PHYSICS 7A
GENERAL PHYSICS

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Physics 7A General Physics

Dina Zhabinskaya

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CHAPTER OVERVIEW

1: Applying Models to Thermal Phenomena

In this chapter we introduce the *Energy-Interaction Model*, which is the primary focus of this course. We will apply this model together with the *Three-Phase Model of Pure Substances* in order to understand various physical phenomena. We will analyze pure substances going through temperature and phase changes and chemical reactions.

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1.1: Where are we Headed?

This page is a draft and is under active development.

In This Chapter

We begin Chapter 1 talking about some familiar phenomena such as phase and temperature changes of pure substances and chemical reactions. The *Energy-Interaction Model* which describes the idea of energy conservation is universal and can be applied to a wide range of phenomena and interactions. So why start with what might seem to be some run-of-the-mill stuff you already know a lot about?

- Reason (1) is you do know a lot about this phenomena, so you are not hit right off the bat with stuff you don't know anything about.
- Reason (2) is that there are some very interesting parts of thermal phenomena that you probably cannot make much sense of right now. And it is fun to finally be able to explain phenomena that you observe on a daily basis.

We will also see that by applying the Energy-Interaction Model to some very strange thermal phenomena, we can make sense of them, we can explain what is going on, and we can answer all kinds of questions about the phenomena. To see the universal applicability of the Energy-Interaction Model, we will also apply this model to several chemical reactions.

One rather simple kind of thermal phenomena you will immediately encounter in this course involves the addition or removal of energy as heat from pure substances. You have encountered this general class of phenomena (changing the temperature of a substance and/or causing it to go through a phase change) in general physical science courses as well as in your chemistry courses. So partly as review, but also as an example of how models need to be extended and modified, we introduce the *Three-Phase Model of Pure Substances* in this chapter. In the next section, we will describe the general structure of the *Energy-Interaction Model* and show how it can be used together with the *Three-Phase Model of Pure Substances.*

In the following section, we will also present some of the kinds of questions we will want to be able to answer, the kinds of explanations we will want to construct, and the kinds of predictions we can make using the models presented in the chapter. We will use a helpful tool, *Energy-Interaction Diagrams*, which was developed specifically for this course in order to help students make sense of energy conservation. As we do this throughout the course, we will become much more aware of the limitations on the kinds of questions and explanations that the particular models, in this case, the *Energy-Interaction Model* can help us with. We will begin to get a much better feeling for when we can *take an energy conservation approach*, i.e., apply the *Energy-Interaction Model* and when we must use a different model.

Keep in mind that in Chapter 1 we deliberately restrict the range of phenomena to which we are applying the *Energy-Interaction Model* to mostly thermal phenomena (and a few examples of chemical reactions). We will wait until Chapter 2 to apply the *Energy-Interaction Model* to mechanical interactions and processes. It is easy to forget that this is the one model that can be usefully applied to essentially any interaction or process that occurs in any branch of physical and biological science.

Contributors

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1.2: Three-Phase Model of Pure Substances

Pure Substances Have a Phase

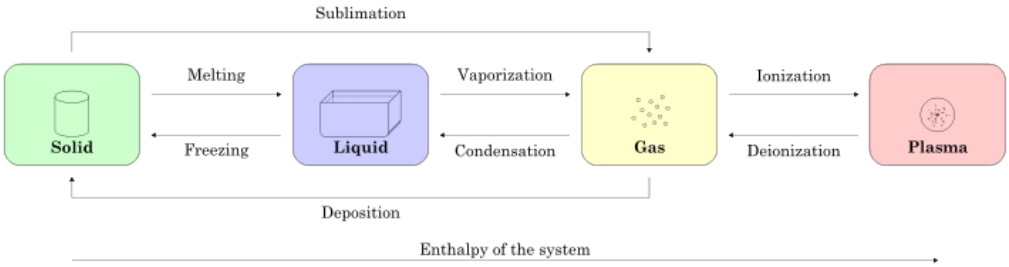
We adopt the standard chemistry definition that a *pure substance* is any material with a definite chemical composition. By “pure”, we simply mean that only one chemical substance is present in the sample. So, water has a definite phase, but mixtures do not. This is partly a disclaimer so that questions such as "is glass a liquid or a solid?" can be put out of mind for now. For the first pass at this model, we treat pure substances as though they are in one of three phases: solid, liquid, or gas.

We are choosing which relevant features to include in our model and which to exclude. The choices will definitely affect the level of detail we can address in our questions and discuss in our explanations. At this time, we are deliberately choosing to be more general to keep the model as simple as possible and at the same time, applicable to as wide a range of phenomena as possible.

Graphical Representation of the Three-Phase Model

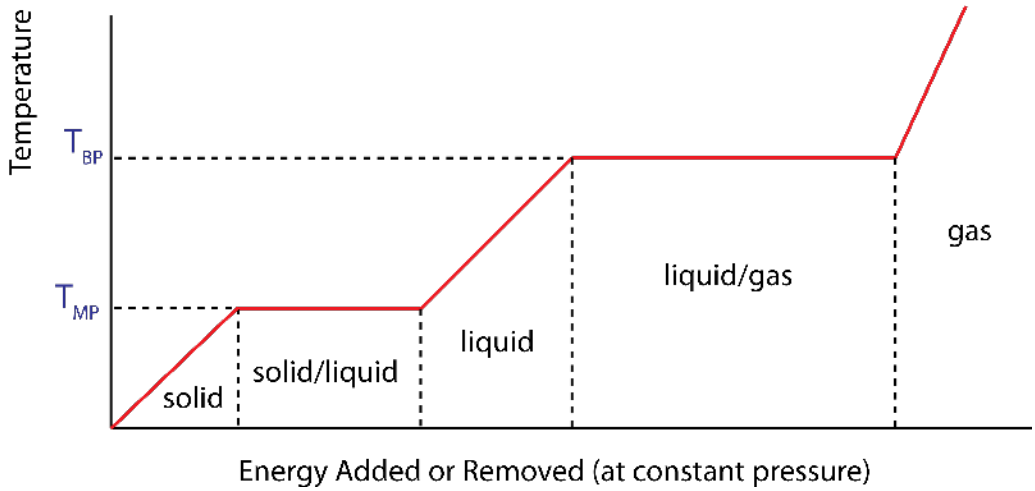
Figure 1.1.1 summarizes phases of matter and terminology of various phase transitions. In the *Three-Phase Model*, we will only focus on the solid, liquid, and gas phases.

Figure 1.1.1 – Summary of Possible Phase Transitions



The graphical representation show below in Figure 1.1.2 summarizes the relationships of the model. The diagram depicts how a pure substance goes through the three basics phases as energy is added (moving to the right along the x-axis) or removed (moving to the left along the x-axis) as a function of temperature. We will discover later in the course that the energy changes of the substance that result in temperature or phase changes can be modeled with a microscopic atomic point of view. Thus, we will refer to these energies as *internal energies* of our system.

Figure 1.1.2 – Temperature vs. Energy Added Diagram



In the simplest form of the *Three-Phase Model of Matter*, the phase changes occur at the same temperature in either direction of the phase transition. That is, the temperature of the change from liquid to solid as energy is removed is the same as the temperature of the phase change from solid to liquid as energy is added. Due to this symmetry, the liquid-solid or solid-liquid phase change

temperature can be referred to as either the *freezing or melting temperature*. Likewise, the liquid-gas or gas-liquid phase change temperature can be referred to as the *boiling or condensation temperature*.

It is very important to realize that the *x-axis* in Figure 1.1.2 represents energies that are added (or removed) to (from) the system, rather than absolute values of energy. The distinction between changes in energy and absolute values of energy, although seemingly subtle, is very crucial to understanding energy and its conservation. We will revisit this point throughout the entire course.

Although the picture appears to have a very simple structure, it is important to dig into the meaning of every piece. You need to ask questions like:

- What is the meaning of the horizontal portions of the graph?
- What is happening at the three slanted portions of the graph?
- What is the state of the substance at the "corners" in the graph?
- Can you explain in you own words “what is going on” physically in your drink with ice during a horizontal portion of the graph?
- Which horizontal portion would correspond to your cold drink?
- Where did the ice start out when you first put it into your cup? When was your drink system in thermal equilibrium, or was it ever in thermal equilibrium?
- Can you picture what is happening in terms of this representation when you boil water to make tea?
- How is this different from putting ice trays into the freezer compartment of your refrigerator?

By asking these kinds of questions you will practice using this representation so it becomes a useful tool to make sense of thermal phenomena and to be comfortable using it to construct explanations for particular phenomena.

Let us look at some of these questions. The plot is telling us that as energy is added to a solid, its temperature will increase until the solid reaches its *melting point temperature*, T_{MP}. At the first "corner" in the diagram at T_{MP}, the substance is still fully solid but at its melting temperature. Once the substance is at this state, any additional energy added will start the melting phase transition, and the substance will be in a mixed solid/liquid phase. When enough energy is added to the substance, the substance will be fully melted (all liquid) at its melting temperature, at the location of the second "corner" in the diagram. The process continues in a similar manner. As more energy is added, the liquid's temperature rises until it reaches its *boiling point temperature*, T_{BP}. As more energy is added, the substance will be found in a mixed liquid gas phase, until enough energy is added to fully vaporize the liquid, resulting in a pure gas. After this, any additional energy will go into increasing the temperature of the gas.

The important thing to notice is that during a *phase change*, temperature *remains constant* even while energy is being added and the substance is in a *mixed phase*. In real life, this could be tested by boiling a pot of water while measuring temperature with a thermometer. If you do this yourself, you will find that the water temperature remains at exactly 100°C throughout the boiling process. Even as the flame continues to pour heat into the pot-water system, the water's temperature will *not change* until all the water is boiled away.

Note:

The same procedure described above follows if energy is being removed instead of added with different definitions of the phase changes: freezing instead of melting, and condensation instead of vaporization.

It is clear that something different is happening physically to the substance during the sloped (when temperature is changing) and the horizontal (when phase is changing) portions of the diagram. Thus, it is useful to give a separate definitions to the internal energy that is changing in the substance during each process. When added energy results in raising the temperature of the substance, we call this type of internal energy *thermal energy*, $E_{thermal}$. When added energy results in changing the phase of the substance, we call this type of internal energy *bond energy*, E_{bond}.

But you might be wondering, how can you find the amount of energy required, for example, to heat up a glass of water from room temperature at 25°C to its boiling temperature at 100°C? Or how much energy is removed from a glass of water, initially at room temperature, when placed in a freezer until it fully freezes? One way to do this is to do an experiment. You can imagine measuring the amount of energy that you add to a glass of water, and recording the amount of temperature that changes as that energy is added. This will lead us to the idea of *specific heat*. Likewise, you can measure the amount of energy required to fully melt or freeze some amount of water, known as *heat of melting*. The quantity associated with the amount of energy required to fully vaporize or condense some amount of substance, is known as *heat of vaporization*. In Chapter 3, we will also attempt to understand this phenomena from a microscopic atomic level, and make connections between atoms jiggling around at faster speeds to

temperature increasing and specific heat. Likewise, we will look at the type of bonds that keep solids and liquids together, and how breaking those bonds or forming them is related to heat of melting.

Some other questions that arise when thinking about the Three-Phase Model may be:

- Does the diagram look different if we doubled the mass of the substance?
- How does the diagram change for different types of pure substances?
- What do the slopes of the solid, liquid, and gas curves represent? Why is the slope of the gas line appears to be steeper in this figure?
- Does it take the same amount of energy to fully melt and fully vaporize the same amount of a given substance?

We will address all of these questions during this course.

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1.3: Energy-Interaction Model

Energy Conservation

The scientific meaning of energy is rather tricky to convey in a sentence or two. There is a good reason for this: energy is an *abstract concept* that took scientists a long time to figure out. Although the concept of energy is truly universal in the sense that energy *changes* are associated with nearly all phenomena and processes, energy is not related to a single property of matter. For example, we all have an intuitive sense of "hotness" and we associate the concept of temperature with this property of matter. We associate the concept of force with the intuitive notion of push and pull. Energy, on the other hand, is associated with many properties or conditions of matter including temperature, force, motion, atomic level, mass, charge, and on and on. It is the fact that energy is so universal that makes it so difficult to define it precisely.

Another reason energy is difficult to pin down, is that the value of energy itself is seldom of importance; rather, it is the *changes* in the values of energy that seem to matter. In fact, we will see that *change in energy* is directly related to "how much" interaction occurred. This is the root of the *Energy-Interaction Model*, it helps explain how energy changes when an interaction occurs. One of the most fundamental conservation law in physics, is the *conservation of energy*, which is the main focus of this course. Mathematically, the statement of conservation of energy is written this way:

$$\Delta E_{total} = Q + W \tag{1.3.1}$$

The left side of the equation represent the sum of all the types of energy that changed in the physical system during a particular interaction, $\Delta E_{tot} = \sum \Delta E$. The right side of the equation represents all the ways that energy can be either added or removed from the physical system. Energy transfer as *heat*, Q, occurs when the system is interacting with an environment which is at a different temperature. Energy transfer as *work*, W, represents all other types of energy transfer that have to do with net force exerted on or by the system. When energy is transferred *to* the system, heat or work is *positive* resulting in an *increase* in the total energy of the system. Likewise, when energy is transferred *from* the system, heat or work is *negative* resulting in an *decrease* in the total energy of the system.

