# Interactive Online Simulations and Curriculum for Teaching and Learning Fundamental Concepts in Molecular Science at the Undergraduate Level

by

Colin Alexander Ashe

Submitted to the Department of Materials Science and Engineering
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 2010

Author ..................................................................
Department of Materials Science and Engineering
May 18, 2010

Certified by ..................
W. Craig Carter
Professor of Materials Science and Engineering
Thesis Supervisor

Accepted by ..................................................................
Christine Ortiz
Chair, Departmental Committee on Graduate Students

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## Abstract

The number of research disciplines that focus, at least in part, on the atomic or molecular level is rapidly increasing. As a result, the concepts that describe the behavior of atoms and molecules, known collectively as "Molecular Science", are becoming an educational necessity for an expanding fraction of college and university students. Unfortunately, these concepts are challenging for students to learn. Because of the growing importance of these concepts and their difficulty, a project was undertaken with the goal of helping students to understand these concepts using simplified, interactive models. Students in their first year of undergraduate study were targeted.

The primary goal of the project was to help students understand the so-called "energy landscape", also known as the "potential energy surface". This concept is central to Molecular Science because it contains information about both equilibrium and kinetic properties of a system. It is also widely used in textbooks and by experts for reasoning qualitatively.

Interactive simulations, along with related curriculum, were created in order to help students understand the energy landscape and explore its implications. The simulations visualize simplified models, which were chosen for their analogic connection to chemical systems as well as their similarity to things with which students could intuitively relate. The primary models used were two- and three-dimensional cardboard boxes, as well as a series of platforms covered with balls. The models were simulated and visualized in Java applets.

Curriculum sequences consisting of applets, exercises, and explanations were carefully constructed to present concepts in a logical order. The materials were made available online at MatDL.org, the materials pathway of the National Science Digital Library. The curriculum sequences were used as a supplemental exercise by students at Kent State University, Carnegie Mellon University (CMU), and the Massachusetts Institute of Technology (MIT). Two large assessments of student learning were conducted: one at CMU and one at MIT, involving over 400 total students. Assessment results demonstrated that using the project materials improved students' performance on the assessment tests with a greater than 99.9% degree of confidence. Free response comments indicated that students found the exercises helpful and interesting.

Thesis Supervisor: W. Craig Carter
Title: Professor of Materials Science and Engineering

# Acknowledgments

The road I traveled toward the completion of this thesis turned out to be longer and more circuitous than I initially anticipated. In hindsight, however, everything has come together more beautifully than I could have imagined. So, in spite of its difficulty, I have benefited greatly from having made the journey. Of course, I was never alone and I am grateful to those who helped me along the way.

First, I would like to thank my thesis advisor, W. Craig Carter, whose advice was as useful as it was unexpected. Through his guidance and sometimes strategic lack thereof, he helped to grow me from a student into a researcher. In addition, his constant concern for my family's well-being and his efforts to ensure their needs were met are particularly appreciated.

I would also like to thank the other members of my thesis committee, Donald Sadoway and Samuel Allen. In addition to helping me meet a fairly tight deadline, they offered helpful insight, thought-provoking questions, and contagious enthusiasm for the work.

Due to the collaborative nature of the project, I had the pleasure of working with a number of people at MIT, Carnegie Mellon University, and Kent State University. I would like to thank all of the project collaborators for creating such an enjoyable atmosphere in which to work and for stimulating conversation over lunch, dinner, and even breakfast.

Of course, I would be remiss if I did not acknowledge my officemates, who helped me in many ways over the years. I have had interesting and useful discussions with all of them, for which I am grateful. In particular, I would like to thank Ming Tang and Dan Cogswell for the numerous conversations we had over the years.

Though they were not nearby, my parents also helped me greatly during my years in graduate school. I am very grateful for their continual support, both moral and financial. I found it comforting to know that they understood my situation, having gone through the Ph.D. experience themselves.

I would also like to thank my parents-in-law for their support. In particular,

conversations with and weekly letters from my father-in-law gave me insight into life as a professor and helped me to evaluate my priorities.

I am very grateful to my children, Elizabeth and Brian, for always keeping me laughing. Their presence helped to lighten the mood when I was in danger of getting stressed out. In addition, their continual affection warmed my heart and helped me to keep things in perspective.

Finally, I would like to thank my wife, Heather, for the many ways she has supported me over the years. First of all, she left friends and family to move to Cambridge with me when I started at MIT. When I was studying and felt pressed for time, she brought me meals on campus. When I was discouraged, she packed little notes of encouragement in with my lunch or sent me encouraging text messages. In addition to supporting me in my work, she always supported my hobbies and interests even if she had no understanding or appreciation of them herself. In these and many other ways, she has enriched my life beyond measure. I am so very grateful for her and I cannot wait to get started on the next chapter in our lives together.

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# Chapter 1

# Introduction

## 1.1 What is Molecular Science?

Over the last few decades research in the physical and biological sciences, as well as the various engineering disciplines, has become increasingly interdisciplinary. This is due, in part, to advances in both theory and technology that have given researchers from these fields unprecedented abilities to understand and control the systems they study on very short length and time scales. For years, such issues had been primarily the concern of chemists and some physicists. However, these concepts have become increasingly important in biology and all of the engineering disciplines.

To reflect the fundamental nature of these concepts, a new term has been coined to describe them: Molecular Science. While this term has not yet been fully brought into the mainstream, it is nonetheless quite widespread. In addition to being used in scholarly articles, a number of universities around the world have created centers and institutes using the term "Molecular Science" in their names to indicate that they are bringing together researchers from disparate fields whose research shares the same underlying focus on the behavior of systems of atoms and molecules.

Because Molecular Science is concerned with the behavior of collections of atoms and molecules, it encompasses the traditional fields of chemical thermodynamics, statistical mechanics, and chemical kinetics. Therefore, Molecular Science does not represent a wholly new field of research; rather, it binds together a set of existing areas of inquiry while providing them with new, exciting applications.

## 1.2 Why focus on Molecular Science?

As described in the previous section, Molecular Science is of central importance to a broad spectrum of research disciplines. Since the educational enterprise exists to impart to students the concepts and skills they will need as they become professional practitioners of their chosen disciplines, it is incumbent upon educators to recognize and respond to the increasing importance of Molecular Science. Unfortunately for both students and educators, the fields that comprise Molecular Science are widely acknowledged to be abstract and difficult to learn. Because of this difficulty, many students fail to properly grasp concepts as they are presented, setting them up for further misunderstanding as they progress to increasingly challenging and nuanced material.

If Molecular Science were central but easily understood, efforts to improve its education would be unnecessary. On the other hand, if Molecular Science were difficult but peripheral, improving educational approaches to its teaching would not benefit many students. However, because Molecular Science is both central and difficult, improving students' abilities to understand it represents an important and valuable contribution both to the educational enterprise as well as our future as a technological society.

## 1.3 Which concepts are addressed?

The primary concept addressed in this work is the so-called energy landscape, also known as the potential energy surface. This construct represents the energy of a chemical system as a function of all the variables that affect its energy. It can be used to understand the energetics of essentially any chemical system including simple molecules, very complex molecules, and even crystalline materials containing defects. While the energy landscape occupies a space of very high dimensionality in the case of complex systems, it can often be dramatically simplified down to two or three dimensions. These two dimensional representations are often used in representing the energetics of chemical reactions and are found widely in textbooks.

This concept was chosen for a number of reasons, including its broad applicability to many fields, its widespread use in higher level education, and the wealth of information it contains. Specifically, the energy landscape has embedded within it information that can be used to calculate the populations of the system's various equilibrium states as well as the rate at which a reaction from one state to another will occur. Equilibrium state populations and reaction kinetics represent the secondary set of concepts that this project aims to address.

Finally, the issue of the degeneracy, or multiplicity, of equilibrium states is addressed as a first step toward helping students to better understand free energy. All of these concepts are presented in greater detail in chapter 2.

## 1.4 What are the goals of this project?

The central objective of this project is to enable students at the early undergraduate level to better understand fundamental concepts in Molecular Science. Although scientific problem solving is a popular topic in education research, this project does not directly address problem solving skills. Rather, the project's aim is to enable students to understand the over-arching principles in Molecular Science by introducing them to the energy landscape and related topics. Simulations are used in order to provide students with concrete experience from which they can create their own intuitive understanding of the concepts.

In order to achieve the central objective of this project, computer simulations were designed and programmed, curriculum to accompany the simulations was written, and these materials were quantitatively assessed among a number of separate student groups in order to ensure that the simulations and curriculum are effective.

Secondary goals of the project include dissemination of the created materials, reuse and reapplication of the created materials, and the development of a community of users.

### 1.4.1 Simulations

Interactive simulations were chosen as the means by which to present the desired subject matter to students for a number of reasons. Chapter 3 elaborates upon these reasons and justifies them based on findings in the literature. In brief, however, interactive simulations were chosen because they are engaging to students and they enable students to develop intuitive understanding by observing and interacting with the simulated system.

While many other projects, discussed in section 3.6, have chosen to directly simulate systems of atoms and molecules, this project chose a different approach. Research has shown that novices often do not notice phenomena or patterns that are obvious to experts (see section 3.4.1). Therefore, rather than directly simulating atoms and hoping students will manage to extract over-arching trends from the simulations, this project focuses on simpler models that represent real systems by analogy.

A principle that guided simulation design was that simulations should be as concrete as possible and only as complex as necessary. For these reasons, models were chosen that students can easily relate to their everyday experiences. Furthermore, in all but one case, the simulations are performed in two dimensions because three dimensions were not needed and would complicate the visualization. So, while systems of atoms and molecules are not directly simulated, the fundamental characteristics of those systems are effectively represented via analogy. Furthermore, through careful model choice it was possible to represent the fundamental concepts to be conveyed while simultaneously eliminating extraneous and distracting peripheral issues. Specifics on the models used are presented in chapters 4, 5, 6, and 7.

The computer simulations that were designed and programmed represent the largest investment of time and effort that went into the project. In addition, this aspect of the project is the one for which the author of this thesis was primarily responsible. For these reasons, this thesis will address the simulations more than any other project element.

### 1.4.2 Curriculum

While the simulations were the main focus of the project, without proper explanation and context, the simulations themselves are of limited value. Therefore, in order to enable students to get the most out of the simulations, a set of supplementary curricula were written. These curricula had varying aims, depending on the objectives of the class in which they were to be used. However, they all shared a common initial focus on presenting the energy landscape concept. Once the energy landscape was presented, one curriculum path pursued the equilibrium properties of a system that can be understood from the energy landscape. The alternate path examined how reaction kinetics can be understood from the energy landscape. These curriculum paths are illustrated in figure 2-1.

The curriculum sequences can be grouped into concept chunks, each of which is focused on a particular simulation and consists of a web page containing the simulation, explanatory text, and a set of activities that the student is asked to perform. The curriculum directs the student's attention to the specific issues to be conveyed but the student remains free to explore and experiment. After spending some time with the suggested activities, students are invited to read explanations of the phenomena involved, sometimes providing answers to particular questions posed in the first part of each segment.

In the latest iterations of the curriculum, the simulation for each segment is available at all times so the student can test out the provided explanations even after he or she has technically completed the suggested exercises.

### 1.4.3 Assessment

One of the central ideas in the education literature is that students often do not learn what instructors think they are teaching. That is, while an instructor may think that he or she has provided students with a brilliant explanation of a concept that could not possibly be misunderstood, the fact that students have a much different body of existing knowledge than the instructor means that students often will not understand the explanation as the instructor intends. Therefore, it is not sufficient to produce instructional materials without also checking to make sure that they are succeeding in their intended role.

The efficacy of the instructional materials produced by this project was tested by means of identical pre- and post-tests. Before working through the developed curriculum, students took an online pretest. They then worked through the curriculum and took an online post-test afterward. The tests were designed to examine students primarily on their understanding of the energy landscape concept. This test consisted of mostly multiple choice questions but some questions also asked students to explain how they arrived at a given answer and allowed a free response.

At the time of this writing, the project materials had been assessed a total of six times: two times at each of the universities involved in this collaboration. In all, these assessments covered more than 400 students. Details on the test and its results are presented in chapter 8.

### 1.4.4 Dissemination

As a project focused on improving education, one of our aims was to make the simulations and curriculum as widely and as easily accessible as possible. In 2010, the internet is obviously the method of choice for the distribution of nearly anything, particularly software and text. Therefore, the material produced by this project has been made available on a website and may be accessed free of charge by anyone with an internet connection. However, rather than creating a new website for distribution of the material, it has been posted on MatDL.org, the Materials Digital Library website, which is part of the National Science Foundation's National Science Digital Library program. This program "is a national network dedicated to advancing STEM [science, technology, engineering, and mathematics] teaching and learning for all learners in both formal and informal settings." [1] This placement connects the materials produced in this project to other material on related topics and a centralized national network of educational materials. The digital library aspect of this project is detailed in [2].

While the website is an important part of the dissemination process, other important decisions were made in an effort to maximize the ability of potential users to take advantage of our materials. The first priority was producing materials that were not locked into a particular hardware or software platform. While there are myriad software platforms available, most students and educators use one or more of the following three operating systems: Microsoft Windows, Apple Macintosh, or Linux. Ensuring support for these separate platforms suggested writing the software in either an interpreted language like Perl or Python, for which platform-specific interpreters are freely available, or a language like Java or Adobe Flash, for which platform-specific runtime engines are freely available.

Past experience on the part of group members, however, indicated that each additional step required to access educational materials results in a reduction in the number of website visitors who actually view the materials. One such step is requiring a potential user to download and install software not already present on the user's computer. Since most students do not already have Perl or Python interpreters installed, writing the simulations in Perl or Python was ruled out. However, most internet users have already installed browser plug-ins for Java and Flash. According to a December 2006 study performed for Adobe by Millward Brown[3], 98.3% of internet-enabled PCs had the Adobe Flash Player plug-in installed, while 86.9% of PCs had the Java plug-in installed. Although more users have Flash installed, Java was chosen as the language to be used in simulation development because its installed base is adequately large, the group was uncertain that Flash would run smoothly enough on users' computers, and because group members were much more familiar with programming in Java, making development easier and more rapid.

Java programs can be distributed either as downloadable applications or as applets that can be embedded in webpages. In an effort to further avoid requiring users to download anything, applets were chosen as the method for displaying the simulations. This method has the advantage that textual descriptions of the applet can be put on the web page containing the applet. This enables the simultaneous display of the simulation and curriculum, described in section 1.4.2.

### 1.4.5 Extensibility

A further goal of the project is extensibility. While the specific simulations used in the curriculum developed during this project are interesting, they are by no means the only conceivable simulations of didactic value. Other instructors may wish to adapt and tailor them to other curricular goals. Ideally, the simulations could be easily adapted without requiring in-depth programming experience.

For this reason, the simulations were designed such that they can be customized through a series of HTML tags in the web page on which the simulation applet is displayed. While the customizability of the simulations is limited to the properties which have corresponding tags, the available tags enable nearly all interesting properties of the system to be modified.

This functionality is discussed in greater depth in section 5.3.4.

### 1.4.6 User community

By providing the ability for instructors to customize the simulations, it is hoped that they will begin to create their own curriculum sequences to match. As they do so, it is our ambition to create a repository of these teaching materials and make them available alongside the materials created by project members. Currently only materials created directly through this project are hosted on the site. However, the project is in the process of reaching out to faculty members at a number of institutions, looking for those who might be interested in not only using the existing materials in their classes, but also adding to the material available on the site.

## 1.5 Who was involved in this project?

The project described in this thesis involved a collaboration between researchers at the Massachusetts Institute of Technology (MIT), Carnegie Mellon University (CMU), and Kent State University (KSU).

At MIT, Donald Sadoway, John F. Elliott Professor of Materials Chemistry and principal investigator provided strategic direction and presented project materials in his *Introduction to Solid State Chemistry* course, which is taken by hundreds of first-year students every year. W. Craig Carter, Professor of Materials Science and Engineering and MacVicar Faculty Fellow acted as the co-PI, providing valuable input on project direction and programming strategy. The author of this thesis was responsible for the user interface design, simulation design, and programming of the simulations described in chapters 4, 5, 6, and 7. Additionally, he created a first draft of the curriculum included in Appendix A and wrote the curriculum included in Appendix B in consultation with Professor Sadoway. Finally, Arthur Barnard, an undergraduate from Cornell University, assisted the author greatly with programming and simulation design during the summer of 2007.

At CMU, the principal investigator was David Yaron, Associate Professor of Chemistry. He was responsible for writing the final draft of the curriculum included in Appendix A and presenting it in his *Modern Chemistry II* class. Jodi Davenport, a post-doctoral researcher with the CMU Department of Psychology and the Pittsburgh Science of Learning Center, provided input on user interface and simulation design and collaborated with Professor Yaron to write the questions used in assessment, presented in Appendices A and B. Mike Karabinos provided support to Professor Yaron and Dr. Davenport as well as logistical support to the other collaborators.

At KSU, Professor Laura Bartolo was the principal investigator and was responsible for updating and maintaining the project website and collecting assessment data from the online pre- and post-tests. She also coordinated our group efforts and kept us on track. Cathy Lowe provided support to Professor Bartolo as well as others. John Portman, Associate Professor of Physics, provided strategic direction and technical insight and offered his class as guinea pigs for our initial assessment efforts.

## 1.6 Thesis organization

This thesis can be divided into three main sections: introductory material (chapters 1, 2, and 3), descriptions of the simulations and curriculum developed during the project (chapters 4, 5, 6, and 7), and assessment of the materials developed (chapter 8).

Following the present chapter, the introductory material continues with chapter 2, which provides an overview of the technical concepts covered in the curriculum developed during this project and discussed briefly in section 1.3. This chapter also provides a road map of the curriculum sequences presented to students. Chapter 3 provides an overview of the general and science education literature that applies to this project.

Chapters 4, 5, 6, and 7 describe the simulations and curriculum that were developed and tested with students. Specifically, these chapters present the models used in the simulations, the visualizations of those models, and the controls available to students to manipulate the models. Each chapter concludes with a description of the activities students carried out when interacting with the simulations.

Chapter 8 presents quantitative assessment data obtained from the tests students took before and after working through the curriculum and highlights specific results of interest.

Finally, chapter 9 offers some concluding remarks and ideas for future work.

# Chapter 2

# A Review of Technical Concepts

## 2.1 Introduction

As explained in section 1.3, this project is centered around the energy landscape concept. During preliminary project discussions this concept was identified as one that ties together many strands that make up Molecular Science. Our group is not alone in this assessment: a research paper by David Wales published in 2005 is titled "The Energy Landscape as a Unifying Theme in Molecular Science"[4]. While Prof. Wales saw energy landscapes as having the power to unite various fields of research within Molecular Science, our group identified it as also having the power to join together concepts that students often fail to connect.

This chapter will discuss the various characteristics of the energy landscape as well as the other concepts that follow from it. These concepts, such as equilibrium state populations and reaction kinetics, are integral to understanding the behavior of systems of atoms and molecules.

It is beyond the scope of this work to present an exhaustive and complete account of these topics; however, for the benefit of those who are new to these concepts and those who may have learned this material many years ago, a simple and brief account is presented. The reader who is interested in acquainting him or herself with these concepts further would be well served to begin by examining the excellent *Molecular Driving Forces* by Dill[5].

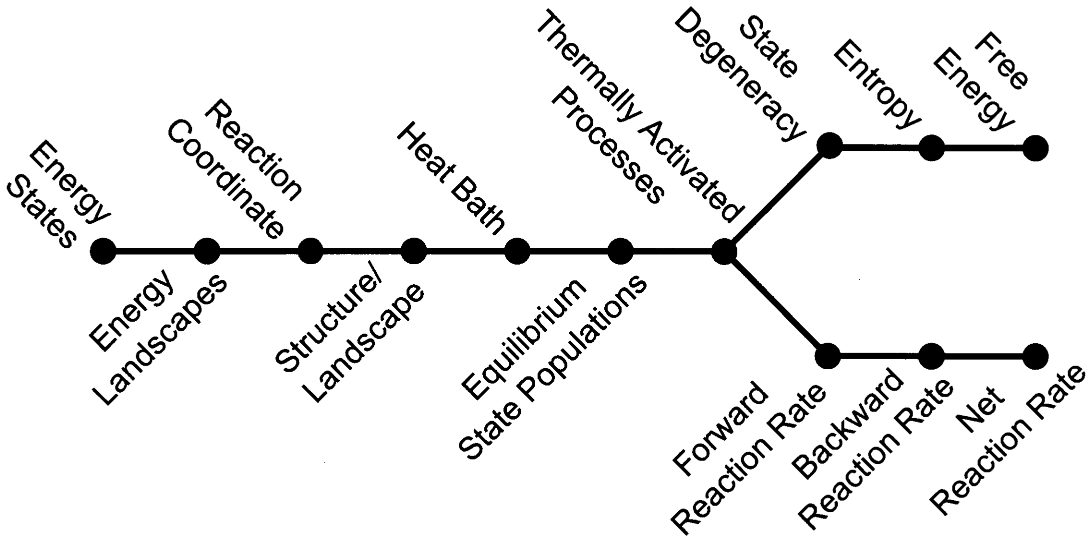


Figure 2-1: Sequence of concepts presented in the curriculum in courses at Carnegie Mellon University (top) and the Massachusetts Institute of Technology (bottom)

## 2.2 Concept road map

The simulations developed by this project have been presented to students as part of curriculum sequences which can be grouped into two major branches. These branches were tailored to fit the syllabi of the courses in which they were presented. A map of the concepts in these two branches is presented in figure 2-1. The top branch of the map represents the concepts covered by the project curriculum as presented in Professor David Yaron's *Modern Chemistry II* course at Carnegie Mellon University. The lower branch represents the concepts covered by the project curriculum as presented in Professor Donald Sadoway's *Introduction to Solid State Chemistry* course at the Massachusetts Institute of Technology. The order of the concepts presented in each branch was chosen carefully to ensure that students could move as smoothly as possible from one concept to the next.

As is clear from figure 2-1 the two curriculum branches share a large number of concepts. They eventually diverge because, in one course, the instructor wished to focus primarily on equilibrium phenomena and in the other, the instructor wished to focus on transient phenomena. While the two branches do eventually diverge they both rely on the energy landscape as the foundation for more advanced concepts.

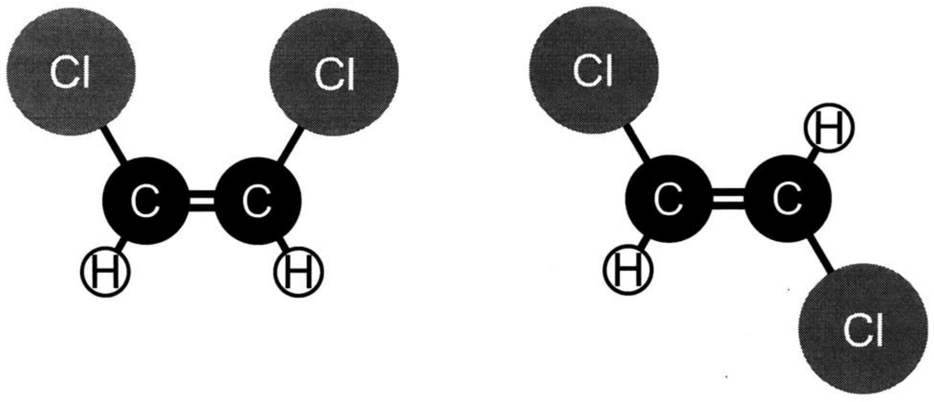


Figure 2-2: Illustration of cis-1,2-dichloroethene at left, and trans-1,2-dichloroethene at right

The concepts presented to students are described in the sections that follow, though the order in which they are presented varies a bit from the order used in the curriculum.

## 2.3 Energy states and the energy landscape

### 2.3.1 States

In approaching energy states and the energy landscape it is wise to begin by considering a simple system. In this discussion, a simple molecule known as 1,2-dichloroethene will be used as the example since it was also used in the curriculum presented to students. This molecule can take on two isomeric configurations, known as cis and trans, illustrated in figure 2-2.

Because the cis configuration has the two large chlorine atoms near one another, it is a higher energy configuration than the trans configuration, which maximizes the separation between the chlorine atoms. Since chemical systems are most stable when the appropriate energy is minimized, the trans isomer represents the stable configuration for this molecule. The cis configuration is known as the metastable state because, while it is relatively stable, it does not represent the most stable configuration. Between the stable and metastable states is a state known as the activated state. This is an unstable, high energy state because it involves twisting

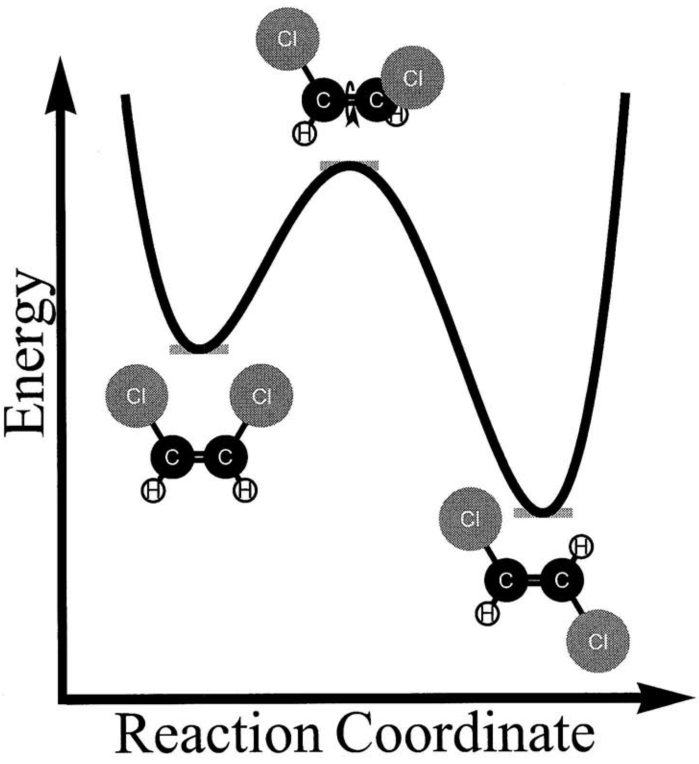


Figure 2-3: Schematic energy landscape diagram depicting 1,2-dichloroethene in its cis (at left) and trans (at right) isomers as well as its activated state (center)

the double bonds between the carbon atoms in the molecule. Consequently, a molecule of 1,2-dichloroethene will spend only a tiny fraction of its time in the activated state. However, in order for the cis isomer to transform into the trans isomer or vice versa, the molecule must pass through the activated state.

### 2.3.2 The energy landscape

The metastable, activated, and stable states of the molecule can be brought together in a diagram known as an energy landscape. Figure 2-3 shows a schematic representation of the energy landscape for 1,2-dichloroethene and matches the important parts of the diagram with the corresponding molecule structures.

#### The reaction coordinate

In the diagram, the meaning of the vertical axis is clear: it represents the potential energy of the molecule due to the forces the atoms exert on one another. However, the meaning of the horizontal axis is less intuitive. The quantity represented on this axis is often called the "reaction coordinate". It can represent many different things, depending on the nature of the system it describes. In the case of 1,2-dichloroethene, it represents the angle through which one half of the molecule must turn in relation to the other half in order to switch from cis to trans or vice versa. Generally speaking, when a system transitions from one state to another, it does so via some path. While the specifics of this path are not important for this discussion, the reaction coordinate can be thought of as the fraction of this path that has been already traversed. For this reason, the quantity represented on the horizontal axis is sometimes also known as the "extent of reaction", indicating that it is a measure of the extent to which the reaction, or the transition from one state to another, is complete.

### Mathematical properties of the energy landscape

In figure 2-3 gray horizontal lines are drawn at the location of the precisely defined thermodynamic states. These states occur where the derivative of the energy landscape function is zero. Because the derivative of an energy is a force, any place on the graph where the derivative of the energy landscape is not zero, a force exists that pushes the system toward a lower energy state.

Locations on the energy landscape where the derivative is zero are said to be equilibrium states. That is, if the system is not disturbed by outside intervention, it will remain in that state indefinitely. Locations where the second derivative of the energy landscape is positive are stable or metastable equilibrium states, while those which have a negative second derivative are unstable equilibrium states. Because the energy landscape rises on either side of stable equilibrium states, if a system initially in such a state moves a small distance away from equilibrium, forces exist that push the system back toward equilibrium. In contrast, at an unstable equilibrium state where the energy landscape falls on either side, these same forces push the system away from the unstable equilibrium.

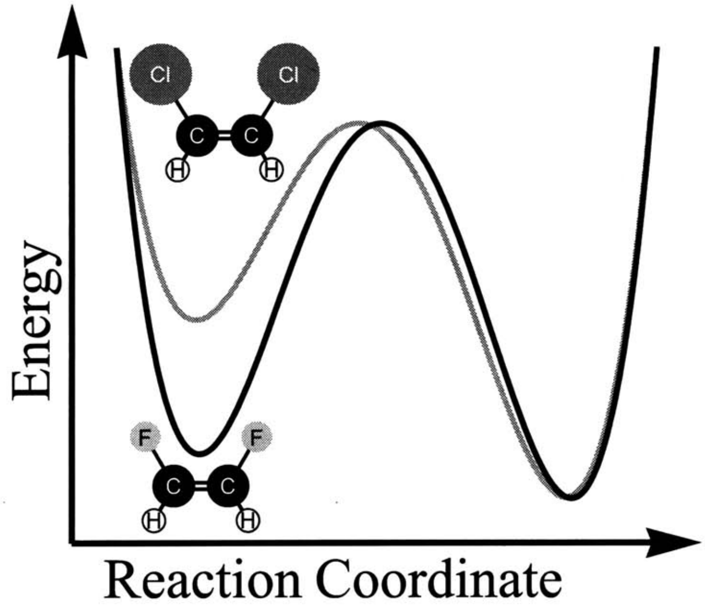


Figure 2-4: Schematic energy landscapes for 1,2-difluoroethene (black) and 1,2-dichloroethene (gray) along with depictions of their molecular structures

### The energy landscape's connection to structure

The attributes of the energy landscape are closely tied to the structure of the system that the energy landscape represents. In figure 2-3 the energy landscape corresponding to 1,2-dichloroethene is presented. To illustrate the idea that a change in molecular structure impacts the energy landscape, consider substituting fluorine atoms for chlorine atoms in 1,2-dichloroethene, resulting in 1,2-difluoroethene. Because fluorine is a smaller atom than chlorine, when the molecule is in the cis configuration, there is less repulsion between the fluorine atoms than there is between the chlorine atoms. The result is that the metastable state for 1,2-difluoroethene has a substantially lower energy than that of 1,2-dichloroethene, as illustrated schematically in 2-4.

### The higher dimensional energy landscape

Systems that are more complex than 1,2-dichloroethene or 1,2-difluoroethene require more variables to determine the system's energy and therefore have more complicated energy landscapes. A schematic example of such a landscape is shown in figure 2-5. This plot depicts just a small section of what could be a much larger energy surface.

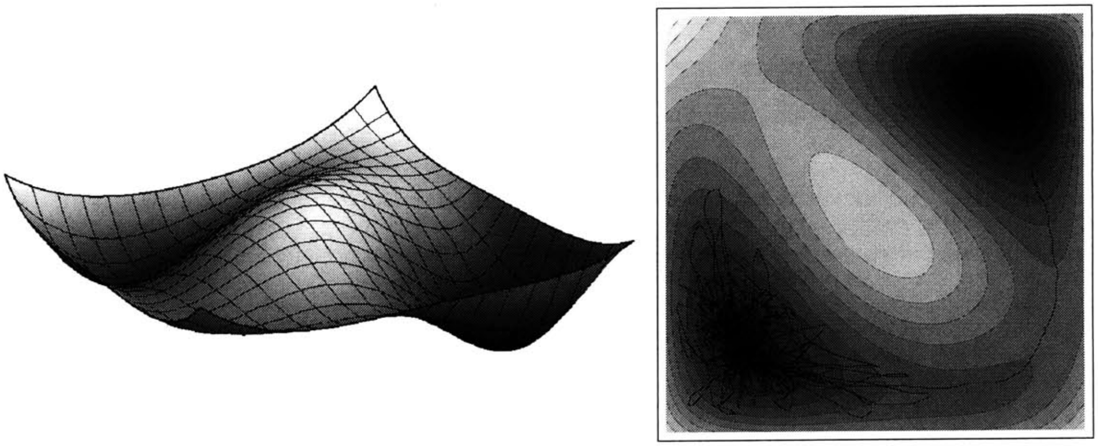


Figure 2-5: Surface plot and contour plot representations of a schematic three-dimensional energy landscape

From the plot it can be seen that a system transitioning from one equilibrium state to another might do so by means of a number of different paths across the surface.

While, in theory, there are many paths that the system could choose in transitioning from one state to another, in practice, the system will predominantly choose the path with the lowest energy barrier. The lowest energy barrier in a multi-dimensional landscape is located at a so-called saddle point, which is analogous to a mountain pass. A path passing from one state to the other past a saddle point is traced out on the righthand image in figure 2-5 as part of a trace of the system's trajectory over time. The system spends much of its time in the vicinity of a minimum and only infrequently crosses the barrier between states.

Because there is one predominant path that the system will follow during a transition, this complicated three-dimensional energy landscape can be easily reduced to the familiar two-dimensional representation. In such a reduction, the energy scale remains unchanged but the original two spatial variables are replaced by a single reaction coordinate, which represents the how far along the transition path the system is. Furthermore, the height of energy barrier in the two-dimensional representation is taken from the height of the saddle point in the multi-dimensional representation.

In reality, the energy landscape of most chemical systems of practical interest is far too complicated to be represented in three dimensions. In fact, the system energy could be a function of hundreds, thousands, or even millions of variables. Fortunately, even in systems such as these, specific areas of interest within the energy landscape can often be represented using the simple two-dimensional representation depicted in figure 2-3.

This discussion only begins to scratch the surface of the energy landscape construct. The reader who is interested in exploring this topic further is urged to examine *Energy Landscapes* by David Wales[6] as it is the authoritative book on the subject.

## 2.4 Equilibrium state populations

When considering chemical reactions or other phenomena in which the objects that make up a system can be in one of a discrete number of states, it is often desirable to know how many objects are in each state. For example, consider a sealed vessel filled with 1000 molecules of 1,2-dichloroethene. One might like to be able to calculate how many of these molecules are cis isomers and how many are trans. Fortunately, it is possible to obtain the information necessary for this calculation from the energy landscape.

The number of molecules in each state can be referred to as the population of the state. In a system with two states of different energy, the ratio of the state populations can be written as:

$$\frac{P_2}{P_1} = \exp\left(-\frac{E_2 - E_1}{RT}\right) = \exp\left(-\frac{\Delta E}{RT}\right) \tag{2.1}$$

where $P_2$ and $P_1$ represent the average populations of the two states being compared and $E_2$ and $E_1$, respectively, represent their energies. $R$ is the so-called gas constant and $T$ represents the system temperature. The quantity $RT$ represents a measure of the thermal energy of the system. By convention, state 1 is normally chosen to be the lower energy state and state 2 is the higher energy, or metastable, state.

Examining this equation, it can be seen that as long as the temperature of the system is known, the only additional piece of information needed to calculate state populations is the difference in energy between the two states. Figure 2-6 illustrates

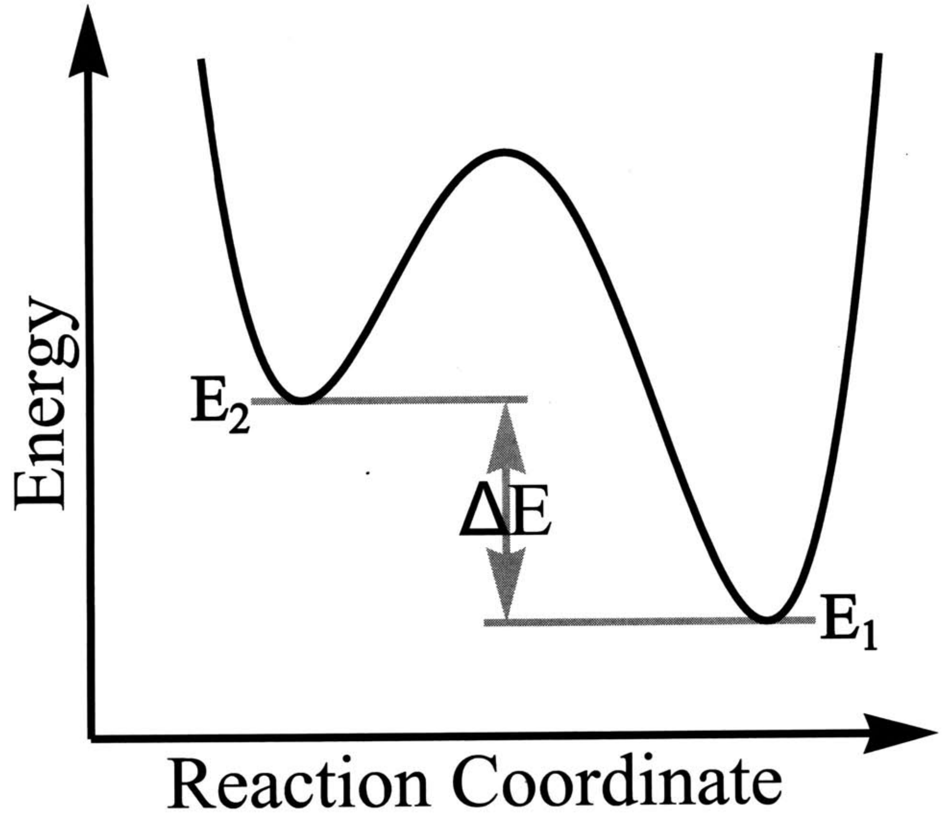


Figure 2-6: A schematic energy landscape diagram showing the difference in energy between the stable and metastable states

how the energy landscape contains this information.

Examining the limiting cases of this equation can be instructive. For example, not surprisingly, when $\Delta E = 0$, the ratio of populations is unity. That is, when the two states have the same energy, they are expected to have equal populations at equilibrium. However, one may not expect that the two states can also have equal populations when the energies of the states are not equal. This is true in the limit where temperature goes to infinity.

Examining a few other cases it can be seen that when $\Delta E/RT = 1$, $P_2/P_1 \approx 1/3$, meaning that the low energy state has a population roughly three times that of the higher energy state. By the time $\Delta E/RT = 5$, the fractional population of state 2 is essentially zero. This illustrates that if the thermal energy of the system is substantially less than the difference in state energies, the low energy state will be strongly favored. However, if the temperature is raised sufficiently high, it is possible

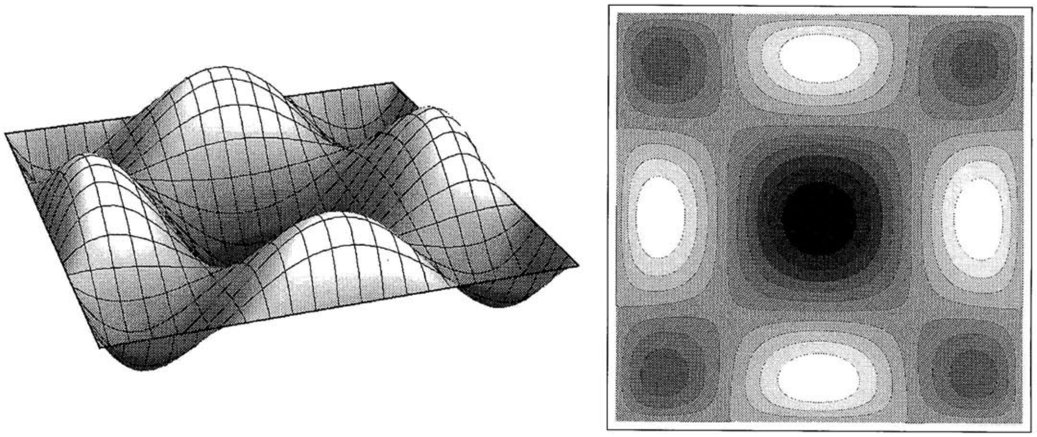


Figure 2-7: Schematic surface and contour plots of an energy landscape containing a central stable state and four equivalent metastable states

for the states to have roughly the same populations regardless of their difference in energy.

Finally, it is important to point out that the equilibrium state populations are a function only of temperature and $\Delta E$ and do not depend on the height of the barrier between the states. The significance of the barrier will be discussed in section 2.6.

## 2.5 Degeneracy, Entropy, and Free Energy

As discussed in section 2.3, a state is simply a configuration of the system under consideration that possesses a given amount of energy. While many simple systems have have only one configuration that corresponds to a given energy value, more complicated systems may have a set of distinct configurations, which all possess the same energy. These states are known as degenerate states and the number of such states in a given set is known as the state's degeneracy.

It may not be immediately obvious how a system could possess multiple configurations which are physically distinct but yet of the same energy. Often this is due to some type of symmetry that the system possesses. A schematic energy landscape containing four degenerate, symmetrically related states is presented in figure 2-7.

State degeneracy is very important because of its relationship with entropy, which is given by the famous Boltzmann equation:

$$S(E) = k_B \ln \Omega(E) \tag{2.2}$$

where $S$ represents the entropy of a system possessing energy $E$, $k_B$ is the so-called Boltzmann constant, and $\Omega$ represents the number of states possessing an amount of energy $E$.

Entropy is important for many reasons but it factors into the present discussion because it is a component of a type of energy known as the Gibbs free energy. The Gibbs free energy is not the same as the energy discussed in the previous sections. That energy is formally known as the internal energy. It is often represented with $E$ but the traditional thermodynamic representation is $U$. The Gibbs free energy differs from the internal energy in that it explicitly accounts for state degeneracy through its inclusion of entropy.

The Gibbs free energy is defined as follows:

$$G = U + pV - TS \tag{2.3}$$

where $G$ is the Gibbs free energy, $U$ represents the system's internal energy, $p$ represents the system's pressure, $V$ represents the system's volume, $T$ represents the system's temperature, and $S$ represents the system's entropy. For the present discussion, it is preferable to ignore the $pV$ term, producing:

$$G = U - TS \tag{2.4}$$

Under real world conditions (i.e. constant temperature and pressure), systems preferentially occupy states that minimize the Gibbs free energy rather than the internal energy. For this reason, Gibbs free energy is the basis of more advanced thermodynamic concepts used to model and understand real world processes.

One of the fundamental ideas in chemical thermodynamics is that, at low temperatures, systems are generally observed in configurations that minimize the internal energy, while at high temperatures, systems generally adopt the configurations that have the highest degeneracy. Illustrating this principle in an interactive manner was the driving force behind the simulations presented in chapter 6.

It is beyond the scope of this thesis and the project described herein to provide an advanced account of the Gibbs free energy. However, by examining systems that possess degenerate states and by understanding how degeneracy affects the energy landscape and resulting state populations, it is possible for students to more fully understand related but more advanced concepts when they are introduced to them.

## 2.6 Chemical kinetics

In section 2.4 the significance of the difference in energy between equilibrium states was discussed. This discussion mentioned that the height of the activated state, otherwise known as the energy barrier, did not play a role in state populations at equilibrium. However, the energy barrier does play an important role in determining how quickly equilibrium is reached when a system is taken out of equilibrium. Chemical kinetics is the study of how quickly chemical changes occur and focuses on processes that are governed by an activation energy, known as activated processes.

Consider again the example from section 2.4: a sealed vessel filled with 1000 molecules of 1,2-dichloroethene. If this system was at equilibrium at a temperature $T_1$ and then is abruptly heated to a new temperature, $T_2$, it is no longer in equilibrium. Recalling equation 2.1, it is clear that a change in temperature will result in a corresponding change in state populations. However, it is not clear how long this change in state populations will take. Equation 2.1 and, in fact, any equation from equilibrium thermodynamics does not provide the ability to obtain such information.

Fortunately, the so-called Arrhenius equation does provide this information. The Arrhenius equation is as follows:

$$k = A \exp \frac{-E_a}{RT} \tag{2.5}$$

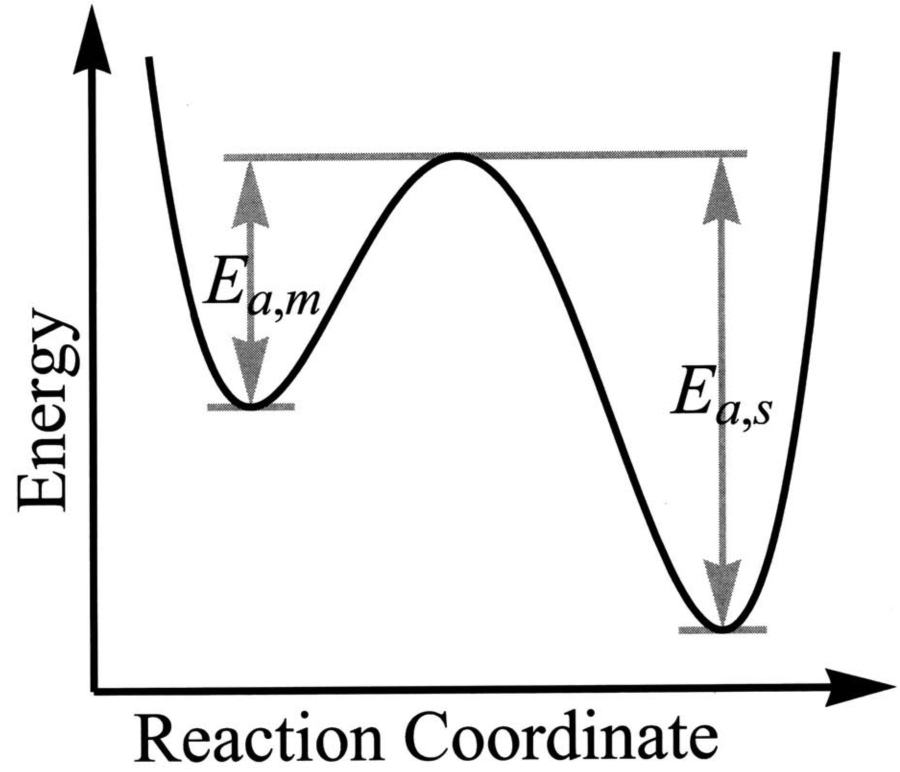


Figure 2-8: A schematic energy landscape diagram showing the activation energies that must be surmounted in order to transition out of the metastable ($E_{a,m}$) and stable ($E_{a,s}$) states

where $k$ represents the reaction rate (not the Boltzmann constant), $A$ is some prefactor, which may or may not be a constant, $R$ is the gas constant just as in equation 2.1, $T$ is the temperature of the system, and $E_a$ is the energy of activation, otherwise known as the energy barrier.

Figure 2-8 brings back the familiar two-dimensional representation of the energy landscape but this time labels the two activation energies present in the system, $E_{a,m}$ and $E_{a,s}$. $E_{a,m}$ represents the amount of energy needed by the system to move from the metastable state to the activated state. Similarly, $E_{a,s}$ represents the energy needed by the system to move from the stable state to the activated state.

In real experiments it is generally only possible to measure the net reaction rate. However, at any given time in a system undergoing a chemical reaction, there is both a forward reaction and a backward reaction underway. If the 1000 molecules of 1,2-dichloroethene are all in the metastable cis configuration, some molecules will successfully surmount the energy barrier and take on the trans configuration. This is the forward reaction. However, once there are a few trans molecules, there is the possibility that they could convert back into cis molecules. This type of conversion represents the backward reaction. Therefore, at any given time, there are really two reactions occurring and their rates are given as follows:

$$k_{forward} = A \exp \frac{-E_{a,m}}{RT} \tag{2.6}$$

$$k_{backward} = A \exp \frac{-E_{a,s}}{RT} \tag{2.7}$$

while the net reaction rate is simply:

$$k_{net} = k_{forward} - k_{backward} \tag{2.8}$$

These reactions occur even when the system is at equilibrium. However, because the forward and backward rates are equal, the net reaction rate is zero, giving the appearance that no reactions are occurring.

One of the central concepts from chemical kinetics is that a chemical reaction's rate depends sensitively upon the activation energy involved. The field of catalysis involves the study of how carrying out chemical reactions under certain conditions or in the presence of additional chemical species can lower the activation energy or create a new reaction pathway with lower activation energy, thereby increasing the reaction rate. The curriculum accompanying the simulations guided students through a series of experiments designed to give them an intuitive understanding of how changing $E_{a,m}$ and $E_{a,s}$ affects forward and backward reaction rates and, consequently, the net reaction rate.

## 2.7 Temperature and its regulation

### 2.7.1 Temperature

The observant reader may have noticed that the term $RT$ appears in both equation 2.1 and equation 2.5. Thus, temperature plays a major role in both equilibrium and kinetic properties of chemical systems. This is because temperature is related to the average kinetic energy of the atoms in the system and the quantities $\exp(-\Delta E/RT)$ and $\exp(-E_a/RT)$ represent the fraction of atoms in the system that have as much or more energy than $\Delta E$ or $E_a$, respectively.

For a monatomic gas, the relationship between average kinetic energy and temperature is given by

$$\overline{E_k} = \frac{3}{2} k_B T \tag{2.9}$$

It is important to note that temperature relates to the *average* kinetic energy of the atoms in the system. This does not mean that every atom has this same kinetic energy. In fact, the kinetic energies of the atoms in the system are distributed according to the so-called Maxwell-Boltzmann distribution. Atoms with a given kinetic energy move with a corresponding speed. The distribution of energies thus gives rise to a distribution of speeds, which is depicted in figure 2-9 for three different temperatures.

Figure 2-9 clearly illustrates that as temperature is increased, the fraction of atoms with a speed above the threshold speed dramatically increases. If the threshold in the picture represents $E_a$ from equation 2.5, for example, then the areas under the curves to the right of the threshold represents the fraction of atoms in the system that have enough energy to scale the energy barrier. Knowing what fraction of atoms in the system have enough energy to do something, like change state, is of tremendous importance in Molecular Science.

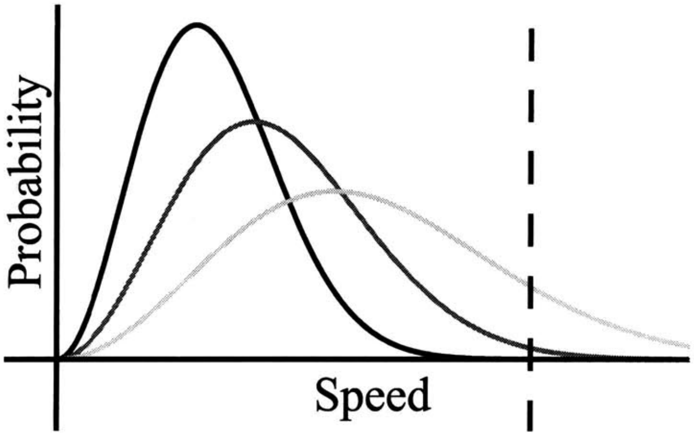


Figure 2-9: Schematic representation of the Maxwell-Boltzmann speed distribution at three different temperatures. Lighter gray indicates higher temperature. The vertical dotted line represents a threshold speed required for some process of interest to occur.

### 2.7.2 The heat bath

When researchers are making calculations related to a chemical system, it is usually assumed to be at constant temperature. This greatly simplifies the calculations. Similarly, when they perform experiments, they generally exert quite a bit of effort to ensure that the system under investigation is kept at a constant temperature. This is generally done by means of a heat bath.

In the laboratory, a heat bath is often a vessel filled with water at a known temperature. The system under investigation is then immersed in this water bath, or reservoir, in order to keep its temperature the same as that of the water. If the system being studied produces heat, this heat is absorbed by the water and the system remains at a constant temperature. Similarly, if a chemical reaction in the system absorbs heat, the heat bath provides this heat to the system and prevents the system's temperature from dropping. As long as the reservoir is much larger than the system under investigation this approach is generally successful.

In thermodynamic calculations, an idealized version of the heat bath is used. In a real laboratory heat bath, if the system under investigation produces too much heat, which the surrounding heat bath absorbs, eventually the temperature of the water will rise to some extent. In contrast, the idealized heat bath, by definition, can absorb any amount of heat from the system without its temperature rising. Similarly, it can also provide any amount of heat to a system with which it is in contact without its temperature decreasing. This idealized heat bath can not exist in the real world, but a sufficiently large reservoir can approximate it.

In the simulations described in chapter 5, 6, and 7, it is necessary that the temperature of the simulated system can be maintained at a given constant value. This is done by simulating a heat bath in contact with the system and giving users the ability to quickly change the temperature of the heat bath. In practice this is accomplished by the following process:

1. The simulation detects when an element of the system (i.e. an atom, molecule, or some other thing) impacts a surface which is in contact with the heat bath. This is generally, at minimum, the bottom boundary of the simulation box.
2. A speed is chosen randomly according to the Maxwell-Boltzmann distribution, shown in figure 2-9.
3. The system element's old speed is replaced with the new speed chosen in step 2.

By randomly assigning new speeds chosen from the Maxwell-Boltzmann distribution to the elements that make up the system, eventually, the actual distribution of speeds in the system becomes approximately equal to the Maxwell-Boltzmann distribution. However, because it takes time for all the system elements to impact the surface in contact with the heat bath, the system does not change its temperature immediately after the heat bath's temperature is changed. Rather, the temperature equilibration takes some time.

## 2.8 Summary and Conclusion

The concepts presented here represent the fundamental concepts included in the curriculum developed by this project and the goal of presenting them effectively informed the decisions made in designing the simulations. As the simulations are introduced in chapters 4, 5, 6, and 7, frequent reference will be made to these concepts.

# Chapter 3

# A Review of Relevant Education Literature

## 3.1 Introduction

Teaching students is difficult and teaching difficult subject matter to students is doubly difficult. This is the situation in which chemistry and physics educators find themselves routinely. Fortunately, because of the difficulty of teaching in general, and teaching science in particular, there is a large body of literature that describes the problems that students and educators encounter, as well as possible solutions to those problems. Furthermore, substantial work by educational psychologists, cognitive psychologists, and even computer scientists has led to a large body of work that lays out a theoretical framework for understanding how people learn. The development of successful theories has helped those involved in educational research to design experiments and interpret the results.

This chapter should not be considered to be a broad review of the education, or even science education, literature. Rather, in an effort to keep this chapter to a manageable size, only the concepts which are directly applicable to project's goals are presented. In particular, this chapter aims to present the concepts that informed the goals and the decision-making process throughout the project's development.

The chapter is divided up into four sections. Section 3.2 introduces the necessary theoretical concepts that provide a foundation for all subsequent discussion. Once the groundwork is laid, section 3.3 presents an overview of literature describing the problems the project attempts to address. Section 3.4 presents concepts that describe some capabilities that, ideally, students will have after working through the project materials. Finally, section 3.5 presents a number of strategies found in the literature that address the problems outlined in section 3.3 and could move students toward the ideal outcomes mentioned in section 3.4.

## 3.2 Theoretical foundations

It may not be obvious that a project which is not specifically about the theory of education or learning would need to be founded on a theory of learning. However, all people, both students and teachers, have a theory of learning even if they are not aware of it. Expectations about what a student should be able to understand given a particular explanation or student evaluations of what constitutes "good teaching" are all based upon deeply held, though not formally expressed, theories of learning.

In research programs that examine ways to effectively teach difficult concepts, it is important that the theory of learning that underlies the work be made explicit[7]. Leveraging a theoretical framework enables researchers to make informed predictions about approaches that are likely to be fruitful. A theory of learning also provides a framework for interpreting the results.

The learning theory that underlies the work on this project is known as *constructivism.* Its influence is not felt strongly in the work described in future chapters but many of the specific strategies employed are based on constructivist principles. In an effort to limit the discussion here to those topics that directly apply to the thesis, discussion of other learning theories, such as behaviorism, will be omitted.

### 3.2.1 Constructivism

The late 1970s saw a learning theory known as constructivism begin to take hold and, during the 1980s and early 1990s, it was the predominantly held theory of learning among education researchers[8]. There are numerous variants of constructivism that have been proposed, including von Glasersfeld's Radical Constructivism[9], Novak's Human Constructivism[10], and the now popular Social Constructivism[8], among others. For the purposes of this literature review, however, it is more illuminating to discuss the common themes shared by constructivist theories of all stripes than to delve into their differences.

### Knowledge is constructed by the learner

The fundamental idea behind constructivism and that which gives it its name is that knowledge and understanding must be constructed by the learner and cannot be passed, unmodified, directly from teacher to learner or from book to learner. In fact, constructivism holds that even scientific researchers are engaged in the construction of understanding about the universe in which we live. Furthermore, constructivism holds that, while the universe is real and there are "truths" about how it operates, researchers can never know that their theories about how it operates are completely true. Rather, they can only know that their interpretations, that is, their constructions of understanding, are consistent with all known experimental results. This idea is reflected in practicing scientists' understanding that a theory can only be disproven and never definitively proven. The history of science, of course, provides many well-known examples of experiments which forced scientists to abandon or revise theories that had been widely accepted.

Constructivism, as applied to education, holds that the process of learning in a student is very much like the scientific enterprise itself. Students synthesize the various pieces of information with which they are presented and, in so doing, construct their own personal understanding of the topics involved. Students cannot simply take explanations presented by teachers and assimilate them in an unmodified fashion. Rather, the explanations themselves are understood by students in light of the student's own pre-existing knowledge and, in order for any new knowledge to be retained, the student must find a way to fit it into their existing knowledge structure.

### Pre-existing knowledge is important

One of the most famous quotes related to this topic comes from the epigraph of David Ausubel's *Educational Psychology: A Cognitive View*[11] and reads "If I had to reduce all of educational psychology to just one principle, I would say this: The most important single factor influencing learning is what the learner already knows. Ascertain this and teach him accordingly."

A student's pre-existing knowledge is very important because it can either help or hinder the student in acquiring new knowledge. This is due to the structure that a person's knowledge takes, which is generally regarded to be an interconnected web of concepts that are, at least to some extent, organized hierarchically[12]. When new concepts are introduced, they must be placed somewhere within the student's cognitive structure. How this proceeds depends upon how well the new concept fits the student's existing cognitive structure, as described in Ausubel's Cognitive Assimilation Theory[13].

In Ausubel's theory, a process known as *subsumption* occurs when a student is presented with new detail-oriented material that can be neatly added to the over-arching concepts already present in a student's cognitive structure[14]. This is a straightforward process if a student's cognitive structure already contains the over-arching concepts necessary to place the new concept in its appropriate context. However, if the over-arching concepts themselves need to be added or changed, as is the case if a student misunderstands a fundamental concept, a process known as *superordinate learning* is necessary. Superordinate learning involves substantial reorganization of the student's cognitive structure and, is therefore, a much more complicated process than subsumption.

Because a student with a wealth of well-organized pre-existing knowledge can learn many concepts through subsumption, learning is easier and more rapid. In contrast, a student with little or poorly-organized pre-existing knowledge will have a much more difficult time learning because his or her cognitive structure will need to be substantially expanded and reorganized.

## 3.3 Literature describing the problem

For decades a common refrain among educators and policy makers has been that education needs to be improved. However, in order to improve anything, concrete problems must first be identified. What follows is a description of three problems identified in the literature that are particularly applicable to the work described in this thesis.

### 3.3.1 Misconceptions

One of the most prevalent types of study in the literature relates to the idea of pre-existing knowledge from section 3.2.1. These studies attempt to ascertain the various common ways that students misunderstand certain concepts, either before or after instruction. Different authors choose different terms for what is being studied but all terms involve the word *conception.*

*Preconceptions* are the conceptions that students have about a topic prior to the study or prior to teaching on the topic. *Misconceptions*, *naïve conceptions*, and *alternate conceptions* focus on conceptions that students have that do not agree with the scientific consensus but *alternate conceptions* is used by some authors to denote the idea that the conception may have value for the student outside of scientific or classroom context[15]. *Non-conceptions* refers to concepts for which the student has no existing knowledge or experience.

These studies are remarkably numerous. In fact, a bibliography of such studies has been compiled and it currently contains approximately 8,400 articles[16]. While most studies have attempted to explore the ways that students misunderstand very specific concepts, some more recent work has attempted to extract patterns from these studies in order to understand whether there are any general ways in which students misunderstand concepts[17].

Unfortunately, the literature related to misunderstanding of Molecular Science topics at the undergraduate level is very sparse[18]. Much of the literature that is available deals with macroscopic thermodynamics, which is not particularly applicable to the present work. However, a helpful bibliography of papers related to heat and thermodynamics has been compiled and contains a few papers of interest[19]. In addition, a recent book directly addresses many common student misconceptions in chemistry[20].

One of the fundamental results of the studies on misconceptions is that students do not alter their conceptions quickly or easily. In fact, unless specific steps are taken by instructors, students often do not recognize that they misunderstand a concept and additional concepts that are linked to the misunderstood concept are also misunderstood[12]. While the present work does not specifically address misconceptions, it can provide students with an opportunity to recognize misunderstandings, as described in section 3.5.3.

### 3.3.2 Novice problem solving

A further problem reflected in the literature is the way in which novices solve problems. Frequently, students attempting to solve a problem will look for an equation from a set of candidates that contains the known variables and the unknown, which they must calculate. Little thought is put into understanding the problem and solving the problem produces little understanding. Novices generally do not recognize the operative underlying principles and therefore may use the same solution technique to solve two problems involving different underlying principles if the problems share superficial characteristics[21].

The difference between novices and experts will be discussed further in section 3.4.1.

### 3.3.3 Length and time scale

While misconceptions and naïve approaches to problem solving can arise in any discipline, one source of difficulty that is particular to Molecular Science is the issue of the time and length scale on which phenomena of interest occur. Students are accustomed to experiencing the world on length scales between millimeters and meters or kilometers and time scales between tenths of seconds and hours. However, in Molecular Science, the operative length scales are on the order of Ångstrøms ($10^{-10}$m) or nanometers ($10^{-9}$m), while the time scale is typically between femtoseconds ($10^{-15}$s) and nanoseconds ($10^{-9}$s). These length and time scales are roughly one billion times shorter than those that students are accustomed to experiencing directly. The large discrepancy between the operative length and time scales for Molecular Science and those that students experience every day makes it very difficult for students to reason qualitatively or develop an intuitive understanding about phenomena in Molecular Science.

In addition, the fact that these atomic scale phenomena have observable consequences on the length and time scales students do experience means students need to simultaneously balance their understanding of these phenomena on multiple length and time scales. In a frequently cited paper, titled *Macro- and microchemistry*[22], Johnstone describes three different levels on which students (in particular, chemistry students) need to be proficient. In a more recent paper[23], he calls these levels *macro*, *sub micro*, and *representation.*

The macro level is the one on which direct observations may be made with the naked eye. The sub micro level occupies the extremely short time and length scales and is often used to explain or justify behavior observed at the macro level. The final level involves representations of chemical phenomena in the form of chemical equations. The correspondence between these levels is obvious to practicing researchers but is often mysterious to students. Enabling students to get a better grip on the three levels is a field of considerable research, some of which is presented in a recent book on the topic[24].

As discussed in section 3.5.1, the project described in this thesis uses models with which students can directly relate rather than simulating anything on the sub micro level. However, within the curriculum that accompanies the simulations, comparisons are made between the simulated models and atoms and molecules in order to encourage familiarity with the sub micro level.

## 3.4 Literature describing the goal

The goal of the educational system is, of course, to educate people. How exactly to go about that is a matter of debate. However, it is safe to say that the ideal outcome of education is the production of experts. While this is not true at the elementary, middle, or even the high school level, it is certainly the goal at universities. If expertise is the clear goal, then it makes sense to attempt to characterize just what expertise means.

### 3.4.1 Expert knowledge and problem solving

The earliest studies specifically aimed at understanding the unique skills of experts were carried out in the mid 1960s. Since then, a large body of knowledge has been accumulated, from which it is possible to draw general conclusions about how experts differ from novices, regardless of the area of expertise.

#### Knowledge

Research has shown that experts' knowledge in their domain is composed of more than just a vast storehouse of individual facts and procedures. While they do possess a large body of domain-specific factual and procedural knowledge, it is all organized around central themes that play important roles in the domain[25]. This is to say, in the language of section 3.2.1, that experts have densely populated, well-organized cognitive structures in their domains of expertise.

#### Problem solving

Because experts' knowledge is organized around central themes or important principles, they are much better than novices at understanding the fundamental nature of a problem they are asked to solve. This was demonstrated in a study in which experts and novices were presented with multiple physics problems and asked to group the problems into categories that they also were asked to define[26]. Novices were found to group the problems on superficial similarities, while experts were found to group them on the fundamental principles involved.

In addition to having the ability to identify the fundamental principles that are relevant to a problem, experts spend much more time than novices thinking about the problem qualitatively, in an effort to *understand* the problem. Experts are also skilled at constantly evaluating their understanding of a problem and determining whether the solution they obtain makes sense[21]. Such skills are commonly labeled *metacognition*.

An additional way that experts differ from novices is that experts tend to draw schematic diagrams when solving a problem. While a problem statement may contain information that is not needed in solving the problem, experts draw pictures that abstract away all but the essential information[27].

While improving student problem solving is not an explicit goal of the present work, the models and visualizations were chosen to familiarize students with a common qualitative picture drawn by experts in the field of Molecular Science: the energy landscape. In addition, the representations and exercises were designed to help students think qualitatively and understand the phenomena. By improving understanding, improved problem solving skills are likely to follow.

### Pattern recognition

Because of their extensive factual knowledge and their over-arching understanding of their domain, experts are able to extract patterns and or other types of meaning from images, data sets or other types of input that may appear meaningless to a novice[21]. This ability may also be due to the fact that the many hours of training logged by the expert have conditioned his or her brain to automatically ignore peripheral issues and concentrate on the phenomena of interest[25]. Without such training, the novice is overwhelmed by stimuli and cannot extract any meaning.

Consequently, although many simulations of atoms and molecules are possible, it is not clear that they would be particularly enlightening for students. Experts find them very interesting but the simulations often involve a lot of simultaneous motion and the untrained eye is ill-equipped to extract meaning from it. For the project described in this thesis, the decision was made to avoid simulations that directly model systems of atoms and molecules in an effort to make the simulations as meaningful as possible for novices. Instead, models were designed from the ground up, specifically to clearly illustrate the topics described in chapter 2.

### 3.4.2 Transfer across domains

A final goal of education that is not specifically linked to expertise is the ability to transfer factual or procedural knowledge from one domain and apply it to another domain. This is of particular value in the sciences and engineering because many phenomena in a given discipline have an analogous phenomenon in another discipline. If a student is able to extend his or her existing domain-specific understanding of the phenomenon to the analogous phenomenon in another domain, a large amount of time and frustration on the part of the student may be saved.

The ability to transfer domain-specific knowledge to another domain is not necessarily a capability that experts in a single domain possess[21]. However, learning experiences can be designed in order to promote transfer of knowledge across domains. Some of the specific approaches to promote transfer that were used in this project are described in sections 3.5.1 and 3.5.2.

## 3.5 Approaches to achieving the goal

Fortunately for those interested in improving education in general, or their own teaching in particular, the education literature does not only contain descriptions of problems or ideal outcomes; rather, it also contains myriad studies that test specific approaches to improving student learning. A few of the ideas from the literature that apply specifically to the present work are presented below. These ideas were used as guiding principles in making decisions about model choice, user interface design, and curriculum design.

### 3.5.1 Modeling and analogy

As described in section 3.4.1, experts are able to separate the important characteristics of a physical system from its peripheral characteristics when solving problems. This type of behavior can be referred to as *modeling*. Modeling involves removing extraneous characteristics of a system and then creating a scheme by which the remaining characteristics can be described mathematically. This is normally what is done in a problem solving or computer simulation context.

Another approach often used in teaching is to substitute a simpler but completely different system for the system of interest. The simpler system is chosen such that there is a one-to-one mapping between the important characteristics of the original system and those of the simpler system. In so doing, an analogy is created between the original system and the simpler system. Choosing an analogic system with which students are already familiar and comfortable makes otherwise unfamiliar concepts accessible.

The use of analogic systems enables concepts to be presented to students in multiple contexts and at a higher level of abstraction than is possible when only the original system is modeled. Presenting material at a higher level of abstraction has been shown to improve students' ability to transfer knowledge to other domains[25].

A number of recent books have examined the issues of modeling and analogy[28, 29, 30] in science teaching. In addition, there are numerous articles in the literature describing analogic systems that have proved useful in teaching common concepts in science and engineering (e.g. [31]).

As described in section 3.4.1, the models used in the simulations developed during this project are all analogic. The actual systems of interest are systems of atoms and molecules. However, instead of directly simulating these systems, analogic models were carefully chosen in order to highlight the concepts of greatest importance. These models are described in detail in chapters 4, 5, and 6.

### 3.5.2 Visualization

The value and importance of visual aids in student learning is a fertile area of current research, as evidenced by the appearance of a few recent books on the topic[32, 33, 34]. The advent and increasing availability of computers has made the creation and distribution of visual aids much faster and cheaper than it had been in the past. As a consequence, custom made visual aids are now much easier to incorporate into curricula. However, guiding principles to be used in designing such visual aids to maximize their didactic potential are still a matter of research.

#### Dynamic motion

One of the major deficiencies of traditional chalkboard lectures and textbooks is the fact that their illustrations are static. Therefore, any dynamic process cannot be properly represented. As a consequence, students are forced to use their imagination in concert with textual descriptions of the system dynamics. For some students this poses no problem; however, the majority of students find this difficult and this impacts their ability to learn concepts effectively.

This project makes use of dynamic visualizations of simulated systems in order to enable students to understand the systems' dynamics. Furthermore, these visualizations are kept simple and only display objects and numerical values when necessary, in an effort to avoid distracting students with irrelevant graphics[35].

#### Multiple representations

One area of research that overlaps with the visualization literature is the field of multiple representations. Research in this field seeks to illuminate how students can more effectively learn when they are presented with multiple different ways of viewing the systems being considered. A clear application is in the field of kinematics, where it might be helpful to students if they could simultaneously view a moving object along with representations of its position, velocity, acceleration, rate of rotation, etc. This use of multiple representations provides students with access to complementary information and, thus, the representations are said to have *complementary roles*[36].

However, multiple representations can be used for more than just displaying complementary information; it can also be used to *constrain interpretation* by presenting one familiar representation along with an unfamiliar representation[37]. In this approach, the more familiar representation is used to help students understand how to interpret the unfamiliar representation.

Finally, multiple representations can be used to *construct deeper understanding*[36] in students, by giving them multiple different perspectives on a concept. This enables them to observe similarities and differences between the different representations and come to a more abstract understanding of the topic. In addition, because of its ability to promote abstract understanding, the use of multiple representations can support the transfer of concepts across domains[25].

In the applets produced by this project, all three uses of multiple representations were employed. Each applet described in chapters 4, 5, 6, and 7 presents both an animated representation of the model itself as well as an auxiliary display that contains a visualization showing information about the model. In the simplest interpretation, these dual representations have complementary roles. However, in chapter 4, the visualization of the system is used to constrain students' understandings of the energy landscape depicted in the auxiliary display. Finally, in the applets described in sections 5.4 and 6.3, multiple different but analogous models are presented side-by-side to help students obtain a deeper, more abstract understanding of the systems.

### 3.5.3 Active learning and guided inquiry

Two approaches to improving education and making it more learner-centered are active learning and guided inquiry. While active learning can take many forms, the unifying trait among its various incarnations is that students are actively engaged in the learning process[38].

In the traditional classroom students sit and absorb information presented by the teacher. In this model, learning is passive. Anyone who has ever been a student knows that passive learning is problematic because of how difficult it is to continually pay attention. Learning cannot occur when students are not paying attention. Therefore, techniques that engage students in the learning process and thereby hold their attention are in a better position to produce real learning.

The applets created by this project represent active learning in that they are interactive. The interactivity of the applets is important because students can move at their own pace, repeat exercises as needed, test out hypotheses, and obtain results that either confirm or reject their hypotheses[25]. The ability to test out hypotheses is important because student learning is enhanced when students invest themselves in a hypothesis prior to observing the result[39]. In addition, when students find that their hypothesis was incorrect, they may be frustrated and attempt to understand where they went wrong. This can have the valuable result that previously unidentified misconceptions can be identified and efforts can be made to rectify them.

Together with the curriculum developed in the project, the applets represent a form of guided or structured inquiry[40]. Students are asked specific questions, which focus their attention on the central ideas to be taught. They attempt to answer these questions by interacting with the model, essentially running simulated experiments. However, they are generally not told what type of outcome to expect and therefore, they are free to experience the fascination of seeing things unfold for themselves.

## 3.6 Other Related Projects

In every age, there is always at least some segment of the population that views technology as the solution to the problem *du jour*. Therefore, as computer technology developed, many researchers and policy makers were interested in the potential applications to education. The application of computers to education began in the late 1960s[41] and continued to gain momentum throughout the 1970s and 1980s. With the advent and wide accessibility of the internet, however, these efforts really took off. As a consequence, there are numerous projects available online that aim to help students learn a multitude of concepts. In fact, there are a number of online educational resources still under active development that cover concepts from Molecular

Science, as described in the sections below.

Whereas the work described in this thesis focuses on using analogic models to teach the fundamental, abstract concepts that underlie Molecular Science, the projects discussed below are primarily aimed at explaining specific phenomena and, as a result, use direct simulation of the systems being investigated. In addition, while these projects all provide some curriculum to accompany the simulations, they differ in how tightly the curriculum is coupled to the simulations.

### 3.6.1 Molecular Workbench

The Molecular Workbench project[42] from the Concord Consortium has grown into a mature, multi-functional simulation and curriculum presentation environment. The curriculum and simulations available from the project website cover a broad range of phenomena, not restricted to Molecular Science. However, as its name suggests, the simulations developed by the project generally involve directly simulating atoms or molecules. While the simulation engine underlying the project can perform many different types of simulations, including classical mechanics, this capability has not been used widely to simulate simple models that represent real chemical systems by analogy. While it would likely have been possible to implement the materials described in this thesis using the Molecular Workbench authoring tools, it was decided to implement things directly ourselves in order to have more fine-grained control over model behavior and presentation.

### 3.6.2 Open Source Physics

The Open Source Physics project[43] is another mature platform for simulation and curriculum dissemination. While its name suggests that it applies only to physics, it does cover selected concepts from Molecular Science under the heading of Thermodynamics and Statistical Mechanics. The name also reveals that its primary focus is on the simulation code. As a result, the project provides numerous simulations of individual phenomena (again, primarily simulating atoms and molecules directly) but does not tie these concepts together into curriculum sequences that are easily navigable on the project website. However, the simulations do make extensive use of multiple representations, providing students with many different data readouts in addition to the animation of the simulated system.

Early in the development of the project described in this thesis, the Open Source Physics code was examined in order to evaluate whether the simulation and curricular goals of the project could be realized using the existing code. However, the code was ultimately not used. This was due, in part, to the unwieldy size and structure of the code, and also because it was not clear that it would be possible to implement the simplifying constraints that are needed to ensure the correct relationship between the simplified model and chemical system it represents.

### 3.6.3 PhET

PhET[44] is another repository of simulations and accompanying curriculum. Like the two presented above, its simulations involve many different physical phenomena and cover diverse topics from chemistry, biology, physics, Earth science and mathematics. While many simulations directly simulate atoms or molecules, it also makes more extensive use of analogy. In fact, one simulation available on the site is quite similar to that presented in chapter 5. However, the PhET simulation and the model described in chapter 5 use substantially different approaches. In addition, the model discussed in chapter 5 is extended to illustrate more advanced concepts. Finally, while PhET simulations are open source, like Open Source Physics, they provide no authoring tools or extensibility options that do not require directly editing the source code.

### 3.6.4 Virtual Molecular Dynamics Laboratory

The Virtual Molecular Dynamics Laboratory[45], developed in the Polymer Science department at Boston University, as its name indicates, uses molecular dynamics simulations to illustrate concepts at very short length scales and time scales. While the website contains a few Java applets and curricular materials, the main project materials must be downloaded and run locally. A new version of the software is due to be released soon and promises to enable some very interesting simulations. However, the focus remains on direct simulation of atoms and molecules.

## 3.7 Summary and Conclusion

This chapter presented a brief review of the concepts from the education literature that apply to the project described in this thesis. The operative learning theory was reviewed, along with literature that describes some of the difficulties with science education. This was followed by discussions of the goals of science education and approaches that can be taken in order to reach those goals. These approaches were used extensively in guiding the decision-making process as project materials were designed and completed.

# Chapter 4

# Introducing the Energy Landscape: the Cardboard Box Model

## 4.1 Introduction

As discussed in chapters 1 and 2, the energy landscape concept is the focus of the simulations and curriculum developed by this project. The purpose of the simulation discussed in this chapter is to introduce students to the ideas of energy states and the energy landscape by using a model that they can relate to their everyday lives: a cardboard box. Figure 4-1 shows the concept road map, introduced in section 2.2, with a highlighted region that covers the concepts addressed by the simulations presented in this chapter.

The model, controls, and activities described in this chapter were designed to help students learn by enabling them to explore the concepts interactively. This chapter includes descriptions of the model itself, the applet's user interface, control that students have over the model, and specific instructional goals of the curriculum along with sample activities for students intended to address those instructional goals.

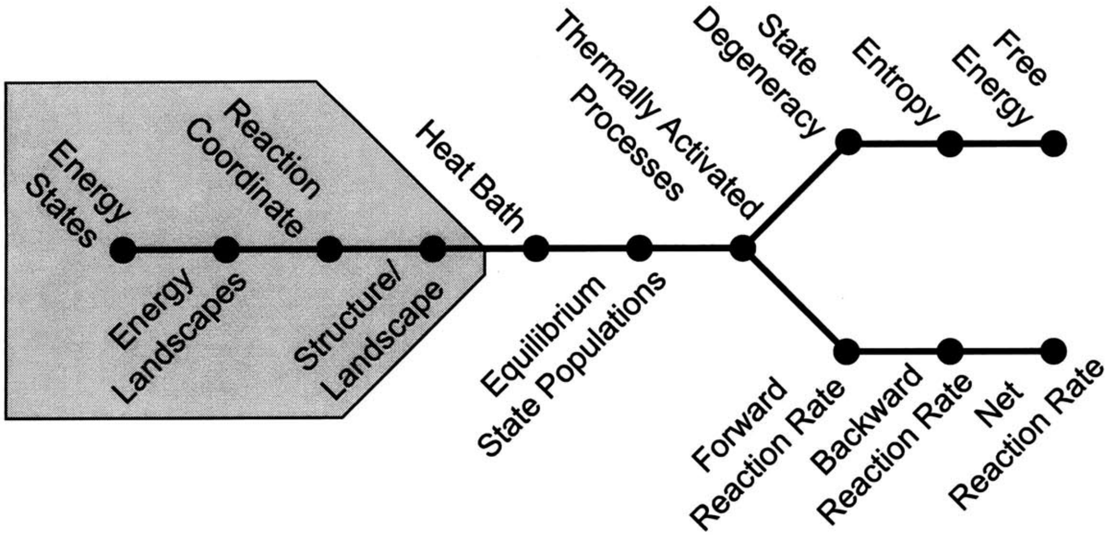


Figure 4-1: The concept road map with the concepts addressed in this chapter highlighted

## 4.2 Description of the model

One of the principles used in guiding decisions made by the group was to always choose the simplest possible model that still exhibits the desired behavior. In addition, if possible, the model should be identical or similar to something that students have interacted with in the real world. In illustrating the energy landscape it was necessary to choose a model that includes a metastable state and a stable state separated by an activated state. In lectures for the course that he teaches at MIT, Donald Sadoway had been using a cardboard box to illustrate the concept of states and the necessity of passing through the activated state in order to transition from metastable to stable or vice versa. Because of its simplicity, its suitable analogic properties, and the fact that it is familiar to all students, the cardboard box was chosen as the model for this simulation. Since the goal of this simulation was to introduce the energy landscape in two dimensions, as presented in section 2.3, it was decided to simulate the box in two dimensions also.

### 4.2.1 What is modeled?

The different possible states of the cardboard box correspond to the orientations in which it can be at rest. As long as the box's width and height are not equal, the box can be characterized as either standing up or lying down. The energy corresponding to each of those states comes from gravitational potential energy.

From introductory physics it is known that the potential energy of an object due to gravity is given by:

$$E_{pot} = mgh_{cm} \tag{4.1}$$

where $m$ is the mass of the object, $g$ is the acceleration of gravity, and $h_{cm}$ is the height of the object's center of mass above some reference point. So, when the box is standing up and its center of mass is high, the box has more gravitational potential energy than when it is lying down with a low center of mass. Furthermore, when the box is up on its corner between standing and lying, its center of mass is at a maximum.

Figure 4-2 shows the cardboard box's three zero-force states in connection with the corresponding parts of the energy landscape. In addition, the three states of 1,2-dichloroethene are depicted to show how the box can represent a real chemical system. Finally, beneath the box in the activated state is an angle represented by $\theta$. This illustrates that the angle formed between the bottom of the box and the surface is used as the reaction coordinate in the energy landscape plot. When the box is standing up, $\theta = 0$ and when the box is lying down, $\theta = \pi/2$ radians.