The following are useful statements about energy. Taken together they constitute a working definition of the concept of energy. This concept will be developed further throughout the course.

Statements that help define energy:

- Energy is an abstract concept that characterizes the interactions of matter.
- The *change* in energy of a physical system is a *quantifiable measure* of the degree of its interactions with other physical systems.

Here are some important things to think about when considering energy:

- Historically, many "forms" or "kinds" of energy have been identified. Sometimes, the form of energy labels the interaction that resulted in a change of energy, e.g., chemical, mechanical, or nuclear. It is often misleading to think of there being different forms, kinds, or types of energy, even though we have these "names of energy" in our vocabulary. Energy is energy, regardless of how it manifests itself. Thus, although kinetic energy and chemical energy might be describing a different physical properties of a system, the idea of energy is equivalent.
- Energy is not a *real physical thing* that resides in systems, even though we often talk about it as if it were a "real thing". Be careful here. Remember there is nothing at all physical about this "thing" we call energy, even when our language sometimes suggests that there is.
- Interactions are modeled by treating energy as something that resides in (can be identified with) particular type of energy. When interactions occur, energies change. This changes in energy might result in an increase or decrease of a particular energy type or a change from one type of energy to another.
- When an interaction occurs, there is a change in one or more energy types. For each energy form that changes, there is an observable (in the sense of being detectable) and quantifiable change in some part of the physical system. The magnitude of the change of each type of energy is determined by the change in its associated observable parameter. We will refer to this observable parameter as the *indicator* associated with a particular type of energy. The questions of how to "divide up" the energy of some physical system and which type of energy to include in the model get to the heart of the modeling process.

Alert

The importance of always being conscious of the word "*change*" as in the phrase "change in energy" and of the way this idea is represented mathematically cannot be overstressed. We signify "change in energy" mathematically by writing "ΔE ". The uppercase Greek symbol "Δ" often is used in science to indicate a change in some quantity. Does "ΔE" look like "E" to you? Of course not, and they have very different physical meanings. A very common misconception is to treat these quantities equally:

CORRECT: $\Delta E_1 + \Delta E_2 + \Delta E_3 + \ldots$ = (net energy transferred into or out of the physical system)

and

INCORRECT: $E_1 + E_2 + E_3 + \ldots$ = (net energy transferred into or out of the physical system)

Only the first statement makes any physical sense.

But if we wrote the second one as:

CORRECT: $E_1 + E_2 + E_3 = E_{total}$

it would make perfect sense.

Yet the statement:

INCORRECT: $\Delta E_1 + \Delta E_2 + \Delta E_3 = E_{total}$

would make absolutely no sense.

The point is, whether we are talking about a change in energy or the value of the energy, it *matters a lot*. You must be always conscious of which you are thinking about and why it is the one you want to think about!

Physical System

We will be analyzing various phenomena as asking the questions, "Is energy conserved?" and "What can we learn from the phenomena using the concept of conservation of energy?". The actual question, "Is energy conserved?", does not have a meaning unless we first define the physical system whose energy we are trying to analyze.

For example, you throw a piece of ice into a drink, place in an insulated container which is initially at room temperature and ask whether the energy of ice is conserved. The answer will be "no", since you observe that the ice will eventually melt. Does this mean that you violated the conservation of energy? Of course, not! Conservation of energy tells us if the energy of your system changed (ice in this example), that means that the energy had to be transferred from the environment (drink in this example). In our ice example, when ice melted its energy increased. Energy conservation then tells us that the energy was transferred to the ice. On the other hand, if we defined our physical system as the ice and the drink combined, then indeed the energy of our system would be conserved. How do we know? If our system is not interacting with other physical systems (the drink and ice are in an *insulated* container), energy is not entering of leaving the system, $Q = W = 0$. Thus, we can conclude that energy is conserved, $\Delta E_{tot} = 0$. Thus, the amount of energy that increased in the ice must equal to the amount of energy that decreased in the the drink.

In reality no system is perfectly *insulated*, but it is a valid approximation to assume energy conservation (or lack of interaction with the environment) within a given time range. If you wait long enough, the drink will eventually come to thermal equilibrium with the environment outside the container. Thus, not only the definition of the physical system is necessary in order to analyze energy conservation, but also the time interval over which the interactions are being analyzed.

Interval

The *time interval* that needs to be considered depends on the question being asked. In situations involving thermal systems, the typical question is, "What is the final state of the physical system once thermal equilibrium is reached?". *Thermal equilibrium* is a state when heat is no longer flowing since all the substances involved in the interaction have reached the same temperature. Thus, thermal equilibrium is often the logical final state for this type of interaction. Or you might want to ask how much ice to add to a drink in order to have a desired final temperature. In physics we often make approximations since it is easier to apply our models to simplified physical situations. You can learn a lot about nature but first starting with the most simplified situations and then slowly building upon them. For example, the drink in an insulated container will reach room temperature if you wait long enough. However, the drink and the ice will reach equilibrium much faster with each other, than the mixture will with the room outside. Thus, on the short time scale of the drink coming to equilibrium with the ice, we can assume that the interactions with the room are negligible.

One of the frequent ways beginning students go astray is to not be perfectly clear in their own mind how the beginning and end of a process or interaction is being determined. Often there is a point in time that can be identified with the beginning and the end of the interaction. This is not usually an actual clock time, such as ten minutes after one, but rather, something happens at a particular time. The "something" that happens can be easily pictured in our mind and remembered. It is when the "ice was placed in the drink", or “ball was thrown”, or “just before the ball hit the ground". Or perhaps it was when "the coffee pot was turned on" or when "the coffee pot was turned off". Something physically happens that we make a conscious decision to identify with the beginning of the time interval and something else happens that we use to identify with the end of the time interval that corresponds to the interaction or process we are interested in. It is crucial to always clearly identify these starting and ending “events,” which precisely determine the interval over which the process or interaction occurs. This will then help us determine what type and how much energy changed during this interval.

Closed and Open Physical Systems

There are two useful ways to express the principle of conservation of energy, one corresponding to closed physical systems and the other to open physical systems.

- **Closed physical system:** in a *closed physical system*, there is no transfer of energy into (or out of) that physical system from some other physical system. (This condition would generally preclude mass transfers as well, since mass transfers would also result in energy transfers.) Another way to state the condition of being closed is that all interactions occur *within* the identified physical system, and there are no interactions with other physical systems. For a closed system the statement of energy conservation becomes:

$$\Delta E_{total} = 0 \tag{1.3.2}$$

- **Open physical system:** in an *open physical system*, there can be a *net* transfer of energy into (or out of) that physical system from some other physical system. Another way to state the condition of being open is that interactions can occur between matter in the identified physical system and matter in other physical systems (which might simply be the *environment)*. For an open system the change in total energy is given by:

$$\Delta E_{total} = Q + W \tag{1.3.3}$$

In ice/drink example, the ice together with the drink placed in an insulated container would constitute a *closed physical system*. If you choose to define the physical system as just the ice, this will then be an *open physical system* which is interacting with other systems, in this case the drink.

Energy Transfers: Heat Q and Work W

When energy is transferred into a *physical system* from *another physical system*, it is customary to name the energy transferred as either *heat* or *work*. The name heat, Q, is given to energy transfers that occur as result of a difference in temperatures. Heat “flows” from the physical system at the higher temperature to the physical system at the lower temperature.

Alert

Historically, the word “heat” was also used to mean what is now more commonly called thermal energy. If you are reading other textbooks, especially older ones, be sure you understand how the authors are using the word “heat”. This is important, because the concept of energy transfer as heat is very different from the concept of thermal energy. We (and most modern authors) now restrict the use of the word “heat” to its meaning as a transfer of energy between physical systems as a result of temperature differences. Thus, stating that a physical system contains some amount of heat does not make sense. As a result, the notation ΔQ will never be used, since this implies a change in a quantity, which Q is not. However, the notation dQ will be used to mean an infinitesimally small amount of energy transferred as heat.

The term work, W, is used to describe the energy transferred between physical systems (objects), which exert forces on one another and move relative to one another. We will examine this type of energy transfer in Chapter 2.

One of the great advantages of an energy model is that we do not have to be concerned with the *details* of how energy transfers occur. We do not need to have a microscopic explanation, for example, of how friction causes increases in thermal energy and decreases in other non-thermal energies. On a microscopic scale, all kinds of energy transfers are taking place between individual atoms and molecules. The energy transfers we are talking about that occur between different physical systems are always the *net* transfers that occur as a result of an interaction between those physical systems.

Energy Changes

State of a Physical System

Related to the discussion regarding the beginning and ending of a process or interaction is the idea also mentioned previously that we are not concerned about the details of the interaction in an energy conservation approach. In fact, all we care about is how the *state of the system* changed from the beginning to the end of the process or interaction, but not what happened in between. By state of the physical system we mean the values of certain parameters that changed. For the *Energy-Interaction Model* we care only about the *indicators* that tell us how much the energy changed in each form of energy. This notion of state of the physical system will become more obvious as we work through more and varied phenomena using the *Energy-Interaction Model*.

Energy Types Related to Thermal and Chemical Processes

When dealing with thermal and chemical processes from a *macroscopic* perspective, it is convenient and useful to define energy types that correspond to the empirically determined enthalpies (the amount of heat added or removed from the substance), ΔHs, that correspond to the process or interaction. These include enthalpies associated with physical phase changes and with the formation of various molecular species. The indicator for the energy associated with these processes would be the *amount of substance* that changed phase or for a chemical reaction, the *amount of substance* that was formed or that "disappeared". We refer to this energy type as *bond energy*, E_{bond}. The general form of the expression for the amount of energy change in these processes is:

$$\Delta E_{bond} = \pm|\Delta m \Delta H| \tag{1.3.4}$$

The indicator for the energy change is the *amount of substance* that changed, Δm. Energy has units of *joules*, *J*. Thus, when Δm will have units of *kg*, ΔH has units of *J/kg*. If the amount of substance is a molar quantity, then Δm will have units of moles, *mol*, and is more commonly written as Δn, and ΔH has units of *J/mol*. We will discuss the $\pm$ sign in the equation shortly.

When the process is either melting or freezing, the enthalpy of melting, or *heat of melting*, is defined as ΔH_{melt}. When the process is either vaporization or condensation, the enthalpy of vaporization, or *heat of vaporization*, is defined as ΔH_{vap}.

When there are no phase changes or chemical reactions occurring and heat is added to a substance, its temperature changes. The amount of temperature change depends on the substance's *heat capacity*. Heat capacity is a quantity that determine how much energy is transferred to a system for a given temperature change:

$$C = \frac{Q}{\Delta T} \tag{1.3.5}$$

We call the type of energy that changes when temperature is changing *thermal energy*, $E_{thermal}$. When only temperature is changing during a process, $\Delta E_{total} = \Delta E_{thermal}$, and if no work being transferred, $W = 0$, Equation 1.3.1 simplifies to $\Delta E_{thermal} = Q$. Combining this with Equation 1.3.5 we can write thermal energy as:

$$\Delta E_{thermal} = C\Delta T \tag{1.3.6}$$

Temperature is the indicator for this energy. The SI units of temperature is *kelvin*, K, thus, heat capacity has units of *J/K*. Sometimes, the units of *celcius*, $^\circ C$, are used, where the conversion between celcius and kelvin is $^\circ C = K - 273$. Thus, 273K corresponds to 0°C.

When temperature of the system increases, so does its thermal energy, and vice versa. Heat capacity depends on the amount of substance you have, it requires more energy to increase the temperature by a given amount of a larger quantity of a substance.

The amount of energy required to increase the temperature of a substance also depends on the type of substance. It is useful to define a quantity which only depends on the type of substance, but not on the amount. This is know as the *specific heat*. For example, it takes more energy to change the temperature of water compared to other common substances. This explains why coastal regions do not have large fluctuations in temperature between day and night. The water's high specific heat does not allow a big drop in temperature when the sun sets. On the other hand, sand has a low specific heat, explaining the large variations in temperature between day and night in a desert.

When the specific heat is given per unit mass, the heat capacity can be written as:

$$C = mc_m \tag{1.3.7}$$

where m is mass in units of *kg*, and c_m is the specific heat in units of $\frac{J}{K \cdot kg}$. When the specific heat is given per amount of moles, sometimes known as *molar heat capacity*, the heat capacity can be written as:

$$C = nc_n \tag{1.3.8}$$

$$C = nc_{mol} \tag{1.3.8}$$

where n is the number of moles and and c_{mol} is molar heat capacity in units of $\frac{J}{K \cdot mol}$.

Separating internal energies into bond and thermal energies is very useful for three reasons:

1. they correspond to changes in indicators we can directly observe.
2. they depend on parameters, ΔH and C, that are tabulated for most substances.
3. During a physical or chemical reaction, only one of them will be changing at a given time.

Both phase changes and chemical reactions involve changes in bond energy that correspond to making and breaking of atomic and/or molecular bonds. Temperature changes corresponding to random atomic motions, results in thermal energy changes. The two types of energy we have defined above are closely related to bond energy and thermal energy we will develop from an atomic perspective in Chapter 3, but are not exactly the same. However, rather than use a different name for the energies involving the empirically determined parameters, ΔH and C, and macroscopic indicators, Δm and ΔT, we will simply refer to them as the bond energy and thermal energy, remembering that we will refine our understanding of these processes in Chapter 3 and see how the macroscopic energies we define here relate to the microscopically defined bond and thermal energies using particle models.