By using the controls discussed in section 4.3.1, the box can be given "kicks". If the box is given a powerful enough kick, it will reach the activated state and transition to the box's other resting state. However, if the kick is too weak, it will stand up on its corner only partially and eventually fall back to its pre-kick state. This type of behavior is understood by students intuitively, though generally not in the formal way that is necessary for useful scientific understanding. The curriculum and exercises discussed in subsequent sections aim to leverage students' intuitive understanding of these behaviors in order that they may come to an intuitive understanding of the

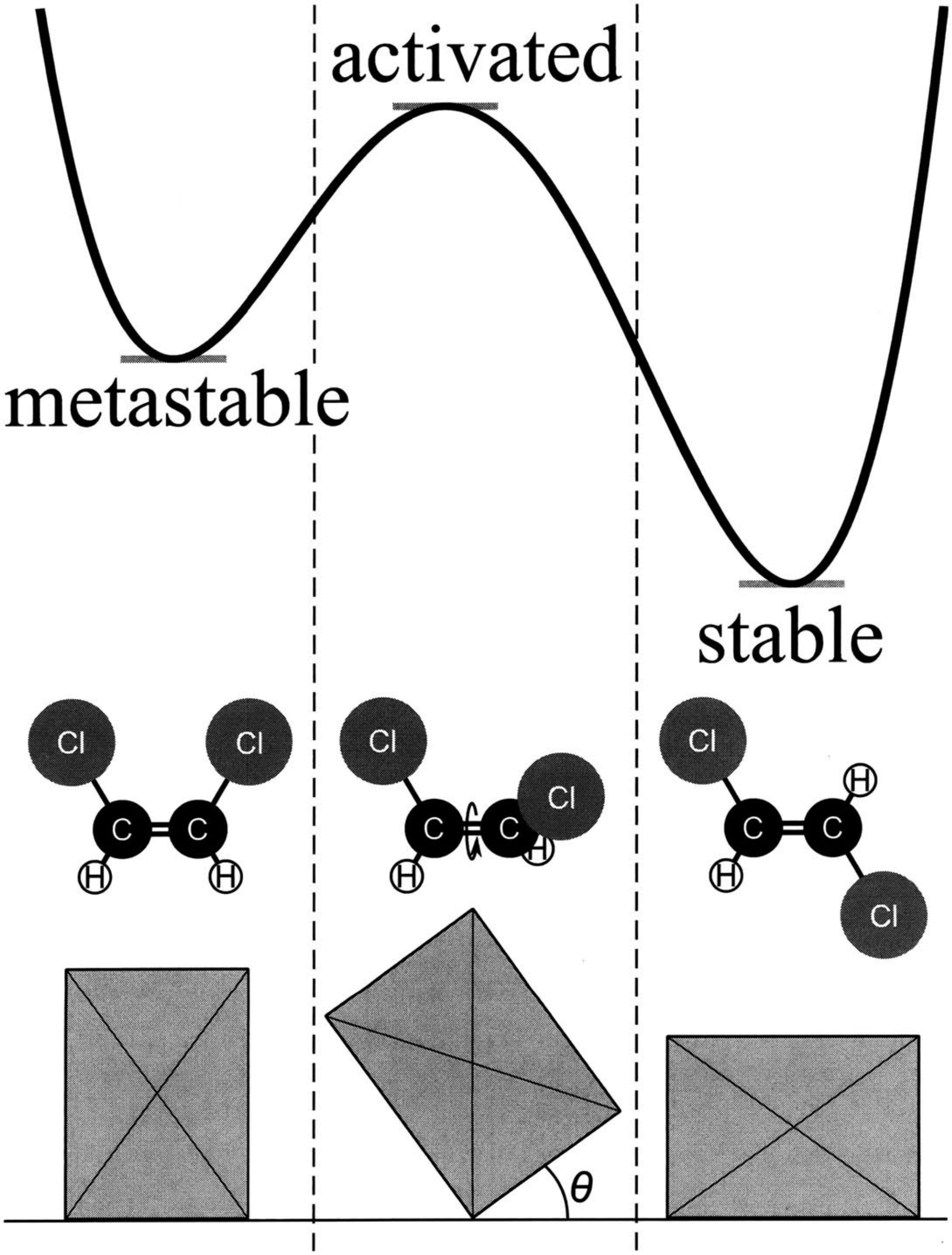


Figure 4-2: Correspondence of box states to those of 1,2-dichloroethene and the schematic energy landscape presented in chapter 2

energy landscape concept.

### 4.2.2 What is not modeled?

While students do understand the behavior of cardboard boxes intuitively, it was necessary to impose several restrictions on the model. The first restriction is that the box must always be in contact with the surface beneath it. That is, it is impossible to give the box a kick such that it leaves the surface and flips through the air.

The second restriction is that the box can only rotate about one corner. There are a couple of practical consequences to this. If one were to kick a real box, even if it did not leave the ground, it might tumble end over end a few times. In this model that behavior is impossible. The box pivots about one corner and can only rotate 90 degrees about that corner. Therefore, if the box has been kicked from one state to another, it is not possible to kick it further in that same direction since this would require rotation about another corner; rather, it must be kicked back to its original state.

These restrictions obviously result in a reduction in the perceived realism of the model. However, they are necessary to keep the model meaningful and simple. If the box were allowed to become airborne, the applicability of the energy landscape would be destroyed. Once the box becomes airborne, its center of mass could take any trajectory. This is unacceptable because the energy landscape depends upon the box's center of mass having a single, consistent trajectory.

The second restriction is not entirely necessary but was imposed in order to make the visualizations simpler and clearer. While figure 4-2 depicts an aperiodic energy landscape, in reality, the cardboard box's landscape is periodic, as can be seen in figure 4-3. Since the box could be rolled end over end for eternity, the box's actual energy landscape is never-ending. In an effort to represent the box's energy landscape in a way that most strongly corresponds to the schematic aperiodic landscape which is in wide use, it was decided to truncate the box's energy landscape and restrict the box's movement to the gray area in figure 4-3.

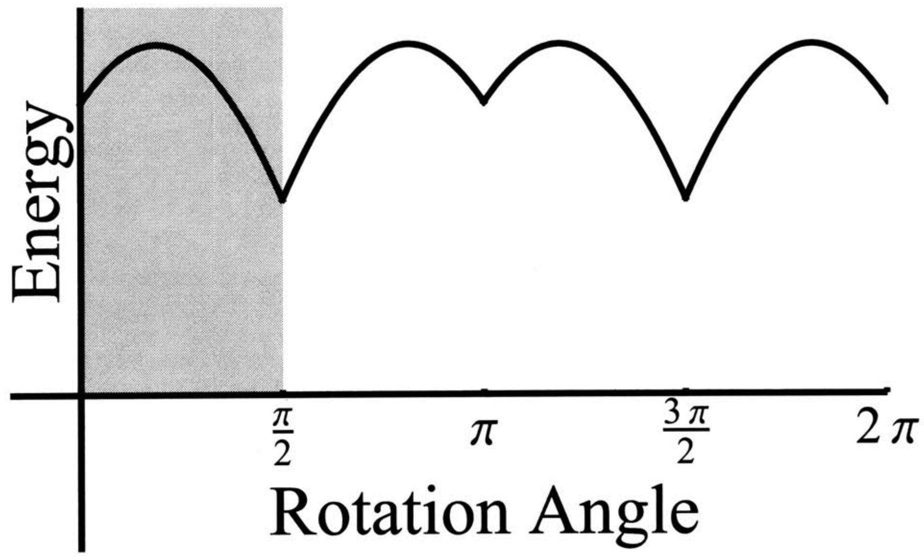
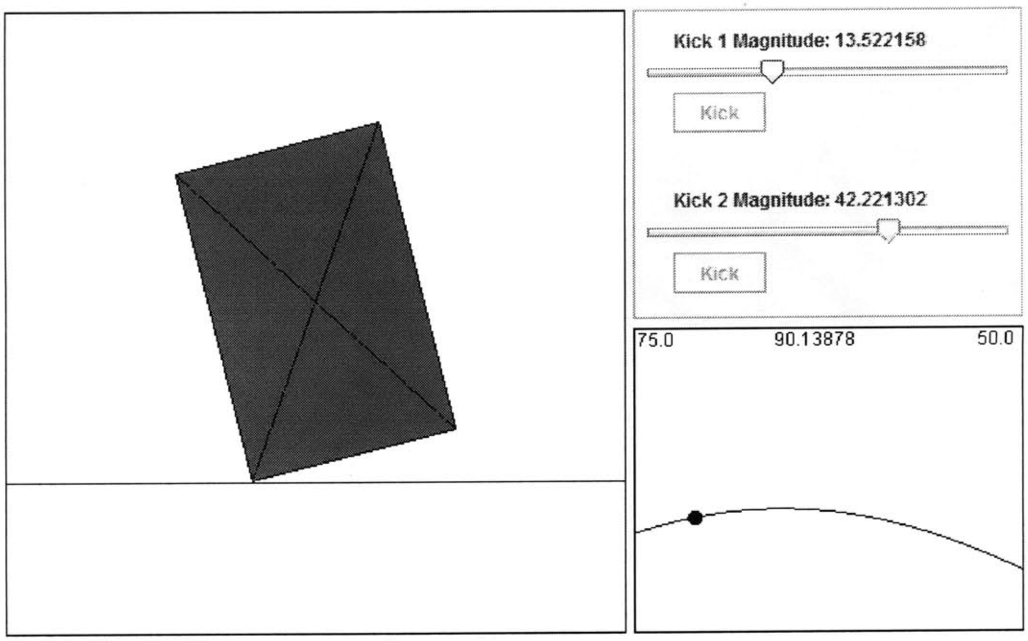


Figure 4-3: The full energy landscape of a cardboard box as it is rolled through $2\pi$ radians. The gray region represents the area to which the box's motion is restricted in the simulation.

## 4.3 Visualization and user interface

As discussed in section 1.4.4, the simulations created for this project were written in Java and made available to students as Java applets. These applets were embedded in web pages along with suggested activities and questions. A screen capture of an applet illustrating the cardboard box model is presented in figure 4-4.

The applet's user interface includes a number of notable elements. These elements are shared across all the applets produced for this project. First, there is a set of controls which can be used to adjust properties of the model or cause the model to do something. Second, there is the main visualization window. This is where the graphical visualization of the model is presented. The visualization responds instantaneously to changes in the model as a result of user input through the controls. Finally, at the bottom right of the applet is the auxiliary data display. In general, this window provides information about the current state of the model or contains some alternate means of viewing the model. In this particular applet, it shows the energy landscape that corresponds to the box depicted in the main visualization window. Each of these user interface components are discussed in the sections below.


Kick 1 Magnitude: 13.522158

Kick 2 Magnitude: 42.221302

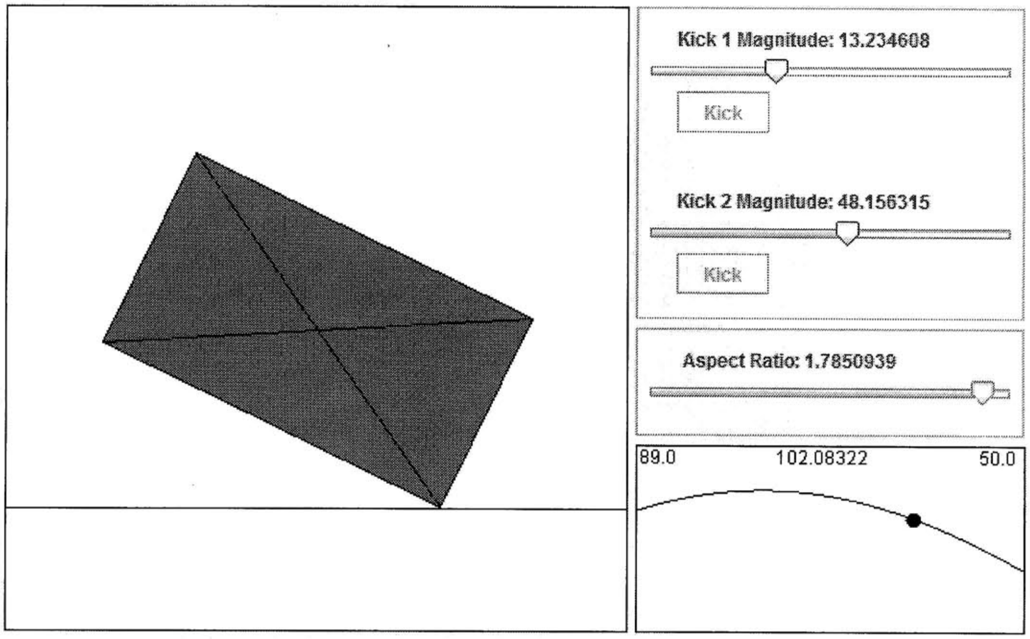
Figure 4-4: Screen capture of the applet

### 4.3.1 Controls

The controls available to the user in this applet are shown in figures 4-4 and 4-5. In both variations of the applet addressed in this chapter the user has access to two sliders, which are used to set the magnitude of the kick to be given to the box. Below each slider is a button labeled "Kick" that actually gives the box a kick of the magnitude selected in the corresponding slider. The numbers above each slider represent the energy of the kick and use the same scale as the numbers that appear in the auxiliary data display, discussed in section 4.3.3.

The top slider governs the magnitude of a kick from the $\theta = 0$ position, so, when the box is in the $\theta = 0$ position, the top kick button is enabled, while the bottom kick button is disabled. When the box is in the $\theta = \pi/2$ position, the bottom kick button is enabled, while the top one is disabled. Finally, when the box is in motion, kicks are not allowed, so both kick buttons are disabled. These disabled buttons are often described as "grayed out", because their text and border are colored gray, rather than black.

A variation of this applet, shown in figure 4-5, includes an additional slider that


Kick 1 Magnitude: 13.234608

Kick 2 Magnitude: 48.156315

Aspect Ratio: 1.7850939

Figure 4-5: Screen capture of the applet with the aspect ratio slider present

controls the box's aspect ratio. When this slider is not present, the box's aspect ratio defaults to 3:2. That is, the box is 1.5 times as high as it is wide. However, by dragging the aspect ratio slider around, the user can change the box's dimensions. The length of the box's base is kept constant while its height is changed in accordance with the slider.

The restrictions placed on the controls, such as the range of possible values the sliders can take and the disabling of buttons under certain conditions are necessary in order to guide students to observe phenomena that support the learning objectives of this applet. In addition, restricting students' options for interacting with the model keeps the activities simple and focused.

### 4.3.2 Main visualization window

The main visualization window in this applet simply contains a depiction of the two dimensional cardboard box model that is simulated internally. It rests on a surface and can be given kicks, which can cause it to change its state. Diagonal lines are drawn across its face to enable easier visual tracking of its rotation, as well as to mark the location of its center of mass at the lines' intersection.

Although section 4.2.2 indicates that the box pivots around one corner, the appearance of the model's motion is not necessarily what one might expect. If the box were allowed to pivot around a point that is fixed in the visualization window, either a larger visualization window or a smaller box would be needed in order to ensure that the entire box could be seen regardless of box orientation. Therefore, it was decided that the box should remain horizontally centered in the visualization window at all times.

This centering can be interpreted in a number of ways:

1. The box's center of mass is constrained to a particular x-coordinate and when the box is kicked, its corner slips across the surface beneath it without any friction.

2. The box actually does pivot around a fixed point on the surface but the box is being watched through a camera that moves in such a way that the box's center of mass stays centered in the viewing window.

3. The box actually does pivot around a fixed point on the surface, but as the box is kicked, the surface is moved such that the box's x-coordinate remains constant.

Internally, the model is simulated as described in interpretation 1 but any of these approaches would produce the same results if done properly.

When a student clicks a "Kick" button, mentioned in section 4.3.1, the box is given an angular velocity corresponding to the value of the appropriate slider. Because gravity is a conservative force and the box is sliding on a frictionless surface, the box's initial kinetic energy is converted into gravitational potential energy as the box turns. If the box was given enough rotational kinetic energy by the kick to surmount the barrier in gravitational potential energy, the box will transition to a new state. Otherwise, it will fall back down to its initial state.

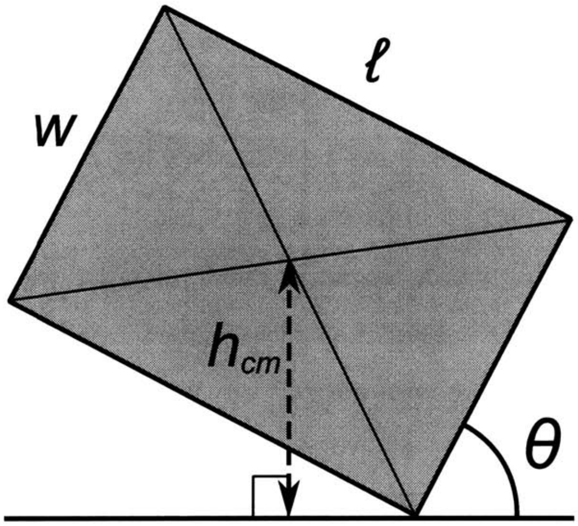


Figure 4-6: The cardboard box model with its dimensions labeled

### 4.3.3 Auxiliary data display

In this applet the auxiliary data display shows the box's energy landscape, as depicted in the gray region of figure 4-3. The vertical axis represents energy and the horizontal axis is the reaction coordinate, which, in this case, is the angle formed between the box's base and the surface beneath it, as depicted in figure 4-6.

One of the most important functions of the auxiliary data display in this applet is to visually connect the box model with the energy landscape. This is done by representing the box's current position on the energy landscape plot with a black dot, as can be seen in figures 4-4 and 4-5. As the box rotates, the dot moves, showing the correspondence between the box and the energy landscape in real-time.

With the cardboard box's dimensions defined as labeled in figure 4-6, the height of the box's center of mass is given by the equation:

$$h_{cm} = \frac{\ell}{2}\cos\theta + \frac{w}{2}\sin\theta \tag{4.2}$$

This equation is plotted in the auxiliary display window and in applets that provide the aspect ratio slider, this plot is updated as the aspect ratio is changed. As stated in section 4.3.1, the box's base is kept constant. So, according to the labeling in figure 4-6, when a student adjusts the aspect ratio slider, $w$ is kept constant while $\ell$

is adjusted.

At the top of the auxiliary data display are a set of numbers. These numbers represent the height of the box's center of mass, measured in pixels, above the surface beneath it for each of the key states the box can be in. These heights are used as a proxy for the actual gravitational potential energy since the box's mass is not addressed anywhere and the acceleration due to gravity is taken to be a constant.

By subtracting the energy of the energy barrier from that of the metastable or stable states, it is possible to calculate the energy needed for the system to surmount the energy barrier and transition from one state to the other. Adjusting the kick sliders discussed in section 4.3.1 such that the slider has the value that was just calculated, it is possible to easily give the box a kick that succeeds in just barely causing a state transition.

## 4.4 Sample curricular activities

Because this applet lays the groundwork for all the concepts that come later, the instructional goals were common to all the classes in which it was presented. The underlying goal was getting students to see the points of correspondence between the visualized model of the cardboard box and the plotted energy landscape. The entire curricula used by students are presented in sections A.1 and B.1.

First, the applet without the aspect ratio slider, as pictured in figure 4-4 was presented. Students were asked to perform the following exercises:

1. Determine the minimum kick magnitude to get the box to transition from the metastable state to the stable state and from the stable state to the metastable state.

2. Observe the relationship between the black dot on the energy landscape and the position of the box in the main visualization window when the box is kicked.

3. Compare the minimum kick magnitudes determined in exercise 1 with the numbers at the top of the energy landscape window. They should note that the num-

bers they found by trial and error correspond to $E_{a,m}$ and $E_{a,s}$, as illustrated in figure 2-8.

4. Identify and describe the box's metastable and stable states, as well as the activated state.

5. Identify the physical significance of the reaction coordinate.

After this set of exercises with the applet lacking the aspect ratio slider, students were presented with the applet including the aspect ratio slider and were asked to complete the following exercises:

1. Move the aspect ratio slider and determine what it controls.

2. If the starting configuration of the system is called state 1, determine the range of aspect ratios for which $E_2 > E_1$, $E_2 = E_1$, and $E_2 < E_1$.

3. Given that a reaction's driving force is $|E_2 - E_1| = \Delta E$, determine the aspect ratio that maximizes the driving force.

4. Find the aspect ratio for which the box is easiest to knock over; i.e. where $E_a$ is minimized.

These exercises give students and opportunity to explore the energy landscape concept using a concrete example. By carrying out the suggested activities, students are exposed to the important features of the energy landscape concept and gain an understanding of the correspondence between the energy landscape and the cardboard box model.

## 4.5 Summary and conclusion

By choosing a simple model and further imposing meaningful restrictions on its behavior, it was possible to illustrate abstract concepts using objects with which students are already familiar. If these abstract concepts can be learned effectively at the introductory level, students will be prepared to learn move advanced concepts both within the context of this project's curriculum but also in general. The effectiveness of this and other applets in conveying the intended concepts will be discussed in chapter 8.

# Chapter 5

# Exploring State Populations: The Platform Model

## 5.1 Introduction

Having laid the groundwork for the energy landscape concept with the cardboard box model presented in chapter 4, this chapter uses a different model to explore concepts that follow from the energy landscape. In addition, the new model helps to reinforce the energy landscape concept itself by simplifying the picture even further.

As highlighted in the gray region in figure 5-1, the simulation presented in this chapter focuses on helping students understand the heat bath concept (section 2.7) as well as introducing how the energy landscape can be used to calculate equilibrium state populations (section 2.4) using the following equation:

$$\frac{P_2}{P_1} = \exp\left(-\frac{\Delta E}{RT}\right) \tag{5.1}$$

While this equation is widely presented in textbooks and lectures, there is a big difference between students being able to use the equation and having an intuitive understanding of the equation. The simulation and exercises presented in this chapter give students the opportunity to experience these concepts visually and interactively.

While the heat bath concept does not follow from the energy landscape concept,

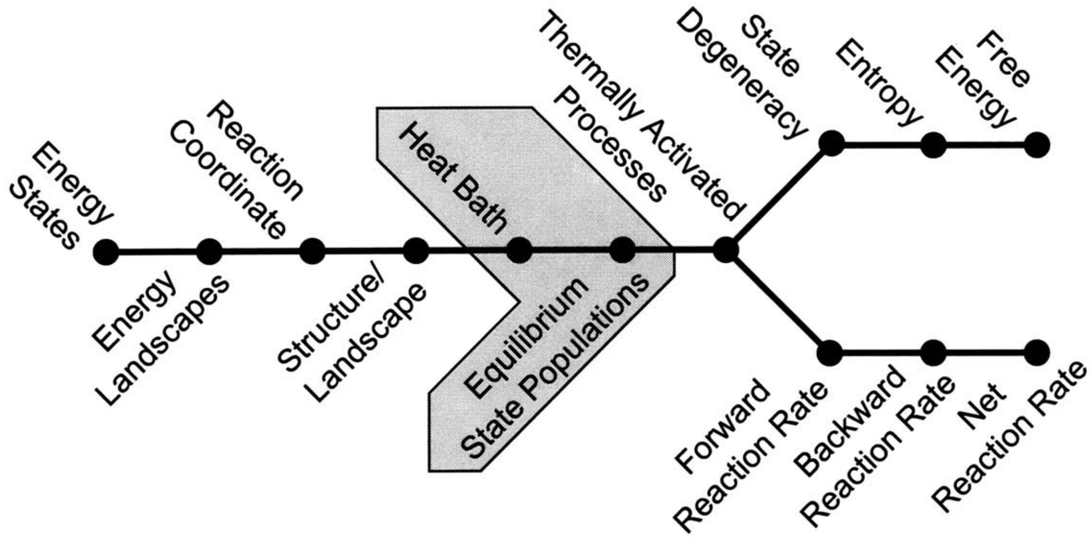


Figure 5-1: The concept road map with the concepts addressed in this chapter highlighted

it must be introduced because of its importance in regulating temperature. Without temperature regulation, it would be impossible to adequately simulate and discuss equilibrium state populations, which are described in this chapter. Descriptions of thermally activated processes, which are presented in chapter 7, also rely on a well-defined system temperature. The importance of temperature and the heat bath are discussed in section 2.7.

The structure of this chapter parallels that of chapter 4 in that it describes the platform model itself, the applet's user interface, the control that students have over the model, and sample activities for students, which address the pertinent instructional goals. Because the development of this model was more difficult than the cardboard box model, this chapter includes more discussion of the development process and ways in which the model was refined during its development.

## 5.2 Description of the model

The model used in the simulations discussed in this chapter consists of a number of balls on top of a set of platforms at different heights, as depicted in figure 5-2.

While it is possible to initialize the platforms in a variety of configurations (discussed in section 5.3.4), the configuration in figure 5-2 provides the clearest analogy between this model and the familiar energy landscape diagram. As can be seen from the figure, each platform corresponds to one of the labeled states in the energy landscape diagram. The platform model simplifies the energy landscape diagram further by removing the sloping regions between well-defined states in favor of flat platforms. For future discussion it is convenient to take the bottom of the figure, which will be called the "floor", as the reference point for ball height.

### 5.2.1 What is modeled?

While the platforms provide the analogic connection with the energy landscape, they are not illustrative of anything on their own. Rather, it is only when the balls are added that the model becomes interesting.

First, it is important to note that these balls are *not* atoms. Rather, they are essentially the same as the black dot in the auxiliary data display discussed in section 4.3.3. Instead of representing anything in and of themselves, they represent the position on a simplified energy landscape of some unseen and unspecified system. However, because this notion is very abstract, it is not explicitly promoted in the curriculum. Instead, the model is described as consisting of a set of platforms which resemble the energy landscape diagrams seen previously in the curriculum. The balls are presented as real balls that are dumped onto the set of platforms and interact with the platforms in interesting ways.

The platforms are modeled so as to simulate contact with a heat bath at a given temperature. As discussed in section 2.7, the heat bath functions by giving the balls kicks with magnitudes taken from the Maxwell-Boltzmann distribution. In practice, this means that each time a ball comes into contact with a platform, its incident velocity is discarded and it is given a new velocity. Since the incident velocity and the reassigned velocity are not identical or even correlated, the balls cannot be said to "bounce" on the platforms even though this is often how it appears. To explain the effect of the heat bath on the balls in terms that are familiar to students, the

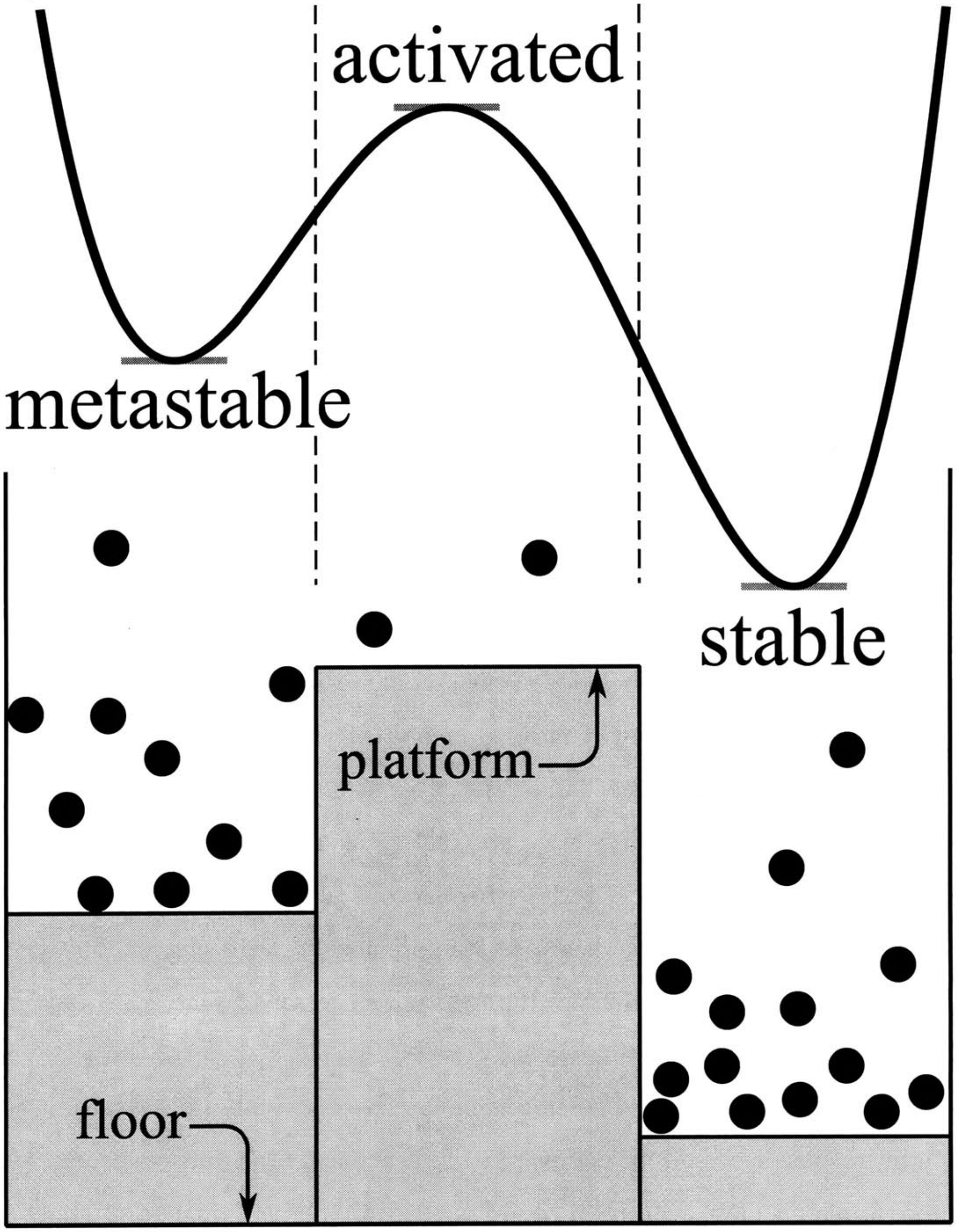


Figure 5-2: The platform model beneath the familiar two-dimensional energy landscape

curriculum introduces the idea that the platforms are vibrating and therefore bump the balls around.

The balls are subject to the force of gravity and therefore fall back down onto one of the platforms after each kick. The total energy of the ball is the sum of the gravitational potential energy and the kinetic energy, as shown in equation 5.2.

$$E_{tot} = E_{pot} + E_{kin} = mgh_{cm} + \frac{1}{2}mv^2 \tag{5.2}$$

where $m$ is the mass of the ball, $g$ is the acceleration due to gravity, and $v$ is the magnitude of the ball's velocity. $h_{cm}$ is the height of the ball's center of mass above a reference point common to all balls, regardless of which platform they are over.

In figure 5-2 the vertical axis can be interpreted simply as representing a spatial coordinate, specifically height. However, because of the connection between height and gravitational potential energy shown in equation 5.2, the vertical axis also provides a measure of the ball's gravitational potential energy at any instant in time. In addition, when the ball is at the apex of its trajectory, the ball's height also represents its total energy.[1]

Because the platform view of the energy landscape is constructed by compressing the sloping inter-state regions until they form vertical lines, the horizontal axis in figure 5-2 can be interpreted as a quantized version of the reaction coordinate from the traditional two-dimensional energy landscape diagram. For example, in the platform model in figure 5-2, the reaction coordinate can take only three values, one corresponding to each platform. While the quantized nature of the platform model might suggest adopting a dynamics scheme that allows balls to occupy only three distinct positions on the horizontal axis, such a scheme would appear unfamiliar to students and consequently impede their understanding.

So, while the reaction coordinate is quantized, the horizontal axis can be simultaneously interpreted as a simple spatial axis. This interpretation allows for the balls to take on natural-looking trajectories that are familiar to students. In this hybrid

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[1] The kinetic energy due to motion along the x-axis is ignored, as explained later.

scheme, the range of horizontal spatial coordinates within the bounds of a given platform map onto a single value for the reaction coordinate that corresponds to that platform's state. While this may seem complicated to explain, it is intuitive to users that the entire width of a platform corresponds to a single state.

Because the primary meaning of the horizontal axis is as the reaction coordinate and because natural-looking motion along this axis is provided mainly for its visual appeal, the kinetic energy of the balls due to motion along the horizontal axis is not factored into energy calculations. In fact, Maxwell-Boltzmann distribution is used only in assigning each ball's vertical velocity. The horizontal velocity is chosen from a uniform distribution. Because the Maxwell-Boltzmann distribution is only used in assigning one component of the ball's velocity, the one-dimensional Maxwell-Boltzmann distribution for speed is used.

### 5.2.2 What is not modeled?

The model as described above contains a few restrictions and simplifying modifications. First and foremost, the balls do not interact with one another. This choice was made initially in order to ensure that the simulations ran acceptably quickly on a broad range of user hardware. Ball interactions are computationally expensive and older computers might not be capable of running the simulations at an acceptable speed if the balls interacted with one another. However, subsequent experience with systems in which balls do interact has shown that ball interaction dynamics is very interesting, even mesmerizing. Because ball interaction is not the *raison d'être* of this simulation, it is important that balls *not* interact, lest it distract students from the simulation's main purpose.[2]

The areas in the system that are in contact with the heat bath are limited to the tops of the platforms. The platforms' sides as well as the walls of the simulation window are not in contact with the heat bath. When balls collide with any vertical

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[2] The system containing many non-interacting balls could also be interpreted as an ensemble of one ball systems superimposed on top of one another. This view was not presented to students in the curriculum but may be of interest to instructors who have introduced the concept of ensembles in their courses.

surface, their horizontal velocity is reversed and they appear to simply bounce off the wall. Limiting the heat bath's contact with the balls to the horizontal surfaces prevents the appearance of visually jarring ball trajectories and it limits the number of places to which students need to pay attention in order to observe the system's interesting behavior.

Although the cell in which the simulation occurs has walls and a floor, it has no ceiling. Very high energy balls are allowed to travel upward indefinitely and, despite passing out of the viewing window, if they are given sufficient time, they will return to view. At low temperatures, this issue does not come into play. However, at high temperatures, many balls might hit the ceiling if there were one. Furthermore, if a ceiling were present, it would invariably cut short the trajectory of some balls, which would appear confusing to users.

### 5.2.3 Model refinements

During the development of the model a number of unexpected issues cropped up, which had to be addressed. These issues are subtle and, had they not been addressed, the ability of the model to demonstrate qualitative behavior would not have been compromised. However, in the interest of making the simulations as useful as possible for as many possible applications, the simulations should also provide quantitative results in line with the equations presented in introductory texts and curriculum. If the simulations produce accurate statistics, then they could be used in a broad range of activities beyond those included in the curriculum developed by this project. The issues discussed below caused inaccuracies in the population statistics and the temperature regulation.

#### Time of flight

As discussed in section 5.2.1, the balls in this model have their velocities reassigned each time they come into contact with a platform. The one-dimensional Maxwell-Boltzmann speed distribution used in assigning the balls' velocity in the vertical

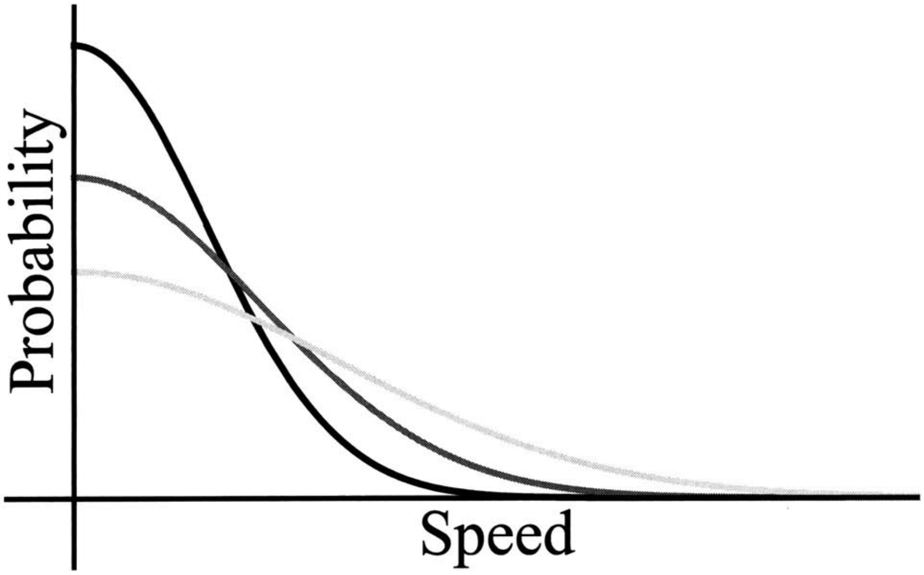


Figure 5-3: Plot of one-dimensional Maxwell-Boltzmann distribution for speed at three different temperatures, where lighter gray indicates higher temperature.

direction is presented in figure 5-3. From this figure it is clear that, when they impact the platform, most balls are given relatively low speeds. However, some fraction of balls are given relatively high speeds, especially at higher temperatures.

Speeds are assigned from the Maxwell-Boltzmann distribution in order that the balls in the system would exhibit a Maxwell-Boltzmann distribution of speeds. However, because of the speed dependence of the so-called "time of flight", the actual distribution of ball speeds in the system does not fit the Maxwell-Boltzmann distribution.

Imagine that all the balls in the system came into contact with a platform at the same time and were all given vertical speeds from the Maxwell-Boltzmann distribution. Because low-speed balls fall back onto a platform more quickly than high-speed balls, the low-speed balls would get new velocities from the Maxwell-Boltzmann distribution before the high-speed ones. However, some fraction of these formerly low-speed balls will be given high speeds from the distribution while the initial set of high-speed balls are still in flight. This results in an over-representation of high-speed balls.

This problem can be solved by adjusting the Maxwell-Boltzmann distribution, taking into account the variation in a ball's time of flight as a function of its speed.

A ball's time of flight is given by the equation:

$$t = \frac{2v_y}{g} \tag{5.3}$$

where $t$ is the time of flight, $v_y$ is the vertical component of the velocity at takeoff, and $g$ is the acceleration due to gravity. By adjusting the Maxwell-Boltzmann distribution to account for the speed dependence of a ball's time of flight, the Maxwell-Boltzmann speed distribution is exhibited by the balls in the system.

This is an important correction because, without it, the actual temperature of a system would be higher than the user-specified temperature of the heat bath. This could result in unexplained discrepancies between measured properties, such as equilibrium state population or reaction rates, and those calculated using the heat bath's specified temperature.

### Excluded volume

When this simulation was first designed, efforts were made to make it visually appealing. In particular, the interactions between the balls and platforms were programmed such that balls would appear to bounce off of the platforms and walls cleanly without ever appearing to sink in. Unfortunately, this approach causes systematic errors in the platform population statistics.

In order to obtain population statistics consistent with equation 5.1 using this model, it is necessary that the platforms all have the same width. As a consequence, the simulations were configured with three platforms of equal width. However, it was found that, depending on the topology of the set of platforms, the time-averaged population statistics were not correct. This is due to an "excluded volume" effect. This effect is illustrated in figure 5-4, which features an over-sized semi-transparent ball in order to make the effect more obvious.

If a ball's coordinates are taken to be at its center and it has a non-zero radius, then there are areas of the system that can never contain a ball's coordinates. These areas are highlighted in figure 5-4. The presence of these areas changes the effective

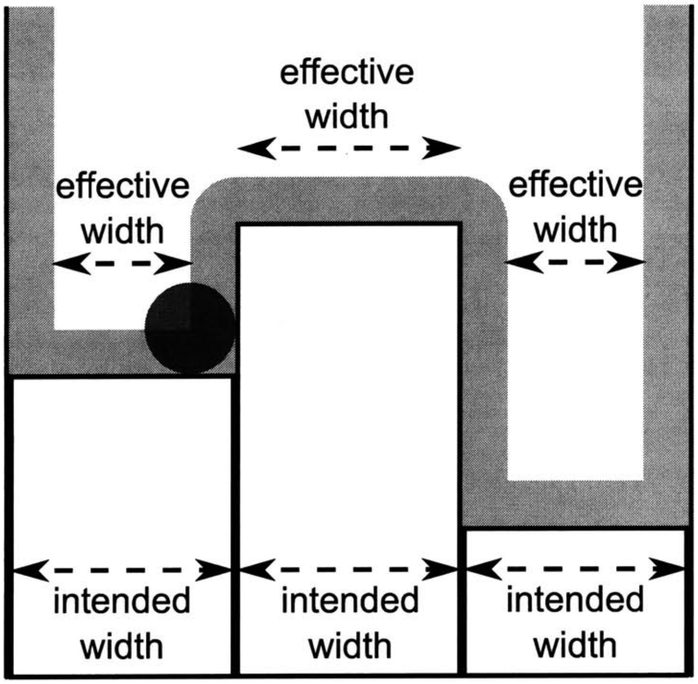


Figure 5-4: Schematic diagram of the platform model highlighting regions of excluded volume in gray

width of some platforms and makes it different from its intended or even its perceived width. As can be seen in the figure, the effective width of the middle platform is greater than that of the other two platforms. Because the two lower platforms are effectively narrower than the middle platform, their equilibrium populations will be lower than those calculated using equation 5.1.

This problem was solved by modeling the balls as 0-dimensional points internally but rendering them as balls with a non-zero radius. This has the unsavory result that the balls appear to sink into the platforms and walls a small distance when they hit them. While this is not ideal, it should not cause any confusion and ensures that the population statistics obtained from the model are in line with equation 2.1.

In subsequent revisions of the software, the ability to choose the way in which balls are rendered may be added as a customizable field like those described in section 5.3.4. This would enable those who are not interested in quantitative activities to obtain a nicer visual experience, while those who value quantitative accuracy could choose that at the expense of visual appearance.