The algebraic signs of thermal and bond energies

It is very important to make sense of the algebraic sign of the change in energy based on what physically is happening. This is actually very simple to do, once you understand the role of an indicator. However, it is easy to make a simple algebraic slip-up when actually calculating numerical values. You should always check to see if the final algebraic sign makes sense.

Any thermal energy for which the temperature increases during the process will always have a positive change in energy. Likewise, any thermal energy for which the temperature decreases will always have a negative change in energy. This is consistent with the simple notion that thermal energy increases with increases in temperature, because at higher temperatures there is “more vigorous” motion of the particles. When doing numerical calculations the sign in the change of thermal energy will correspond to the sign in the change in temperature, as indicated by Equation 1.3.6.

Any bond energy for which bonds are broken during the process or interaction will always have a positive change in energy. Likewise, any system for which bonds are formed during the process or interaction will always have a negative change in energy. This is consistent with the common experience of having to *add energy* (and thus increase the bond energy) to vaporize liquid water that is at 100°C. The bonds that had existed in the liquid phase disappear (are broken) in the process of the liquid changing to a vapor. You will probably need to struggle mentally with this last point: broken bonds have more energy than intact bonds. Work on this until it “seems obvious” to you. Therefore, when the substance is either melting or vaporizing the change in bond energy is positive (a plus sign is chosen on the right-hand-side of Equation 1.3.4). When the substance is either freezing or condensing the change in bond energy is negative (a minus sign is chosen on the right-hand-side of Equation 1.3.4).

Alert

A very common misconception is to think that bond energy should increase when bonds are formed and decrease when bonds break. In other words, bond energy is misinterpreted as the the energy stored in bonds. It is important to analyze each energy term in terms of the *Energy-Interaction Model*, which states that if energy is transferred to a system, the system's energy must increase, and vice versa. The *Three-Phase Model* tells us that energy needs to be added to a substance when it is vaporizing from a liquid to a gas, and removed when it is condensing from a gas to a liquid. Thus, the system's energy (bond energy in this case) increases as bonds break and decreases as bonds form.

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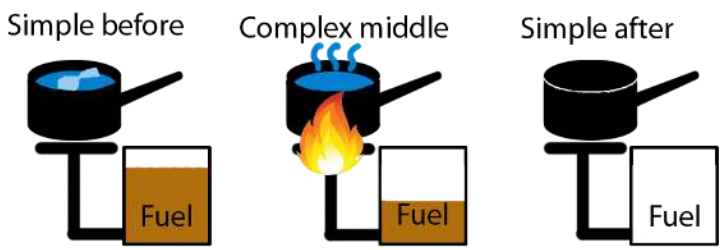
1.4: Working With the Energy-Interaction Model

This page is a draft and is under active development.

Energy-Interaction Diagrams

When solving complex energy interaction problems, it is often helpful to use a tool that was developed for this course, the *Energy-Interaction Diagram*. Energy-Interaction diagrams illustrate the types of energy transformations that occur when an open physical system is interacting with its environment, or with two or more substances which defined a closed physical system interact with each other. The diagram helps make clear the physical systems involved, the particular types of energy involved, and the changes in those energies resulting from the interaction over a given time interval. The initial and final states of the systems should be clearly indicated on the diagram. These diagrams are “before-to-after” diagrams. That is, they indicate the state of the systems before the interaction occurs and the state of the systems after the interaction has occurred, while not specifying any details of how the system got from the initial to the final state. We use Energy-Interaction diagrams because they are useful. They help us to systematically apply the energy conservation approach to a particular physical situation using the *Energy-Interaction Model*.

Figure 1.3.1: Illustration of the "before" and "after".



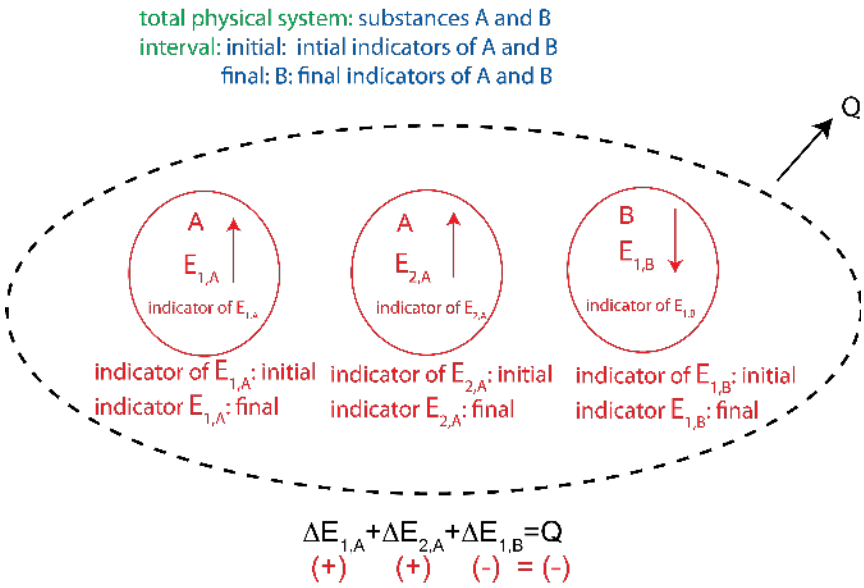
Drawing Energy-Interaction Diagrams When Modeling an Interaction in a *CLOSED* System:

1. The beginning and ending of the interaction is specified by explicitly writing down a condition of the physical system that corresponds to the beginning and end of the time interval over which the interaction occurs. These times are referred to as the *initial* and *final* times.
2. The types of energy that changed during the specified time interval are indicated by circles and labeled sufficiently to identify the type of energy.
3. If transfers of energy to the environment are significant, due to friction, for example, include the thermal system of the environment on the Energy-Interaction diagram. That is, enlarge the boundary of the closed system to include the environment.
4. The change in each energy, whether an increase or decrease, is indicated, when known, with an “up” or “down” arrow.
5. Changes in the observable parameter (indicator) associated with each type of energy that occur as a result of the interaction should be shown. If the quantitative change in the value is known, it should be given. If not, an “up” or “down” arrow can be used following the symbol of the indicator to indicate an expected increase or decrease.
6. Draw a *solid oval* around all the "energy circles" to indicate the system is closed.
7. Below the diagram write the energy-conservation equation. You may also indicate which quantities are positive or negative for each term in the equation.

Drawing Energy-Interaction diagram Diagrams When Modeling an Interaction in an *OPEN* System:

The important difference between open and closed systems is that energy from outside the open physical system can be transferred into or out of the physical system as heat, Q, or work, W. (By definition, these transfers do not occur for a closed system.) The only difference, then, in the Energy-Interaction diagram for the two types, is that the diagram for an open system needs to explicitly show the transfer of Q and/or W. This is done by drawing a *dashed oval* around all of the energies (to indicate the open physical system boundary) and drawing arrows pointing toward or away on the boundary to show a Q or a W transfer in or our, respectively. A generic example of the Energy-Interaction Diagram for an open system is shown below.

Figure 1.3.2: Generic Example of an Energy-Interaction Diagram in an open physical system with two substances, three types of energy, and heat leaving the system.



Comments:

1. What is shown in the diagram above is the minimum that must always be written down. Most of the hard thinking will have been done to get to this point. Often, many explanations of physical phenomena can be constructed using this diagram without going further and substituting in explicit expressions for the individual change in energy terms and numerical values for various parameters. Even if you are required to continue the process through to a numerical result, you must do the mental work of constructing the Energy-Interaction Diagram to this point prior to doing any numerical calculations.
2. In an open-system diagram, the arrow showing energy transfer into the system is drawn in the direction of energy flow and labeled with *Q* or *W*. Do not write "-Q" or "-W" when energy is transferred out of the system. The arrow pointing away from the system is the indication that *Q* or *W* is a negative quantity. The variable itself is a quantity that could be either positive or negative. The sign is added when the variable is converted to a numerical value.

General Process of Constructing an Energy-Interaction Diagram

Listed here are some general questions you need to ask yourself as you use the *Energy-Interaction Model*. The order suggested is logical, but it is often necessary to cycle back to previous questions depending what is known about the interaction. The *Energy-Interaction diagram* is a tool to help you use the *Energy-Interaction Model*, which helps you keep track of the many important details you need as you construct the model corresponding to the particular physical situation you are interested in.

Here is a list of common questions:

1. *What happened?* State the essence of the physical phenomenon of interest *in your own words*. You do not need to write this down, but you should have an “internal dialogue” with yourself.
2. *What is the boundary of the physical system you are modeling?* Answer this question by *listing the physical things* you intend to include in the physical system. (Examples of “physical things” are: air, H_2O, your hand, heat pack, all of the chemicals.)
3. *What is the extent of the process or interaction?* This means identifying the beginning and end of the time interval corresponding to the process/interaction that *you defined* and explicitly writing this on the diagram.
4. *Which energy types do you include in your diagram?* Answer: Which *indicators* are changing? Each indicator that changes corresponds to a type of energy that changes. Put these energies into your diagram as *labeled circles* (for example, “H_2O $E_{thermal}$”). Include the indicator for each type of energy inside the labeled circle with an up or down arrow showing whether the indicator increased or decreased during the process, if known.
5. *What are the values of the indicators at the times corresponding to the start and end of the interval you chose in step (3)?* Record the initial and final values of the indicators next to their respective energies. Remember that all of the initial and final values of indicators should correspond to the *same* initial and final times. Note: It is not *always* necessary to identify specific initial and final values for all indicators. *Sometimes*, depending on the question, you only care about the *change* in the indicator

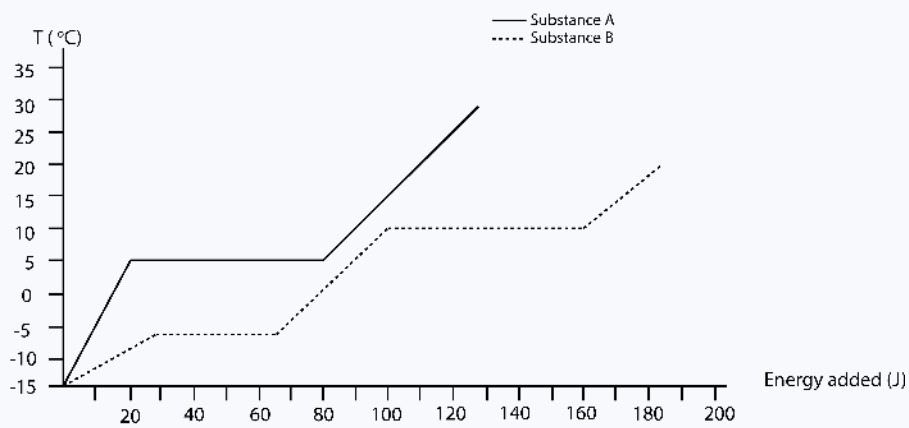
(e.g., ΔT). At other times, you may only know that the final value of the indicator is greater than (or less than, or equal to) the initial value. The point is not to memorize a series of steps, but to be as specific as possible about what you know. The diagram is not an end in itself, but a tool to lead you through your analysis and help you organize your thoughts. The diagram helps you connect the particular physical phenomenon to the particular model you are constructing.

6. *Is the physical system in your particular model open or closed?* If you are modeling the phenomenon as an *open* physical system, draw a dashed oval enclosing all of the energies, and use an arrow that stops or starts on the oval to show heat or work entering or leaving the physical system. You may find it necessary to go back to step (2) and modify the boundary of the physical system.
7. Write an equation expressing energy conservation *for your particular Energy-Interaction diagram*, in terms of the ΔEs, Q, and/or W. Each term in your conservation of energy equation must correspond to an "energy circle" in your diagram. Note, the main purpose of drawing the *Energy-Interaction diagram* is to help you write down the energy-conservation equation. If you get very comfortable with this model, you can go directly to this step and skip drawing the diagram, unless you are explicitly asked to do so.

Of course, much more complicated paths than following steps 1)-7) are possible. The following example illustrates how this is handled.

Example 1.4.1

Depicted below are temperature vs. energy added plots for substances A and B. Substance A is initially at -5°C. Substance B is initially in the gas phase at its boiling temperature of 10°C. Assume all phases exist for both substances. When the two substances are brought into contact, they eventually reach thermal equilibrium. During this process 30 joules are released to the environment.



a) Label on the above plot the initial and final states for both substances.

b) Depict this process using an Energy-Interaction diagram.

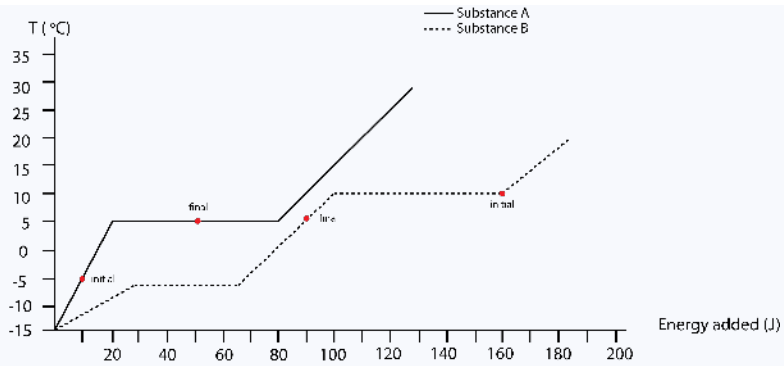
Solution

a) Substance B is initially at a higher temperature than A, thus it will be losing energy and A will be gaining energy. Energy conservation tells us that the energy gained by A plus the energy lost by B have to equal to the energy released to the environment:

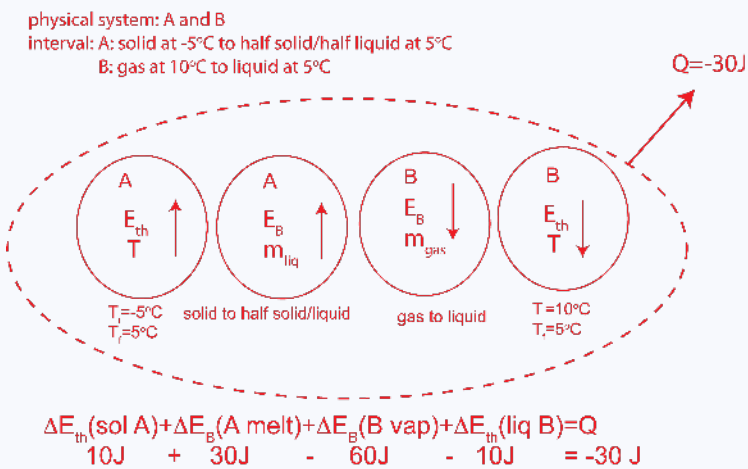
$$\Delta E_{tot}(A) + \Delta E_{tot}(B) = Q = -30J$$

Thus, B will loose 30 more joules than A will gain.

Starting points, which are stated in the problem, are marked on the plot below. Let us assume B will condense completely to liquid. This will result is a loss of 60J for B, thus a gain of 30J for A. If A gains 30J its temperature will be 5°C, B is at 10°C, so equilibrium is not yet achieved. For B to go to 5°C requires $\Delta E_{tot}(B) = -70J$. This means $\Delta E_{tot}(A) = 40J$, where A is still at 5°C exactly half melted as shown by the "final" dot on the plot.



b) Based on the initial and final states, A will go through a thermal energy change in the solid phase and bond energy change from all solid to half solid/liquid. B will go through a bond energy change all gas to all liquid, and a thermal energy change in the liquid phase. The Energy-Interaction Diagram for this process is shown below.



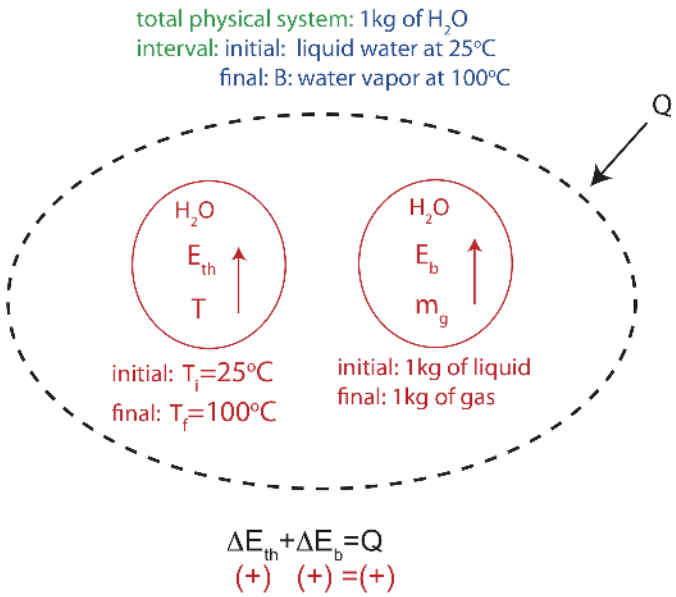
Boiling a Pot of Water

Let us consider the physical situation of a pot of water left on an unattended kitchen stove top. We might wish to estimate how long it would take for 1.0 liter (1.0 kg) of water in the pan to boil away and heat the pan to dangerously high temperatures, perhaps igniting the plastic handle. Let us also suppose we have previously determined the rate at which energy is transferred from the stove burner to the pan by doing a simple experiment to see how long it takes to heat the 1 kg of water in the pan by 10°C, giving a calculated power input to the water of 1.0 kW. *Power* is a useful measure of energy transfer, since it tells us how fast energy is transferred, or the rate of energy transfer. Thus, power has units of energy per unit time. Watts is defined as $W = J/sec$.

In this example we are both heating the water starting from room temperature of 25°C and changing its phase. Thus, we need to include both the thermal and bond energies of the water. Since we know there is a heat input to the pan of 1.0 kW, it makes sense here to model the water as an open system with the heat input from "the outside." However, can we assume that all the energy is transferred to the water and neglect any transfer to the pan or the environment? If the mass of the water (1.0 kg) is several times larger than the mass of the pan (typically the case), the heat capacity of the pan will be considerably less than the water, since the specific heat of the water is so much greater than steel or aluminum and the amount is also larger in this case. The energy transfer to the environment from the pan is tougher to estimate. We do know from experience that water does boil when left on the burner for awhile. So the transfer to the environment is definitely less than from the stove to the pan. We can initially leave this out of the model, and consider whether to put it in when we have made the time calculation.

So at this point, our Energy-Interaction Diagram would look like this:

Figure 1.3.3: Energy-Interaction Diagram for boiling water



Plugging in the algebraic expressions for each kind of energy (Equations 1.3.4 and 1.3.6):

$$mc_{liq}\Delta T + m\Delta H_{vap} = Q \tag{1.4.1}$$

Looking up the values for water in Table 1.4.3, $c_{liq} = 4.18\ kJ/Kkg$ and $\Delta H_{vap} = 2257\ kJ/kg$ and plugging into the above equation:

$$(1kg)(4.18\ kJ/Kkg)(75K) + (1kg)(2257\ kJ/kg) = 2571\ kJ = Q \tag{1.4.2}$$

Since the heat input is 1 kW or 1 kJ/s, it would take about 2571 sec or 43 min to boil away the water.

Now let us examine whether our numerical predictions make sense. First, notice that the calculated change in bond energy is about seven times greater than the change in thermal energy. This is at least consistent with the values of heat capacities and heats of vaporization listed in the data table. (We will develop a much deeper understanding of this difference when we further develop our particle model of matter in Chapter 3.) This difference in heats also implies that the water would come to boiling much quicker than it would take to boil it away (about 5 minutes compared to 38 minutes). Does this correspond to your personal experience when cooking? Earlier, we raised the question whether the pan had an effect on the system. If we included the pan, which energies would we need to add? How would this affect our prediction of the time to boil away all of the water?

Example 1.4.2

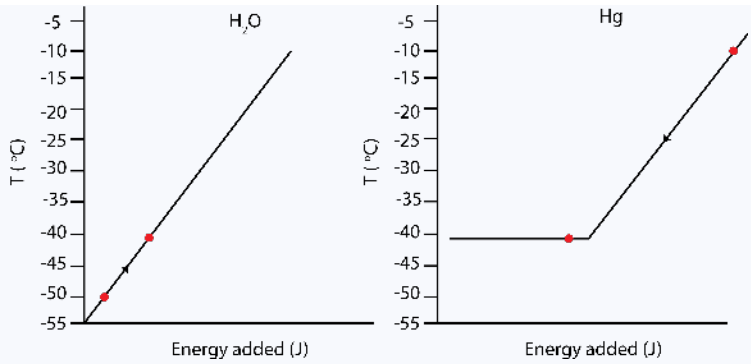
In an experiment 0.5kg of ice initially at -50°C is mixed some mercury initially at -10°C in an insulated container. Once the two substances come to thermal equilibrium 0.2 kg of mercury has frozen. Assume the total mass of Hg is bigger than 0.2kg. Use Table 1.4.3 to look up any relevant constants.

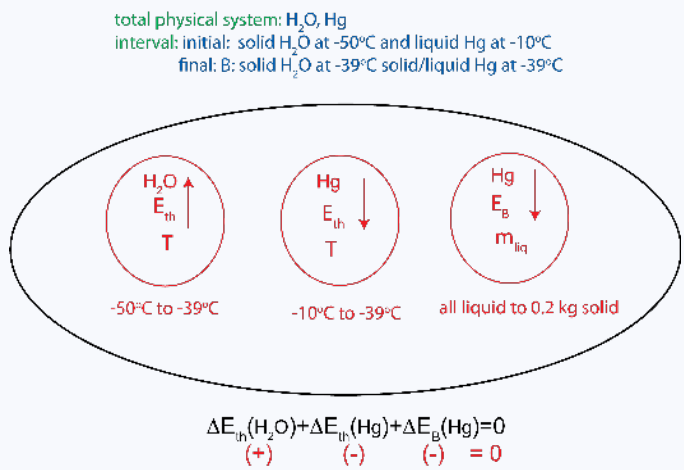
a) Depict the process using an Energy-Interaction diagram and Temperature vs. Energy added plots. Briefly explain how you determined the final temperature.

b) Calculate the total mass of mercury.

Solution

a) Since mercury has only partially frozen when the system reaches equilibrium, the final temperature has to be at the melting temperature of Hg, which is $-39^{\circ}C$ from Table 1.4.3. The Energy-Interaction diagram and the Temp. vs. E added plots are shown below.





b) The equation of conservation of energy for this interaction is:

$$m_{ice}c_{ice}\Delta T_{ice} + m_{Hg}c_{Hg,liq}\Delta T_{Hg} - \Delta m_{Hg}\Delta H_{Hg,melt} = 0$$

Solving for m_{Hg}:

$$m_{Hg} = \frac{\Delta m_{Hg}\Delta H_{Hg,melt} - m_{ice}c_{ice}\Delta T_{ice}}{c_{Hg,liq}\Delta T_{Hg}}$$

Looking up the relevant values in Table 1.4.3, $c_{ice} = 2.05\ kJ/Kkg$, $c_{Hg,liq} = 0.141\ kJ/Kkg$, and $\Delta H_{Hg,melt} = 11.3\ kJ/kg$. Plugging in numbers:

$$m_{Hg} = \frac{(0.2kg)(11.3\ kJ/kg) - (0.5kg)(2.05\ kJ/Kkg)(-39^oC + 50^oC)}{(0.141\ kJ/Kkg)(-39^oC + 10^oC)} = 2.22\ kg$$

Once the system reaches equilibrium, there is 2.02kg of liquid Hg and 0.2kg of solid Hg, since the total mass is 2.22 kg.

Application to Chemical Reactions

Similar to substances going through phase transitions, chemical reactions involve breaking and forming of bonds. Thus, it seems logical that the concept of bond energy with the *Energy-Interaction Model* can be applied to various chemical reactions as well.

The bonds in *reactants*, chemical substances at the start of the reaction, break. While bonds in *products*, the resulting chemical substances in a reaction, form. Using the same arguments as we did for phase changes, forming bonds releases energy and breaking bonds requires energy. Thus, the change in bond energy of a chemical substance whose bond is broken is positive. When *n* number of moles of a chemical substance are broken, $\Delta E_{bond} = n\Delta H$, where ΔH is the enthalpy of the molecule. When a bond is formed the change bond energy is negative. For *n* moles of formed bonds, $\Delta E_{bond} = -n\Delta H$. Chemical reactions can be *exothermic* when heat is transferred into the environment, thus, the total change in energy is negative. Other reactions are *endothermic* which require an input of energy, thus, the total change in energy is positive. One can determine whether a reaction is exothermic or endothermic by adding up all the total enthalpies of the reactants and subtracting the total enthalpies of the products:

$$Q = \Delta E_{bond} = \sum n_i \Delta H_{reactants} - \sum n_i \Delta H_{products} \quad (1.4.3)$$

$$Q = \Delta E_{tot} = \sum_i n_i \Delta H_{reactants} - \sum_i n_i \Delta H_{products} \tag{1.4.3}$$

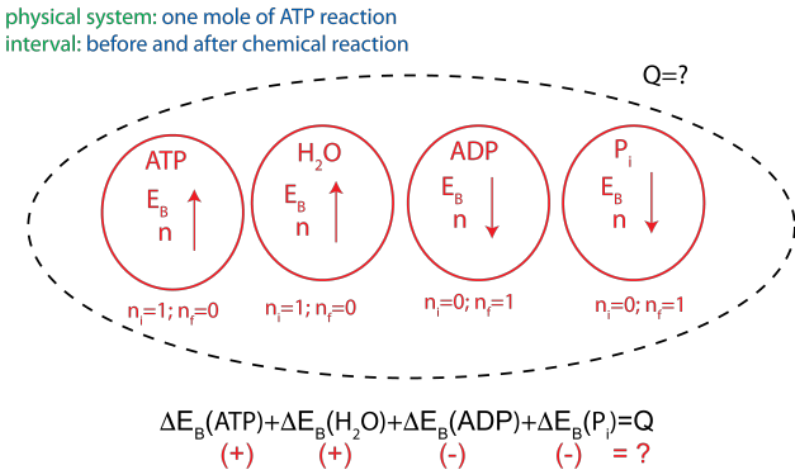
For example, living cells use ATP as a source of energy for other reactions. The chemical reaction for ATP hydrolysis is shown here:

$$ATP + H_2O \rightarrow ADP + P_i \tag{1.4.4}$$

A common misconception about ATP is that "breaking ATP releases energy". This statement is clearly inconsistent with what we have learned so far about bond energy, "breaking bonds requires an input of energy". So why do we say that ATP is the source of energy for life? Let us take a more careful look at this chemical reaction using the *Energy-Interaction Model*. When ATP and H_2O breaks down into its constituents, energy is required to break these bonds. However, when ADP and Pi are formed, energy is released.