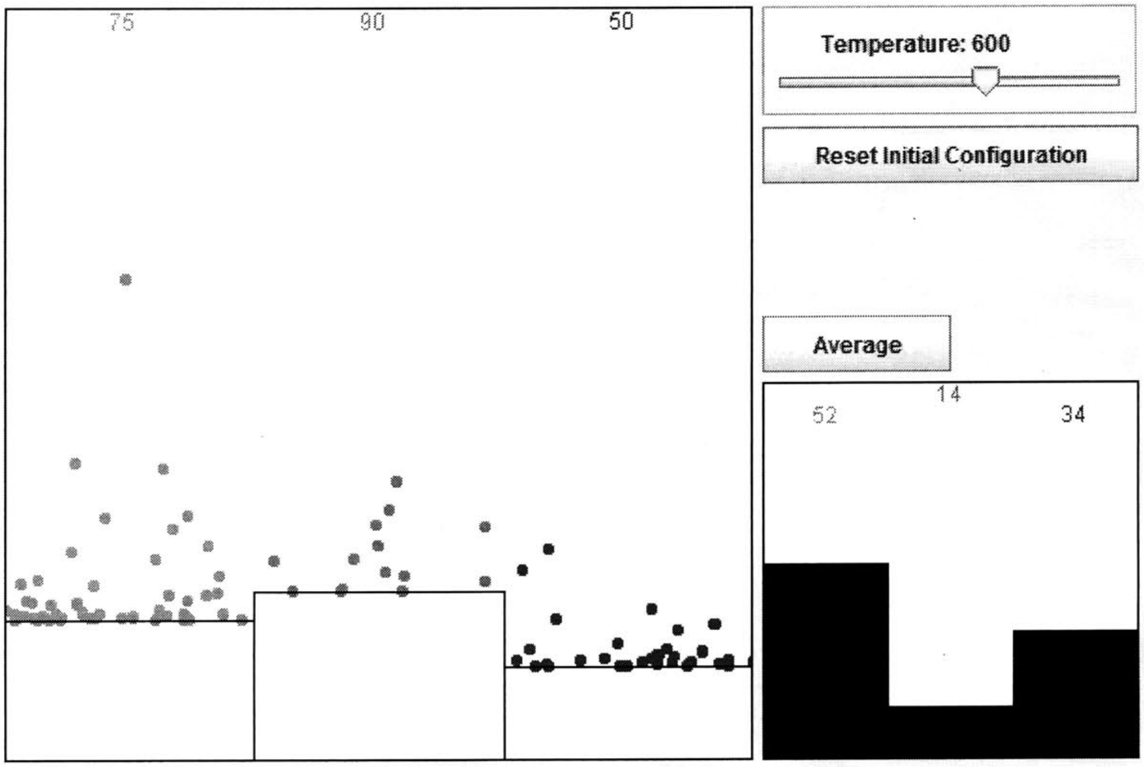

Temperature: 600

Figure 5-5: An applet depicting the platforms model

## 5.3 Visualization and user interface

The exact appearance of the applets presented to students varies, depending on the goals of the exercise. However, figure 5-5 presents a representative example. The general layout of the applet is the same as that presented in chapter 4. It contains a large main visualization window at left, an auxiliary data display at bottom right, and controls at top right. These components will be discussed in detail in the following sections.

### 5.3.1 Controls

Applets simulating the platforms model for the purpose of examining equilibrium state populations or understanding the heat bath (as opposed to those presented in chapter 7) have a number of controls. Clearly visible in figure 5-5 is a slider and two buttons.

The slider is used to set the temperature of the heat bath to a value between 0 and 1000. At 0, the motion of the balls effectively stops. It does not entirely stop because the balls' horizontal velocities are chosen from a uniform distribution that is independent of temperature. At 1000, many balls appear to shoot out of the top of the visualization window, but they drop back into the window after their trajectories peak outside of the window. The absolute numbers for the temperature are not significant but are provided in order to facilitate activities that call for a particular temperature to be set.

The button marked "Reset Initial Configuration" does as its label suggests and returns the system to the state in which it was started. What that initial state is depends upon the goals of the exercise. As described in section 5.3.4, the initial state can be customized such that each platform can have a specified number of balls placed over it. In simulations focused on kinetics, generally all balls are placed in the metastable state; in simulations focused on equilibrium properties, the balls might be evenly spread across the platforms.

The button marked "Average" applies to the auxiliary data display and affects whether real-time data or time-averaged data is displayed. Averaging begins when the button is pressed, not from the beginning of the simulation. This behavior is advantageous because many systems go through a transient period during which the populations change quite quickly and might skew the time-averaged population figures. By giving students the ability to start averaging after the system appears to have reached equilibrium, these transient effects can be minimized.

In addition to the visible sliders and buttons, users may have additional controls depending on whether they are allowed in the system configuration parameters described in section 5.3.4. These additional controls enable direct editing of the platforms by either changing platform heights or grouping two or more platforms together to form a single platform.

If it is allowed, users may adjust platform heights by placing the mouse cursor near the top of chosen platform. The cursor changes from the normal arrow into a hand with an extended index finger. The user can then move the platform up or down by holding down the left mouse button and dragging the mouse up or down. When the user releases the left mouse button, the platform is left at its current height. The ability to adjust platform heights enables students to explore how changing $\Delta E$ or changing $E_a$ affects the system.

The ability to group platforms together is not of tremendous utility in examining equilibrium state populations or kinetic phenomena, however, it is very useful when the discussion moves to degeneracy. As discussed in chapter 6, degenerate states may be initialized as a set of platforms with common widths and heights. The population statistics of the entire set of degenerate states is more interesting than the populations of each individual platform. Therefore, it is useful to have the ability to group all the degenerate states together so they form a single wide platform. This enables users to get the population statistics of the set of degenerate states taken as a whole.

To group platforms, the user must first click on the body of a platform. This highlights the platform with a red boundary. The user then presses and holds down the `CTRL` key on the keyboard. With the `CTRL` key held down, the user then clicks on a platform adjacent to the highlighted platform in order to group those two platforms together. This process can be repeated as needed. As shown in section 5.3.4, platforms can be marked as not "groupable". Any platform so designated will ignore the actions that normally lead to grouping.

This set of controls enables a broad range of possible activities with the model. The activities presented to students in the project curriculum will be discussed in section 5.5.

### 5.3.2 Main visualization window

The applet's main visualization window presents a real-time view of the simulated model, including the platforms and moving balls. It is not obvious from the grayscale image of the applet in figure 5-5 but the balls are rendered with a color that corresponds to the platform they are above. In addition to the platforms and balls, the main visualization window contains numbers at the top that represent the height of each platform in pixels. These numbers are rendered in the same color as the balls on each platform.

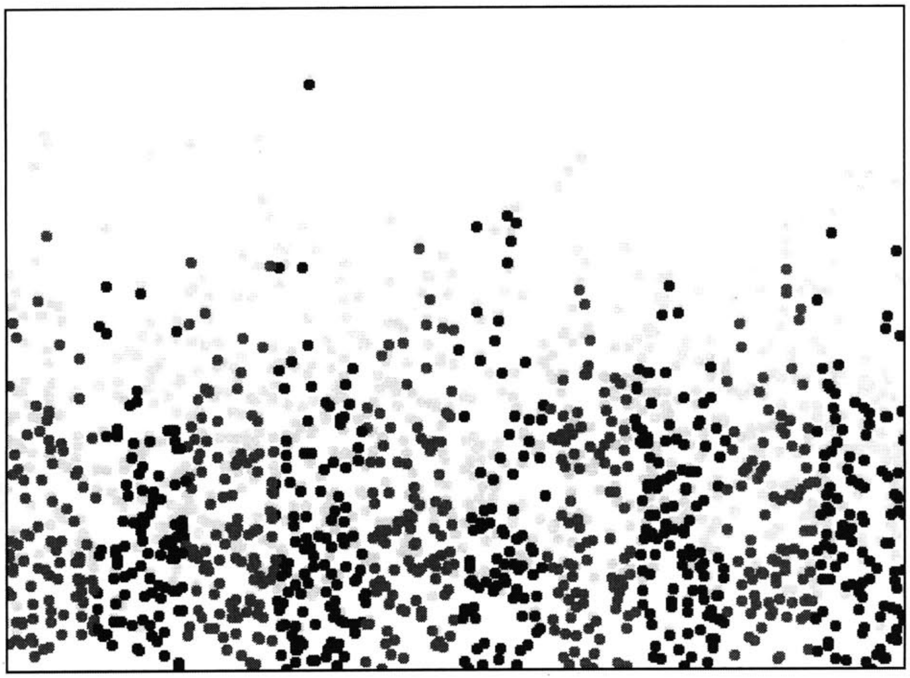


Figure 5-6: Screen capture of a visualization window containing both real balls (gray and dark gray) and their total energy ghosts (light gray)

The treatment of the balls as zero-dimensional points and its repercussions are discussed in section 5.2.3 and will not be discussed further in this section.

The approach to rendering the balls evolved as the project developed. Initial efforts to clearly convey the idea that the vertical axis represented energy, as discussed in section 5.2.1, led to the development of a so-called "ghost" ball representation, which rendered an additional ghost ball for each real ball, as depicted in figure 5-6. These ghost balls did not have normal dynamics. Rather, each ball's coordinate along the vertical axis was fixed at its total energy, as given in equation 5.2. The ghost tracked its corresponding real ball along the horizontal axis and they coincided when the real ball was at its trajectory's apex. One such real/ghost pair can be observed readily at the top of figure 5-6. The visualization window could display only the real balls, only the ghost balls, or both at the same time.

While this was an interesting way of viewing the model, it was ultimately discarded. When both the real and the ghost balls were viewed simultaneously, the visualization window appeared overly cluttered. It was difficult to see what was going on because there was simply too much going on. When the ghost balls were viewed alone, their unfamiliar dynamics prevented them from being especially instructive. In addition, it was ultimately decided that emphasizing the balls' total energies was not necessary, since the temperature is related to only their kinetic energies.

Beyond the ghost concept, this early prototype had a number of other interesting features, including the following:

- the ability to choose between the Maxwell-Boltzmann and a uniform distribution when assigning ball velocities
- the ability to choose whether platforms are in contact with the heat bath or are insulated, which results in the balls bouncing with no energy loss
- the ability to choose whether ball velocities should be assigned from the chosen distribution or whether the balls' total energies are assigned from the distribution

Ultimately none of the features listed above were included in the simulations presented to students. They were deemed to be either confusing or unnecessary. However, programming these features and experimenting with the simulations was instructive and valuable in that it enabled the truly useful features to be identified and extracted from a broad range of possibilities.

In all the simulations produced, the colors used for rendering the balls have been in some way related to the platform above which the ball is located. This approach was taken in order to make it clear when a ball transitions from one platform to another when it is high above both platforms. However, in the preliminary simulations, ball colors simply alternated between red and blue. This behavior is what is responsible for the gray and dark gray balls in figure 5-6, since, upon converting the image to grayscale, the red balls become gray and the blue balls become dark gray. Alternating colors proved to be confusing to students, however. During preliminary testing at Kent State University, discussed in section 8.2, some students inferred that red and blue were indicators of hot and cold and had difficulty reconciling this view with the energy landscape or the balls' speeds. Alternately, some students thought that the color of the balls somehow represented a type of ball, which should be static. This view also cannot be reconciled with the fact that the ball "types" never appear to mix.

As a result of the feedback, the customization scheme described in section 5.3.4 was created to allow ball colors to be specified on a per level basis. When choosing the colors used for each platform in the simulations, students' ideas that color somehow represented temperature or energy were taken into account. Therefore, the activated state has been often represented with red, while the stable state is generally represented in blue. The metastable state has been represented using magenta since it is mix of blue and red. Although the idea of ball color representing a static ball type has not been addressed in the simulation, better explanations are included in the curriculum to attempt to avoid confusion on this point.

### 5.3.3 Auxiliary data display

In this applet the auxiliary data display shows the numbers of balls above each platform, either in real-time, which is the default behavior, or averaged over time. This population is represented as a bar graph, with each platform getting its own bar. The actual population numbers are displayed above each bar, as shown in figure 5-5. The colors used for displaying a given platform's population number is the same as the color of the balls above that platform.

If platforms are grouped together, bars corresponding to the grouped platforms are combined into one and the number displayed above the bar is the sum of the populations above all of the platforms in the group.

### 5.3.4 Applet customizability

As mentioned in section 1.4.5, one of the goals of this project was to make the models easy for people to modify without requiring any programming ability. Such capability enables instructors to tailor the applets to simulate systems that are of particular relevance to their course's subject matter. This is accomplished by using special tags on the web page containing the applet.

To embed an applet on a web page written in `html`, the `APPLET` tag is used. At minimum, this tag tells the web browser where to locate the applet in the server's file structure and what the applet's width and height should be. However, it is also possible to use the `APPLET` tag to pass any number of special parameters to the applet using `PARAM` tags. These tags can be used to customize the applet's appearance and behavior. Below is the `APPLET` tag used to generate the applet pictured in figure 5-5, which contains a number of `PARAM` tags nested inside the `APPLET` tag.

```
<APPLET code="VirtualLab.class" width=615 height=410>
    <PARAM NAME="LESSON" VALUE="51">
    <PARAM NAME="NUMBER_OF_LEVELS" VALUE="3">
    <PARAM NAME="LEVEL_WIDTHS" VALUE="100,100,100">
    <PARAM NAME="LEVEL_HEIGHTS" VALUE="75,90,50">
    <PARAM NAME="LEVEL_ADJUSTABLE" VALUE="FALSE,FALSE,FALSE">
    <PARAM NAME="LEVEL_GROUPABLE" VALUE="TRUE,FALSE,TRUE">
    <PARAM NAME="INIT_BALLS_PER_LEVEL" VALUE="100,0,0">
    <PARAM NAME="BALL_COLOR_BY_LEVEL" VALUE="MAGENTA,RED,BLUE">
</APPLET>
```

Each `PARAM` tag consists of a name/value pair. The `NAME` field requires a unique identifier for the parameter and the `VALUE` field contains a value or set of values that are linked to the name. In order for these parameters to have any effect on the applet, special functions are required within the Java code to handle the parameters and set the values of any internal variables linked to these parameters. The necessary handler functions have been written for all the `PARAM` tags in the `APPLET` tag shown above. The `PARAM` tags have the following meanings, options, and conditions:

- `LESSON` sets the internal lesson number, which calls a specific initializer function that is specific to that lesson. These initializer functions determine which model (two-dimensional cardboard box, platform, 3D box, etc.) is presented in the applet. The subsequent `PARAM` tags apply only if the platform model is chosen.

- `NUMBER_OF_LEVELS` specifies the number of platforms the model should use. Acceptable values are integers greater than 0. Each of the following parameters is an array of values that specify the properties of the platforms from left to right. Because each value in the array sets a property for one platform, the number of entries in each array must equal `NUMBER_OF_LEVELS`.

- `LEVEL_WIDTHS` is an array of values that specify the width (in pixels) of each platform in the visualization window. The values in the array must sum to the total width (in pixels) of the visualization window.

- `LEVEL_HEIGHTS` is an array that specifies the height (in pixels) of each platform.

- `LEVEL_ADJUSTABLE` is an array of boolean values (either `TRUE` or `FALSE`) that specify whether a user is allowed to adjust the height of each platform.

- `LEVEL_GROUPABLE` is an array of boolean values that specify whether a user is allowed to add each platform to a group of platforms. This is discussed in section 5.3.1

- `INIT_BALLS_PER_LEVEL` is an array that specifies how many balls should be above each platform when the system is initialized.

- `BALL_COLOR_BY_LEVEL` is an array that specifies what color should be used to render the balls above each level. The possible values for this are `BLACK`, `DARK_GRAY`, `GRAY`, `LIGHT_GRAY`, `WHITE`, `MAGENTA`, `RED`, `PINK`, `ORANGE`, `YELLOW`, `GREEN`, `CYAN`, and `BLUE`.

This set of parameters allows instructors and students plenty of flexibility in adapting the platform model to their own needs. By simply editing a few lines in an `html` file they can create very interesting systems and initialize them however they please.

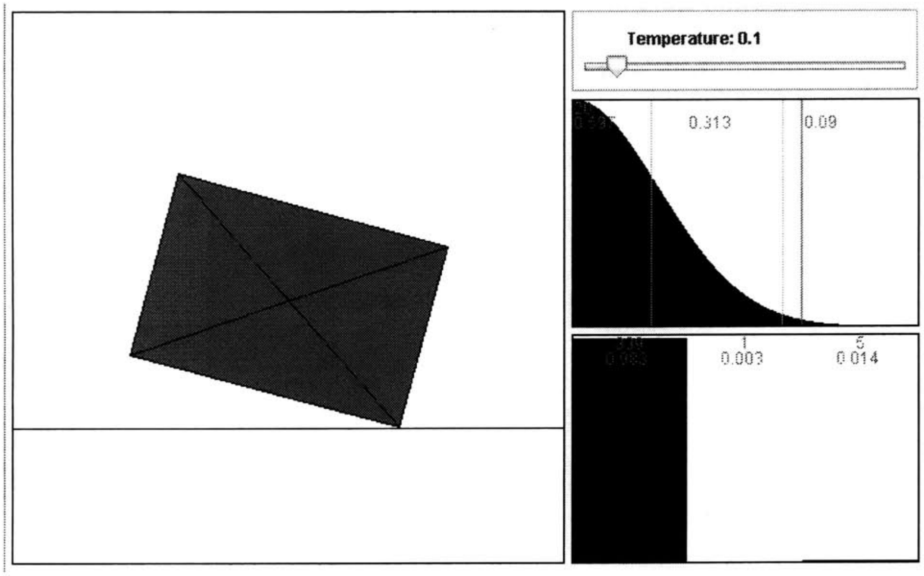


Figure 5-7: Prototype applet for teaching the heat bath concept

## 5.4 The cardboard box revisited

One of the foundations of the project is the idea that multiple different representations of the same or similar models helps students to learn abstract concepts more effectively. Therefore, if it is possible to return to familiar models to illustrate new concepts, this is done. This section describes how the cardboard box model presented in chapter 4 can be used to illustrate both the heat bath and equilibrium state populations.

### 5.4.1 Heat bath applet

During the initial curricular design, quite a bit of effort went into devising ways to effectively introduce the heat bath concept since it does not flow logically from the energy landscape. One idea was to use the two-dimensional cardboard box model presented in chapter 4, except using automated kicks from the Maxwell-Boltzmann distribution rather than manual kicks of user-specified strength. As mentioned in section 5.2.1, the box could be imagined to sit on a vibrating platform, causing it to jump around. An applet depicting this model and some additional elements is presented in figure 5-7.

As seen in figure 5-7, the applet also includes two auxiliary data displays. The first one shows the Maxwell-Boltzmann distribution just like those in figure 5-3, which is used in assigning the kick magnitudes. The most recent kick given to the box is shown as a vertical line superimposed on the distribution. In addition, the critical kick magnitudes necessary for the metastable→stable and stable→metastable transitions are superimposed on the distribution as light gray vertical lines, dividing it up into three regions, which, from left to right are: no transition possible, metastable→stable transition possible, and stable→metastable transition possible. In the second auxiliary data display, a histogram showing how many kicks from each region have been recorded. This is displayed both in absolute numbers and as a fraction of all kicks.

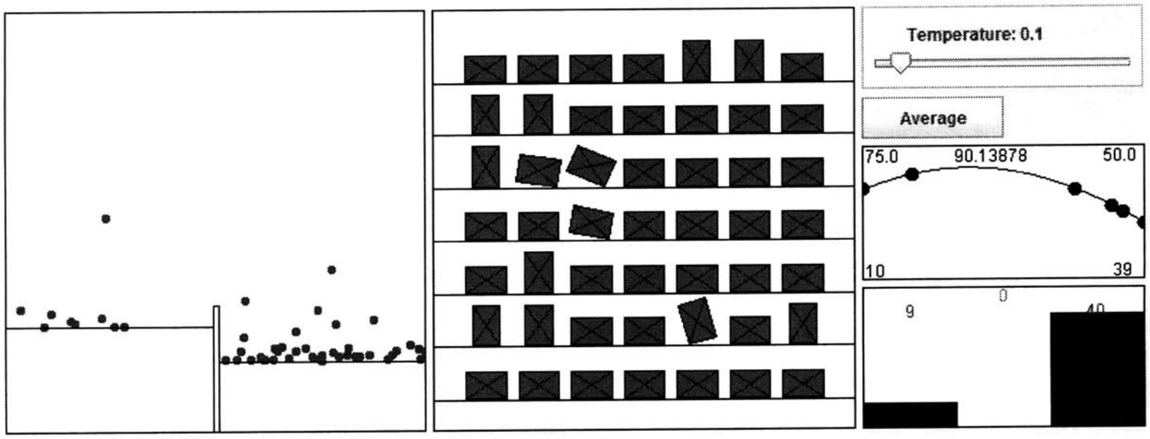
By adjusting the temperature, students can see the distribution shift toward higher energies. In addition, students can see how the frequency of higher energy kicks goes up when the temperature is higher by observing the histogram at bottom right.

In the end, this applet was not included in the curriculum presented to students. This is mostly because teaching the Maxwell-Boltzmann distribution was not an explicit priority and this particular applet design focuses very heavily on the properties of this distribution.

### 5.4.2 Equilibrium state populations

While the applet depicted in figure 5-7 was not used in the curriculum presented to students, the model was included in an applet that was presented to students. In this applet, an array of independent boxes sits on an unseen vibrating platform and is given kicks from the Maxwell-Boltzmann distribution automatically, as described in the previous section. This array of boxes is analogous to the balls in the platform model and serves to reinforce the idea of equilibrium state populations. This applet is shown in figure 5-8.

As can be seen from the figure, this applet includes both the platform model and the cardboard box model side by side. For each of the two main visualization windows there is also an auxiliary data display of the same type described when the two models were described: the energy landscape display for the box model and the



Temperature: 0.1

Figure 5-8: Applet depicting both the platform and cardboard box models

histogram display for the platform model. The auxiliary data display depicting the box's energy landscape is enhanced from the one described in section 4.3.3 in that it contains one dot for each box in the visualization window. In addition, it includes state population numbers, which are at the display's bottom corners. These numbers make it easy for students to compare the populations of each state between models.

It is important to note that the two models are not linked in any way. A box can undergo a state transition without any ball in the platform model switching platforms. Similarly, a ball can transition from one platform to the other without any change in the box model. They are presented side by side in order to facilitate comparison between the models and highlight the fact that despite having very different physics, the two models have comparable state population distributions at equilibrium.

Of course, it is possible to display the array of boxes by itself, without the platform model, if that is preferable. If both models are displayed, the number of balls in the platform model should be equal to the number of boxes in order that the state populations of the two models are directly comparable. In figure 5-8 there are 49 boxes and 49 balls. The data displays in the figure also show that the state populations of the two models are very similar.

## 5.5 Sample curricular activities

As illustrated in the concept road map for this chapter (figure 5-1), the main educational goals are teaching students about the impact of the heat bath and equilibrium state populations. These concepts are presented in greater detail in sections 2.7 and 2.4, respectively. While the platform model was designed to facilitate the teaching of these concepts, students still need guidance and suggestions on what phenomena to look for and how to manipulate the system in illustrative ways. The activities presented in this section were included in the curriculum (see sections A.1 and B.1) to help to guide students in their exploration of the model.

### 5.5.1 Heat bath

The general approach taken in helping students to understand the heat bath was to have them simply observe the behavior of balls on the platforms. Such an approach could have been carried out with the balls on a single platform. However, in the curriculum presented to students, the simulation included two platforms, as seen in figure 5-9.

Students were shown this applet and asked to carry out the activities listed below. The activities suggested at CMU and MIT varied a bit and are listed separately.

- **CMU:** Increase the temperature of the system.
  - What happens to the average height of the bouncing balls?
  - Compare the average height of the bouncing balls on the upper platform to the lower platform.
- **MIT:** Try increasing the temperature of the system.
  - What happens to the average height of the low-bouncing balls?
  - What happens to the average height of the balls that bounce the highest?
  - Does the frequency with which high-bouncing balls are observed increase or decrease when the temperature is raised?

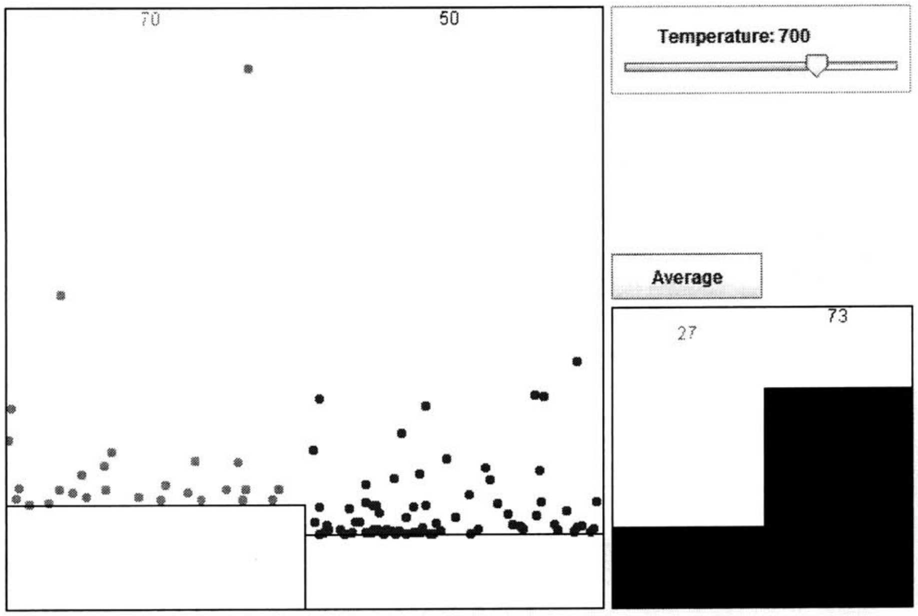

Temperature: 700

Figure 5-9: Applet used for illustrating the behavior of the heat bath and equilibrium state populations

In these exercises, the goal was to demonstrate to students the practical results of the behavior of the Maxwell-Boltzmann distribution and its dependence on temperature, as illustrated in figure 5-3. That is, as the temperature is raised, the frequency with which balls are given a high speed increases dramatically. This is important because the presence of high speed balls is required for balls to jump up from the stable state into the metastable state.

### 5.5.2 State populations

The goal in examining the behavior of state populations was to impress upon students that the ratio of balls in one state versus the other depends on two factors: the difference in energy between the states and the temperature. This is discussed further in section 2.4. The applet depicted in figure 5-9 was used again for these exercises. The two platform model was used instead of the three platform model depicted in figure 5-5 because the activated state is not included in the discussion of population ratios and its presence only slows down equilibration.

### CMU

At CMU, the students were asked to complete the following activities and questions:

- 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 balls 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 balls on the upper platform going from about 14 to 28.)

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

Students were then presented with the applet in figure 5-8 on page 97 and asked to complete the following activities:

- 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 $\Delta E$ and $T$, however, the detailed manner in which the system reaches this steady state depends on the details of the dynamics.

It is worth noting that in this curriculum sequence, students are not prompted to change the heights of the platforms. If platforms were raised or lowered in the platform model in figure 5-8, the aspect ratio of the box would also need to change in order that the energy landscape would be comparable to the platform model.

### MIT

At MIT, students were asked to complete the following activities and questions based on the applet in figure 5-9:

- When the system is initialized there are equal numbers of balls on each platform. What happens as time progresses and why?

- Compare the average number of balls on the upper platform to that of the lower platform (ratio = upper platform population / lower platform population). What is the ratio like at low temperatures? (Don't choose too low a temperature and make sure that you give the system some time to find equilibrium.) Does the ratio increase or decrease as you raise the temperature?

- Try lowering the upper platform (but keep it higher than the other platform). How does this affect the ratio described above? How would the ratio change if you lowered the higher platform until both platforms were the same height? How would the ratio change if you now raised the left platform again? If you wanted to make the population ratio as close to zero as possible, what would you do?

The applet depicting both the platform and boxes model (figure 5-8) was not presented at MIT because the curriculum sequence was more focused on kinetic properties than on equilibrium properties.

In both the CMU and MIT curriculum sequences, answers and explanations were provided for each question asked. By first allowing students to explore the behavior of the systems modeled in the applets with the assistance of suggested activities and then following up on these activities with answers and explanations, students have the chance to first attempt to figure things out for themselves and then fill in any gaps in their understanding by reading the explanations.

## 5.6 Summary and conclusion

As illustrated in the various descriptions in this chapter, the platform model provides a simple, yet powerful means to present the important concepts of the heat bath and equilibrium state populations. In addition, the cardboard box model can be repurposed to reinforce lessons presented using the platform model. Together these two models offer instructors a number of options for interactively teaching concepts that are normally taught only using a few equations and maybe a graph. As will be seen in chapters 6 and 7, the platform model can be applied to yet more situations, helping to teach ideas of degeneracy and chemical kinetics.

# Chapter 6

# Exploring Degeneracy: The 3D Box Model

## 6.1 Introduction

This chapter introduces a new model designed to help students explore the ideas of state degeneracy, entropy, and free energy, as shown in figure 6-1. Although this model is different from those presented in the preceding chapters, it can be thought of as an extension to the model presented in chapter 4. Where a cardboard box was represented in two dimensions in that model, the present model extends the picture to three dimensions.

As discussed in section 1.4.1, the models and visualizations presented in the applets were kept as simple as possible and confined to two dimensions when possible. The present model, however, benefits greatly from the move to three dimensions and the simulations do not become overly complicated or difficult to interpret. Furthermore, because students have already seen the two-dimensional model presented in chapter 4 and because the three-dimensional model retains much of the two-dimensional box's behavior, the extension of the model to three dimensions is very manageable for students.

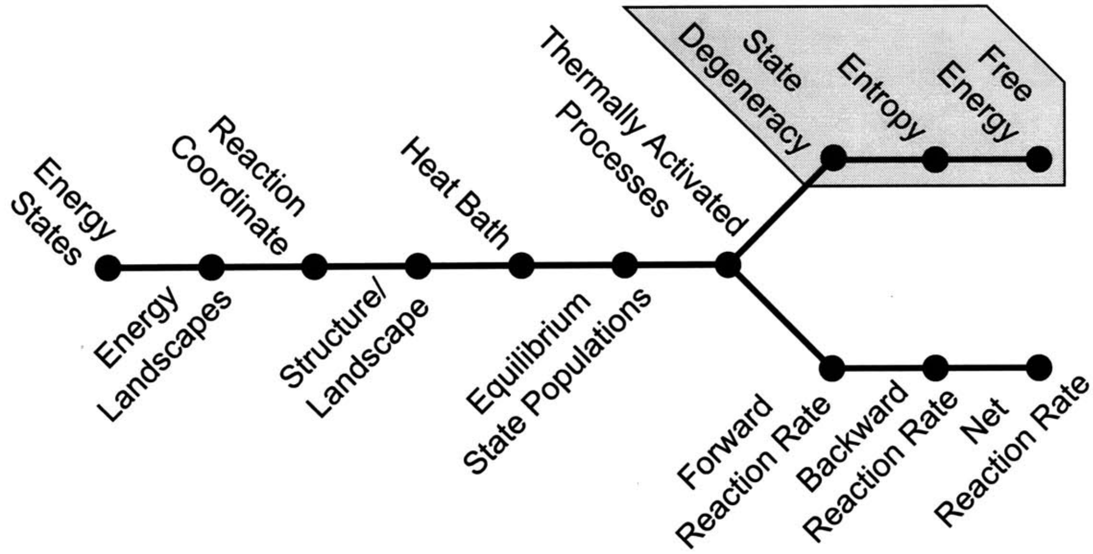


Figure 6-1: The concept road map with the concepts addressed in this chapter highlighted

## 6.2 Description of the model

The model used in this applet was designed to help students understand the idea of state degeneracy. As discussed in section 2.5, one of the important take-home ideas from chemical equilibrium is that, at low temperature, systems prefer to be in configurations that minimize their internal energy, while at high temperatures, they preferentially adopt states that have the highest degeneracy. The three-dimensional box model was designed such that this concept could be presented qualitatively without requiring a rigorous, quantitative analysis.

A three dimensional box composed of all 90° angles will have three pairs of degenerate faces in its most general case, as the box's length, width, and height are all different. Such a box is not particularly instructive in the context of this curriculum because each pair of equivalent faces has the same degeneracy. However, by setting the length and height equal, the box is made to have only two sets of degenerate faces, one set with a degeneracy of two and one set with a degeneracy of four. Such a box is illustrated in figure 6-2.

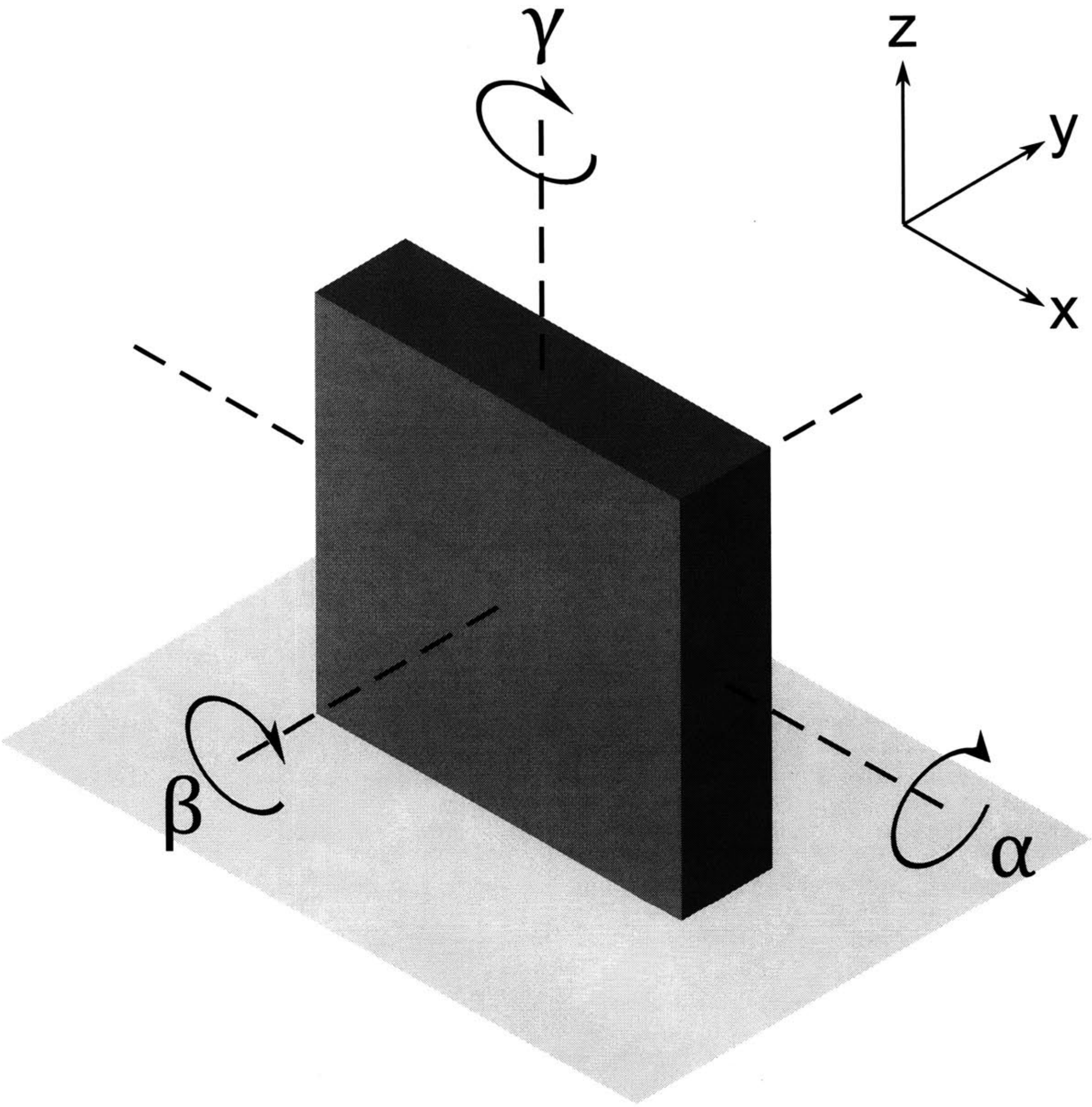


Figure 6-2: The three-dimensional box model

### 6.2.1 What is modeled?

The three-dimensional box rests on a surface, which is said to be vibrating. These vibrations provide "kicks" to the box, just as they did for the two-dimensional model discussed in section 5.4. As described above, the box has two square faces and four rectangular sides. When it is lying on one of the faces, its center of mass is at its global minimum; when it is standing up on one of the rectangular sides, its center of mass is at a local minimum. Therefore, the box lying on one of its faces represents the stable state. When the box is standing on one of its rectangular sides it is in the metastable state. Thus, the box has a low energy/low degeneracy state (box faces) and a high energy/high degeneracy state (box sides).

In this model there are two distinct types of state transitions that can occur:

1. metastable ⟷ stable

2. metastable ⟷ metastable

Transition type 1 occurs when the box rolls over an edge separating a square face from a rectangular side. There are four such edges for each square face, for a total of eight. Transition type 2 occurs when the box rolls over an edge separating a rectangular face from another rectangular face. There are a total of four such edges per box. Due to the box's topology, a direct stable→stable transition is not possible.

As in the two-dimensional box model, the three-dimensional box's center of mass is kept centered. That is, its $x$ and $y$ coordinates are kept fixed. As a consequence, it rotates about the dotted lines depicted in figure 6-2, which are at 90° angles to one another and go through the box's center of mass. In transitions of type 1 above, the rotation can be represented as $\alpha = \pm 90°$, while type 2 transitions can be represented as $\beta = \pm 90°$. When the box receives a kick, the direction of the kick is chosen randomly and the magnitude of the kick is chosen from the Maxwell-Boltzmann distribution.

### 6.2.2 What is not modeled?

There are a number of restrictions on the model that serve to simplify its behavior and maintain the validity of its relationship to the energy landscape concept. The first restriction is taken directly from the two-dimensional box model: the box must always remain in contact with the surface beneath it. As discussed in section 4.2.2, this restriction is necessary to maintain a connection between the box model and an energy landscape-type representation of its gravitational potential energy.

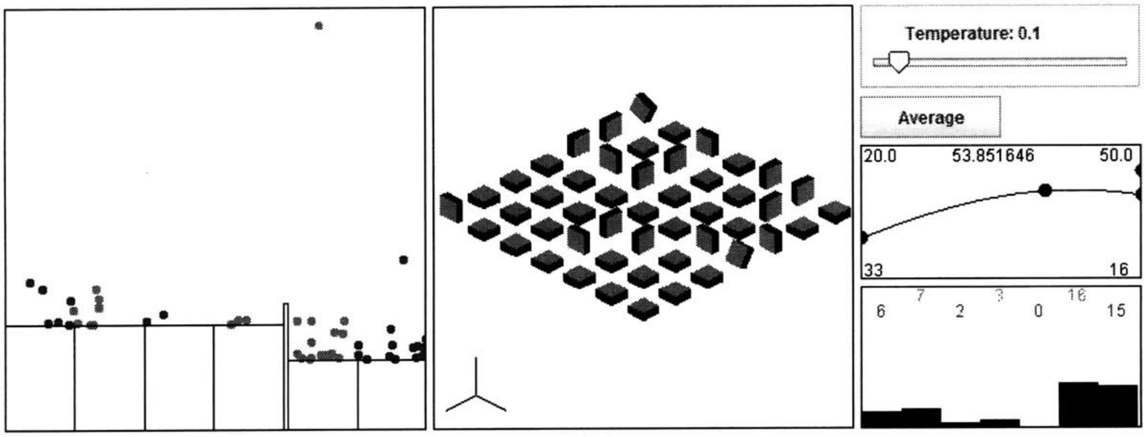
A restriction that is new to the box model is the constraint that the box is never allowed to stand up on a vertex. Any transition must occur via rotation over a box edge (e.g. $\alpha = \pm 90°$ or $\beta = \pm 90°$). This restriction helps to simplify the model and it also simplifies the energy landscape used to represent the box's energy. This will be discussed further in section 6.3.3.

The box is also not allowed to rotate about the $z$-axis. That is, $\gamma$ is constrained to be always 0. This restriction is imposed because such a rotation does not represent a transition from one state to another. In fact, such a rotation does not change the box's gravitational potential energy at all, since the box's center of mass remains at the same height. Such motion, therefore, accomplishes nothing and its inclusion would only complicate the model.

Finally, the box's motion is always stopped when a rotation about a single box edge is completed. As a consequence, even a kick of a very large magnitude will not result in the box flipping end over end repeatedly. When a rotation about a single edge is complete, the box is taken to be at rest in either the metastable or stable state and receives a new kick. While the box is not at rest, it cannot receive any kicks and it moves in accordance with the kick it received while at rest.

## 6.3 Visualization and User Interface

Because a single box can only be in one state at a time, watching a single box is not particularly helpful if the aim is to demonstrate that higher degeneracy states are preferred at higher temperatures. While it would be possible to use a single



Temperature: 0.1

Figure 6-3: Screen capture of applet depicting both the platform and 3D box models

box and follow the fraction of time the box was observed in the low energy/low degeneracy state versus the high energy/high degeneracy state, such an approach is a bit too indirect. Rather, if an array or ensemble of boxes is used, students can simply observe which state predominates at any moment. This approach is analogous to the approach taken with the platform model, which simulates what can be interpreted as an ensemble of non-interacting balls, each of which can be above only one platform at a time.

A single three-dimensional box was never incorporated into an applet. In fact, the only applet presented to students contained both an ensemble of three-dimensional boxes and a corresponding platform model, as depicted in figure 6-3.

The applet shown in figure 6-3 is very similar to the applet presented in section 5.4.2 and depicted in figure 5-8. The only difference is the use of the three-dimensional box model in place of the two-dimensional model.

### 6.3.1 Controls

As is clear from figure 6-3, a temperature slider is provided in order that students may adjust the temperature of the system. In addition, a button is provided so that students can toggle between real-time data and time-averaged data.

Within the visualization window for the platform model, platforms may be adjusted in height and grouped, as described in section 5.3.1. The value of grouping will be discussed further in section 6.3.2.

Within the visualization window for the three-dimensional box, there are no controls that alter the system. However, the array of boxes can be rotated and zoomed in order to provide a closer or more convenient look at the boxes.

### 6.3.2 Main Visualization Window

As seen in figure 6-3, this applet contains two main visualization windows. These will be addressed separately below. However, it is worth reiterating here that, while efforts were made to maximize the analogic relationship between the visualized models, the two models are not physically linked during the simulation. They can change independently and they do change independently. They are presented side by side to emphasize the fact that two models, involving totally different physics, can produce approximately equivalent population distributions at equilibrium. However, it can be seen that they are not linked by the fact that their population distributions are not always equal and fluctuate independently.

#### 3D box model

In the visualization window depicting the three-dimensional box model, a 7-by-7 box array is presented in an isometric projection. This projection enables students to easily observe box transitions in any direction. Box faces and box sides are rendered in different colors to maximize students' ability to visually track the motion of boxs. This also aids students to visually estimate which state (lying down or standing up) predominates at any given time.