The goal is to figure out whether this is an exothermic or an endothermic reaction and how much energy is either given off to the or taken from the environment. The Energy-Interaction diagram for the reaction (before performing the calculation) is shown below:

Figure 1.3.4: Energy-Interaction Diagram for ATP hydrolysis



At standard conditions, $|\Delta H_{ATP}| = 2982\ KJ/mol$, $|\Delta H_{H_2O}| = 287\ KJ/mol$, $|\Delta H_{ADP}| = 2000\ KJ/mol$, and $|\Delta H_{P_i}| = 1299\ KJ/mol$. Plugging into the above equation the enthalpy values for each molecule with the correct signs for the reactants and products we get: $Q = 2982 + 287 - 2000 - 1299 = -30\ kJ/mol$. This shows that the reaction is *exothermic*, so energy is released into the environment. Thus, although energy is required to break down ATP the net result of this reaction is production of energy. Now you can go back to the Energy-Interaction Diagram and modify it with heat, *Q*, leaving the system.

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1.5: Units, Data Tables, and Equations

This page is a draft and is under active development.

Units for Energy

The historical development of the energy concept separately for thermal and mechanical interactions, as well as the widespread use of several different systems of units, has created a multitude of energy units. But energy is energy and all forms can and should be expressed in the same basic energy unit. Fortunately, essentially everyone within the scientific and technical community has now embraced the International System (SI) system of units. The SI unit of energy is the joule, J, (rhymes with cool). All other energy units are related to the joule through an appropriate conversion factor. We will generally use SI units in this course. However, in those instances where non-SI units are commonly used, we will use both, and expect you to be able to convert back and forth. An advantage of working *exclusively* in SI is that you don't have to be concerned about unit conversions (and keeping track of them for that purpose).

The SI base units for mass, length, and time are kilogram (kg), meter (m), and second (s), respectively. Other SI units can be expressed in base units when desired. For example, a Joule is a kgm^2/s^2. The kelvin (K), the SI unit for temperature, is another independent base unit. The zero of the kelvin scale is at thermodynamic zero, the so-called "absolute zero" of temperature. (Note that "kelvin" is used without the word "degree" attached.) Although the zero of the Celsius, or centigrade, scale is not at absolute zero, the kelvin is the same size as the Celsius degree. Thus, when dealing with temperature *differences*, it is sometimes convenient to use Celsius degrees for ΔT. For example, the SI unit for specific heat, J/kg K is equal to (and will sometimes be written as) J/kg C°.

A concept closely related to energy is power: the time rate of energy change or energy transfer. The SI unit of power is a joule per second, J/s and is given the name watt, W.

Table 1.4.1: Some common energy units and conversions to SI:

- 1 kWh = 3.6 MJ
- 1 erg = 10^{-7} J
- 1 cal = 4.184 J
- 1 food Calorie (big "C" calorie) = 1 kcal = 4.184 kJ
- 1 $ft \cdot lb$ = 1.36 J
- 1 eV = 1.602×10^{-19} J
- 1 BTU = 778 $ft \cdot lb$ = 252 cal = 1.054 kJ

Table 1.4.2: SI Units related to energy:

SI Unit	Construct	Abbreviation	Expressed in base units
Joule	energy	J	$\frac{kgm^2}{s^2} = Nm$
Watt	power	W	$\frac{kgm^2}{s^3} = \frac{J}{s}$
Newton	force	N	$\frac{kgm}{s^2}$
Pascal	pressure	Pa	$\frac{kg}{ms^2} = \frac{J}{m^3} = \frac{N}{m^2}$

Thermal Data

Below is a very useful table for this course. It includes experimentally determined values of melting and boiling temperatures, heats of melting and vaporization, and specific heats for some commonly used pure substances. The subscript "p" in c_p refers to specific heat measured at constant pressure. We will discuss the importance of this in Chapter 3. We will also discuss in Chapter 3 why specific heats for solids, liquids, and gases are different.

Table 1.4.3: Table of Melting and Boiling Points, Heats of Melting and Vaporization, and Specific Heats of Some Common Substances

(at a constant pressure of one atmosphere):

Substance	Symbol (phase)	Melting Temperature T_{MP} (K)	Boiling Temperature T_{BP} (K)	Heat of Melting ΔH_{melt} (kJ/kg) (kJ/mol)	Heat of Vaporization ΔH_{vap} (kJ/kg) (kJ/mol)	Specific Heat c_p (J/Kmol) (kJ/Kkg)
Aluminum	Al(s)	933	2600	(389.18) (10.5)	(10790) (291)	(24.3) (0.900)
Bismuth	Bi(s)	544	1693	(52.2) (10.9)	(722.5) (151)	(25.7) (0.123)
Copper	Cu(s)	1356	2839	(205) (13)	(4726) (300.3)	(24.5) (0.386)
Gold	Au(s)	1336	3081	(62.8) (1.24)	(1701) (33.5)	(25.4) (0.126)
Ice (-10°C) Water Water vapor	H_2O(s) H_2O(l) H_2O(g)	273	373	(333.5) (6.01)	(2257) (40.7)	(36.9) (2.05) (75.2) (4.18) (33.6) (1.87)
Lead	Pb(s)	600	2023	(24.7) (5.12)	(858) (177.8)	(26.4) (0.128)
Sodium	Na(s) Na(l)	371	1154	(114.8) (2.64)	(4306) (99)	(28.2) (1.23) (32.7) (1.42)
Silver	Ag(s)	1235	2436	(88.2) (9.50)	(2323) (250.6)	(25.4) (0.233)
Mercury	Hg(s) Hg(l) Hg(g)	234	630	(11.3) (2.3)	(296) (59.1)	(28.3) (0.141) (28) (0.140) (20.8) (0.103)
Tungsten	W(s)	3410	5900	(184.1) (33.86)	(4812) (884.9)	(24.6) (0.134)
Nitrogen	N_2(g)	63.14	77	(25.7 (0.72)	(199.1) (5.58)	(29.0) (1.04)
Oxygen	O_2(g)	54.39	90.18	(13.9) (0.444)	(213.1) (6.82)	(29.16) (0.911)
Iron	Fe(s)	1535	3135	(247.1) (13.8)	(6260) (349.6)	(25.1) (0.449)

Useful Grouping of Energy

Below is a list of different types of energies used in this course. The types of energies are split into two categories:

- **Mechanical Energy:** Sum of kinetic and potential energies associated with the physical "objects" as a whole, not with the internal energies of the objects.
- **Internal Energy, U:** Sum of kinetic and potential energies associated with the individual molecules/atoms comprising a substance, as well as the energies associated with their atomic and nuclear energies. In Chapter 1 we mostly deal only with *changes in the energies* associated with thermal and bond energies (chemical energies).

For each energy an *indicator* characterizes an observable that directly tells us whether the corresponding energy changes. The algebraic equation for each energy tells us how that energy depends on its indicator. A summary of energies used in the course is given in the table below.

Table 1.4.4: Common Types of Energy:

Energy Type	Indicator	Algebraic Equation for Change in Energy
Internal:		
Thermal energy	temperature, T	$\Delta E_{th} = C\Delta T$

Bond energy: phase	mass of sample in a given phase, m	$\Delta E_{bond} = \pm\lvert\Delta m \Delta H\rvert$
Bond energy: chemical	number of moles of sample, n	$\Delta E_{bond} = \pm\lvert\Delta n \Delta H\rvert$
Mechanical:		
Kinetic energy	speed, |v|	$\Delta KE = \frac{1}{2} m \Delta(v^2)$
Gravitational potential energy	height, y	$\Delta PE_g = mg\Delta y$
Spring potential energy	displacement from equilibrium, |x|	$\Delta PE_{spring} = \frac{1}{2} k \Delta x^2$

Note: This list is by no means complete, and the mechanical energy systems listed here will be used in Chapter 2. They are listed here only for reference.

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1.6: Looking Ahead

Let's reflect on what we have done in the course up to this point. Our focus has been on developing an energy model, which we have called the *Energy-Interaction Model*, and on understanding how to apply it to some particular thermal phenomena. We have used this model to begin to understand some of the more general thermal properties of matter. We will continue to develop the *Energy-Interaction Model* as we apply it to new kinds of phenomena in Chapter 2.

The next step is to add additional types of energies to our repertoire, so we can handle other types of phenomena with different kinds of interactions. Fortunately, there are not that many different energies. So, after we have added just a few more, we will be in a position to tackle questions about many more phenomena than we could even deal with in one quarter. But that is precisely the power of this approach. It is so universal that you do not need to be shown how to use it for each different phenomenon. Once you are comfortable with the approach, it becomes your own powerful tool, which you can use anytime you need it.

What have we left out in what we have done so far? Think back over all of the phenomena we have discussed and the questions we can answer with this approach. Basically, we can get at the values of quantities, or more precisely the changes in these values that occur as a result of the interaction, but we cannot get information about the details of the interaction or what goes on during the interaction.

When we want to know something about the details of an interaction or the dynamics of the phenomenon, we will need to use an approach, or model, that incorporates these details. But precisely because we have to incorporate more detail, the models will not be nearly so general as the *Energy-Interaction Model*. In Physics 7B we will devote considerable effort to understanding the Newtonian model, which allows us to very accurately calculate motions of objects. In Physics 7C we focus on a very useful wave model of motion and field models that allow us to make sense of electric and magnetic phenomena. We need these detailed models because we want to be able to answer questions that the Energy-Interaction model can't help us with. But, alas, we will miss the simplicity and generality of the energy model.

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CHAPTER OVERVIEW

2: Applying Models to Mechanical Phenomena

In this Chapter we continue to work with the *Energy-Interaction Model*. We add all kinds of *mechanical* interactions to the thermal interactions we treated in Chapter 1. (Note: the term “mechanical” as in the phase “mechanical interactions” is typically used to imply everything other than thermal. Since the *Energy-Interaction Model* literally applies to every kind of *interaction* that scientists have ever encountered, we will be just scratching the surface of the realm of applications of this powerful model. We will, however, devote some attention to one area of application that occurs frequently in many phenomena–all kinds of things vibrate, from atoms and molecules to bridges and skyscrapers; that is, they move back and forth or oscillate in very predictable ways.

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2.1: Where Are We Headed?

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Overview

In this second chapter we continue to work with the *Energy-Interaction Model*. We add all kinds of *mechanical* interactions to the thermal interactions we treated in Chapter 1. The term term “mechanical” is typically used to imply everything other than thermal. Since the *Energy-Interaction Model* literally applies to every kind of *interaction* that scientists have ever encountered, we will be just scratching the surface of the realm of applications of this powerful model. We will, however, devote some attention to one area of application that occurs frequently in many phenomena–all kinds of things vibrate, from atoms and molecules to bridges and skyscrapers; that is, they move back and forth or oscillate in very predictable ways. A fundamental understanding of *vibrational* (or *oscillatory* as it is often called) motion is very useful. Therefore, we introduce the *Intro Spring-Mass Oscillator Model* in this chapter as an application of the *Energy-Interaction Model*. The *Intro Spring-Mass Oscillator Model* will also play an important role in Chapter 3 when we develop particle models of matter.

In Chapter 2 we continue our focus on interacting systems. We intentionally focus on the systems as they exist *before* the interaction and then immediately *following* the interaction; we stay away from the *details* of what happens during the interaction itself. This is a very general and a very powerful approach. We saw in Chapter 1 that energy transfers are fundamentally related to interactions.

When one physical system interacts with another, or when parts of the same physical system interact, we were able to identify different *types of energy* that either increased or decreased. If the physical system is closed, i.e., we have included all of the energies that change during the interaction, then energy conservation tells us that the total of all the increases equals the total of all the decreases. If the physical system is open, then the net change in all of the energies of the system equals the net energy *added* to the physical system from the outside or *removed* from the physical system to the outside. We continue this approach in Chapter 2 with non-thermal types of energies. A surprising result for many of us is that when we consider typical activities such as driving a car or riding a bike, most of the energies involved ultimately end up being transferred to various thermal systems. Thermal energy seems to have a way of “grabbing and hanging on to” most of the energy. (This tendency has to do with the vast number of particles involved in thermal systems. We explicitly discuss this in Chapter 4.)

Thermal energies are associated with the *random* or *disordered* motions of the particles making up matter. In this chapter we turn our attention to energies in which the *common motion* all of the particles making up the matter is important. We can often describe this common motion with just two variables: a position variable (x) and a speed variable (v). These energies (ones that can be described by position and speed of the *entire object*) are commonly called *mechanical energies*.

As you begin reading this chapter, you might be tempted to ask, “How many kinds of energy can there be?”. The answer is simple and reassuring: there are only *two* fundamental kinds: these are energies that depend on the square of the speed of a particle or object (kinetic energy, abbreviated KE) and energies that depend on the positions or configurations of particles or objects (potential energy, abbreviated PE). All energies, no matter what names we give them, are either a kinetic energy or a potential energy or some combination of the two. This is true for the two energies we have discussed up to this point: bond energy and thermal energy. Bond energy depends on the positions of the atoms making up the molecules, so it is a potential energy. Thermal energy is a *combination* of the kinetic energies of the individual atoms *and* the potential energies associated with the motions of the atoms about their equilibrium positions. We will discuss these relations in much greater detail in Chapter 3.

Where are we going with this energy stuff and why? You will begin to see that using the *Energy-Interaction Model* allows us to answer many interesting questions about sports, bikes, objects falling off buildings, and other common (or not so common) everyday activities. Mechanical energies involve position and speed variables, and because transfers of mechanical energy involve work (instead of heat), we need to understand a little more about *work*. Work involves the notion of forces acting through distances, which means we will have to know a little more about *force* itself. The payoff is that we will be able to calculate or predict many unknown distances, speeds, and forces *without ever having to know the details* of the interactions. And the beauty of this approach is that it works for all kinds of physical situations. We do not have to learn lots of different ways of approaching questions that depend on the particulars of the situation!

Another significant benefit of starting the way we did in Chapter 1 with thermal phenomena is that we can also look much more realistically at *real-world phenomena* where *friction* is always present. If you look at a conventional introductory physics text, you will find that for the first third of the book, it seems everyone just *pretends* that there is no friction! It is as if we lived in a distant galaxy where friction didn't exist. But that is a pretty idealized galaxy. Because we are treating energy within a general model that works for mechanical energies as well as thermal energies, rather than from a purely mechanics approach. We can deal directly with the transfers of energy to thermal systems and treat a lot of phenomena much more realistically than we could if we narrowly focused on the mechanics of *frictionless* systems.

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2.2: Force

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Overview

We can apply the *Energy-Interaction Model* used in Chapter 1 to mechanical energy as well as to thermal and bond energy. When discussing macroscopic objects, *mechanical energies* have to do with the movement of the object as a whole, while thermal energy is related to the random atomic motion within the object. Mechanical interactions obey the same rules and can be understood in the same way as the interactions we studied in Chapter 1. Because energy conservation still holds, regardless of the kind of interaction, Energy-Interaction Diagrams prove to be just as useful in describing the interactions that take place when a ball falls, as in describing the interactions taking place in a pot of boiling water. We will also be able to make numerical predictions of various parameters in mechanical interactions, just as we were able to do for thermal interactions.

With thermal and bond energies, we could infer changes in the energy of a system through changes in observable properties, the indicators, such as temperature for the change of thermal energy, mass in phase changes, and number of moles in chemical reactions. In the mechanical systems introduced in this chapter, we infer changes in energy by looking at changes in position and speed. Mechanical energies we describe can exchange energy with each other or with the thermal and bond energies. In Chapter 1, we labeled the energy transferred into or out of a physical system due to a difference in temperature between the physical system and its surrounding environment as *heat*, Q. In this chapter, we introduce another type of energy transfer, which is given the label *work*, W.

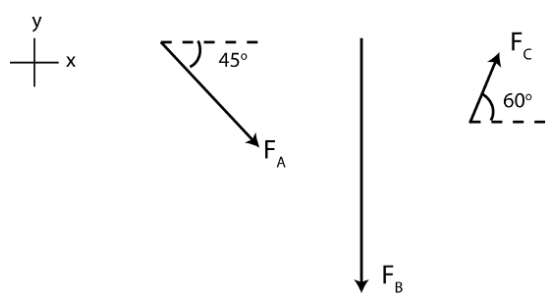
Heat has to do with a temperature difference between two systems, while *work* has to do with a *force* applied to a system by another system over some distance. Before discussing work explicitly, we will introduce a basic description of force. We will come back to a more detailed overview of forces in Physics 7B. For right now, we just need a few fairly simple ideas related to force.

Force is a Vector

In general terms, ***a force is any push or pull between two objects.*** Variables such as temperature and mass are known as *scalars*, since there is only a quantity (or magnitude) associated with them, but not direction. Others variables, such as force, velocity, and acceleration, are known as *vectors*. Vectors have a *magnitude* (how large is the force?) and *direction* (which way does the force point?). We will not study vector mathematics in great detail until Physics 7B, but we need to understand the basics in order to understand how energy is transferred through work. Both direction and magnitude affect the amount of energy that one physical system transfers to another physical system. So we need to explore vectors a little bit further. A vector is typically represented by either a bold face, **A**, or an arrow over the symbol, $\vec{A}$.

One way to represent vector quantities is to simply draw an arrow pointing in the direction the vector points (think of the direction of a pull or push for a force), and let the length of the arrow represent the magnitude of the vector (how hard is the push for a force). Shown below are several forces represented in this way with arrows:

Figure 2.2.1: Graphical representation of force vectors.



In the above examples, force $\vec{F}_A$ points in a direction 45˚ below the +*x* axis, or we can say it points Southeast. Force $\vec{F}_B$ is about twice the magnitude of $\vec{F}_A$ since the length of the arrow is double, and it points in the –*y* direction, or South. Force $\vec{F}_C$ is about half the magnitude of $\vec{F}_A$ and points in a direction 60˚ above +*x* axis, or Northeast.

Force is the agent of interactions of TWO OBJECTS

Forces are the agents of interactions between two “objects”. (The quotes around the word “object” signify that it is being used in a general way that includes matter in the form of gases or liquids as well as matter in the solid phase. Sometimes it might even be a single atom or electron. We will omit the quotes from now on, but remember we are using the word object in this more general sense.) Just as there cannot be an interaction involving only one object, there cannot be a force involving only one object.

We normally say, “the force on (name of an object) by (name of another object)” to make clear which two objects are involved in the interaction. For example, we could say, “the force on ball by bat”, or symbolically $\vec{F}_{\text{on ball by bat}}$. Generally, a force applied on object A by object B can be expressed in this notation:

$$\vec{F}_{\text{on A by B}} \tag{2.2.1}$$

To realize that this is something you already know and actually does *make sense* think of the following: use the word “push” in a sentence that refers to you actually pushing. What did you have to say? Did you name an object that you pushed on? Who did the pushing? Can you push without pushing on something? Remember that sometimes it might be something pretty squishy, such as air (which is still a “something,” still an "object"). Can an object be pushed unless there is “something” pushing on it? This is what we mean when we say that *force* is the *agent* of an interaction of *two objects*. There simply cannot be an interaction without there being two objects. And there cannot be a force without there being two objects.

Two Types of Force

Let us consider the example of the force on ball by bat. Does the force by the bat continue to act on the ball after the bat is no longer touching the ball, or does the force act only while the ball and bat are in contact? Recall that force is an agent of interaction, so another way to ask the question is whether the ball and bat continue to interact after they are no longer in contact. The answer is they interact *only while in contact*. Thus, the force the bat exerts on the ball (and, likewise, the force that the ball exerts on the bat) acts only while the two objects are in contact. Consequently, we call this type of force a *contact force*.

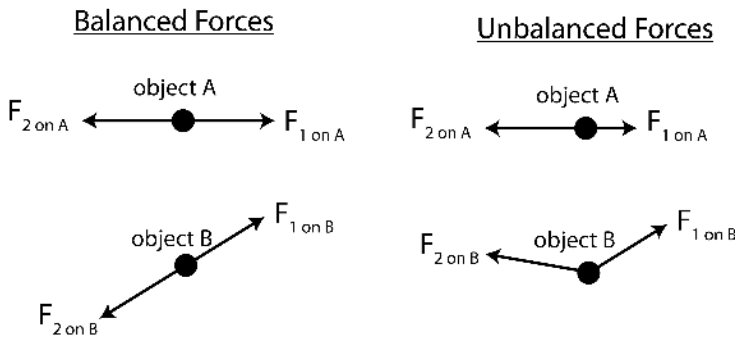
Some forces act even when the objects are not touching, some even when extreme distances separate the objects, and these are referred to as *long-range forces*. Think about the force of gravity. The Earth pulls down on all objects near its surface. Note that we have *two objects*: the Earth and the object being pulled down. We know from everyday experience that the gravitational force of the Earth on an object is present whether the object is touching the Earth or not. Apparently the interaction between the Earth and a nearby object is unlike the force between the bat and the ball. The interaction and the force, the agent of the interaction, continue to exist even when there is no direct contact. The gravitational force is a *long-range force*. The force of gravity between our sun and each the planets in our solar system does indeed get weaker as the distance between the sun and the particular planet increases, but it is definitely still there. The gravitational force is truly *long-range*.

There are also non-contact forces that act between objects that are not touching, but “die off” or “go to zero” as soon as the objects get more than a *little distance* apart. Most of the forces that hold atoms together into molecules and hold the particles of solids and liquids together are like this. The interaction and the agent of the interaction, the force, exists, even though the particles are not touching, but the force decreases to zero in magnitude pretty fast as the particles begin to separate just a little bit from each other. We will see examples of this behavior in Chapter 3 when we study the forces between neutral atoms or molecules. Sometimes this kind of force is said to be a *short-range force*.

Balanced and Unbalanced Forces

There is one last important idea that we will need to use, but is also part of our common experience with pushes and pulls. We can easily imagine two people pushing on a table from opposite sides. If person A pushes harder than person B, the table moves. If both people push with the same strength but in opposite directions, the table does not move. In the first case, we say the forces applied on the table (one object) by the two objects (the two persons) were *unbalanced*, and as a result, the table moved. In the second case, the two objects applied equal and opposite forces on the table and the table did not move. We say the forces applied by the two persons were *balanced*. The figure below provides a few examples of balanced and unbalanced forces on an object using the graphical representation of a vector.

Figure 2.2.1: Graphical representation of balanced and unbalanced forces



Note, you can have forces of the same magnitudes but still be unbalanced. Picture a scenario of two people pushing a table with the same strength and in the same direction, the table will clearly move. For the unbalanced forces in the figure above, can you guess which direction the object will move? The reason it is important to consider the total force acting on an object, is that it is precisely the total force that matters when considering the work done on our object. Once we know the total force, we will be able to calculate work and figure out how the energy of the object changes due to this total force.

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2.3: Work

Definition of Work

Work, W, is a transfer of energy from one physical system to another via a force acting between the two through a distance. Only the part of the force that acts parallel to the displacement contributes to work. The general algebraic expression for work done along a path s from point A to B is:

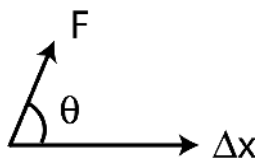
$$W = \int_A^B \vec{F}_{net} \cdot \vec{ds} \tag{2.3.1}$$

The "·", known as the *dot product*, in the equation above means that only the component of force that is parallel to the path contributes to work. When the force is constant along some displacement, Δx, Equation 2.3.1 simplifies to:

$$W = |\vec{F}||\overrightarrow{\Delta x}|\cos\theta \tag{2.3.2}$$

where $|\vec{F}|$ is the magnitude of the force, $|\overrightarrow{\Delta x}|$ is magnitude the displacement vector, and θ is the angle between these two vectors as shown in the figure below. The term, $|\vec{F}|\cos\theta$, determines the amount of the force that points in the direction of displacement.

Figure 2.3.1: Force and displacement resulting in work.



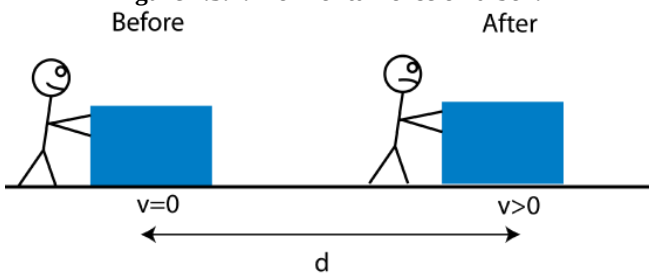
When Does Work Happen?

In order to accomplish work on an object there must be a net force applied on the object, and the object must move in the direction of the net force. If either of those conditions are not met, then there is no work. For example, if an object is traveling freely with no forces acting on it (such as a comet moving at constant speed in outer space far from other objects), there is no work being done on the object despite it moving through a distance. The reverse is also true: if an object has forces acting on it, but is not moving (as in the example of two people pushing on a table with equal but opposite forces), there is also no work being done on the table. What matters is the net force, not the individual ones. There is one last way for no work to be done. Imagine someone carrying a weight across a room while walking at a constant speed. Your intuition may be tempted to tell you that there is a force being exerted through a distance, and therefore work is being done, but as is often the case in physics, your intuition would be wrong! The force you exert while carrying an object is entirely *up*, but the displacement while walking is completely *horizontal*. The best way to improve your intuition about work is to work through examples, apply the definition, and see where it leads you.

Like heat, work is a scalar (i.e., has no direction associated with it) and is measured in the SI unit of energy, joules. A joule is equivalent to a newton·meter, or $J = N{\cdot}m$, since a newton is the SI unit of force.

Consider a box being pushed horizontally along a frictionless surface as shown in the figure below.

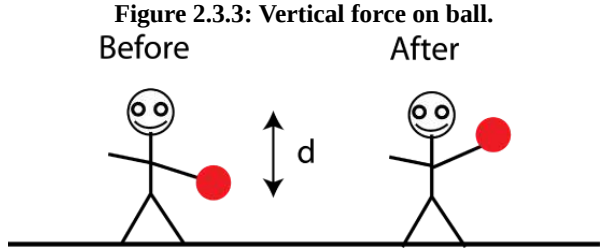
Figure 2.3.2: Horizontal force on a box.