If students have any difficulty understanding what is going on, they may zoom in on the visualization window by holding down the `SHIFT` key, holding down the left mouse button, and dragging down to zoom in or dragging up to zoom out. Holding down the left mouse button and dragging the cursor around rotates the array of boxes. In order to help students understand the boxes' orientation as the scene is rotated, the axes in the bottom left of the visualization window also rotate.

If a user observes the boxes for a while, he or she may conclude that some boxes do not receive any kicks for a prolonged period of time. In reality, all boxes are given a kick when all boxes are at rest. However, much of the time, the kicks are so small that they are not visible. This is due to the nature of the Maxwell-Boltzmann distribution.

### Platform model

The visualization window depicting the platform model is configured with four platforms of intermediate height in a group at left, two platforms of low height in a group at right, and one very narrow but tall platform between the two groups. Each platform of intermediate height in the group of four represents one of the box's four rectangular sides. Each short platform represents one of the box's two square faces. The tall narrow platform represents the eight edges between the square faces and rectangular sides mentioned in section 6.2.1. Because this applet is not focused on the population of the activated state, nothing is lost by making it very narrow. Furthermore, the fact that it is very narrow means that it can often be crossed by balls in a single jump, which speeds up equilibration.

What is not represented at all is the four box edges separating one rectangular side from another. Because the box can transition from one metastable state to another by crossing a metastable→metastable activated state, in order to be strictly correct, there should be tall, narrow platforms between each of the platforms on the left of the visualization window. However, ultimately, metastable→metastable transitions are of little interest and including the activated state between degenerate metastable states would unnecessarily complicate the picture.

As mentioned in section 5.3.1, the capability to group platforms is most useful when degenerate states are modeled. This is because the individual degenerate states can be collapsed into a single platform representing the entire set of degenerate states. Figure 6-4 shows what the applet looks like when the degenerate states are grouped into the appropriate sets.

When the degenerate states are grouped into a single platform, it becomes clear

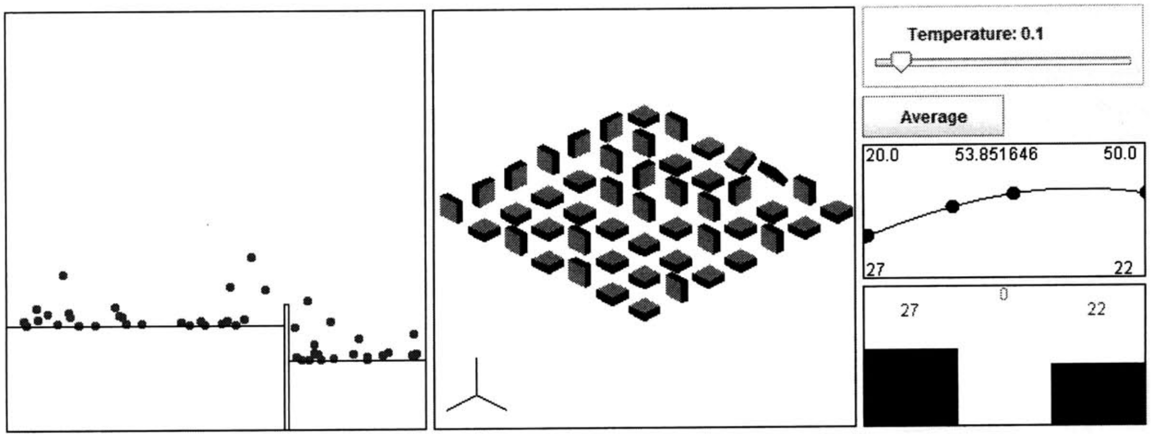


Figure 6-4: Screen capture of the applet shown in figure 6-3 with the platforms grouped

that the width of a platform is a measure of the state's degeneracy. Students can then see the effect of degeneracy and its interplay with temperature by running the simulation at different temperatures. At low temperatures, it is easy to see that the low energy state is preferred. However, at high temperatures, the width of the higher energy state coupled with the diminished importance of $\Delta E$ results in the higher energy state having the larger population. This a concept that often mystifies students. However, students' understanding of this concept improved after using the applets and curriculum (see question 14 in section A.2 and test results in section 8.4.2).

The curriculum presented along with this applet uses the discussion of degeneracy to introduce students to entropy and, ultimately, free energy. However, this is done by means of mathematical derivations, not additional models or modifications to existing models.

One recent idea that may be added in the future is a so-called "group" button. This control would group each set of platforms with a common height into a single platform with a width equal to the sum of the constituent platforms' widths. This would be useful because the platform model is most instructive in only two forms: a form in which each degenerate box face has a corresponding platform in the platform model and a form in which each *set* of degenerate faces has a single platform with a width proportional to its degeneracy. Having the ability to toggle back and forth between these views would be valuable.

### 6.3.3 Auxiliary Data Display

As seen in both figures 6-3 and 6-4, the applet includes two auxiliary data displays. It must be emphasized that the top display corresponds to the three-dimensional box model and the bottom display corresponds to the platform model. This is not immediately clear from the applet itself.

Various arrangements for the displays were considered during the applet's development and, while others that would have been more clear were considered, ultimately this arrangement was chosen for its compactness. As a result, all users can view the entire applet on their computer screens without needing to scroll side to side. By eliminating the need to scroll, all of the applet's information is available at a glance, which makes comparisons between the two models much more convenient. As computer screen resolutions increase, particularly in width, this becomes less of a problem.

#### Energy landscape

In the energy landscape display there is one black dot for each box in the main visualization window. In addition, the number of dots on each side of the activated state is displayed at the bottom of the display.

The main way in which this display differs from the one used for the two-dimensional box is that there are two reaction coordinates. The most obvious reaction coordinate is the rotation angle of the box as it transitions from lying down (stable) to standing up (metastable). This is the horizontal axis in the display and it corresponds to the angle $\alpha$ labeled in figure 6-2. However, the rotation angle $\beta$ is also represented, though the axis representing it extends into the screen or page. This is illustrated in figure 6-5, where the frame on the left represents the display shown in the user interface. The frame marked with $\beta$ depicts the portion of the energy landscape that

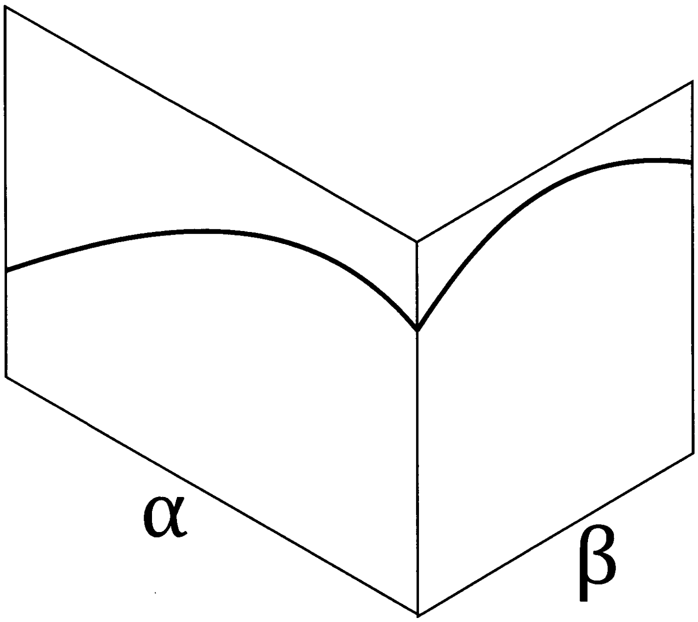


Figure 6-5: Three-dimension depiction of the energy landscape for the three-dimensional box model

extends into the screen.

This representation was chosen because, while metastable⟷stable transitions (i.e. rotations in $\alpha$) are of primary interest, it was also desirable to show the box's energy increases when it executes a metastable→metastable transition. The correspondence between boxes undergoing transitions and the appearance of dots in the energy landscape is depicted in figure 6-6. A more complicated three-dimensional view was not used because it might have the effect of de-emphasizing the metastable⟷stable transition, which is of greatest importance. In addition, the two-dimensional view is used frequently earlier in the curriculum, so it is familiar to students. Therefore, barring a compelling reason to change the view, the two-dimensional view is preferred.

### Histogram

The histogram used as the auxiliary data display for the platform model is the same as that used in the applets described in chapter 5. However, it is worth highlighting the fact that when platforms are grouped, as described in section 6.3.2, the histogram changes to reflect the change in number of platforms present in the model. As a result,

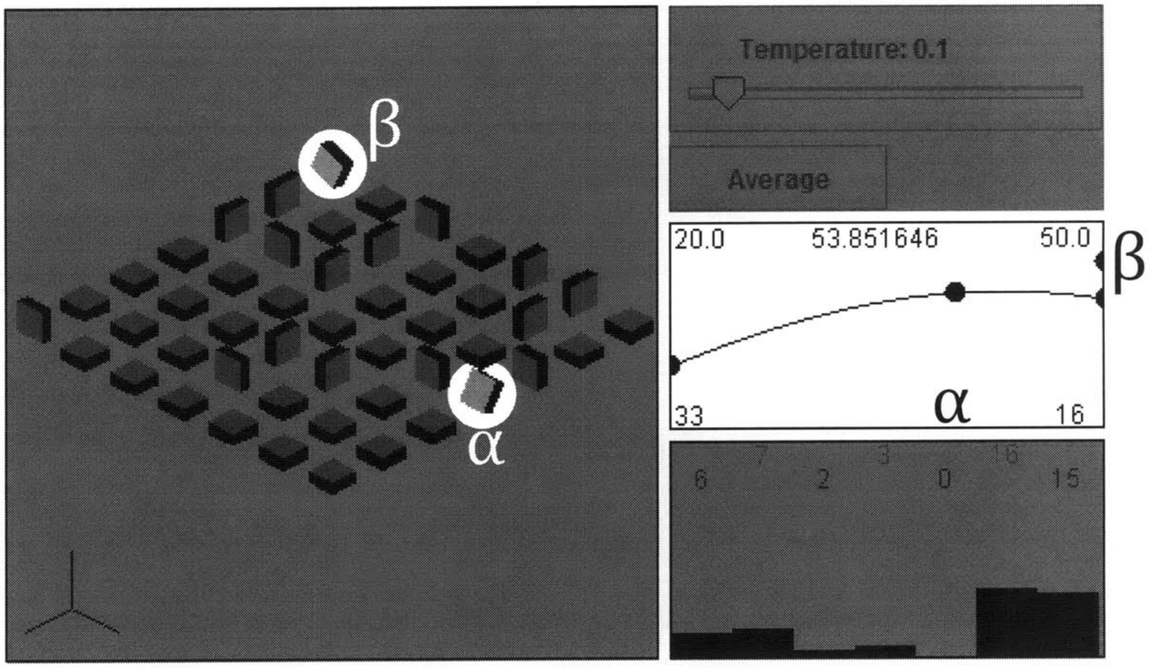


Figure 6-6: Screen capture highlighting the correspondence between boxes and dots on the energy landscape

the population numbers presented in the histogram represent the entire population of the set of degenerate states rather than the population of a single degenerate state. This facilitates more direct comparison of the populations in the box model and the platform model.

## 6.4 Sample curricular activities

The main goal of this applet was to help students understand how degeneracy affects the distribution of state populations as a function of temperature. Therefore, students are asked to simply run the applet at different temperatures and observe what happens. In particular, the CMU students who used the curriculum were asked to do the following:

- Notice how the populations of the higher and lower energy states behave at different temperatures.
- 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)?

The full curriculum seen by CMU students is presented in section A.1. Students at MIT did not see this applet because it did not fit into the curricular goals of the course.

By observing the simulations over a period of time and analyzing the simulations in order to answer the question, students can obtain a qualitative understanding of the effect of state degeneracy on the equilibrium population distribution of generic systems. This helps to underscore the validity of the observation that at low temperatures, low energy states are preferred, while at high temperatures, high degeneracy states are preferred.

## 6.5 Summary and Conclusion

The model and applet presented in this chapter introduced students to the idea of state degeneracy. By choosing appropriate parameters for the three-dimensional box and imposing a few necessary restrictions on its behavior, it was possible to illustrate the target concepts and tie the model back to the platform model. These two models taken together helped students to understand how collections of states can be degenerate and how that degeneracy can affect the state population distribution at different temperatures.

This model represented the end of the curriculum line focused on equilibrium properties, as seen in figure 6-1. However, it sets the stage for a meaningful discussion of entropy and free energy and by providing an opportunity for students to directly observe the effects of state degeneracy, it helps to make these concepts much more concrete and less elusive.

# Chapter 7

# Exploring Reaction Kinetics: Platform Model Revisited

## 7.1 Introduction

As described in chapter 2, the energy landscape provides information that can be used to understand kinetic properties of systems as well as equilibrium properties. Whereas the difference in energy between the metastable and stable states is the quantity of importance in equilibrium properties, the activation energies, as described in section 2.6, are the quantities of interest when looking at a system's kinetic properties.

Because the platform model, described in chapter 5, approximates an energy landscape (see figure 5-2), it can be used to explore kinetic processes as well as equilibrium phenomena. This chapter describes the application of the platform model to the study of kinetic properties. As seen in figure 7-1, particular emphasis is put on understanding how the net reaction rate is composed of both the forward reaction rate and the backward reaction rate.

Because the model is described in detail in chapter 5, it will not be described here any further.

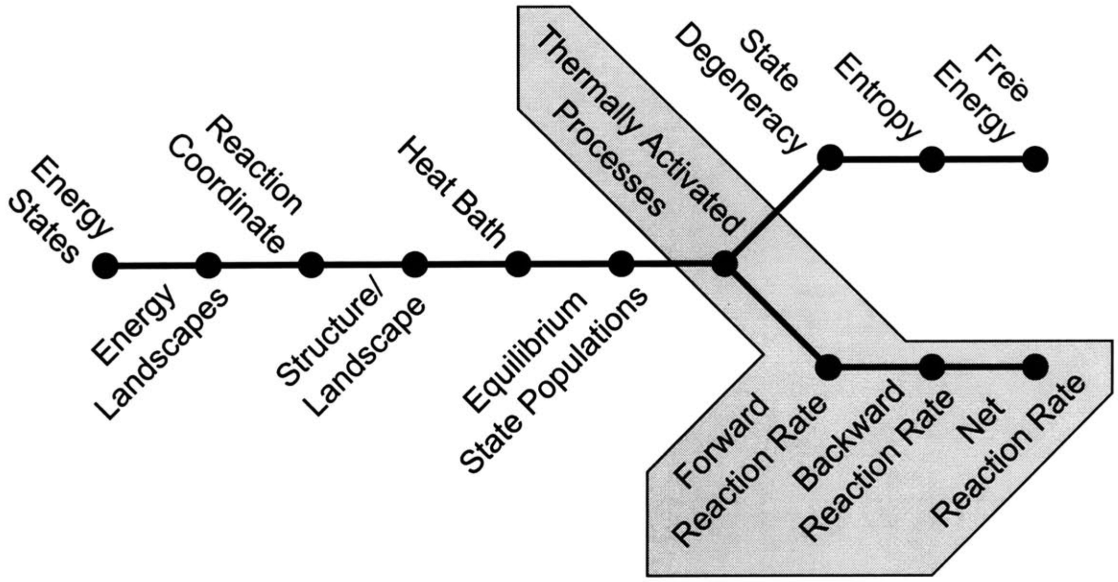


Figure 7-1: The concept road map with the concepts addressed in this chapter highlighted

## 7.2 Visualization and User Interface

The user interface of the applet is very similar to those described in chapter 5, in particular figure 5-5, as can be seen in figure 7-2.

There are two main differences between figures 5-5 and 7-2. The first is the width of the platforms and the second is the addition of a start/stop button. The significance of these differences is discussed below in sections 7.2.1 and 7.2.2, respectively.

### 7.2.1 Main Visualization Window

In the main visualization window, the platform model is depicted. In this particular configuration, the activated state is represented by a much narrower platform than either the metastable or stable states. This is done mostly as a matter of convenience. If the activated state's platform were wider, balls would generally need to successfully execute a number of rightward jumps on top of the activated state in order to complete a metastable→stable transition. This slows down the rate at which the system evolves. In order to maintain student engagement, any tedious or overly slow processes should be avoided. Therefore, the activated state's platform was reduced

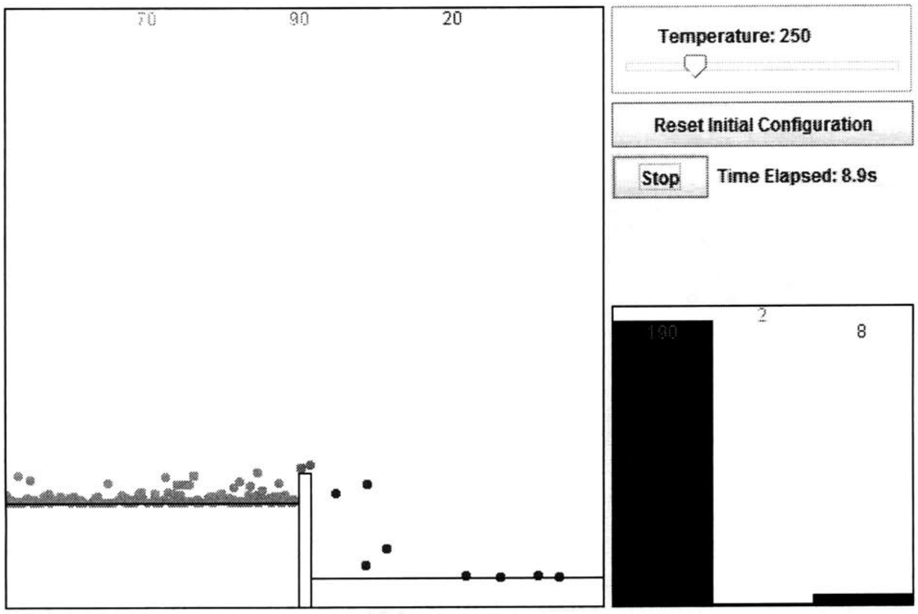


Figure 7-2: Screen capture of the kinetics applet

in width in order that students would see balls transition from one state to another more quickly. This does not cause problems because the goal in this applet is not to analyze equilibrium state populations.

### 7.2.2 Controls

When the system is initialized, all the balls begin, seemingly frozen in space, over the metastable platform. The simulation can be started by clicking the button labeled "Start". This button's label changes to "Stop" once the simulation has been started. The label to the right of the "Start"/"Stop" button shows the time that has elapsed since the simulation began. After the elapsed time reaches 15 seconds, the simulation is automatically stopped. This is done to facilitate specific exercises, described in section 7.4. When the simulation ends, the "Start"/"Stop" button is disabled.

After the simulation has ended, a student can run another simulation from the beginning by clicking on the "Reset Initial Configuration" button. This resets all the balls over the metastable platform and enables the "Start" button. Students can begin the simulation again by clicking on "Start".

It should be noted that, while the temperature slider is visible, it is disabled. This is due to issues discussed in section 7.3 below.

Finally, students can adjust the heights of the platforms in the main visualization window. This capability is crucial for exploring the effect that $E_{a,m}$ and $E_{a,s}$ have on the reaction rate. The platform heights can be adjusted before the simulation is started, while it is running, or afterward, in preparation for a new simulation run.

### 7.2.3 Auxiliary Data Display

The auxiliary data display in this applet is a histogram just like the one found in the applets presented in chapter 5. It is most useful in that it reports the number of balls above each platform. The exercises students are asked to complete call for them to report the number of balls in the stable state after the 15 second simulation is complete. The histogram view provides an easy way for students to get this data without having to manually count each ball on the stable platform.

## 7.3 Problems with the model

When developing this applet, the goal in mind was to help students understand the dependence that reaction rate has on both activation energies and temperature. In particular, the goal was to illustrate to students that halving $E_{a,m}$ would increase the rate of the metastable→stable transition more than doubling the temperature. This fact is at the heart of catalysis. While it would be possible to increase the rate of a reaction by simply increasing the temperature, this is less effective than figuring out ways to lower the activation barrier.

Reducing the activation barrier for the forward reaction is more effective than increasing the temperature because of the difference between how these two approaches affect the backward reaction rate. When $E_{a,m}$ is halved, $E_{a,s}$ is not reduced as much. This is because $E_{a,s} = \Delta E + E_{a,m}$ and, even if $E_{a,m}$ is reduced substantially, $\Delta E$ remains unchanged. However, if $E_{a,m}$ were kept constant and $T$ is doubled, the backward reaction rate is increased more markedly. This leads to a net reaction rate that is increased less than if $E_{a,m}$ were halved.

Unfortunately, the platform model with its current dynamics scheme does not produce the behavior that was to be presented to students. The short-term solution to this problem was to confine the discussion to a single temperature, exploring only the effects on the net reaction rate that result from changing $E_{a,m}$ and $E_{a,s}$. This is why the temperature slider is disabled, as mentioned in section 7.2.2.

### 7.3.1 A description of the problem

As discussed above, halving $E_{a,m}$ should result in a greater increase in the net reaction rate than doubling the temperature. In the applet, the net reaction rate is evident by counting the number of balls in the stable state after 15 seconds have elapsed. However, during internal testing prior to distributing the applets to students, the opposite of this behavior was observed. That is, doubling the temperature was found to increase the reaction rate more than halving $E_{a,m}$.

It was found that this behavior is due to the topology of the platform model. Whenever a real system is given enough thermal energy to reach the activated state, it actually does transition to the activated state. From there, it may transition to the stable state or back to the metastable state. However, if one observes the behavior of balls in the platform model, it becomes clear that balls often receive enough thermal energy from the heat bath to reach the activated state but because of their position on the wide metastable platform, they do not actually transition to either the activated or the stable state. This is particularly true at low temperatures, when balls have relatively low speeds and therefore, low and short trajectories.

At high temperature, however, many balls receive quite high speeds from the heat bath. This, in turn, produces high, far-reaching trajectories that often easily clear the activation barrier and transition into the stable state. As a consequence, the increase in the net reaction rate when the temperature is doubled is greater than that when $E_{a,m}$ is halved.

### 7.3.2 Possible solutions

Early attempts to solve the problem without radically reworking the model were unsuccessful. The first solution attempt involved dramatically increasing the velocity of the balls in the horizontal direction. It was hypothesized that doing so should increase the fraction of balls that successfully reach either the activated state or the stable state after receiving a reasonably high speed from the heat bath. However, the results were less than satisfactory. Balls that were already quite close to the activated state's platform were often reflected back into the metastable state because they were not high enough in their trajectory before encountering the side of the activated state's platform. Balls that were far away from the activated state still did not succeed in making a transition. In addition, any ball that was kicked in the opposite direction from the activated state never succeeded in making a transition. This approach was tried at multiple values for the $x$-velocity but none were successful.

A second possible solution that was tried involved making the metastable and stable platforms much more narrow. This seemed to produce reasonable statistics but it was very confusing to watch. The balls were impossible to distinguish from one another and it was visually very unappealing.

A third possible solution has been considered but not yet implemented. This solution would involve artificially manipulating the trajectories of balls in order to ensure that all balls which receive enough energy from the heat bath to reach the activated state actually do transition to the activated state. This could be implemented by checking each ball's kinetic energy immediately after it receives its new velocity from the heat bath. If its kinetic energy is enough to ensure that the apex of its trajectory is at least as high as the height of the activated state's platform, the $x$-velocity necessary to make it land on the activated state is calculated and given to the ball. In this way, the platform model could be made to reflect the fact that real systems, when given enough energy to reach the activated state, actually do transition to the activated state.

This solution could be implemented with either the narrow activated state shown

| Configuration | $E_{metastable}$ | $E_{activated}$ | $E_{stable}$ | $E_{a,m}$ | $E_{a,s}$ | $\Delta E$ | Ball Count |
|---|---|---|---|---|---|---|---|
| 1 | 70 | 90 | 20 | *20* | *70* | *50* | |
| 1 | 70 | 80 | 20 | *10* | *60* | *50* | |
| 1 | 70 | 75 | 20 | *5* | *55* | *50* | |
| 1 | 70 | 75 | 65 | *5* | *10* | *5* | |
| 1 | 70 | 90 | 65 | *20* | *25* | *5* | |

Table 7.1: A table students are asked to complete in order to understand forward, backward, and net reactions rates

in figure 7-2 or an activated state with the same width as the metastable and stable states. While this solution is guaranteed to produce the correct results, it is not guaranteed to be easily understood by students. Therefore, it would need to be tested with students before being whole-heartedly adopted.

## 7.4 Sample curricular activities

The goal of the activities presented to students is to help them understand how the height of the activation barriers for both the forward and backward reaction affect the net reaction rate (see section B.1.4). This is accomplished by asking students to carry out five 15-second trials involving different values of the various quantities of interest. Table 7.1 contains the values that students were asked to use in each trial.

In the table header row $E_{metastable}$ represents the height of the metastable platform, which is displayed at the top of the main visualization window, as seen in figure 7-2. $E_{activated}$ and $E_{stable}$ represent the heights of the activated and stable platforms, respectively. $E_{a,m}$ and $E_{a,s}$ represent the activation barrier to the forward (metastable→stable) and backward (stable→metastable) states, respectively. In the body of the table, the values in the normal font face were provided to students. Students were asked to calculate the values that appear in italics and to fill in values in the blank cells by carrying out trials with the applet. Students were provided with the following equations to help them calculate the italicized values:

$$E_{a,m} = E_{activated} - E_{metastable} \tag{7.1}$$

$$E_{a,s} = E_{activated} - E_{stable} \tag{7.2}$$

$$\Delta E = E_{metastable} - E_{stable} \tag{7.3}$$

In addition to determining the number of balls in the stable state after the 15-second trial had elapsed, students were asked to carefully watch the activated state to observe the direction in which balls were crossing from one state to the other. The applet was designed to stop automatically after a specified amount of time had elapsed in order that students would not need to watch the clock and could, instead, watch the system evolve. Fifteen seconds was chosen as the interval length because it was long enough to reliably obtain more than one ball in the stable state and it was short enough that the system would not reach equilibrium before it elapsed. It has the additional advantage of not being long enough to cause students' attention to wander.

After completing the table, students were asked the following questions about the data in the table:

- Which quantities affect the number of balls in the stable state after each 15-second trial and how?
- Which quantities have no direct effect?
- If you were asked to design a chemical reaction that maximizes the reaction rate, how would you do it?

Between the activities students performed with the applet and the answers and explanations provided afterward, students had the opportunity to learn about reaction rates and the importance of activation barriers both interactively and through step-by-step explanation.

## 7.5 Summary and Conclusion

Although the more complete picture of the dependence of reaction rates on both activation energies and temperatures was not presented due to problems with the model and its visualization, the applet described in this chapter nonetheless presented students with the opportunity to explore a very interesting set of ideas from chemical kinetics. By systematically varying the model according to the values in table 7.1 students were able to obtain a dataset with significant didactic power. In addition, the general structure of the platform model and the terminology used points back to the energy landscape concept, helping students to understand that kinetics, as well as equilibrium properties, are captured in the energy landscape concept.

# Chapter 8

# Assessment of Student Learning

## 8.1 Introduction

As discussed in section 1.4.3, the project not only developed simulation applets and corresponding curriculum, but also deployed them in undergraduate courses in order to assess their efficacy. At the time of this writing, the applets and curriculum have been tested with students on six different occasions, two times at each of the three universities collaborating on the project: Carnegie Mellon University (CMU), Kent State University (KSU), and the Massachusetts Institute of Technology (MIT). These six deployments have introduced at least 550 students to the project materials and over 400 have completed both pre- and post-tests to assess the impact that the materials had on their learning.

Although the materials have been deployed six times, many of these deployments were very small. The two tests that resulted in the greatest student response were those conducted in David Yaron's *Modern Chemistry II* at CMU in April 2008 and Donald Sadoway's *Introduction to Solid State Chemistry* at MIT in November 2009. In these two deployments the number of students who completed both the pre- and post-tests was 69 and 334, respectively. Because of the large number of students involved, these two deployments produced over 90% of all student responses recorded to date.

In an effort to keep the discussion in this chapter meaningful and concise, the small-scale deployments will not be presented. Rather, with the exception of some preliminary testing performed at Kent State University, discussion will focus exclusively on data obtained from students in the two large-scale deployments mentioned above.

## 8.2 Preliminary Testing

Preliminary testing occurred at Kent State University in November 2007. The students were upper level undergraduates in a biophysics course taught by John Portman. The students' primary purpose was to identify any aspect of the applets that they found confusing and to suggest ways the applets could be improved. The tests were done during a class period in a computer laboratory on the KSU campus. During testing, project personnel were present to observe the ways in which students interacted with the applets.

In addition to sharing verbal feedback with the researchers, students completed a questionnaire that asked them to identify the analogic connection between certain items depicted in the applet user interface and physical concepts or quantities. This feedback led to the change in ball color scheme described in section 5.3.2. In addition, students took great pride in causing the simulations to break or produce erroneous results. As a result of their efforts, a number of programming errors were detected and remedied. While students did complete a feedback survey, they did not complete the pre- and post-tests that are the basis for the quantitative assessment data presented below.

## 8.3 Assessment methodology

As discussed previously, the focus of this project was to develop interactive online materials that would enable students to learn fundamental concepts from Molecular Science. Thus, the question posed during the assessment of these materials is "Do the applets and corresponding curriculum result in improved student understanding of Molecular Science concepts?" However, to answer this question using accepted statistical methods it is necessary to refine the question further[46]. Given the possibility that the materials actually reduce students' understanding, the question can be restated as "Do the applets and corresponding curriculum produce any change in students' scores on a test of Molecular Science concepts?" This question will be referred to as question 1.

While this question is interesting and can validate the project's approach overall, it is not capable of offering any insight into ways in which the applets and curriculum could be improved. In order to identify such improvement opportunities, it is necessary to take a more finely-grained approach. This approach involves asking the question "Do the applets and corresponding curriculum produce any change in the proportion of students who correctly answer a given conceptual question?" This question will be referred to as question 2.

In order to answer these questions, a test was designed by David Yaron and Jodi Davenport. This test consists of a set of true/false, multiple choice, and free response questions. The version given to CMU students is presented in section A.2, while the version given to MIT students is presented in section B.2. In both deployments, described in sections 8.4 and 8.5 below, the test was given to students as a pre-test before they used the applets and curriculum, and then again as a post-test after students had completed the material. At both CMU and MIT students were given, as a homework assignment, the completion of the pre-test, curriculum sequence, and post-test. Therefore, they completed the assessment materials outside of a classroom setting rather than in a computer laboratory, as was done during preliminary testing.

The pre-test and post-tests were administered online and students' responses were saved and subsequently analyzed. In order to answer question 1, each student's responses were scored like a normal test: correct answers were awarded one point and incorrect answers were awarded zero points. The number of correct answers was divided by the total number of questions to obtain a mean score. The mean score of each student's set of responses was averaged to obtain a mean for all respondents. This procedure was carried out for both the pre-test and the post-test. The pre-test and post-test means were compared using a two-tailed paired sample $t$-test with the null hypothesis that the mean of student scores was unchanged after using the applets and curriculum. The results of this analysis are presented in the sections below.

In order to answer question 2, student responses were aggregated in order to calculate the proportion of students who answered a given question correctly. This was done for each question for both the pre-test and the post-test. This data was then analyzed using a two-tailed dependent test of proportions[47] using the null hypothesis that students' use of the applets and curriculum produced no change in the proportion of students who provided the correct answer to a given question. The results of this analysis are presented in the sections below.

## 8.4 *Modern Chemistry II* at CMU

The use of the applets and curricular materials in David Yaron's *Modern Chemistry II* course in 2008 was the first large-scale deployment of the project materials among students. His course is generally taken by students in the second semester of their first year, following the first course in the sequence. In total 112 students participated, though the number of fully usable responses was quite a bit smaller, as discussed in section 8.4.2.

### 8.4.1 Curricular Goals

As depicted in figure 2-1 on page 28, the curriculum sequence used in this course covers energy states, the energy landscape, the heat bath, equilibrium state population distributions, activated process, degeneracy, entropy, and free energy. The curriculum used to explain concepts and direct student use of the applets is presented in appendix A. While some of the exercises were originally written by the author of this thesis, much of the in-depth explanation and all the graphics were produced by David Yaron.

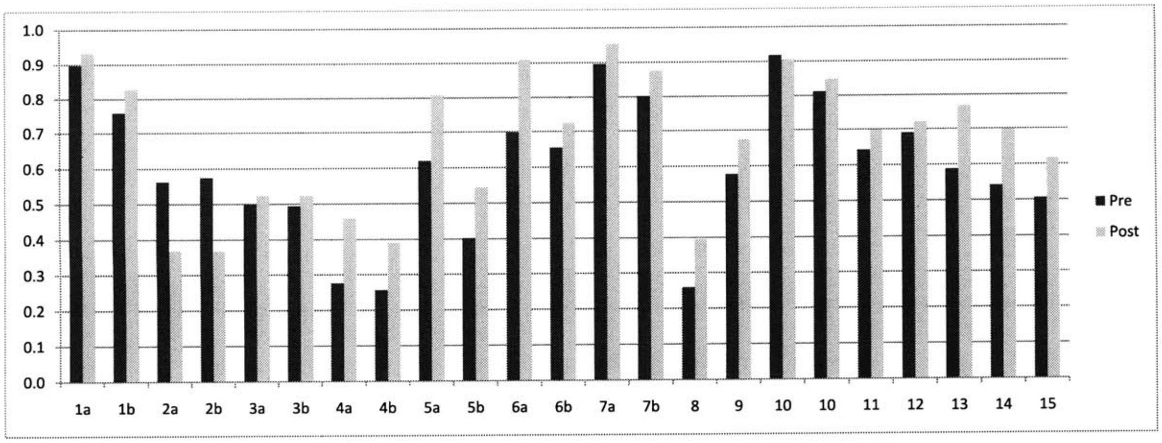


Figure 8-1: Fraction of students providing the correct answer for each question in the pre-test (dark gray) and post-test (light gray) at CMU

### 8.4.2 Selected assessment data and discussion

Figure 8-1 presents a histogram plot which shows, for each question on the pre-test and post-test, what proportion of students answered correctly. Looking at the data, there is a clear trend that the light gray bars, representing the post-test, are higher. This indicates that a higher proportion of students are answering questions correctly after using the applets and curriculum. While it is tempting to look for trends in order to verify that the applets and curriculum are having the intended effect, this is not sufficient. Rather, in order to establish that this observed trend is statistically meaningful, accepted statistical techniques must be used to analyze the data. In the sections below, questions 1 and 2, posed in section 8.3 will be addressed through appropriate statistical analyses.

#### Question 1

In this section, the question "Do the applets and corresponding curriculum produce any change in students' scores on a test of Molecular Science concepts?" is addressed. In order to do this, students' performance on the test as a whole was examined by Jodi Davenport.

Although 90 students took the pre-test and 89 students took the post-test, only 69 students completed both. By eliminating incomplete data and removing those students from the dataset who did not take both the pre- and the post-test, a pair of matching samples was created. That is, each student who appears in the pre-test dataset, also appears in the post-test dataset. As described above, each student's test was scored, awarding one point for a correct answer and zero points for an incorrect answer. This score was then divided by the total number of questions to obtain the fraction of questions that a student answered correctly. Finally, after this score was calculated for each student in both the pre-test and post-test datasets, the mean score for each dataset was calculated. By this procedure the mean for the pre-test was calculated to be $M = 0.59$ and the mean for the post-test was calculated to be $M = 0.67$.

In order to go beyond simply pointing to the increased mean as proof of the project's effectiveness, a two-tailed paired sample $t$-test was used. This is a standard tool for comparing mean scores from two different samples in order to ascertain whether the means have a statistically significant difference or whether their observed difference could be just due to random variability. The null hypothesis is that there is no difference in the true mean between these two samples and that the difference between them is due to chance. However, in this case, the analysis found $t_{68} = 4.638$, $p < 0.001$. The high $t$ value and very small $p$ value enable the null hypothesis to be rejected with confidence. That is, to a 99.9% degree of confidence, the difference between the measured means in the two tests is not due to random variability, but rather due to a real difference. Thus, on the basis of the $t$-test results, it is possible to answer question 1 in the affirmative: the applets and curriculum *do* result in a change in students' test scores. Specifically, the change observed is positive, indicating that students' use of the applets and curriculum improved their understanding of Molecular Science concepts.

### Question 2

While it is encouraging that students do appear to benefit from using the applets and curriculum created by the project, researchers always like to refine and improve their work. Unfortunately, the $t$-test presented above does not provide any clues about how or in what areas the applets or curriculum could be improved. In order to fill this gap, research question 2 is used.

By asking the question "Do the applets and corresponding curriculum produce any change in the proportion of students who correctly answer a given conceptual question?", it is possible to find specific aspects of the curriculum that could be improved. In particular, the question is whether statistically significant differences in the proportion of students who answer a given question correctly are observed between the pre- and post-tests. As discussed in section 8.3, this is done by performing a two-tailed dependent test of proportions on each question. This analysis found that questions 2a, 2b, 4a, 5a, 6a, 13, and 14 all display statistically significant changes in the proportion of students who answer them correctly, based on a 95% confidence level. The proportion of students who answered each question correctly is displayed in figure 8-1.

In order to more clearly observe the differences between students' responses to pre-test and post-test questions, figure 8-2 plots the fraction of students who answered a given pre-test question correctly subtracted from the fraction of students who answered the same question correctly on the post-test. One of the surprising features, which is immediately obvious upon looking at the data, is that the proportion of students who provided a correct answer to questions 2a and 2b decreased markedly after using the applets and curriculum. This is a clear area that needs some attention, especially given that questions 2a and 2b are two of the seven questions found to display statistically significant differences between the pre-test and post-test. Fortunately, as discussed in section 8.5.2, this result was not observed among MIT students who used the applets but with a somewhat different curriculum. These results indicate that student confusion at CMU may be related to the curriculum used there and is not the result of some fundamental flaw in the approach.

Figure 8-1 provides some insight into why some questions were not found to exhibit statistically significant changes: the initial proportion of students who answered the question correctly was already very high on the pre-test. With very high pre-test scores, there was little room for improvement. Questions 1a, 7a, and 10 are clear

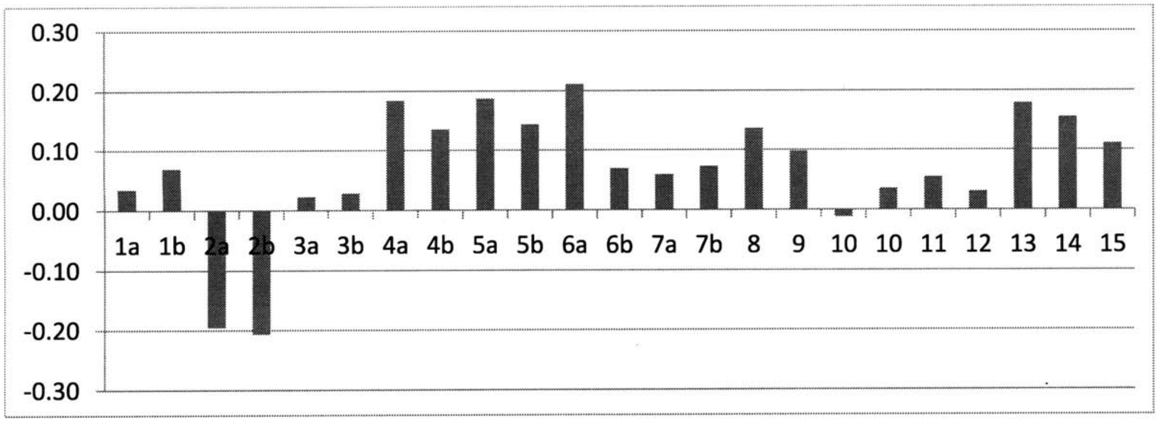


Figure 8-2: Change (post-test minus pre-test) in proportion of students who answered correctly for each question on the test at CMU

examples of this. Given that these questions were answered correctly by the vast majority of students, it is clear that students are comfortable with the concepts covered by these questions and additional work to clarify or expand on these concepts is not the most fruitful area into which to invest time and energy.

In contrast, question 4a is very interesting because, while it displays a statistically significant increase in the proportion of students who answered it correctly after using the project material, the proportion of students who answered the question correctly still remains below 50%. So, while the applets and curriculum are helping students to understand the material better, more effort is clearly needed to clarify the concept with students.

### 8.4.3 Selected student feedback

In addition to completing the pre- and post-tests, students were asked to fill out a feedback form in order to help project personnel understand students' ability to understand the analogies used and students' affective responses to the applets and curriculum.

While there are potentially many interesting conclusions to be made from the survey, one student's response provided explicit validation of the approach taken by the project. In response to the open-ended statement "This simulation helped me to understand...", one student in a humanities major wrote:

> what I knew or didn't know. It was sort of a metacognitive tool... the questions throughout prompted me to assess my learning of the last little chunk of material and to gauge my understanding vs what i [sic] was expected to have learned.

In addition to the above response, the survey indicated that students appreciated the interactivity of the applets and their visual nature.

## 8.5 *Introduction to Solid State Chemistry* at MIT

The deployment of project materials in Donald Sadoway's *Introduction to Solid State Chemistry* at MIT in the fall of 2009 involved, by far, the largest student participation of any of the deployments to date. His course is a first-semester undergraduate course and is one of two possible courses students can choose in order to satisfy a requirement that is universal to all students, regardless of major. Because of the requirement and his popularity as a lecturer, his class is always very large and thereby represents an excellent venue for testing materials developed in this project.