The person exerts a force on the box, and we observe the box moving with an increasing speed along the surface. This force results in work being done on the box, since the force is in the same direction as the displacement *d*, and there are no other horizontal forces acting on the box. The work being done implies that the energy of the box must be increasing. From Equation 1.2.1, we obtain $\Delta E_{tot} = W$. The next question we want to ask is what type of energy is changing? The physical property we observe increasing is the speed of the box. The energy associated with speed of objects is known as *kinetic energy*, *KE*, where *speed* is its indicator.

In another example, a person lifts a ball vertically.

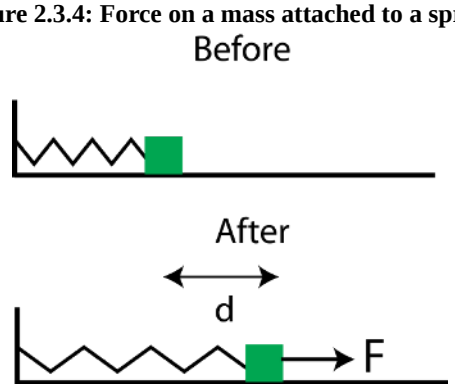
Figure 2.3.3: Vertical force on ball.



In this example we assume that the speed of the ball is zero before and after it is lifted. The person does work on the ball, since a force by the hand on the ball is exerted in the same direction as the displacement *d* on the ball. Thus, the energy of the ball must have increased in this interval. What type of energy is this? The only physical characteristic of the ball that changed is its height, since the speed remained at zero. The energy associated with height is known as *gravitational potential energy*, PE_g, where *height* is its indicator.

Another system we will study intensively in this course is the *spring-mass system*. In the figure below a mass attached to a spring (*spring-mass system*) is mounted to a wall. When there is no force acting on the spring-mass ("before" in the figure), we say that the spring-mass system is in its *equilibrium position*. In the particular interval shown in the figure, a horizontal force is applied on the spring-mass displacing the spring-mass by a distance *d* from equilibrium.

Figure 2.3.4: Force on a mass attached to a spring.



Again, we assume that the speed of the mass remained zero, while the person holds the mass in place when stretched. Work is being done since the force, $\vec{F}$, is in the same direction as the displacement *d*. The physical characteristic that changes in this particular interval is the displacement from equilibrium of the spring-mass system. We call the energy associated with this change, the *spring-mass potential energy*, PE_{sm}, where *displacement from equilibrium* is its indicator.

Note, the indicators for both potential energies introduced here, PE_g and PE_{sm}, depend on the position of the physical system. We will look at these three energies in greater detail in the coming sections.

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2.4: Mechanical Energy

Kinetic Energy

As we discussed in the previous section, forces cause objects to move. When a net force acting on a physical system has a component in the direction of its motion, there is work done. Recalling the Energy-Interaction Model, when work is being done Equation 1.2.1 becomes:

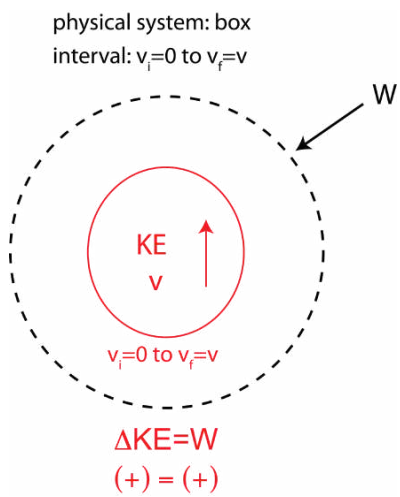
$$\Delta E_{tot} = W. \tag{2.4.1}$$

When you push a box across the floor, you do work on the box, and the box speeds up. The energy whose indicator is speed is known as *kinetic energy*, which depends on both speed and mass in the following manner:

$$KE = \frac{1}{2}mv^2 \tag{2.4.2}$$

Looking back at Figure 2.3.2 we can calculate the final speed of the box after it has been pushed for a distance *d* with a force of magnitude *F* using the Energy-Interaction Model. Assume the box starts from rest, the Energy-Interaction diagram for this situation looks like this:

Figure 2.4.1: Energy-Interaction diagram for work done on box.



Assuming the force is constant over the distance *d*, and using definition of work from Equation 2.3.2, we find $W = Fd$. The initial kinetic energy is zero, since $v_i = 0$, and $KE_f = \frac{1}{2}mv^2$. Plugging this into the energy-conservation equation from the figure above, $KE_f - KE_i = W$ we get:

$$\frac{1}{2}mv^2 = Fd \tag{2.4.3}$$

Solving for *v*:

$$v = \sqrt{\frac{2Fd}{m}} \tag{2.4.4}$$

Given some fixed displacement *d*, the final speed is proportional to the magnitude of force (the harder you push the faster the box will move). And the speed is inversely proportional to mass (the heavier the box the harder it is to push it).

Force of Gravity

An object near the surface of the Earth is attracted to the Earth with a force commonly referred to as the *force of gravity*. This force is proportional to the object's mass and is nearly constant everywhere on the surface of the Earth. The constant of proportionality is often referred to as "g", but properly it should have a subscript "E" to indicate that it is the Earth that is interacting with the object, and not, e.g., the moon. If the downward force of gravity is balanced by an upward force acting on the object (object is placed on a surface), then the object's velocity remains constant (balanced forces). If the object exerting the upward force on the object is a

scale or balance, then it reads the "weight" of the object, which is equal in this case of balanced forces, to the gravitational force acting down on the object.

The term weight is often taken to mean the gravitational force. This is OK when forces are balanced and the object's motion does not change. If the object's velocity is changing, the weight (what a scale reads) can be very different from the gravitational force. The force of gravity acting on the astronauts in the space shuttle is only slightly less than the force of gravity acting on them when they are standing on Earth, yet they are "weightless" in the orbiting shuttle! (We will study the interesting state of weightlessness in 7B.)

Force of gravity is written as:

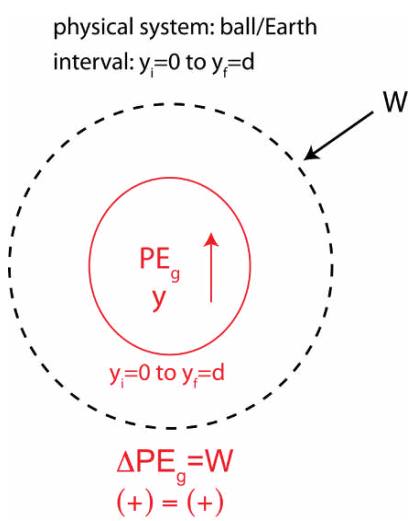
$$F_{gravity} = mg \tag{2.4.5}$$

where *m* is the mass of the object and $g = 9.8m/s^2$ (or in units of *N/kg*) near the surface of the Earth. (Note, in this course we will often approximate $g \simeq 10m/s^2$ for simplicity of numerical calculations.) This gravity equation is an extremely accurate approximation when near the surface of the Earth, but it will not hold if the object changes elevation by a sizeable fraction of the Earth's radius.

Gravitational Potential Energy

Gravitational potential energy, PE_g, exists when two objects interact by the gravitational force. If we are talking about an object near the surface of the Earth and the Earth itself, the energy of this object changes as some other object (perhaps you) does work on the object by raising it to a higher elevation as we saw in Figure 2.3.3. Since the ball and the Earth are interacting, we need to include both in the physical system. Assuming the motion of the ball does not change in this interval (speed is constant throughout), implies that all the work goes into changing the gravitational potential energy. We call this a "potential" energy, because the energy depends only on the relative positions of the object and Earth. It does not depend on the route taken to get to these positions or on the speeds the object and Earth might have. The Energy-Interaction Diagram for the situation in Figure 2.3.3 is:

Figure 2.4.2: Energy-Interaction diagram for work done ball.



Since the motion of the ball remains constant, forces on the ball are balanced. Thus, the force exerted by the hand on the ball must equal the force of gravity acting on the ball, $|\vec{F}|_{\text{by hand on ball}} = mg$. This results in $W = mgd$, for the force mg acting over distance *d*. Thus, the change in gravitational potential energy becomes, $\Delta PE_g = mgd$. More generally, gravitational potential energy of an object at height *y* is given by:

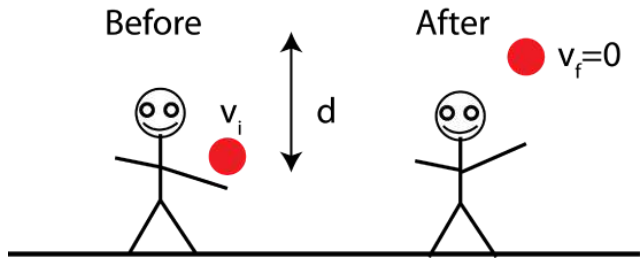
$$PE_g = mgy \tag{2.4.6}$$

Notice that ΔPE_g does not depend on distance moved parallel to the surface of the Earth, but only on the change in vertical distance, since gravitational force points toward the center of the Earth, thus, only has a vertical component.

Instead of lifting the ball, imagine that you now threw it directly upward, giving it some initial speed. You notice that eventually the ball starts to fall back down. Can we figure out the maximum height this ball will reach in term of its initial speed? Let us focus on

the interval after the ball was just thrown to its maximum height. At its maximum height, we call *d*, the speed of the ball goes to zero (in order for an object to turn around, it first has to stop). This situation is depicted in the figure below.

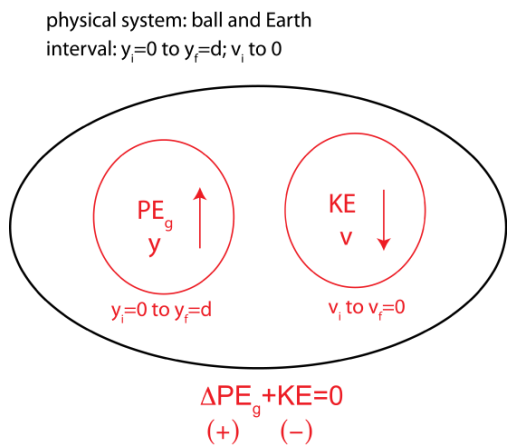
Figure 2.4.3: Throwing a ball upward.



We observe that the ball's kinetic energy decreases, since it slows down and eventually stops at the top of its trajectory. Let us define the physical system to include both the ball and the Earth. If we neglect air friction, we can conclude that the ball/Earth physical system is not interacting with any other objects in the given interval. (Note, the person is not *in contact* with the ball during this interval.) Therefore, we can conclude that this system is closed, $\Delta E_{tot} = 0$. Since kinetic energy is decreasing, this means that another type of energy must be increasing in the ball/Earth system. It is precisely gravitational potential energy which increases, since the ball's height is increasing.

The Energy-Interaction Diagram for this situation is:

Figure 2.4.4: Energy-Interaction diagram for a ball thrown upward.



Using Equations 2.4.2 for *KE* and 2.4.6 for PE_g we get:

$$mg(y_f - y_i) + \frac{1}{2}m(v_f^2 - v_i^2) = 0 \tag{2.4.7}$$

Plugging in values of the indicators for each energy and solving for the maximum height, we find:

$$mgd - \frac{1}{2}mv_i^2 = 0 \tag{2.4.8}$$

$$d = \frac{v_i^2}{2g} \tag{2.4.9}$$

One interesting feature of this result is that the maximum height does not depend on the mass of the ball, which at first may seem counterintuitive. How can we explain why a dropped ball hits the ground before a feather dropped at the same time? You will be able to answer this after reading the next subsection. Also, notice that the maximum height is inversely proportional to *g*. On the moon the value of *g* is much smaller than on the Earth, this is why astronauts are able to jump much higher on the moon.

You might ask, why did we choose $y_i = 0$ at the height where the ball was thrown? Why not at the ground, which might seem a more logical place for $y = 0$? When applying the Energy-Interaction Model to various phenomena only the change in a particular energy matters. Our choice of the origin of the coordinate system used to measure “y” does not matter, since we are always subtracting two heights. There will be instances where defining an "absolute" gravitation potential energy, PE_g, rather than a

change ΔPE_g, will be useful. We will see that gravitational potential energy of so many joules will mean it has this amount relative to where we picked the origin of our coordinate system, which is completely arbitrary. We will come back to this point later in Section 2.6.

Mechanical and Thermal Energies

Let us go back to our example of a person doing work on a box and, thus, increasing its kinetic energy. Instead, let us imagine a situation where the box, while pushed, is moving at a constant speed for some interval. This scenario is plausible from everyday experience. If the box is moving horizontally ($\Delta PE_g = 0$) and at a constant speed ($\Delta KE = 0$), implying that $\Delta E_{tot} = 0$, thus the change of energy is zero. So, how can this situation be consistent with the Energy-Interaction Model that states that when work is done on our system there must be a change in the system's energy?