### 8.5.1 Curricular goals

As seen in figure 2-1 on 28, the goals for *Introduction to Solid State Chemistry* are the same as those for *Modern Chemistry II* up to the concept of thermally activated processes. The project curriculum used at MIT differs from that used at CMU in that it does not include degeneracy, entropy or free energy. As a consequence, questions pertaining to these concepts were omitted while the remainder of the test was identical. Specific questions intended to address the additional concepts presented in the MIT curriculum were not added to the pre-test or post-test, though the test already contained some questions related to reaction rates.

### 8.5.2 Selected assessment data and discussion

The research questions and analysis procedures used in assessing student learning during the MIT deployment mirror those presented in section 8.4.2. As such, the discussion here will be more direct.

#### Question 1

In order to determine whether, on the whole, student understanding of Molecular Science concepts improved as a result of using the applets and curriculum, a two-tailed paired sample $t$-test was conducted by Formative Evaluation Research Associates (FERA). After eliminating duplicates and removing students who did not complete both the pre- and post-tests, a pair of samples with $N = 334$ was obtained. The mean score for each sample was calculated and the pre-test mean was found to be $M = 0.66$, while the post-test mean was found to be $M = 0.77$. The $t$-test found $t_{333} = 12.285$, $p < 0.001$. This $t$ value is huge and indicates that the null hypothesis can be safely rejected. This result provides strong support to the idea that the applets and curriculum do, in fact, promote student learning of Molecular Science concepts.

#### Question 2

Figure 8-3 represents, for each question on the pre- and post-tests, what fraction of students answered correctly. The questions about degeneracy, entropy, and free energy are omitted, leaving blanks in the graph. This was done in order to preserve question numbering so comparison between CMU and MIT results would be straightforward. Qualitatively, the data looks similar to that obtained at CMU, in that the proportion of students answering questions correctly increases after they use the applets and curriculum.

In order to identify opportunities to improve the applets and curriculum, a two-tailed dependent test of proportions was performed for each question. In this analysis, all questions apart from 1a, 1b, 2a, 2b, and 10 involved statistically significant changes in the proportion of students who answered them correctly after using the project

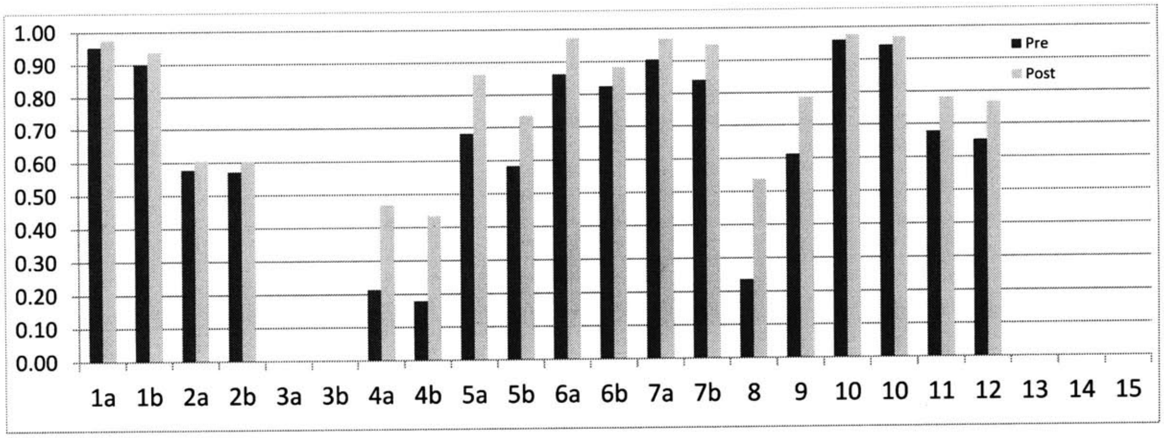


Figure 8-3: Fraction of students providing the correct answer for each question in the pre-test (dark gray) and post-test (light gray) at MIT

materials. Furthermore, questions 1a, 1b, and 10 were answered correctly by more than 90% of respondents during the pre-test. Thus, there was very little room to improve.

Questions 2a and 2b, which were discussed in section 8.4.2 are noteworthy because in the CMU test, the proportion of students who answered them correctly decreased significantly after using the project materials. Interestingly, in the MIT test, students did very slightly better on these questions after using the project materials, as seen in figure 8-4, but not in a statistically significant manner. Because the applets used in both deployments are the same, the discrepancy is assumed to be due to differences in the curriculum accompanying the applets. The source of student confusion will need to be investigated.

Like the CMU test, the proportion of students who correctly answered questions 4a and 4b was still very low on the post-test, even after a statistically significant improvement in comparison to the pretest. The fact that this question has proved to be so difficult for both students at CMU and MIT using different curricula may indicate that it is a very challenging and potentially subtle issue, or perhaps there is some semantic issue in the the questions that is causing student difficulty. This question also merits further investigation.

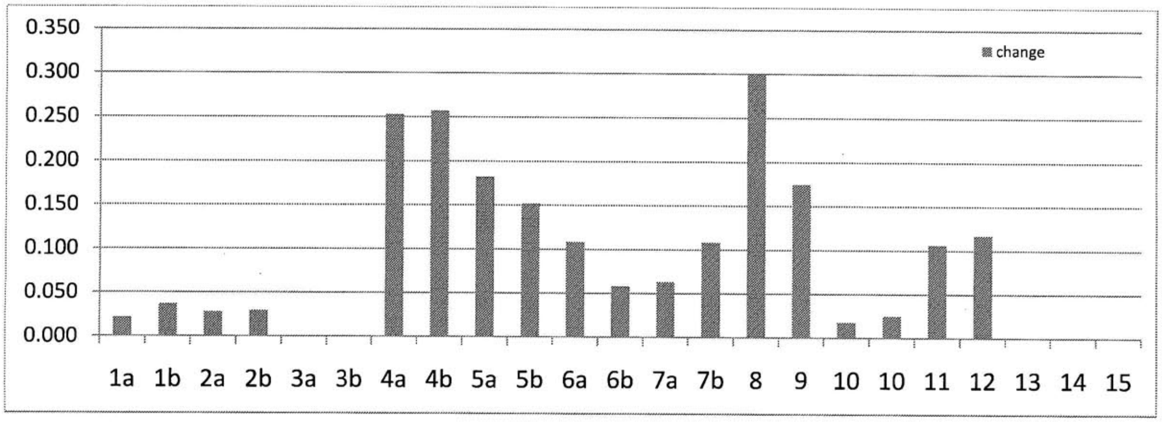


Figure 8-4: Change (post-test minus pre-test) in proportion of students who answered correctly for each question on the test at MIT

### 8.5.3 Selected student feedback

Like the deployment at CMU, the student feedback information obtained at MIT offers a number of insights. Students were asked to state whether they agree or disagree with a number of statements about the applets and curriculum. Possible responses were strongly agree, slightly agree, neither agree nor disagree, slightly disagree, or strongly disagree or disagree and only one response could be chosen to describe each statement.

In response to the statement "This activity helped me connect concepts in new ways", one quarter of respondents strongly agreed, while half of respondents slightly agreed. In response to the statement "This activity helped me see how the same principles apply to different topics", 70% of students either strongly or slightly agreed. Furthermore, 65% of students agreed that the activity "gave me a deeper understanding of principles I already knew" and nearly 70% of respondents agreed that the activity "was easy to understand".

## 8.6 Summary and Conclusion

In order to ascertain whether the materials created by this project actually succeed in enhancing student learning of Molecular Science concepts, a number of statistical tests were performed. The *t*-tests measuring overall student performance on pre-tests and post-tests enable the null hypothesis to be rejected. In fact, the large $t$ values provide strong support for the claim that the project materials *do* help students to understand concepts from Molecular Science. The tests of proportions performed by the author indicate students' performance on many of the individual questions on the pre- and post-tests, even when evaluated alone, is enhanced by using the project materials. Furthermore, the analysis of the individual questions helped to identify areas that need some improvement. In particular, these areas relate to students understanding of representations of kinetic energy in the applets and energy landscape diagram (questions 2a and 2b), and the availability of information related to the reaction rate in the energy landscape diagram (questions 4a and 4b). However, even in the face of these areas of potential improvement, statistical analysis indicates that the project materials already deliver on their promises.

# Chapter 9

# Future Work and Conclusion

## 9.1 Future work

During the development of the project described in this thesis, new and interesting ideas presented themselves daily. These ideas often related to additional phenomena to which the applets could be applied, or to ways the applets could be improved or expanded. In addition, concurrent to the work described elsewhere in the thesis, work on a new applet was begun, which is aimed at enabling students to understand interatomic interactions. Work that is planned on this and other ideas is presented in the rest of this section.

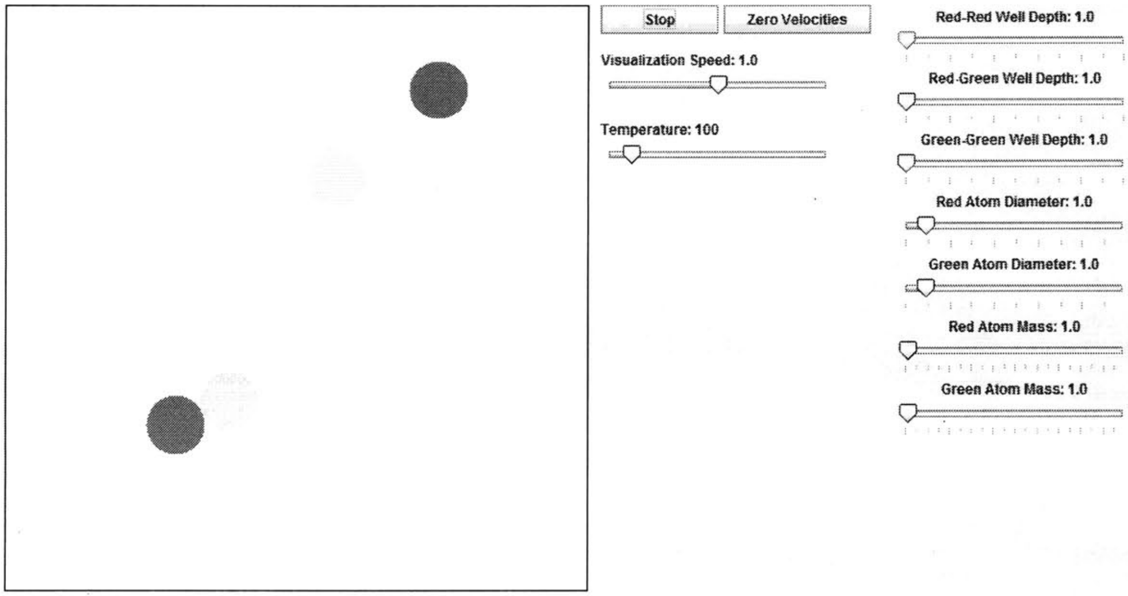
### 9.1.1 User-variable molecular dynamics

Molecular dynamics (MD) is a powerful computational tool that permits the simulation of systems of atoms and molecules according to classical mechanics[48]. Because classical mechanics produces atom trajectories that appear natural, students are comfortable viewing MD simulations. Therefore, MD simulations represent a useful tool in enabling students to observe and hopefully understand phenomena at very short length and time scales[49]. Fortunately, modern personal computers are now powerful enough that simple MD simulations can be run on student-owned computers, even within web browsers, as Java or Flash applets. There are many projects available online that already offer this type of capability[42, 43, 45]. In fact, most of the online materials aimed at presenting Molecular Science concepts use MD simulations to do so.

## Motivation

While the available MD simulations are useful, they are also somewhat limited. The author believes that by giving students greater control over system parameters, they could be made more valuable and instructive. The MD simulations cited above offer some level of interactivity, though the ability to specify system parameters is sometimes locked once the simulation begins running. Rapaport[50] describes a MD simulation that allows system parameters to be changed by the user on the fly, during the simulation. Expanding on those ideas, the author has developed an MD simulation framework that allows students to manipulate nearly all system parameters during the simulation, including the mass, radius, and interatomic interaction strength of atoms.

Most MD simulations used in education are written by researchers who use MD to explore real problems. As such, they require that the simulated atoms behave like real atoms as much as possible. However, the author believes that MD simulations for education need not be constrained to be realistic. That is, if only "real" atoms are simulated, certain fundamental relationships are obscured. By constraining an atom in a simulation to have a static mass, it becomes difficult for students to probe how an atom's mass affects its behavior. Even allowing an atom to change to a different chemical species on the fly does not remedy the problem, because, in that case, mass is convoluted with other parameter changes, like atom radius and interaction strength. By providing students with the ability to change each of these parameters separately while a simulation is running, it is hypothesized that they will be able to more readily understand over-arching trends governing interatomic interaction.



Visualization Speed: 1.0

Temperature: 100

Red-Red Well Depth: 1.0

Red-Green Well Depth: 1.0

Green-Green Well Depth: 1.0

Red Atom Diameter: 1.0

Green Atom Diameter: 1.0

Red Atom Mass: 1.0

Green Atom Mass: 1.0

Figure 9-1: Screen capture of interactive molecular dynamics applet

### Applet capabilities and research question

In keeping with the goal of the materials described in the rest of the thesis, the goal of an interactive MD simulation is to provide students with the tools necessary to explore a model system and acquire a qualitative, intuitive understanding of its behavior. Giving students the ability to manipulate many aspects of the system could enable them to explore the system more fully and answer questions that occur to them as they interact with it. As seen in figure 9-1, the applet in its current form allows students to manipulate the temperature as well as all the parameters that define each atomic species. Students may also reposition atoms within the visualization window by dragging them with the mouse or lock an atom in place by clicking on it. Other controls, including one that would allow the student to change the number of atoms in the system, could also be added.

However, in order to avoid overloading the student with options, this applet should be used as part of a curriculum sequence in which students are given the ability to manipulate different aspects of the system at different times rather than all at once.

Future work to develop curriculum materials around this applet is planned. Of particular interest is the following research question: "Does enabling students to dynamically adjust single atom properties independent of others have a positive or negative effect on student understanding?" While enabling students to adjust atom masses could help students to observe how the frequency of vibration of atoms in a diatomic molecule varies with mass, the fact that the mass can be varied continuously could introduce confusion in other areas. This question deserves to be explored.

### 9.1.2 Applet improvements

In addition to pursuing how to effectively present new ideas to students, there are a number of ways in which the applets described in chapters 4, 5, 6, and 7 can be enhanced. Many of these additions or changes would not be difficult to implement and have the potential to improve the experience of the user.

#### Platform model: ball rendering scheme

As discussed in section 5.2.3, rendering the balls in the platform model as disks with a non-zero radius resulted in errors in state population statistics. The chosen solution was to model the balls as zero-dimensional points but render them with a non-zero radius. This results in the balls overlapping the platforms and walls to some extent. This was seen as a reasonable price to pay in order to recover statistical accuracy.

However, some educators may not be concerned with quantitative analyses and may wish to use the more visually pleasing approach. Therefore, one way in which applets using the platform model could be enhanced is by adding the modeling scheme to be used as a customizable parameter, like those discussed in section 5.3.4. This would enable educators who prefer statistical accuracy to meet their needs, while those concerned only about illustrating the system's qualitative behavior could choose a scheme that looks more natural. In addition, advanced students could be asked to compare the two approaches and explain source and significance of the discrepancies between them.

### Adding temperature to kinetics applet

As described in section 7.3, the platform model does not produce the desired behavior in the net reaction rate when comparing the relative effects of halving the energy barrier versus doubling the system temperature. A number of potential solutions were presented in section 7.3.2. Future revisions of the software will artificially manipulate ball trajectories in order to guarantee that balls with enough energy to reach the activated state do, in fact, land on the activated platform. Student understanding of this visualization will also be examined in order to ascertain whether the dynamics are confusing to students. If this approach does prove to be confusing to students, alternate approaches will be sought.

### Simultaneous aspect ratio and platform adjustment

In the applet described in section 5.4.2 the platform model is displayed side by side with an array of two-dimensional boxes. Currently, it is possible to adjust platform heights but this should not be the case without some modifications. In order to enforce the correspondence between the platform model and the two-dimensional boxes, changing a platform's height should also change the aspect ratio of the boxes. Because changing the aspect ratio of a box also affects the energy barrier between the metastable and stable states, adjusting the height of the metastable or stable platform should also result in an adjustment of the narrow energy barrier platform. Implementing this behavior is planned for a future revision of the software.

### Auto-grouping of platforms

Section 6.3 describes an applet that presents the platform model side by side with the three-dimensional box model. When students use this applet, they can group platforms representing degenerate microstates into one large platform. However, the current method of grouping is not especially straightforward. The platform model only makes sense if the platforms corresponding to degenerate microstates are either fully grouped or fully ungrouped. Therefore, a button that would perform the grouping or ungrouping would simply operation of the applet for students. The addition of this functionality is planned for a future revision of the software.

### 9.1.3 Learning questions

Chapter 8 raised some interesting questions about student performance on the pre- and post-tests. A number of the questions raised are worth exploring in future deployments of the project materials.

#### Kinetic energy in modeled systems

One of the issues that students at both CMU and MIT found most difficult was the representation of kinetic energy in the applets. This issue was probed in the pre- and post-tests in questions 2a and 2b. At CMU, the fraction of students who answered these questions correctly decreased markedly after using the project materials, as noted in section 8.4.2. At MIT, while the proportion of students who answered these questions correctly did not decrease after using the project materials, it did remain quite low, as discussed in section 8.5.2. This difficulty may be due to insufficient explanation that the energy landscape, which is also known as the potential energy surface, only explicitly represents the potential energy of the system. This issue should be addressed in order to identify ways in which the concepts may be made clearer to students.

#### Speed of reaction in the energy landscape

As discussed in section 2.6, the energy landscape contains information that can be used to calculate the rate of a chemical reaction. However, as indicated in sections 8.4.2 and 8.5.2, students largely fail to recognize this. Even after using the project materials, fewer than half of the respondents at both CMU and MIT stated that the energy landscape diagram contained information about the speed of reaction. Determining the cause of this lack of understanding and finding ways to remedy it is a priority for future revisions of the curriculum.

#### Equilibrium state population distributions at high temperature

Sections 8.4.2 and 8.5.2 also indicate the students have difficulty understanding how population distributions function at high temperature. Although student understanding of this concept was improved substantially after using the project materials, only about 40% of CMU students and just over 50% of MIT students answered the post-test question on this topic correctly. It appears that students believe that at low temperature the stable state is favored, while at high temperature, the metastable state is favored. This is only partially true. At low temperature, the stable state is highly favored. However, at very high temperature, the stable and metastable states are roughly equally likely. Finding ways to improve student understanding of this concept will be a focus of future revisions to the curriculum.

### 9.1.4 Dissemination and user community

As mentioned in chapter 1, the project aimed to effectively and broadly disseminate the project materials in addition to developing a vibrant community of users. Now that the initial work on the project is complete, it is possible to improve the dissemination of the materials as well as to build a community of users.

#### Dissemination

While project materials are available at MatDL.org, simply making the materials available does not ensure that many potential users will find and take advantage of them. Therefore, it is necessary to build awareness of the project among the base of potential users. This potential user base consists of two distinct groups: instructors and students. In an effort to inform instructors about the materials, a number of talks have been given at various professional society meetings over the last few years. These efforts will continue and will be expanded to include papers in appropriate journals, such as the Journal of Chemical Education.

In addition to raising awareness of the project through conferences and journals, direct conversations with faculty at community colleges have also been initiated. It is predicted that the project materials could be especially effective with community college students, whose academic preparation tends to be weaker than that of students at CMU or MIT. In forging partnerships with community colleges, it is hoped that many students can benefit from the project materials.

While efforts have been made to inform instructors about these materials, little work has been done to raise the awareness of the project among students themselves or among learners who are unaffiliated with a university. To address this shortcoming, a number of efforts are planned. Because students tend to be heavily involved in online social networking, it makes sense to create a presence for the project within these social networks. At minimum, the project will get involved with Twitter and Facebook. Other social networks may be added as time goes on. In addition, in order to raise the project's visibility when users perform an online search, buying a few carefully chosen Google AdWords could help to ensure that the project is visible to those who are looking for related resources.

### User community

In addition to dissemination, growing the community of users is a priority for the project going forward. While finding instructors at other universities who are interested in using project materials within their own courses is a big part of this effort, it is also necessary to find instructors who are willing to help in the creation of new materials. As discussed in section 5.3.4 it is possible for instructors to customize the platform model without any programming experience. In order to facilitate this type of customization, documentation of the customization procedures will be added to the project web site.

However, it is possible that some instructors may want to modify the simulations more than is possible with the existing options for customization. In order to allow those with programming experience to tailor simulations to their exact needs, the publication of the simulation source code is also planned. Ideally, interested users could add functionality and contribute it back to the main project code base.

The project website will also be expanded to allow users to submit modified simulations and curriculum sequences. In so doing, it is hoped that the project website becomes a hub for instructors interested in teaching and developing new curriculum for Molecular Science concepts.

## 9.2 Summary and Conclusion

This thesis presented work undertaken by a group of collaborators at Carnegie Mellon University, Kent State University, and the Massachusetts Institute of Technology in an effort to help beginning undergraduate students learn Molecular Science concepts that form the basis of many science and engineering disciplines. In order to achieve the goal of helping students obtain a qualitative, conceptual understanding of these concepts, interactive online Java applets were designed and programmed. These applets used carefully designed models to teach students specific concepts through analogic connection to real chemical systems. The analogies used and the areas of applicability of the models were presented and discussed in the curriculum that was presented to students along with the applets. This curriculum also included specific exercises that students were asked to complete in order to draw their attention to the most meaningful aspects of the models.

Two main curriculum sequences were developed: one to fit the educational goals of David Yaron's *Modern Chemistry II* course at CMU and one to fit the curriculum of Donald Sadoway's *Introduction to Solid State Chemistry* course at MIT. These curriculum sequences were given to students as homework assignments in each class. The ability of the applets and the respective curriculum sequences to improve student understanding of molecular science concepts was tested using online pre-tests and post-tests. Statistical analysis of the results indicate that, at both CMU and MIT, student understanding did improve in a statistically significant manner, both overall and for many individual questions.

As a consequence of its ability to help students improve their understanding of Molecular Science concepts, this project represents a valuable contribution to the field of undergraduate science education. In addition, because of its free availability on the internet, it is easy for students and educators to use it, either personally or in a classroom setting. The customizability of the platform model also makes it possible for educators to tailor it to their own specific educational goals. It is hoped that as the work becomes more broadly known, a community of users will develop around it and contribute both specially-tailored applets as well as curriculum suitable for teaching an expanded set of concepts.

# Appendix A

# Curriculum and Test Given to Students at Carnegie Mellon University

## A.1 Curriculum and applets

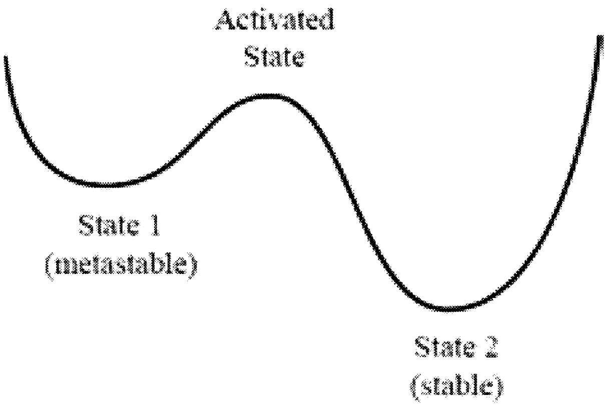
In this section, the online curriculum sequence used by students in the deployment at CMU will be presented without commentary. Some commentary on the curriculum and exercises is presented in chapters 4, 5, 6, 7, and 8. The curriculum is organized into pages. For each applet, there is a page of introduction. Once students have read the introduction they can click on a link to open the page containing the applet and exercises.

The pages containing the applets and exercises are divided into two frames. The top frame contains the applet and the bottom frame contains the exercises. After students have completed the suggested exercises, they can click on a link in the bottom frame to explanations of what they have just observed. Because the page is divided into frames, the applet is still accessible to students while they read the explanations. This enables them to use the applet to verify the explanations provided without having to navigate to a different page.

## A.1.1 Activity 1

### 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.



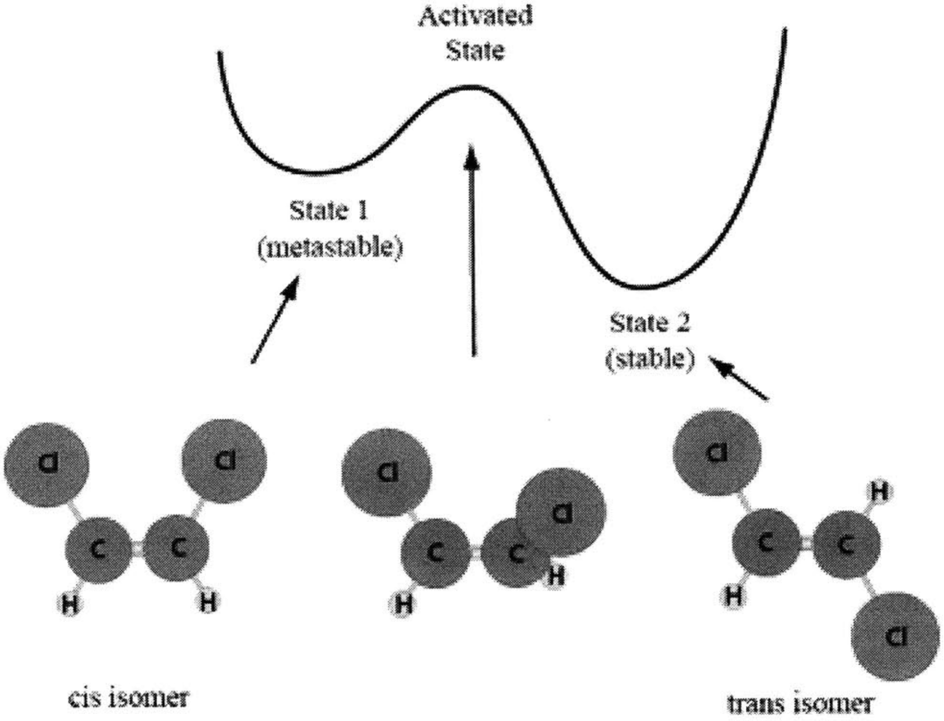
The diagram shows the energy associated with a thermally activated process in which a chemical system transitions between two states, labeled state 1 and state 2. State 2 is a stable state because it corresponds to the lowest energy configuration. State 1 is a metastable because, although it has higher 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.

### A.1.2 Activity 2

#### The reaction coordinate

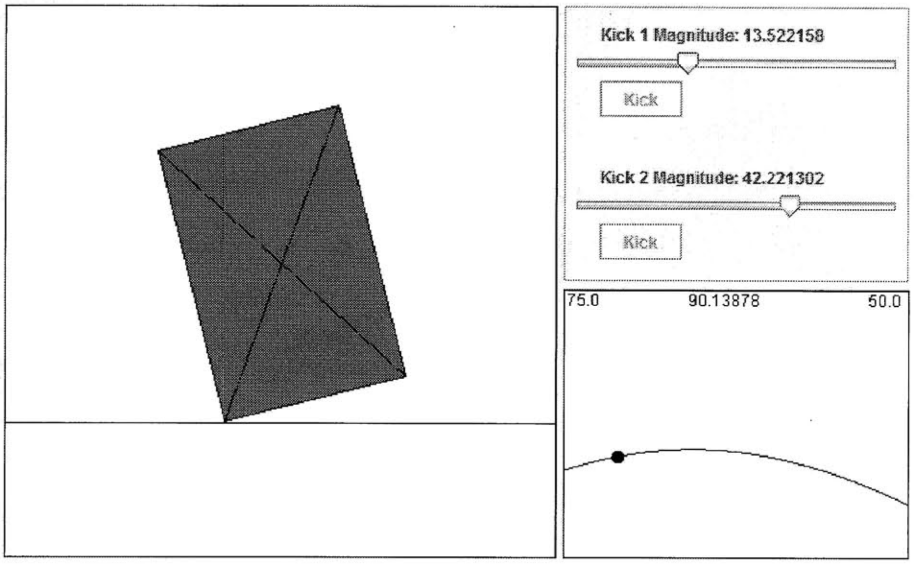
The first feature we will explore is the meaning of the x-axis in the above figure, which is known as the reaction coordinate Q. For a system to get from state 1 to state 2 it must follow some pathway. In most cases, we don't have detailed information on the precise nature of this pathway, but it is 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 $< 90°$ to correspond to the cis isomer (state 1) and all angles $> 90°$ 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.

### Applet for reaction coordinate


Kick 1 Magnitude: 13.522158

Kick 2 Magnitude: 42.221302

**Description of how to use the applet**

In this virtual lab, you are presented with a representation of a cardboard box. You can "kick" the box by clicking on the buttons marked "Kick!". You can use the sliders to adjust the magnitude of the kicks that you give to the box. If you give the box a large enough kick, you can cause the box to transition from one state to another.

**Activity: The Reaction Coordinate**

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.

**Question:** 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.)

**Question:** 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.)

**Question:** 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?

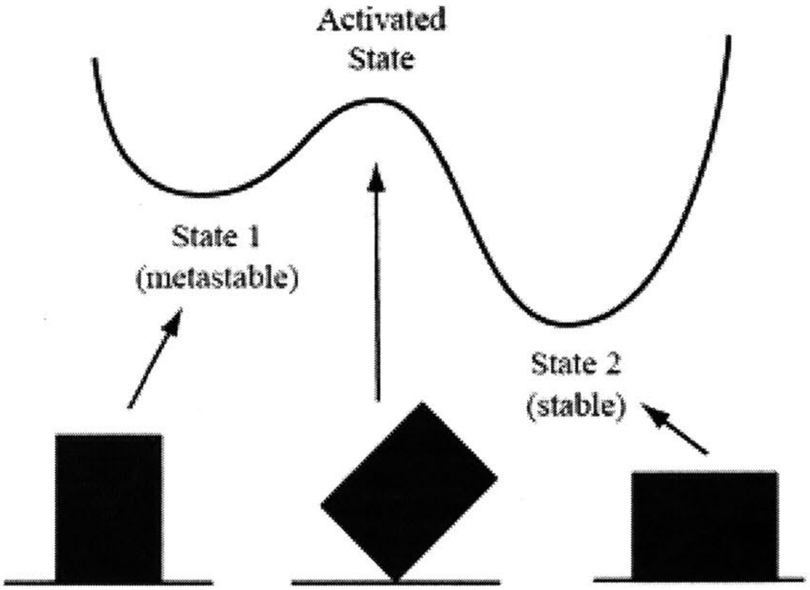
Notice the relation between the position of the box and the dot on the energy landscape. The landscape shows the gravitational potential energy of the system. What is Q for this system? What is state 1 and state 2? Which state is stable and which state is metastable? What does the transition state look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

Click the 'next' button for the answer...

## Answers

**Answer:**

The following diagram 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.



You can now close this window and return to the online activity.

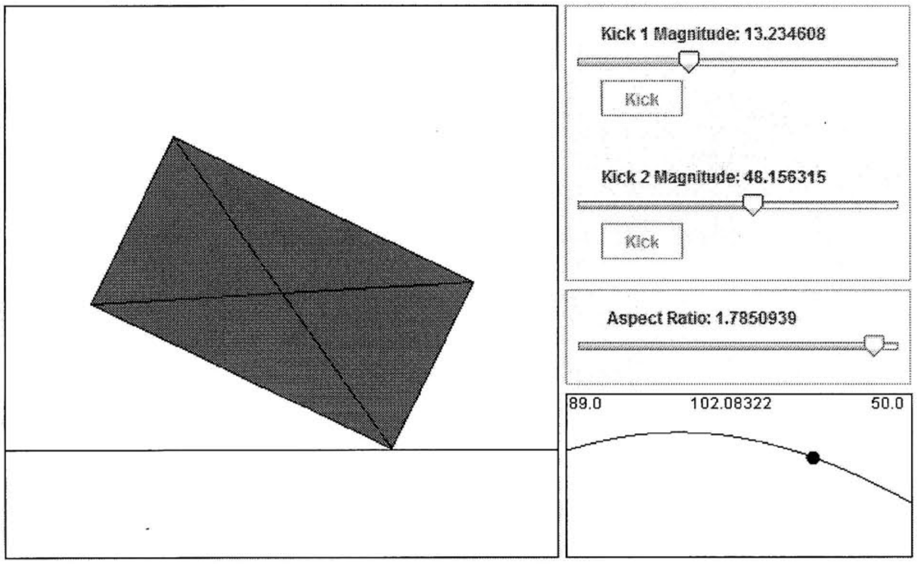
## A.1.3 Activity 3

### The energy landscape

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

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 on the previous page with flourines, we alter the energy landscape for the cis-trans isomerization. The van der Waals ratio (i.e. size) of Flourine is less than that of Chlorine. How do you think the energy landscape changes when you replace Cl with F?

### Applet for energy landscape



Kick 1 Magnitude: 13.234608

Kick 2 Magnitude: 48.156315

Aspect Ratio: 1.7850939

### Description of how to use the applet

This virtual lab is identical to the applet from the last lesson except that an additional control has been added. This additional control allows you to adjust the "aspect ratio" of the box in the visualization window. The aspect ratio of an object is simply the ratio between its length and its width.

### Activity: The Energy Landscape

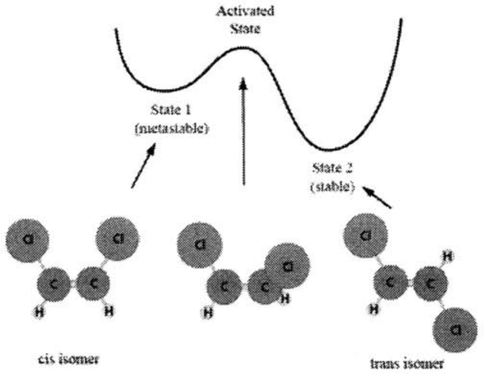
Try moving the "aspect ratio" slider and see what it alters.

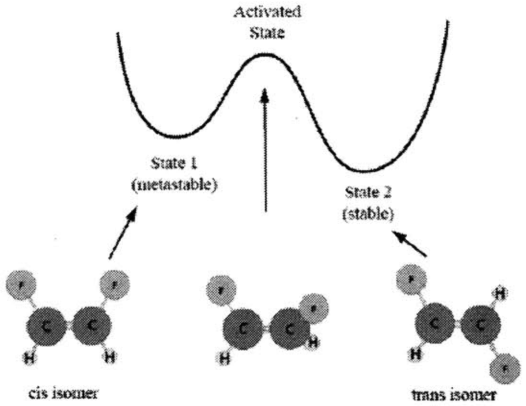
**Question:** For which aspect ratios is the reaction uphill in energy (energy of state 2 > energy of state 1)? For which aspect ratios is it a downhill reaction?

**Question:** 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?

### Answers

**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.

## A.1.4 Activity 4

### Population distributions

In the previous 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.

**Virtual Activity**

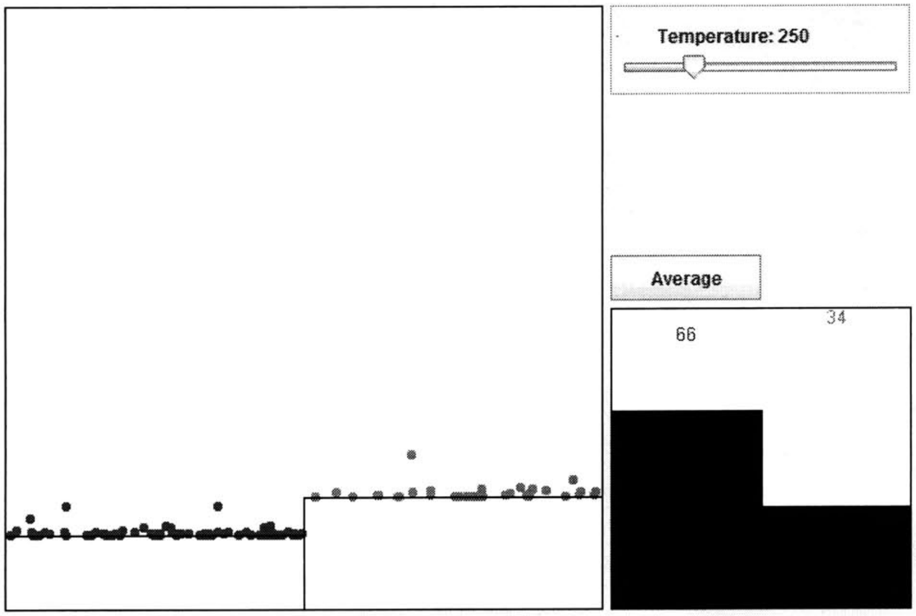
Population distributions(Java 1.5) [Opens in a separate window]

In the above activity, the ratio between the number of particles in state 2 and the number in state 1 is equal to:

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

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 $\Delta E$ and RT. $\Delta E$ 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.

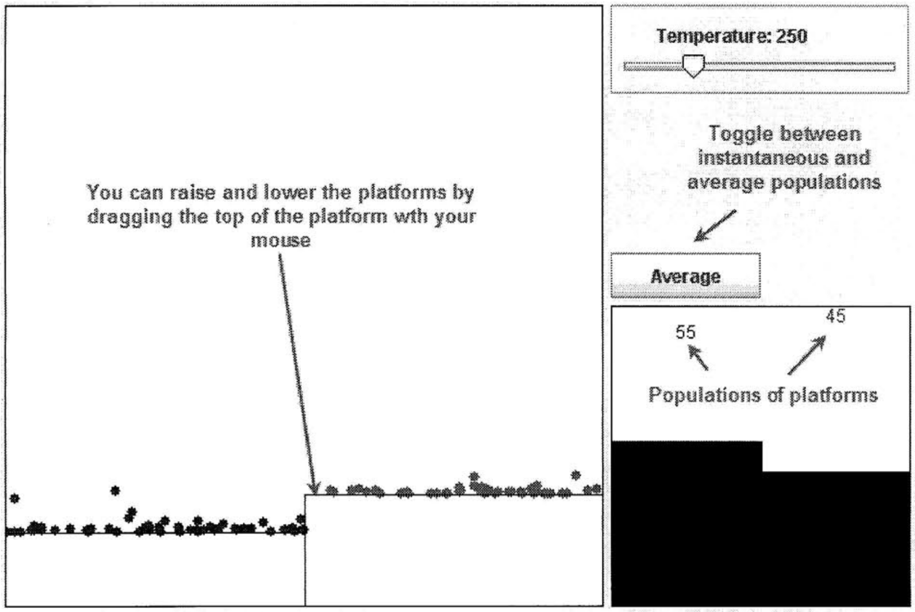
### Applet for population distributions



### Description of how to use the applet

The visualization window in the above virtual lab consists of a number of balls bouncing on raised platforms. (Please see image below for an annotated description.) The platforms' heights may be adjusted by positioning the mouse cursor near the top of the platform. The cursor icon will become a hand with the pointer finger extended. When this occurs, the platform may be made taller or shorter by pressing the left mouse button and dragging the mouse up or down.

The temperature of the system can be changed using the temperature slider at the top right. The histogram window at the bottom right shows the occupancy of each platform in real time. However, by clicking the "Average" button, the histogram shows the occupancy of each platform averaged over time. Clicking the "Average" button again changes the histogram back to displaying real-time occupancy.



Temperature: 250

You can raise and lower the platforms by dragging the top of the platform wth your mouse

Toggle between instantaneous and average populations

Populations of platforms

**Activity: Population distributions**

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.)

**Question:** 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?

### A.1.5 Activity 5

#### Motion at a constant temperature and exchange of energy with the heat bath

In this activity, we explore the motion of molecules at a constant temperature.

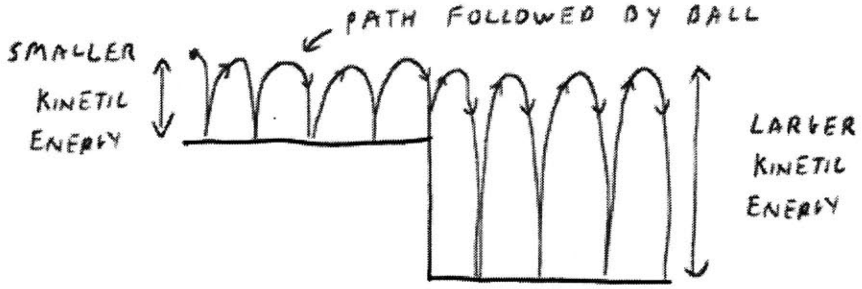
**Virtual Activity**

Motion at constant temperature, and exchange of energy with the heat bath (Java 1.5) [Opens in a separate window]

In the above activity, 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,

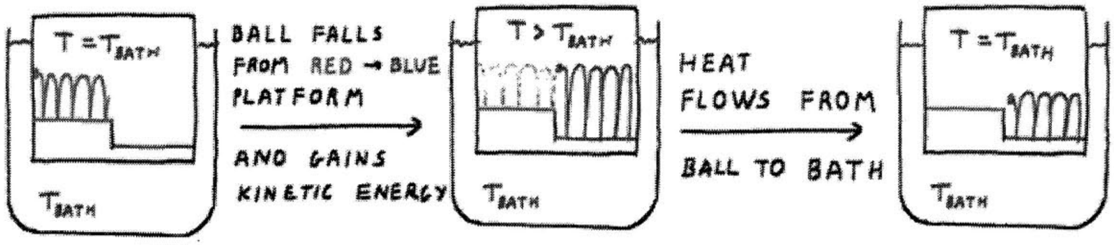
$$\langle \text{Kinetic energy per degree of freedom} \rangle = \frac{1}{2}kT$$

where k is the "Boltzmann constant" with a value 1.3806503 x 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.

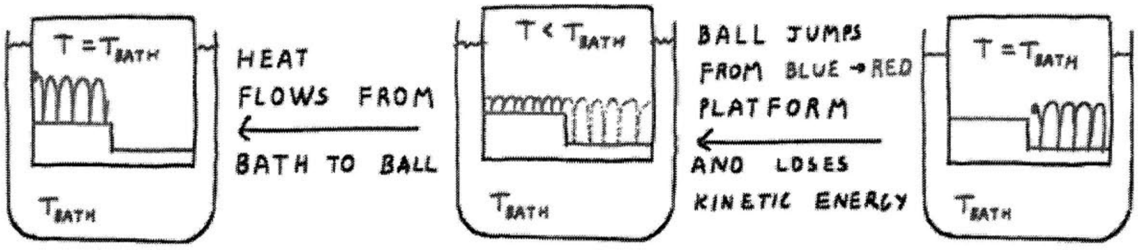


When the ball falls to the lower platform, gravitational potential energy is converted into kinetic energy, so the degree of bouncing is higher on the lower platform than it was on the upper platform. This means the average kinetic energy of the ball has increased. Since temperature is directly proportional 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¿Tbath), so heat flows into the heat bath until the temperature of the ball becomes equal to that of the heat bath (T=Tbath). 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.

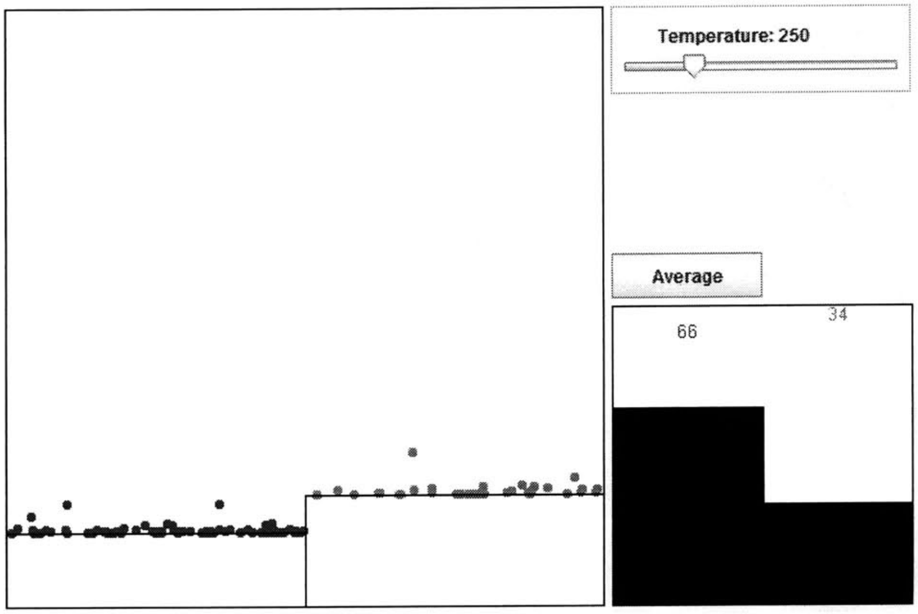


As the ball moves from state 1 (upper platform) to state 2 (lower platform), heat flows into the heat bath. The opposite is true for a transition from state 2 to state 1. Following the figure below from right to left, we see that as the ball transitions from the lower to the upper platform, it loses 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.



Question: 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?

### Applet for constant temperature motion and the heat bath



#### Description of how to use the applet

This activity uses the same applet as the last activity (Population distribution).

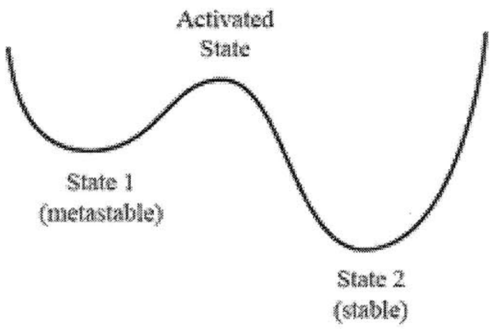
**Activity: Motion at constant temperature, and exchange of energy with the heat bath**

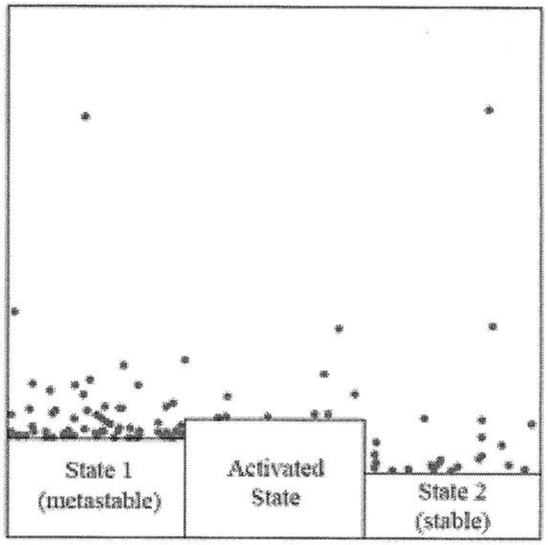
Increase the temperature of the system. What happens to the average height of the bouncing particles? Compare the average height of the bouncing balls on the upper platform to the lower platform. Are they different?

## A.1.6 Activity 6

### 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.





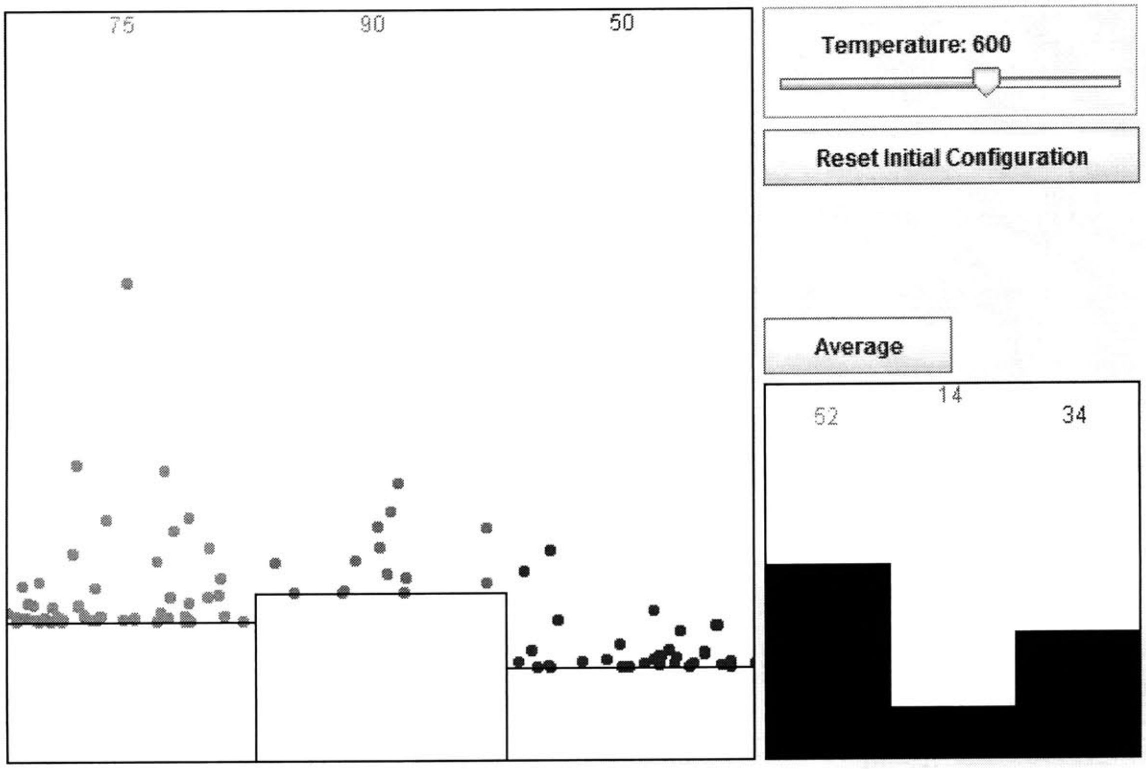
**View Virtual Lab**

Thermally activated processes (Java 1.5) [Opens in a separate window]

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 $\exp(-E_a/RT)$ 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 $\exp(-E_a/RT)$.

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 that 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.

### Applet for thermally activated process



### Description of how to use the applet

This simulation is similar to the previous lesson except that an additional platform has been added. The left and right platforms represent the metastable or stable states, respectively. The center platform represents the transition state between the metastable and stable states. Balls that make it onto this middle platform can be considered "activated", since they have enough energy to make it over the barrier to the stable state. In this lesson, all the balls start on the left, metastable side of the reaction. You can reset the simulation at any time to this starting distribution by clicking the 'Reset initial configuration' button. As before, the platforms' heights may be adjusted and the temperature of the system can be changed using the temperature slider at the top right.

### Activity: Thermally activated processes

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

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

**Question:** 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?

### A.1.7 Activity 7

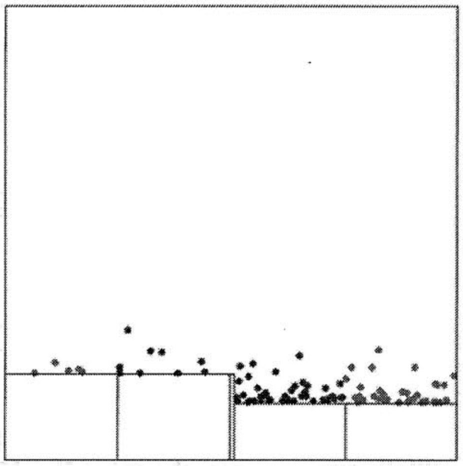
#### Energy and temperature determine the populations

Once a system reaches thermal equilibrium, the relative populations of two states is related only to the difference in energy between the states, $\Delta E$, and the temperature T, through the relation $P_2/P_1 = \exp(-\Delta E/kT$. The details of the dynamics do not play a role. This next activity illustrates this concept.

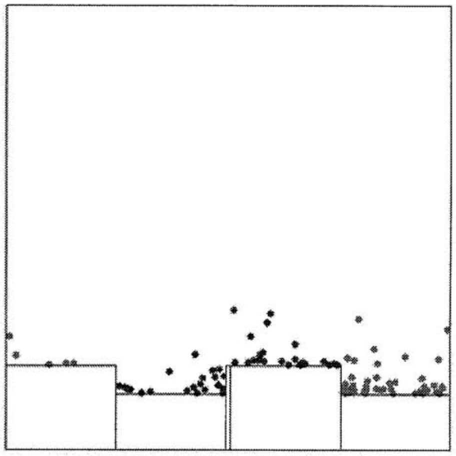
**View Virtual Lab**

Energy and temperature determine the populations (Java 1.5) [Opens in a separate window]

Now 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.



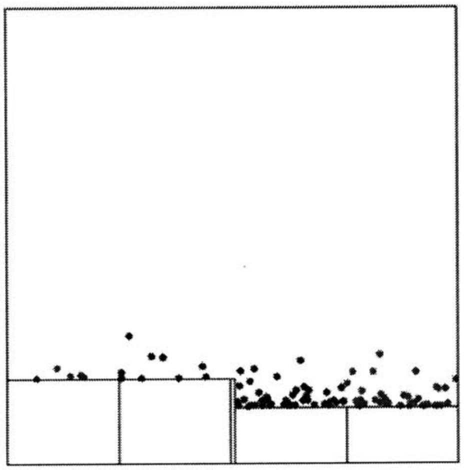
Arrangement 1



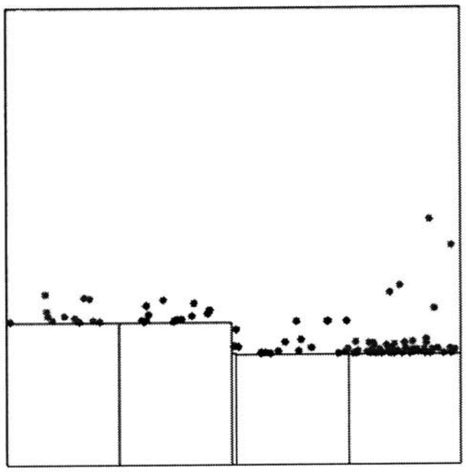
Arrangement 2

**Question:** 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 3



Arrangement 4

**Question:** At thermal equilibrium, with 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:

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

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 $E_2 > E_1$?

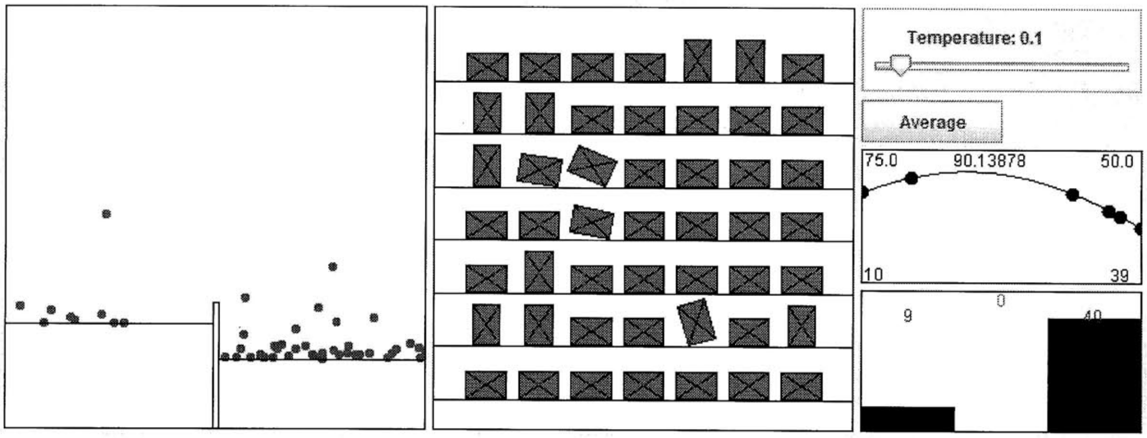
Click next to find the answer...

**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 an 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:

$$\frac{P_2}{P_1} = \exp\Big( - \frac{\Delta E}{R\infty} \Big) = \exp(-0) = 1$$

where we have used the fact that $1/\infty = 0$

## Applet for energy and temperature determine the populations


Temperature: 0.1

### Description

The relative populations of two states is related only to the difference in energy between the states, ?E, and the temperature T, through the relation $P_2/P_1 = \exp(\Delta E/kT)$. The details of the dynamics do not play a role. This 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 and two are at low energy. 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 $\Delta E$ and T, however, the detailed manner in which the system reaches this steady state depends on the details of the dynamics.

### A.1.8 Activity 8

**Entropy and Free Energy**

This simulation introduces entropy into the systems. The simulation extends the above two-dimensional boxes to three dimensions.

**View Virtual Lab**

Entropy and free energy (Java 1.5) [Opens in a separate window]

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 | |

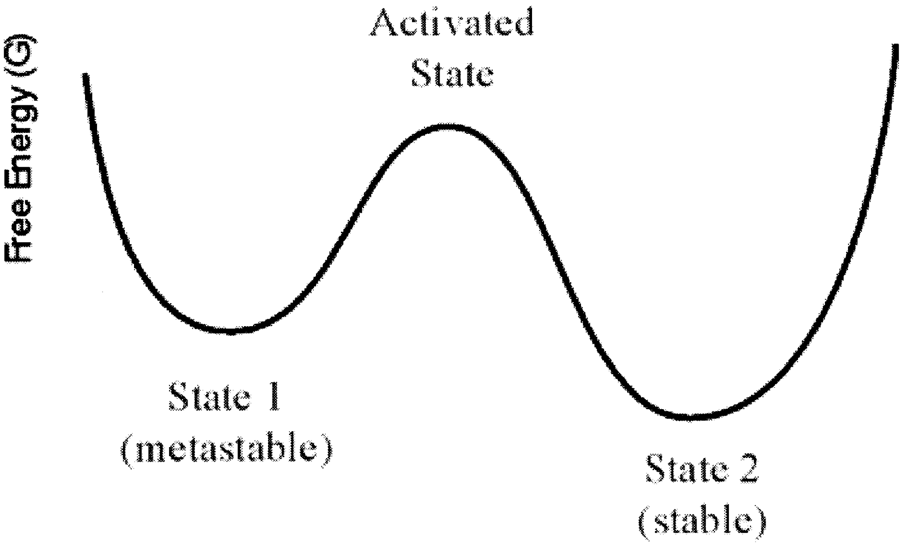
Or, equivalently, we can say the following reactions: box laying down $\Longrightarrow$ box standing up ball on lower 2 platforms $\Longrightarrow$ ball on upper 4 platforms are entropy-driven but not enthalpy-driven.

This interplay of energy and entropy is captured mathematically by the free energy: $G = H - TS$ 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.

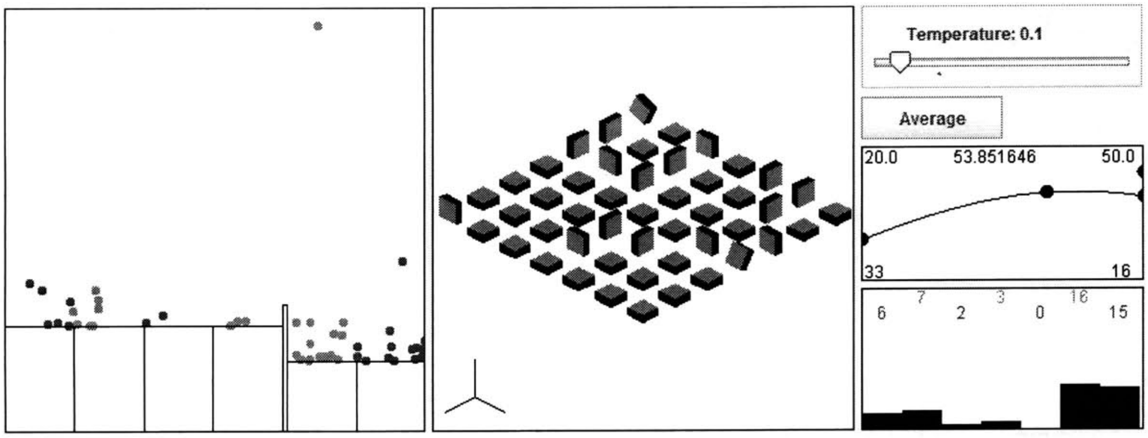
We will show below that we can include the entropy effects by replacing energy with free energy in our population expression:

$$\frac{P_2}{P_1} = \exp\left(-\frac{G_2 - G_1}{kT}\right) = \exp\left(-\frac{\Delta G}{kT}\right)$$

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



### Applet for entropy and free energy



#### Description

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: Entropy and free energy

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

**Question:** 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)?

## A.1.9 Activity 9

### Mathematical derivation of free energy

Above, we used the expression:

$$\frac{P_2}{P_1} = \exp\left(-\frac{\Delta E}{kT}\right)$$

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:

$$\frac{P_{\text{a short side}}}{P_{\text{a long side}}} = \exp\left( - \frac{\Delta E}{kT}\right)$$

(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:

$$\begin{aligned} P_{\text{all standing-up configurations}} &= P_{\text{short side 1}} + P_{\text{short side 2}} + P_{\text{short side 3}} \\ &\quad + P_{\text{short side 4}} \\ &= 4 \cdot P_{\text{a short side}} \end{aligned}$$

Similarly, the total population of boxes lying down is:

$$\begin{aligned} P_{\text{all lying down configurations}} &= P_{\text{long side 1}} + P_{\text{long side 2}} \\ &= 2 \cdot P_{\text{a long side}} \end{aligned}$$

The ratio is then:

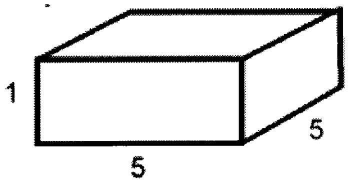
$$\frac{P_{\text{all standing-up configurations}}}{P_{\text{all lying-down configurations}}} = \frac{4 \cdot P_{\text{a short side}}}{2 \cdot P_{\text{a long side}}} = \frac{4}{2} \exp\left( - \frac{\Delta E}{kT}\right)$$

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

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} \exp\left(-\frac{\Delta E}{kT}\right) = \frac{\Omega_2}{\Omega_1} \exp\left(-\frac{E_2 - E_1}{kT}\right)$$

where $\Omega_n$ 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).

**Question:** Consider a box with dimensions as shown below. Suppose the difference in energy between the box standing up and laying down is ?E. What is the ratio between the total population 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:

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} \exp\left(-\frac{\Delta E}{kT}\right)$$

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

$$\frac{P_2}{P_1} = \frac{\Omega_2}{\Omega_1} \exp\left(-\frac{\Delta E}{kT}\right) = \frac{\Omega_2}{\Omega_1} \exp\left(-\frac{E_2 - E_1}{kT}\right) = \frac{\Omega_2 \exp(-E_2/kT)}{\Omega_1 \exp(-E_1/kT)}$$

If we want the effects of $\Omega$ to be comparable to the effects of energy, we need to move $\Omega$ 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 $kT$

$$\Omega = \exp\left(\frac{kT\ln\Omega}{kT}\right)$$

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

$$\Omega = \exp\left(\frac{TS}{kT}\right)$$

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

$$\frac{P_2}{P_1} = \frac{\Omega_2\exp(-E_2/kT)}{\Omega_1\exp(-E_1/kT)} = \frac{\exp(TS_2/kT)\exp(-E_2/kT)}{\exp(TS_1/kT)\exp(-E_1/kT)}$$

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

$$\frac{P_2}{P_1} = \frac{\exp(\frac{TS_2}{kT})\exp(-\frac{E_2}{kT})}{\exp(\frac{TS_1}{kT})\exp(-\frac{E_1}{kT})} = \frac{\exp(-\frac{E_2-TS_2}{kT})}{\exp(-\frac{E_1-TS_1}{kT})} = \frac{\exp(-\frac{G_2}{kT})}{\exp(-\frac{G_1}{kT})} = \exp\left(-\frac{\Delta G}{kT}\right)$$

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.)

## A.2 Pre- and post-test

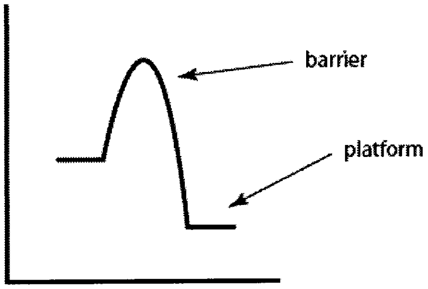
This section contains the test that was given to students as both the pre-test and post-test. Here the correct answers to the questions are marked with an asterisk but the correct answers were not indicated on the tests students received.

### A.2.1 Test

*Please complete the following 15 questions. When prompted to explain your answer, please explain your reasoning in a sentence or two.*

*For questions 1-7, please refer to the graph below.*

*Free energy diagrams convey qualitative information about chemical reactions. For each question, a) Determine whether each piece of information is available in the diagram; and b) what aspect of the diagram allows you to make the inference.*



1a. Is information about the relative potential energy differences between states available in the diagram above?

____ Yes* ____ No

1b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms*

____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available

2a. Is information about the relative kinetic energy differences between states available in the diagram above?

____Yes ____No*

2b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms

____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available*

3a. Is information about the relative entropy between states available in the diagram above?

____ Yes ____ No*

3b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms

____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available*

4a. Is information about the speed of reaction available in the diagram above?

____ Yes* ____ No

4b. What aspect of the diagram allows you to make this inference

____ Height differences between platforms

____ Height of barrier*

____ Number of barriers

____ Number of platforms

____ Information not available

5a. Is information about the number of transition states available in the diagram above?

____ Yes* ____ No

5b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms

____ Height of barrier

____ Number of barriers*

____ Number of platforms

____ Information not available

6a. Is information about the number of stable states available in the diagram above?

____ Yes* ____ No

6b. What aspect of the diagram allows you to make this inference

____ Height differences between platforms

____ Height of barrier

____ Number of barriers

____ Number of platforms*

____ Information not available

7a. Is information about whether the reaction is endothermic or exothermic available in the diagram above?

____Yes* ____ No

7b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms*

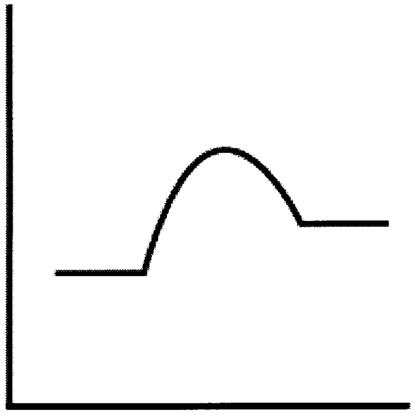
____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available

**Questions 8-9 refer to the following diagram**



8. At very high temperature which of the following is true:

____ The number of molecules in State 1 will be roughly equal to the number in State 2.*

____ The number of molecules in State 1 will be much less than the number in State 2.

____ The number of molecules in State 1 will be much greater than the number in State 2.

____ Cannot determine based on given information.

Please explain how you determined your answer: ________________

9. At very low temperature which of the following is true:

____ The number of molecules in State 1 will be roughly equal to the number in State 2.

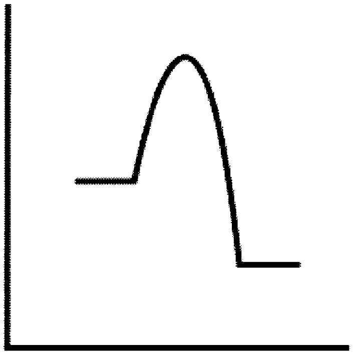
____ The number of molecules in State 1 will be much less than the number in State 2.*

____ The number of molecules in State 1 will be much greater than the number in State 2.

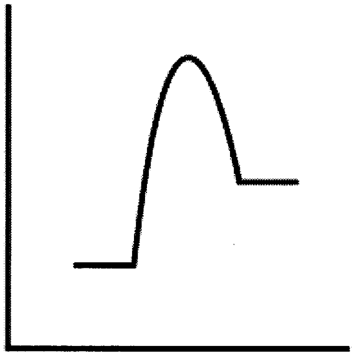
____ Cannot determine based on given information.

Please explain how you determined your answer: ________________

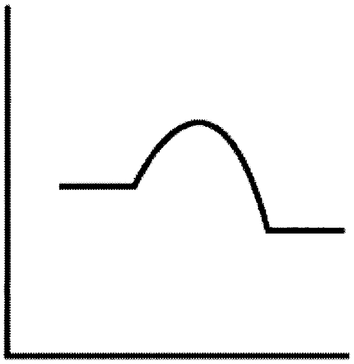
**Questions 10-12 refer to the following diagrams.**



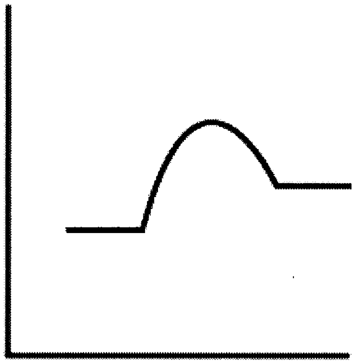
a.



b.



c.



d.

10. Which of these reactions give off heat from State 1 to State 2? (Check all that apply)

____ Graph a*

____ Graph b

____ Graph c*

____ Graph d

____ Can't tell

Please explain your answer: ________________

11. A system starts will all molecules in State 1 (on the left). Which of the following systems will take the longest to reach equilibrium?

____ Graph a

____ Graph b*

____ Graph c

____ Graph d

____ Can't tell

Please explain your answer: ________________

12. A system starts with all molecules in State 1 (on the left). Which of the following systems will reach equilibrium the fastest?

____ Graph a

____ Graph b

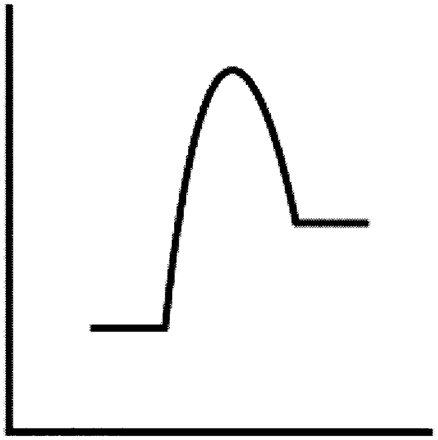
____ Graph c *

____ Graph d

____ Can't tell

Please explain how you arrived at your answer: ________________

**Questions 13-15 refer to the following diagram:**



13. As temperature increases:

____ The ratio of molecules in State 2/State 1 increases. *

____ The ratio of molecules in State 2/State 1 decreases.

____ The ratio of molecules in State 2/State 1 remains the same.

____ Cannot tell from given information.

Please explain how you arrived at your answer: ________________

14. If the majority of molecules are in State 2, this chemical process is:

____ energy driven

____ entropy driven*

____ exothermic

____ inconsistent with conservation of energy

____ none of the above

Please explain your answer: ________________

15. If the majority of molecules are in State 1, the chemical process is:

____ energy driven*

____ entropy driven

____ exothermic

____ inconsistent with conservation of energy

____ none of the above

Please explain your answer: ________________

# Appendix B

# Curriculum and Test Given to Students at the Massachusetts Institute of Technology

## B.1 Curriculum and applets

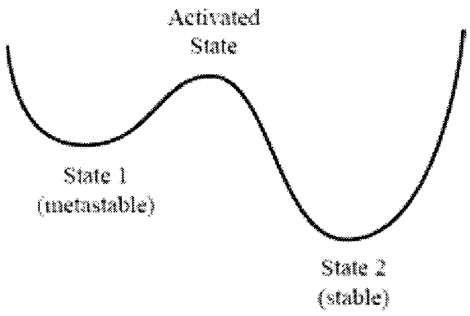
In this section, the online curriculum sequence used by students in the deployment at MIT will be presented without commentary. Some commentary on the curriculum and exercises is presented in chapters 4, 5, 6, 7, and 8. The curriculum is organized into pages. For each applet, there is a page of introduction. Once students have read the introduction they can click on a link to open the page containing the applet and exercises.

The pages containing the applets and exercises are divided into two frames. The top frame contains the applet and the bottom frame contains the exercises. After students have completed the suggested exercises, they can click on a link in the bottom frame to explanations of what they have just observed. Because the page is divided into frames, the applet is still accessible to students while they read the explanations. This enables them to use the applet to verify the explanations provided without having to navigate to a different page.

### B.1.1 Lesson 1

#### Introduction

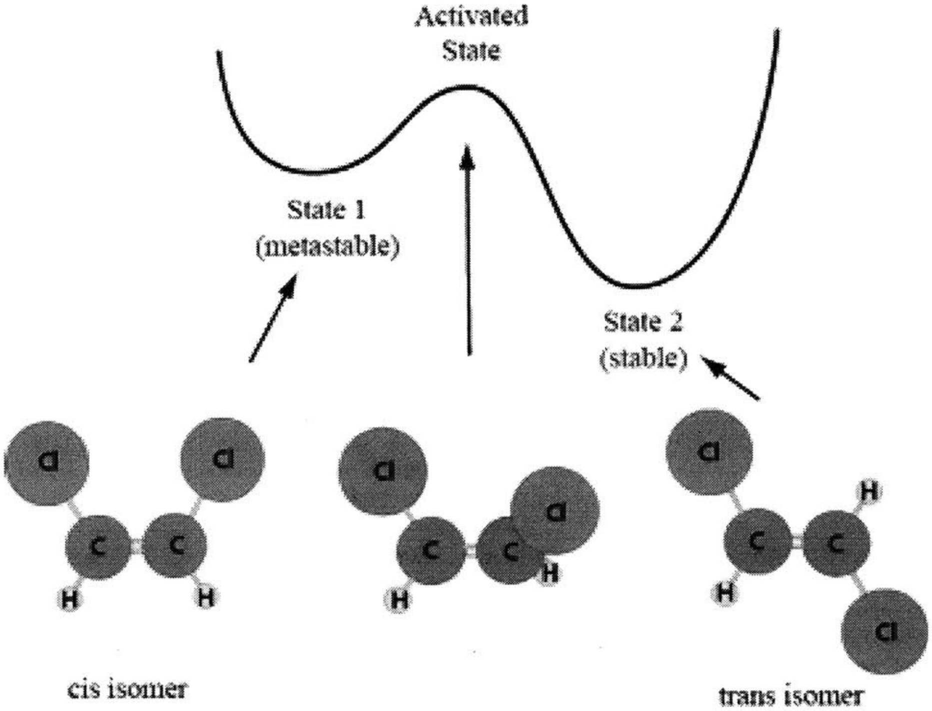
Introduction The goal of this activity is to provide insight into the ways modern science views the effects of temperature on chemical reactions, particularly thermally activated processes. Schematic energy diagrams of the type shown below have tremendous power as tools for thinking about chemical reactions at the molecular level.



The diagram shows the energy associated with possible states of a thermally activated process,labeled state 1 and state 2. The y-axis represents the amount of energy. From the diagram, we can infer that state 2 is a stable state because it corresponds to the lowest energy configuration. State 1 is metastable because, although it has higher energy than state 2, the system must overcome an activation barrier (represented by the hill between the states) 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 begin by exploring the meanings of various features of the above diagram and how it is used to think about chemical processes.

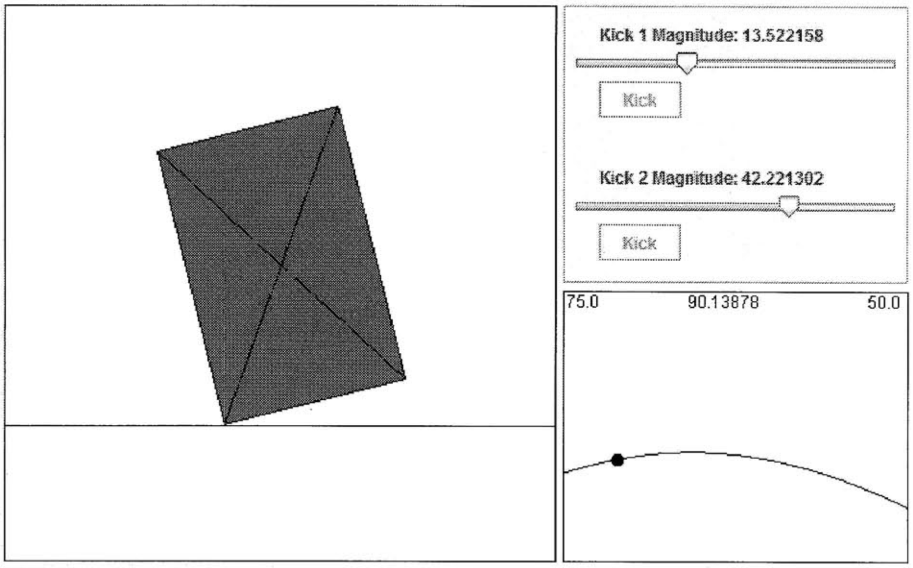
The reaction coordinate The first feature we will explore is the meaning of the $x$-axis in the above figure, which is known as the reaction coordinate $Q$. For a system to get from state 1 to state 2 it must follow some pathway. In most cases, we don't have detailed information on the precise nature 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 $< 90°$ to correspond to the cis isomer (state 1) and all angles $> 90°$ 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.

### Applet for lesson 1



Kick 1 Magnitude: 13.522158

Kick 2 Magnitude: 42.221302

### Description of how to use the applet

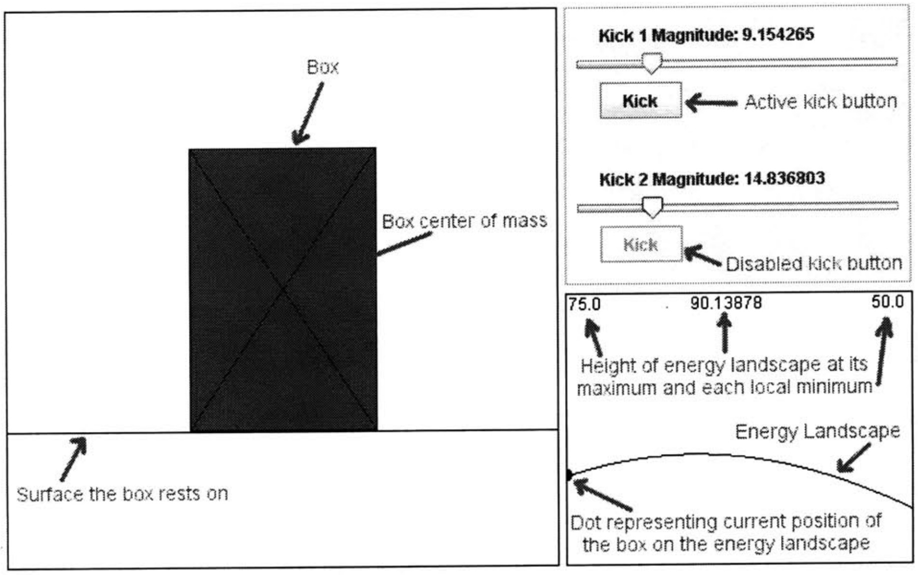
In this virtual lab, you are presented with a representation of a cardboard box. Professor Sadoway used a similar box in class to introduce you to the concepts of a state and an energy barrier between states. This applet lets you explore those concepts in greater detail.

Before starting with the activities, let's describe the applet and what is represented in the applet. Let's call the state that the box is in initially "state 1". There are two types of kicks you can give to the box: kick 1 and kick 2. Kick 1 is the kick given to the box when it's in state 1, while kick 2 is the kick given to the box when it's in state 2. You can use the sliders to adjust the magnitude of these kicks.

In order to actually give the box a kick, click on the button labeled "Kick" in black (not gray). If you give the box a large enough kick, you can cause the box to transition from one state to another. Note that it is not possible to give a kick when the box is in motion. It is also not possible to give a box kick 1 when the box is in state 2 and vice versa.

The window on the bottom right of the applet is a graph of the box's potential energy versus the reaction coordinate. Such a graph is normally called an "energy landscape". The hill shape you see in this graph is similar to the hill at the center of the energy landscape illustration you saw on the main page for this set of activities. The black dot sits on the left side of the hill when the box is in state 1. If the box is kicked, the black dot moves along the energy landscape and shows, in real-time, the potential energy of the box as the height of its center of mass changes. If the kick is large enough to cause the box to transition from state 1 to state 2, the dot will make it over the top of the hill in the energy landscape and come to rest in state 2 on the right side of the window.

See the figure below for descriptions of all the controls and displayed information in the applet.



### Activity: The Reaction Coordinate

- Try kicking the box over (with the upper kick button). Once it falls over, try kicking it back up (with the lower kick button).
  - Determine the minimum kick needed in each direction and write these numbers down.
- Notice the relation between the position of the box and the dot on the energy landscape. Recall that the landscape shows the gravitational potential energy of the system as a function of the reaction coordinate, Q.

  - What is Q for this system?
  - Describe the box when it's in state 1 and state 2.
  - Which state is stable and which state is metastable?
  - Describe the box in when it's in the transition state.

Think about these questions before clicking to the next page...

### Answers

Let's examine the answers to the questions asked on the previous page.

- Determine the minimum kick needed in each direction and write these numbers down.
  - **Answer:** *You should have determined that the minimum magnitude of Kick 1 necessary to produce a transition is 15.169926.*
  - **Answer:** *For Kick 2, the minimum magnitude that will result in a transition is 40.01698.*
  - Note that these values could also be obtained by subtracting the height of the energy landscape at its maximum from its height at the two minima. These three values are displayed at the top of the energy landscape window. The difference in height between the maximum and each minimum represents a difference in gravitational potential energy. By giving the box a kick with kinetic energy nearly equal to these potential energy differences, the box is able to surmount the barrier between the two states and it crosses the barrier with nearly zero kinetic energy. Note that the discrepancies between the minimum kick values calculated from the potential energy values in the energy landscape window and those observed through trial and error are due to numerical issues in the simulation and are not meaningful.
- What is Q for this system?

  - **Answer:** *The reaction coordinate for this system is the angle that one of the box faces makes with the surface it's resting on. Depending on which box surface you choose for measuring the angle, Q runs between 0 and 90 degrees or 90 and 0 degrees.*

- Describe the box when it's in state 1 and state 2.

  - **Answer:** *When the box is in state 1, it is standing up on its end. When it's in state 2, it's lying on its side.*

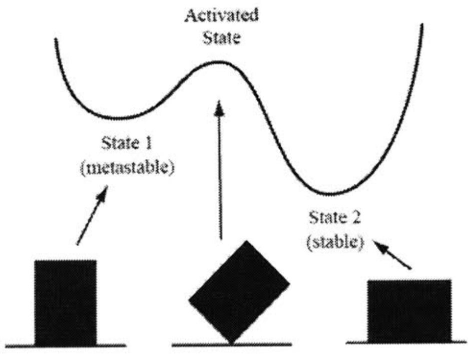
- Which state is stable and which state is metastable?

  - **Answer:** *Because the center of mass of the box is higher in state 1, state 1 is metastable. State 2 is stable because it has the lowest center of mass and, consequently, the lowest gravitational potential energy. This conclusion should also be clear from the kick magnitudes you recorded. A larger kick is always necessary to transition out of a stable state than out of a metastable state. As you discovered, the minimum kick needed to transition out of state 2 (Kick 2) is almost 3 times as large as the kick necessary for the reverse transition, demonstrating that state 2 is stable while state 1 is metastable.*

- Describe the box in when it's in the transition state.

  - **Answer:** *The transition state is the state in which the box's center of mass is highest. This occurs when the box is standing up on one corner and one of the diagonal lines drawn on the box is vertical.*

Many of the answers above can be seen in the following figure:

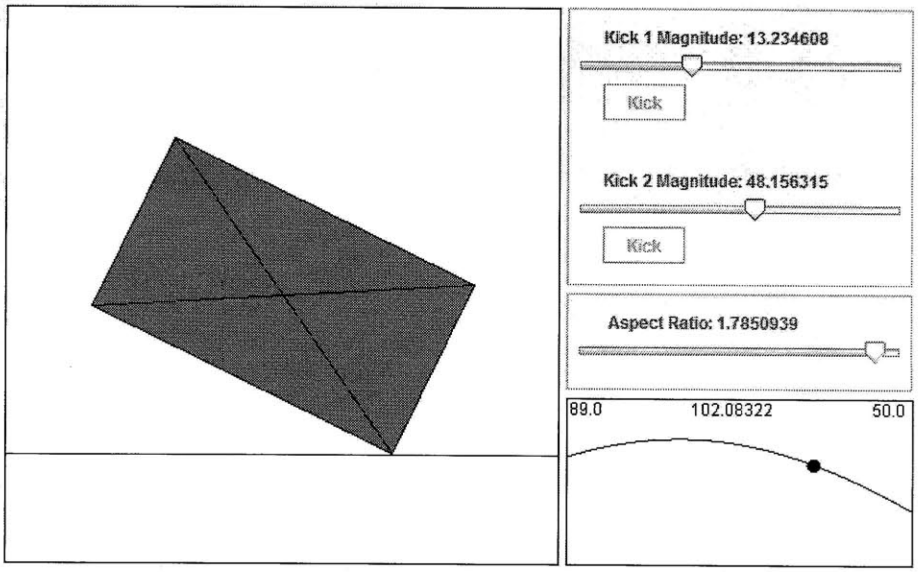


## B.1.2 Lesson 2

### The energy landscape

What factors determine the curve of the energy landscape? In this activity, we explore the factors that establish this curve.

### Applet for lesson 2



Kick 1 Magnitude: 13.234608

Kick 2 Magnitude: 48.156315

Aspect Ratio: 1.7850939

### Description of how to use the applet

This virtual lab is identical to the applet from the last lesson except that an additional control has been added. This additional control allows you to adjust the "aspect ratio" of the box in the visualization window. The aspect ratio of an object is simply the ratio between its length and its width. The goal of this lesson is to help you explore how changing the structure of the system causes changes in the energy landscape.

**Activity: The Energy Landscape**

- Try moving the "aspect ratio" slider.
  - What does it control?
- Recall from the last lesson that the box is initially in state 1, represented by the minimum on the left side of the energy landscape window.

    - For which range of aspect ratios is the energy of state 2 greater than the energy of state 1?
    - For which range of aspect ratios is the opposite true?
    - Which aspect ratio value separates these two regions?

- 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?

Think about these questions before clicking to the next page...

### Answers

- Try moving the "aspect ratio" slider.
    - What does it control?
        - **Answer:** *In this applet, the size of the box's base is kept fixed, so the aspect ratio slider basically just controls how tall the box is. However, by changing the height of the box, the box's center of mass is also changed. The center of mass is what controls the box's gravitational potential energy, so changes in the box's center of mass also produce changes in the energy landscape.*
- Recall from the last lesson that the box is initially in state 1, represented by the minimum on the left side of the energy landscape window.
    - For which range of aspect ratios is the energy of state 2 greater than the energy of state 1?
        - **Answer:** *Note that decreasing the aspect ratio reduces the energy of state 1 while the energy of state 2 remains fixed. If you reduce the aspect ratio until the height of the energy landscape for state 1 is lower*

*than that of state 2, you should find that state 2 has a higher energy than state 1 for aspect ratios below 1.*

  - For which range of aspect ratios is the opposite true?
    - **Answer:** *The energy of state 1 is greater than the energy of state 2 for aspect ratios greater than 1.*
  - Which aspect ratio value separates these two regions?
    - **Answer:** *When the aspect ratio is different from 1, one state has a higher energy than the other. However, when the aspect ratio is 1, the two states have the same energy.*

- 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?
    - **Answer:** *From the answer above, we know that the driving force is minimized (actually, equal to zero) when the aspect ratio is 1. If you start at an aspect ratio of 1 and increase or decrease the aspect ratio, you'll find that a change in either direction results in an increase in the driving force. In this applet, the aspect ratio is limited to values between 0.5 and 2. Within those limits, the driving force is maximized when the aspect ratio is 2.*

      *However, if we didn't have those limitations, we would find that the largest driving force occurs when the aspect ratio is infinity. This is because the energy of state 2 is fixed at 50 (since the size of the rectangle's base is fixed) and if the aspect ratio were 0, the driving force would be 50 (i.e. 50 - 0). However, if the aspect ratio were infinity, the driving force would be infinity (i.e. infinity - 50).*
  - For what aspect ratio is it easiest to knock the box over?
    - **Answer:** *When considering the driving force, we looked at the difference between the energies of states 1 and 2. However, in trying to*

*figure out the aspect ratio that makes the box easiest to knock over, we need to look at the difference in energy between the activated state and the stable and metastable states.*

*As discussed previously, the amount of kinetic energy that the box needs to be given in a kick in order to reach the activated state is equal to the difference in potential energy between the activated state and the box's initial state. In this case, we will confine our discussion to the metastable state since we know that the difference in energy between the activated state and the metastable state is always less than the difference between the activated state and the stable state.*

*If you start with an aspect ratio of 1 and change the aspect ratio, you will notice that the difference in energy between the activated state and the metastable state (which is state 1 when aspect ratio* $>$ *1; state 2 when aspect ratio* $<$ *1) decreases in both directions. Clearly, this quantity is maximized when the aspect ratio is 1. Thus, we should expect the quantity to be minimized away from an aspect ratio of 1.*

*It turns out that when the aspect ratio is 0 or infinity, the difference in potential energy between the activated state and the metastable state goes to zero and the box is trivially easy to push over. This is because the height of the energy landscape on each end of the diagram is related to the lengths of the box's sides while the height of the energy landscape for the activated state is related to the length of the diagonals drawn inside the box. When the aspect ratio is 0 or infinite, those diagonals have the same length as the longest side, meaning that the activated state has the same height as the metastable state.*

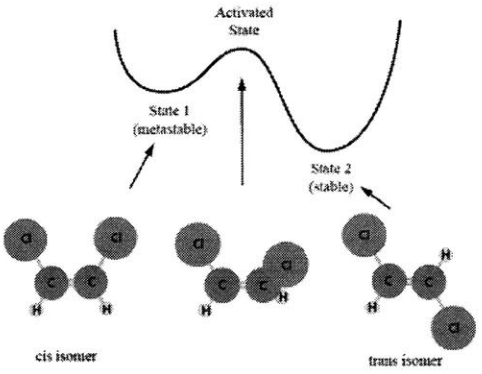
*You may have also noticed that when the aspect ratio is 1, the activated state is directly in the middle of the graph, but as the aspect ratio is increased, the activated state moves to the left. If you were able to increase the aspect ratio to infinity, this trend would continue until the activated state and the metastable state at the left of the graph merged* *into a single activated state.*

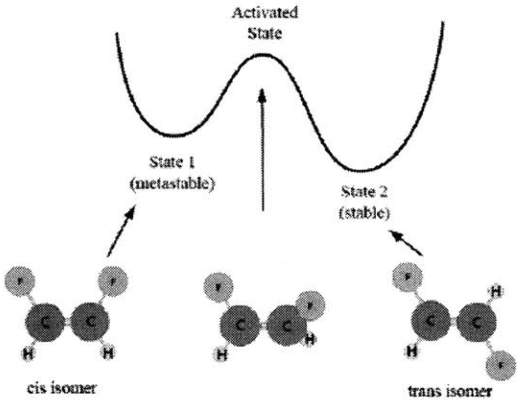
This activity illustrates that the energy landscape is established by the structure of the system. For a chemical system, it is established by the molecular structure. For instance, if we replace the chlorines of the molecule shown in the introduction to lesson 1 with fluorines, we alter the energy landscape 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?

Think about these questions before clicking to the next page...

**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.

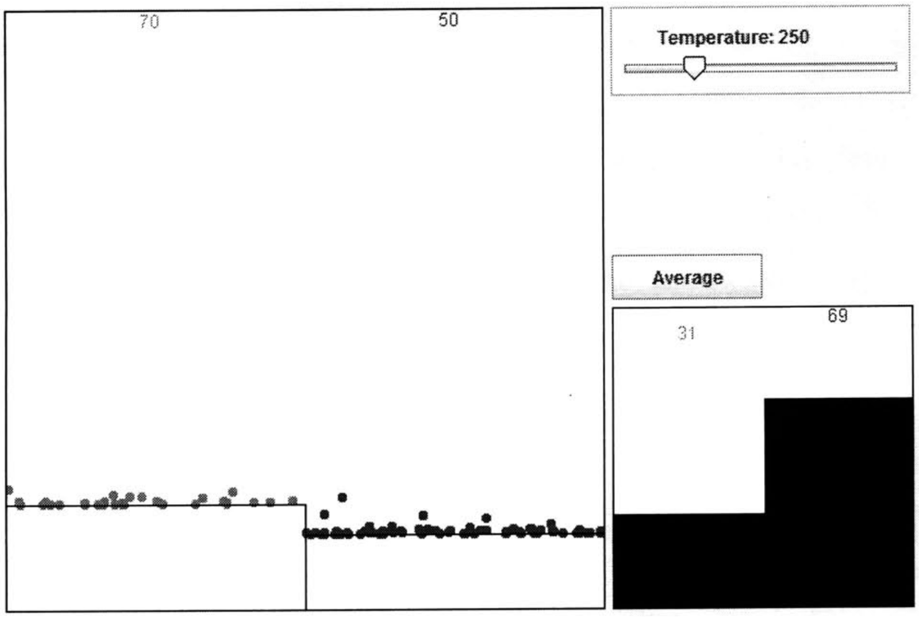
### B.1.3 Lesson 3

#### The effects of a heat bath: Motion at constant temperature

In the above simulations, you determined the strength of kick needed to change the state of the box (either 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 kinetic 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. However, instead of boxes, let's now consider placing balls on the platform.

#### Applet for Lesson 3



#### Description of how to use the applet

The visualization window in the above virtual lab consists of a number of balls bouncing on raised platforms. (Please see image below for an annotated description.) Each platform represents a state similar to the stable and metastable states we examined with the box simulation. The array of platforms represents the energy landscape for the balls. That is, each platform represents a state and each platform's height represents the potential energy of the state.

The top surface of each platform is in contact with a heat bath. Because of this connection to the heat bath, whenever the balls hit the top surface of the platforms, they are given kicks (i.e. kinetic energy), which cause them to rise above the platform in an arc. While they travel upwards, the conservative force of gravity causes their kinetic energy to be converted into potential energy. When they are at the apex of their trajectories, all their initial kinetic energy has been converted to potential energy. Thus, at the apex of their trajectories, their heights above the platforms that kicked them are an indicator of how much kinetic energy they received when they were kicked. Of course, the speed of the ball immediately after it is kicked also indicates how much kinetic energy it received from the kick.

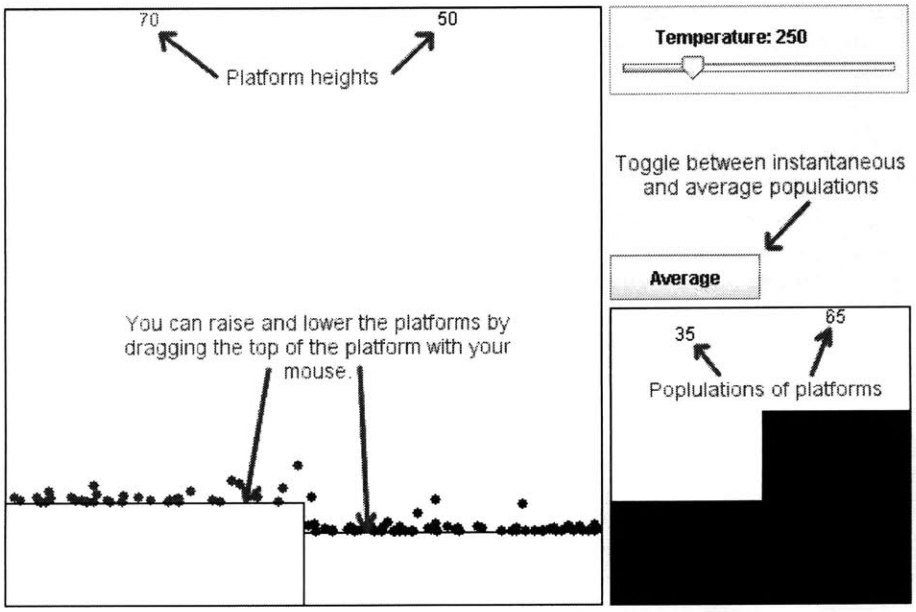
Without getting into too many details, you should know that a heat bath basically acts as a temperature regulator. As you probably know, temperature is proportional to the average kinetic energy in the system. If we set the temperature of the heat bath to a certain value but the system has too much kinetic energy, some of that kinetic energy will be removed from the system as the balls interact with the heat bath, which, in this simulation, occurs on the top surface of the platforms. (You can watch this happen by setting the temperature very high for a few seconds and then very quickly reducing the temperature.) Of course, if the system initially has too little kinetic energy, as the balls interact with the heat bath, they will be given greater amounts of kinetic energy. We will cover further properties of the heat bath later.

To make this simulation more interesting, you may manipulate the energy landscape: the platforms' heights may be adjusted by positioning the mouse cursor near the top of the platform. The cursor icon will become a hand with the pointer finger extended. When this occurs, the platform may be made taller or shorter by holding down the left mouse button and dragging the mouse up or down. The height of each platform is displayed at the top of the window.

The temperature of the heat bath can be changed using the temperature slider at the top right, either by clicking and dragging with the mouse or by clicking on it with the mouse and using the left and right arrow keys to decrease or increase the value.

The histogram window at the bottom right shows the occupancy of each platform in real time. However, by clicking the "Average" button, the histogram shows the occupancy of each platform averaged over time. Clicking the "Average" button again changes the histogram back to displaying real-time occupancy.

Note that the balls are treated as zero dimensional points but they are rendered with a finite (non-zero) size. This means that they will appear to overlap with the platforms a bit. It is necessary to treat the balls as points in order to ensure that there is no "excluded volume", which could prevent us from collecting accurate population statistics.



### Activity: Being kicked by a thermal bath: Motion at constant temperature

- When the system is initialized there are equal numbers of balls on each platform.
  - What happens as time progresses and why? (If you need to start the simulation over, just click the reload button on your browser.)

- Try increasing the temperature of the system.
  - What happens to the average height of the low-bouncing particles?
  - What happens to the average height of the particles that bounce the highest?
  - Does the frequency with which high-bouncing particles are observed increase or decrease when the temperature is raised?
- Compare the average number of particles on the upper platform to that of the lower platform (ratio = upper platform population / lower platform population).
  - What is the ratio like at low temperatures? (Don't choose too low a temperature and make sure that you give the system some time to find equilibrium.)
  - Does the ratio increase or decrease as you raise the temperature?
- Try lowering the upper platform (but keep it higher than the other platform).
  - How does this affect the ratio described above?
  - How would the ratio change if you lowered the higher platform until both platforms were the same height?
  - How would the ratio change if you now raised the left platform again?
  - If you wanted to make the population ratio as close to zero as possible, what would you do?

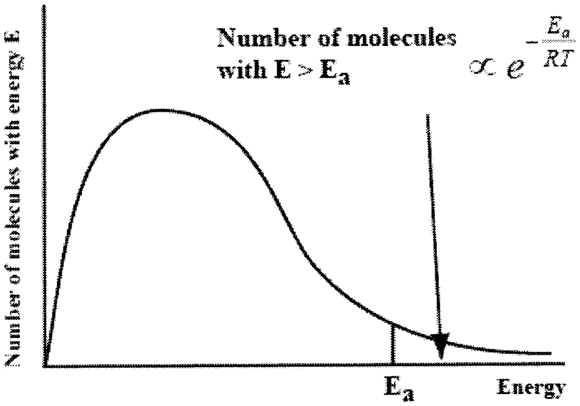
Think about these questions before clicking to the next page...

### Answers

Here is a discussion of the general concepts you need to understand in order to answer the questions asked on the previous page.

The balls on the upper platform can be viewed as being "activated", since they have higher potential 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.

In lecture 22, the number of activated molecules was discussed in terms of the Maxwell-Boltzmann distribution. The number of activated molecules, i.e. particles on the upper platform, is proportional to $\exp(-E_a/RT)$ where $E_a$ is the difference in energy between the two platforms. This is illustrated in the figure below, which shows the Maxwell-Boltzmann distribution.



More generally, the ratio between the number of particles in the higher state and the number in the lower state is equal to

$$\frac{P_{\text{high}}}{P_{\text{low}}} = \exp\left(-\frac{E_{\text{high}} - E_{\text{low}}}{RT}\right) = \exp\left(-\frac{\Delta E}{RT}\right)$$

where $P_{high}$ and $P_{low}$ are the "populations" of the upper and lower states, respectively. That is, they represent the average number of particles in each of these states.

Note that $P_{high}/P_{low}$ depends only on $\Delta E$ and $RT$. $\Delta E$ 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 $P_{high}/P_{low}$, 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.

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 frequency with which a system gets a strong enough kick to reach an activated state, represented here as a tall platform.

Now that you understand the fundamental mechanisms that govern the behavior of these particles, let's look at the answers to the questions.

- When the system is initialized there are equal numbers of balls on each platform.
  - What happens as time progresses and why?
    - **Answer:** *You observed that many particles move from the high platform to the low platform until a small number of particles are left on the high platform. This is because the initial configuration is not the equilibrium configuration. In particular, the initial population of the higher platform is much too high. So, particles leave the high platform until equilibrium is reached. Equilibrium occurs when the frequency with which particles move from the high platform to the low platform equals the frequency with which particles make the opposite transition.*
- Try increasing the temperature of the system.
  - What happens to the average height of the low-bouncing particles?
    - **Answer:** *It increases a bit.*
  - What happens to the average height of the particles that bounce the highest?
    - **Answer:** *It increases quite a lot. That is, it appears to increase much more than the height of the low-bouncing particles.*
  - Does the frequency with which high-bouncing particles are observed increase or decrease when the temperature is raised?
    - **Answer:** *High-bouncing particles are observed more frequently when the temperature is increased. All of these behaviors are essentially properties of the Maxwell-Boltzmann distribution.*
- Compare the average number of particles on the upper platform to that of the lower platform (e.g. $P_{high}/P_{low}$).

  - What is $P_{high}/P_{low}$ like at low temperatures?
    - **Answer:** *At low temperatures it's easy for particles to move from the high platform to the low platform but difficult for particles to jump from the low platform up to the high platform. Thus, at low temperature when the system is at equilibrium, there are very few particles on the high platform but many particles on the low platform. This implies* $P_{high}/P_{low}$ *is small.*

      *Note that this ratio can only take values between 0 and 1. Think about the circumstances required in order for those limiting values to be observed.*
    - Does $P_{high}/P_{low}$ increase or decrease as you raise the temperature?
      - **Answer:** *Because large kicks become more frequent at high temperatures, there are more opportunities for particles from the low platform to move to the high platform. Therefore, as temperature is increased, the number of particles on the high platform increases, which raises the value of the ratio defined above.*

- Try lowering the upper platform (but keep it higher than the lower platform).
  - How does this affect $P_{high}/P_{low}$?
    - **Answer:** *By reducing the size of the jump needed for a particle which was initially on the low platform to move to the high platform, lowering the high platform increases the number of particles on the high platform and decreases the number of particles on the low platform. Thus,* $P_{high}/P_{low}$ *increases as the high platform is lowered.*
  - How would $P_{high}/P_{low}$ change if you lowered the higher platform until both platforms were the same height?
    - **Answer:** *If both platforms have the same height, their populations will be the same, on average. Thus, the ratio will be 1.*
  - How would $P_{high}/P_{low}$ change if you now raised the left platform again?

  - **Answer:** *If the left platform were raised then $P_{high}/P_{low}$ would go down. This is because the jump required for particles to transition from the low platform to the high platform would increase. If the jump required for the transition gets larger, then the frequency with which such a jump is observed goes down. This means that the rate with which particles transition from the lower platform to the higher platform goes down. Hence, a larger fraction of the particles will be on the lower platform, meaning that $P_{high}/P_{low}$ will be reduced.*

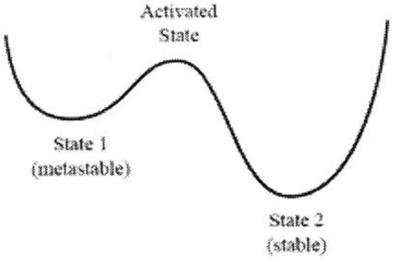
- If you wanted to make $P_{high}/P_{low}$ as close to zero as possible, what would you do?

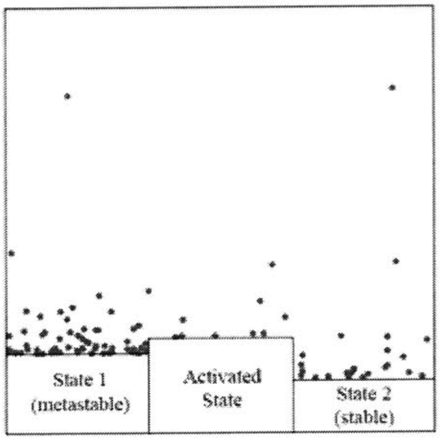
  - **Answer:** *To make $P_{high}/P_{low}$ almost zero, you want to make $P_{high}$ as low as possible. In order to do this, you need to make it incredibly difficult for a particle to ever jump from the low platform up to the high platform. This can be done by increasing the height of the high platform and simultaneously reducing the temperature of the system. By raising the height of the platform you dramatically increase the size of the kick that is needed to move a particle up to the high platform and by reducing the temperature, you dramatically reduce the probability of observing a kick of that magnitude.*

### B.1.4 Lesson 4

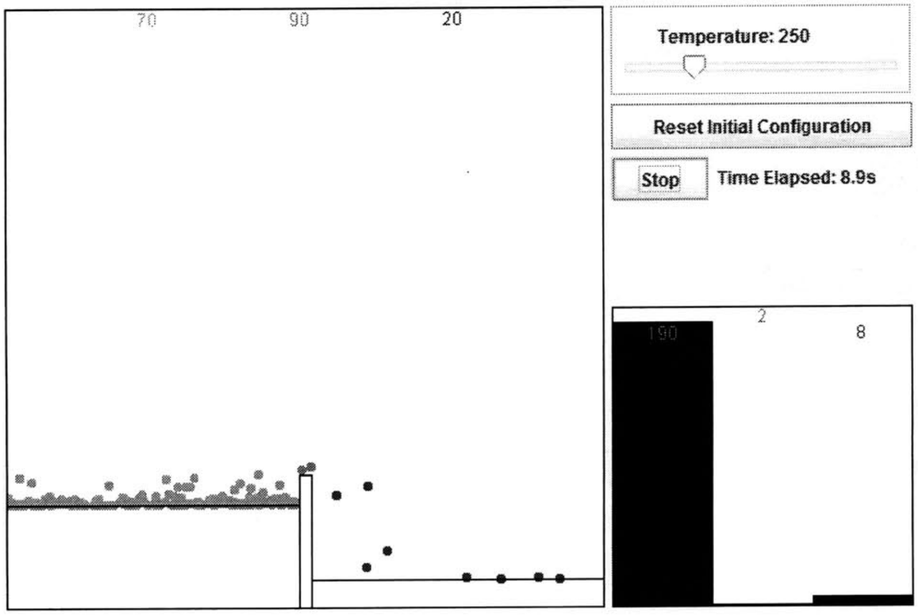
#### Thermally activated processes

The previous activity considered the number of particles that can reach a certain activation energy. In this activity, we explore how the number of particles that can reach a certain energy affects 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.





## Applet for lesson 4



## Description of how to use the applet

This virtual lab is similar to the previous lesson except that an additional platform has been added. The left platform represents the metastable state and the right platform represents the stable state. The center platform can be thought of as an activated state or an energy barrier between the two other states. In this lesson, all the balls start on the left (metastable) side of the reaction. Notice that each platform's height (i.e. the potential energy of that state) is displayed at the top of the simulation window.

To start the simulation, click the button labeled "Start". It will automatically run for 15 seconds and then stop. You may pause the simulation by clicking the button again (now labeled "Stop") in order to more closely inspect the system at any time. The number of seconds that have elapsed while the simulation is running is displayed to the right of this button. Once 15 seconds has elapsed and the simulation has stopped, you must click the 'Reset initial configuration' button in order to run another simulation. Note that this puts the balls back over the left platform and resets the timer. It does not reset the platform heights if you have changed them.

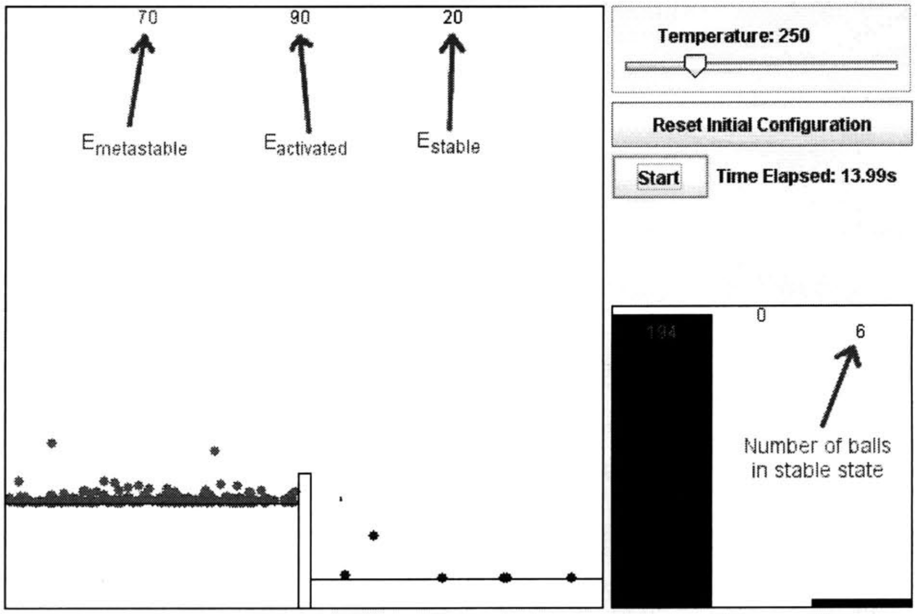
In this exercise you will be asked to adjust the height of the platforms by dragging the top of the platform with your mouse. However, unlike the last lesson, you will not be asked to change the temperature, so the temperature slider has been disabled.

### Activity: Thermally activated processes

Below is a table that describes the configuration of four different simulations you need to perform. Each row in the table corresponds to a different simulation. Your task is to fill in all the empty cells. The first three empty cells (from left to right) in each row can be filled in by simply calculating $E_{a,forward}$, $E_{a,backward}$, and $\Delta E$, where these quantities have the following definitions:

$$\begin{aligned} E_{a,forward} &= E_{activated} - E_{metastable} \\ E_{a,backward} &= E_{activated} - E_{stable} \\ \Delta E &= E_{metastable} - E_{stable} \end{aligned}$$

In order to fill in the last empty cell in each row, you need to run the simulation and record a value displayed in the histogram window on the applet. The figure below highlights the location of the quantities you need to pay attention to on the applet.



Temperature: 250

Time Elapsed: 13.99s

Before running each simulation, you need to adjust the levels of the platforms in the simulation window so they match the values specified in the row you're working on. Once all the platforms are the right height, click on the button labeled "Start". The simulation will then run for 15 seconds before stopping automatically. Once the simulation has stopped, write down the number of balls in the stable state, which can be read from the right-hand side of the histogram window.

While the simulation is running, you don't need to watch the clock. Rather, you should watch the balls crossing the activated state. In particular, pay attention to how many balls are crossing in each direction. You don't need to count them, but you should try to get a general sense for relative amounts.

After completing each row, click on the button labeled "Reset Initial Configuration" to put all the balls back in the metastable state and reset the clock.

| Configuration | $E_{metastable}$ | $E_{activated}$ | $E_{stable}$ | $E_{a,m}$ | $E_{a,s}$ | $\Delta E$ | Ball Count |
|---|---|---|---|---|---|---|---|
| 1 | 70 | 90 | 20 | | | | |
| 1 | 70 | 80 | 20 | | | | |
| 1 | 70 | 75 | 20 | | | | |
| 1 | 70 | 75 | 65 | | | | |
| 1 | 70 | 90 | 65 | | | | |

- Which quantities affect the number of balls in the stable state after each 15-second trial and how?

- Which quantities have no direct effect?

- If you were asked to design a chemical reaction that maximizes the reaction rate, how would you do it?

Examine your results and think about these questions before clicking to the next page...

### Answers

Here are the issues you need to understand in order to correctly answer the questions from the previous page.

In order to transition from the metastable state to the stable state, a ball must first get enough energy from the heat bath (vibrating platform) to reach the activated (middle) platform. (Note: in this simulation, a ball can also jump over the middle platform if it has a higher energy than the activated state.) Once on the activated platform, each ball will fall to the right, into the stable state, with a given probability. Therefore, the number of balls reaching the stable platform in a given time period is proportional to the number of activated balls. The number of activated balls is proportional to $\exp(-E_a/RT)$ where $E_a$ is the difference in energy between the activated and metastable platforms. Since the number of balls reaching the stable state is proportional to the number of activated balls and the number of activated balls is proportional to $\exp(-E_a/RT)$, the rate of this thermally activated process is therefore proportional to $\exp(-E_a/RT)$.

However, the rate at which the balls accumulate in the stable state depends not only on the rate at which balls are added to the stable state from the metastable state (i.e. the forward reaction), but it also depends on the rate at which balls in the stable state jump back to the metastable state (i.e. the backward reaction). It turns out that the analysis in the preceding paragraph applies to both the forward and the backward reactions. For the forward reaction $E_{a,forward} = E_{activated} - E_{metastable}$, whereas for the backward reaction, $E_{a,backward} = E_{activated} - E_{stable}$. Clearly, $E_{a,backward}$ will be larger than $E_{a,forward}$, and since the rate is proportional to the negative exponential of these energies, the backward rate will always be smaller than the forward rate.

The net rate for the reaction is the forward reaction rate minus the backward reaction rate. In the simulations you were instructed to run on the previous page, you recorded the number of particles in the stable state, which is the time integral of the net reaction rate. However, you were also asked to pay close attention to the balls that crossed the middle platform in order to observe both the forward and backward reactions taking place. Did you observe the backward reaction? In what configurations was it most obvious?

The table below fills in all the cells you were asked to fill in. Although you were asked to run each simulation only once, the number of balls in the stable state given in the table below was calculated as an average of 100 trials in order to ensure accurate statistics. The standard deviation is given in parenthesis.

| Configuration | $E_{metastable}$ | $E_{activated}$ | $E_{stable}$ | $E_{a,m}$ | $E_{a,s}$ | $\Delta E$ | Ball Count |
|---|---|---|---|---|---|---|---|
| 1 | 70 | 90 | 20 | *20* | *70* | *50* | 9.14 (2.79) |
| 1 | 70 | 80 | 20 | *10* | *60* | *50* | 34.91 (5.18) |
| 1 | 70 | 75 | 20 | *5* | *55* | *50* | 72.24 (7.93) |
| 1 | 70 | 75 | 65 | *5* | *10* | *5* | 64.08 (6.53) |
| 1 | 70 | 90 | 65 | *20* | *25* | *5* | 8.38 (2.57) |

- In configuration 1 very few balls reached the stable platform.

- In configuration 2, $E_{a,forward}$ was cut in half, $E_{a,backward}$ was only reduced a bit, and $\Delta E$ was kept constant in comparison to configuration 1. However, in this configuration many more balls ended up in the stable state. Since it had the largest percentage change, we can attribute the higher reaction rate to the reduction in $E_{a,forward}$. Recall that because the rate is proportional to the negative exponential of the activation energy, $E_{a,forward}$, a decrease in $E_{a,forward}$ leads to an increase in reaction rate.

- In configuration 3, $E_{a,forward}$ was cut in half again. $E_{a,backward}$ was again only reduced a bit, while $\Delta E$ was still kept constant. Again, the reaction rate saw a dramatic increase. Like configuration 2, in configuration 3, this increase in rate can be attributed to the halving of $E_{a,forward}$.

- In configuration 4, $E_{a,forward}$ was kept constant but $E_{a,backward}$ was dramatically reduced. (This also implies that $\Delta E$ was reduced) The reduction in $E_{a,backward}$ meant the rate of the backward reaction was increased. So, while the forward reaction occurred at the same rate as in configuration 3, the increased rate of the backward reaction meant that fewer balls ended up in the stable state at the end of 15 seconds.

- In configuration 5, $\Delta E$ was kept constant while $E_{a,forward}$ and $E_{a,backward}$ were increased. The reduction in reaction rate can be mostly attributed to the increase in $E_{a,forward}$. However, the fact that the number of balls in the stable state for configuration 5 is less than configuration 1 could be attributed to a lower $E_{a,backward}$ in configuration 5, allowing for a slightly higher backward reaction rate.

From the discussion and data above we can draw the following conclusions:

- The forward reaction rate (metastable $\longrightarrow$ stable) is proportional to $\exp(-E_a/RT)$, where, in this case, $E_a = E_{a,forward}$. It does not depend on $\Delta E$ at all.

- The backward reaction rate (stable $\longrightarrow$ metastable) is proportional to $\exp(-E_a/RT)$, where, in this case, $E_a = E_{a,backward}$. It does not depend on $\Delta E$ at all.

- The net reaction rate is the forward rate minus the backward rate.

In this lesson, the applet was not allowed to continue until the system reached equilibrium. However, it is important to realize that the ratio of the equilibrium populations for the stable and metastable platforms is determined solely by $\Delta E$ and is not affected at all by the height of the activated state. A higher energy barrier means it will take the system longer to reach equilibrium, but the equilibrium populations are independent of the height of the energy barrier. This is basically the same idea we discussed in lesson 3 when we looked at $P_{high}/P_{low}$ in the system with only 2 platforms.

Now, we can answer the specific questions from the previous page:

- Which quantities affect the number of balls in the stable state after each 15-second trial and how?
  - **Answer:** *The quantity that primarily affects the net reaction rate is Ea,forward because it controls the rate of the forward reaction. However, Ea,backward can also affect the net reaction rate. If it is only a bit larger than Ea,forward, the backward reaction will convert products back into reactants at a noticeable rate, thus reducing the net reaction rate. We see this by comparing configuration 4 to configuration 3 above.*
- Which quantities have no direct effect?
  - **Answer:** $\Delta E$ *controls the ratio of populations of the states at equilibrium but it has no direct effect on the reaction rates.*
- If you were asked to design a chemical reaction that maximizes the reaction rate, how would you do it?
  - **Answer:** *In order to maximize the net reaction rate, you would want the forward reaction to go as quickly as possible and you would want the backward reaction to go as slowly as possible. This means you want to minimize* $E_{a,forward}$ *and you want to maximize* $E_{a,backward}$.

## B.2 Pre- and post-test

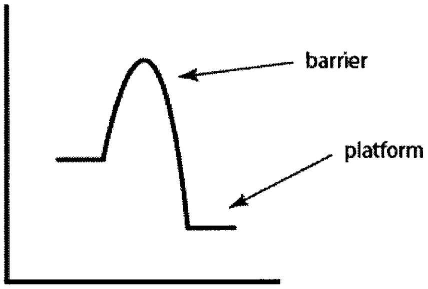
This section contains the test that was given to students as both the pre-test and post-test. Here the correct answers to the questions are marked with an asterisk but the correct answers were not indicated on the tests students received. The test presented here is identical to that presented in section A.2 except that questions 3a, 3b, 13, 14, and 15 have been omitted. For comparison purposes, the question numbering used in section A.2 has been retained here. However, when students received the test, the numbering was sequential.

### B.2.1 Test

*Please complete the following 15 questions. When prompted to explain your answer, please explain your reasoning in a sentence or two.*

*For questions 1-7, please refer to the graph below.*

*Free energy diagrams convey qualitative information about chemical reactions. For each question, a) Determine whether each piece of information is available in the diagram; and b) what aspect of the diagram allows you to make the inference.*



1a. Is information about the relative potential energy differences between states available in the diagram above?

____ Yes* ____ No

1b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms*

____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available

2a. Is information about the relative kinetic energy differences between states available in the diagram above?

____Yes ____No*

2b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms

____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available*

4a. Is information about the speed of reaction available in the diagram above?

____ Yes* ____ No

4b. What aspect of the diagram allows you to make this inference

____ Height differences between platforms

____ Height of barrier*

____ Number of barriers

____ Number of platforms

____ Information not available

5a. Is information about the number of transition states available in the diagram above?

____ Yes* ____ No

5b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms

____ Height of barrier

____ Number of barriers*

____ Number of platforms

____ Information not available

6a. Is information about the number of stable states available in the diagram above?

____ Yes* ____ No

6b. What aspect of the diagram allows you to make this inference

____ Height differences between platforms

____ Height of barrier

____ Number of barriers

____ Number of platforms*

____ Information not available

7a. Is information about whether the reaction is endothermic or exothermic available in the diagram above?

____Yes* ____ No

7b. What aspect of the diagram allows you to make this inference?

____ Height differences between platforms*

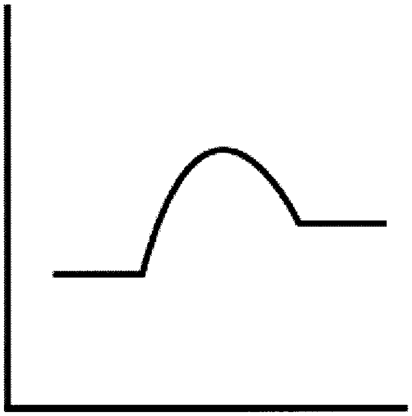
____ Height of barrier

____ Number of barriers

____ Number of platforms

____ Information not available

**Questions 8-9 refer to the following diagram**



8. At very high temperature which of the following is true:

____ The number of molecules in State 1 will be roughly equal to the number in State 2.*

____ The number of molecules in State 1 will be much less than the number in State 2.

____ The number of molecules in State 1 will be much greater than the number in State 2.

____ Cannot determine based on given information.

Please explain how you determined your answer: ________________

9. At very low temperature which of the following is true:

____ The number of molecules in State 1 will be roughly equal to the number in State 2.

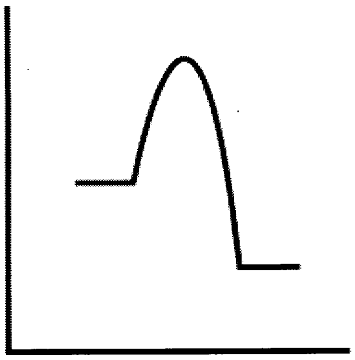
____ The number of molecules in State 1 will be much less than the number in State 2.*

____ The number of molecules in State 1 will be much greater than the number in State 2.

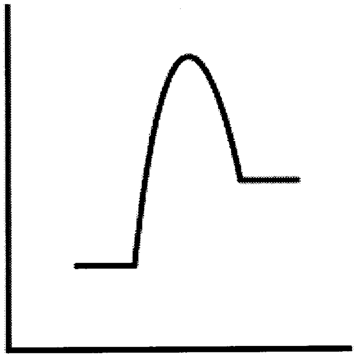
____ Cannot determine based on given information.

Please explain how you determined your answer: ________________

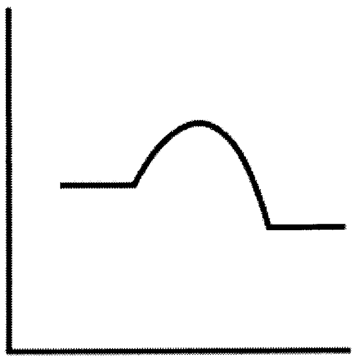
**Questions 10-12 refer to the following diagrams.**



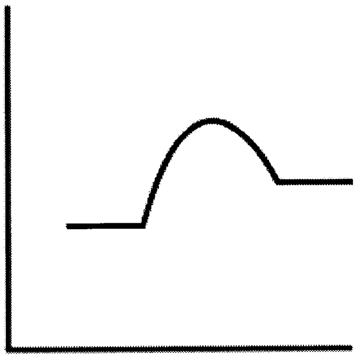
a.



b.



c.



d.

10. Which of these reactions give off heat from State 1 to State 2? (Check all that apply)

____ Graph a*

____ Graph b

____ Graph c*

____ Graph d

____ Can't tell

Please explain your answer: ________________

11. A system starts will all molecules in State 1 (on the left). Which of the following systems will take the longest to reach equilibrium?

____ Graph a

____ Graph b*

____ Graph c

____ Graph d

____ Can't tell

Please explain your answer: ________________

12. A system starts with all molecules in State 1 (on the left). Which of the following systems will reach equilibrium the fastest?

____ Graph a

____ Graph b

____ Graph c *

____ Graph d

____ Can't tell

Please explain how you arrived at your answer: ________________

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