The only solution out of this conundrum is that some other object (except for the person) must be doing work on the system in such a way that it cancels the work done by the person. Another object that the box is interacting with is the surface it is in contact with, which can indeed exert a force, known as *friction*. Taking friction into account for a box which is moving horizontally at a constant speed, we get:

$$\Delta E_{tot} = 0 = W_{friction} + W_{person} \tag{2.4.10}$$

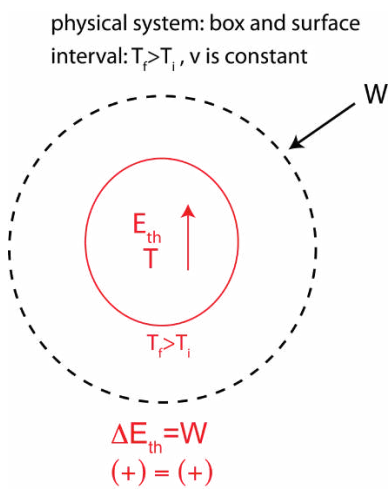
The force due to friction acts in the opposite direction of motion, $W_{friction} = -F_{friction}d$, which must be equal and opposite to the work done by the person,

$$W_{friction} = -W_{person} = F_{applied}d. \tag{2.4.11}$$

This results in equal and opposite (balanced) forces applied by the person and by the surface generating friction.

Another way to approach this problem is to define the physical system as the box and the surface together. This leaves the person the only outside "object" interacting with our system doing work, W_{person}, on the surface/box physical system. (Note, although the Earth is also interacting with the box, it does not contribute to work when the box moves horizontally, so we do not include it in this scenario.) Since both $\Delta KE = 0$ and ($\Delta PE_g = 0$) for a box moving horizontally at constant speed, and the net work done is no longer zero for the newly defined physical system, there must be another energy that is changing. We have now included the effects of friction inside our physical system, the interaction between the surface and the box contributes to a thermal energy change of our system. Friction is a complicated force, but for now, we can think about it in terms of subatomic particles applying forces onto each other and, thus, speeding up. As subatomic particles move around faster, the temperature of our system increases, resulting in an increase of thermal energy. The Energy-Interaction diagram for this scenario is:

Figure 2.4.5: Energy-Interaction diagram for box moving horizontally at a constant speed.

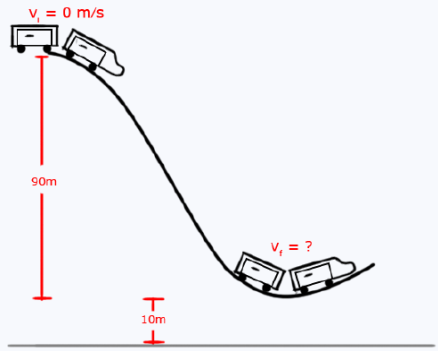


In Chapter 1, we saw that transfer of energy can happen between thermal types of energy. Other transfers of energy can happen between mechanical energies, like ball being throw upward or dropped down (assuming effects of air friction are negligible). And yet, other transfers can occur from mechanical to thermal types of energies, when friction cannot be neglected. If we assume that only mechanical energy transfer is possible for a falling object, the Energy-Interaction Model predicts that a ball and a feather should fall at the same rate, since Equation 2.4.9 is independent of mass. However, this is clearly not what we observe in our daily

experiences. The feather is clearly affected by air friction more than the ball, thus transferring its mechanical energy to thermal energy at a much greater rate.

Example 2.4.1

A roller coaster with mass of 8,000 kg reaches an initial height of 100 m above ground, before plummeting to 10 m above the ground. At the top the roller coaster is at rest.

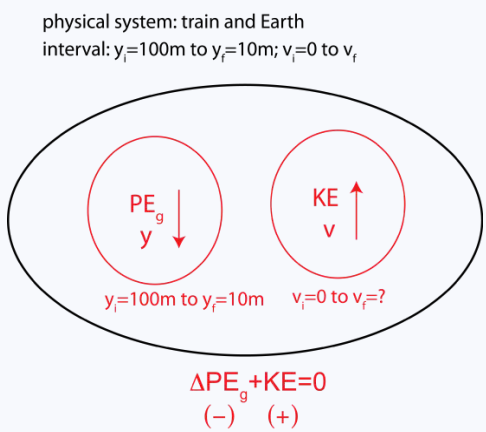


a) Assume the track is frictionless, find the final velocity of the train.

b) You measure the velocity of the train at 10 m to be 2m/s slower compared to what you predicted in part a). Calculate the change in thermal energy of the track/train physical system.

Solution

a) The Energy-Interaction Diagram for this process is shown below:



The equation below the above Energy-Interaction Diagram in terms of the energy indicators is:

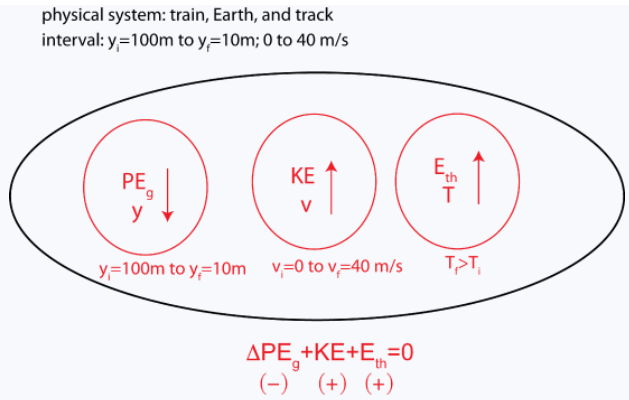
$$mg(h_f - h_i) + \frac{1}{2}m(v_f^2 - v_i^2) = 0$$

Plugging in values into the equation:

$$m(9.8m/s^2)(10 - 100) + \frac{1}{2}m(v_f^2 - 0) = 0$$

and solving for v_f, we get $v_f = 42m/s$.

b) The Energy-Interaction Diagram for this process is shown below:



Plugging in values into the equation:

$$(8000kg)(9.8m/s^2)(10m-100m)+\frac{1}{2}(8000kg)((40m/s)^2-0)+\Delta E_{th}=0$$

and solving for ΔE_{th}*, we get* $\Delta E_{th}=656kJ$.

The next type energy we take up is so important for future work, that we give it its own model: the *Intro Spring-Mass Oscillator Model*.

Contributors

- Template:Phys7A

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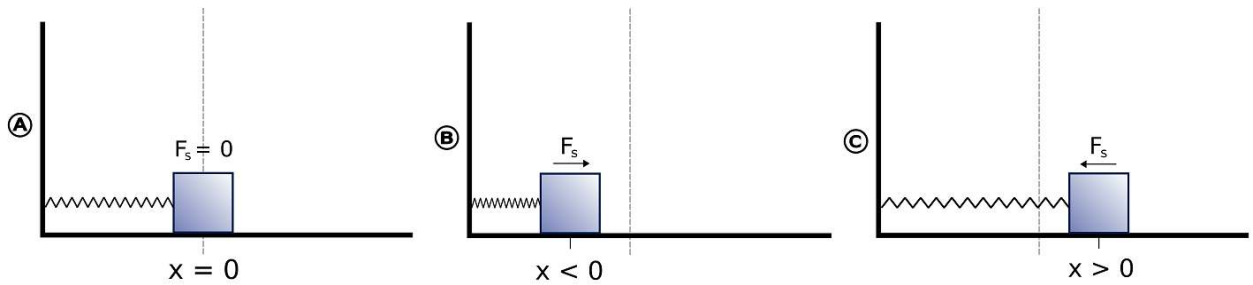
2.5: Spring-Mass Oscillator

This page is a draft and is under active development.

Spring-Mass Force

Take a look at the three scenarios depicted below for a horizontal spring-mass system. In picture A) the spring-mass is at its equilibrium position (x=0), which means that it is not experiencing a net force. The equilibrium position is where the spring-mass system "wants" to naturally be. When the mass is displaced from the equilibrium, the force, known as *restoring force*, will always point back toward equilibrium. In picture B) the spring is compressed and the force pushes the mass back toward equilibrium, where in picture C) the spring is stretched, and the restoring force pulls the mass back to the left.

Figure 2.5.1: forces experienced by a spring-mass system.



The force with which a spring pulls back when stretched (or pushes back when compressed) is proportional to the amount of stretch from equilibrium, provided the spring is not stretched too far. Historically, this linear proportionality between the force and amount of stretch is referred to as *Hooke's Law* behavior, which is true if the mass of the spring is negligible. We write the *restoring force* as:

$$F = -kx \tag{2.5.1}$$

where *k* is the "spring constant" or "force constant" (and depends on the stiffness of the particular spring), and *x* is the displacement from equilibrium. The *minus sign* indicates that the force is the opposite direction to the direction the spring was stretched or compressed. In other words, if you are applying a force on the spring-mass that displaces it from equilibrium, the restoring force will act in the opposite direction of the applied force. An important point to notice in the expression for the force of the spring is that *x* is measured from the un-stretched position of the free end of the spring.

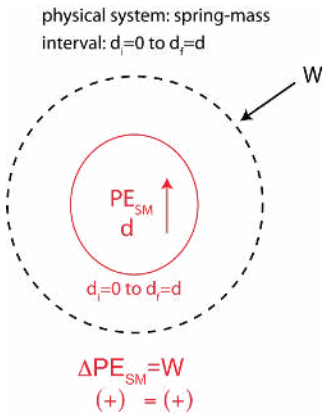
In order for the force to have units of newtons, the units of *k* must be newtons per meter (*N/m*). The force that you (an external agent) have to exert on the spring to stretch it a distance x is in the opposite direction to the restoring force and is equal to $F_{applied} = +kx$.

Hooke's Law breaks down at the extremes of a spring's motion. For example, when stretched to the point of breaking or permanent deformation, a spring's behavior will begin to deviate substantially from the linear expectation. Also, when compressed so far that it begins to touch itself, and the forces at play change. For these reasons, it is usually assumed that springs stretch only within a small portion of their maximum deformation.

Spring-Mass Potential Energy

Let us refer back to Figure 2.3.4. Work is done when the mass is pulled away from equilibrium. Assuming the kinetic energy stays constant (spring-mass is motionless at equilibrium and held in place when stretched), the work done contributes only to increasing the potential energy of the spring-mass system. We call this type of energy, the *spring-mass potential energy*, P_{sm}. The change in potential energy depends on the amount of work done. Work is proportional to force which depends on the distance away from equilibrium. This suggests that the indicator for P_{sm} is *displacement from equilibrium*, denoted by *d* or |x| or sometimes |y| for vertically hanging springs. Note, the absolute value sign around "|x|" implies that the potential energy does not depend on whether the spring is compressed or stretched, since *Hooke's Law* is symmetric about the equilibrium position. Assuming the spring-mass is stretched a distance *d* from equilibrium, the Energy-Interaction diagram for the interval depicted in Figure 2.3.4 is:

Figure 2.5.2: Energy-Interaction diagram for stretching a spring-mass system.



The restoring force, $F = -kx$, is not constant since it depends on displacement *x*. That is, the force is proportional to the distance the spring has been pushed or pulled. So we can no longer used the simplified version of work, but will use the general Equation 2.3.1 for work. The applied force does work when the spring is stretched from distance of zero to a max of *d*, in this example. Thus, the work done on this system:

$$W = \int_0^d kx dx = \frac{1}{2}kd^2 \tag{2.5.2}$$

Notice that while the force scales linearly with deformation, the work required to deform the spring scales as the square of deformation. This also confirms that the potential energy will depend on the magnitude of the displacement only, and not the direction. Using the energy-conservation equation from Figure 2.5.2 we get $\Delta PE_{sm} = \frac{1}{2}kd^2$. Generally, the spring-mass potential energy is given by:

$$PE_{sm} = \frac{1}{2}kx^2 \tag{2.5.3}$$

where *x* is displacement from equilibrium. Upon stretching the spring, energy is stored in the springs' bonds as potential energy. This potential energy is released when the spring is allowed to oscillate. The maximum speed is accomplished when the spring returns to its equilibrium position ($PE_{sm=0}$), and all energy is kinetic energy.

Example 2.5.1

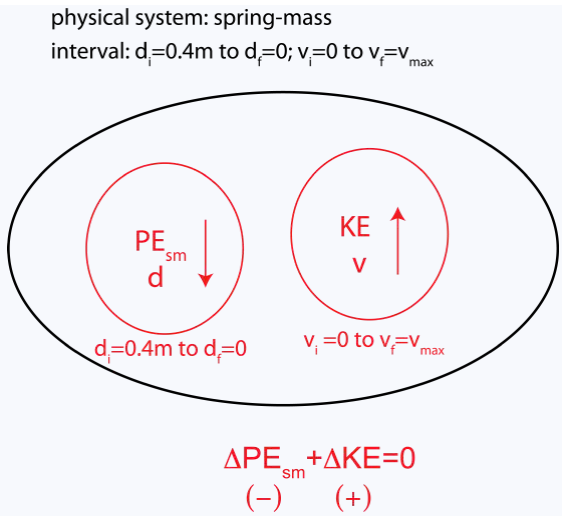
A spring of negligible mass and a spring constant of 120 N/m is fixed to a wall and is free to oscillate. On the other end, a ball with a mass of 1.5 kg is attached. The spring-mass is then stretched 0.4 m and released.

a) What is the maximum speed of the attached ball? Neglect any effects of friction.

b) The spring-mass looses 2 Joules of energy per oscillation. Find the maximum displacement of the spring-mass after 4 oscillations.

Solution

a) Let us focus on the interval once the ball is released until it is at equilibrium when the speed is maximum.The spring-mass system is closed since it is not interacting with other systems in this interval. As the spring-mass oscillates potential and the kinetic energies change, $\Delta E_{tot} = \Delta PE_{sm} + \Delta KE = 0$. The Energy-Interaction Diagram for this process is shown below:



Using definitions of potential and kinetic energies:

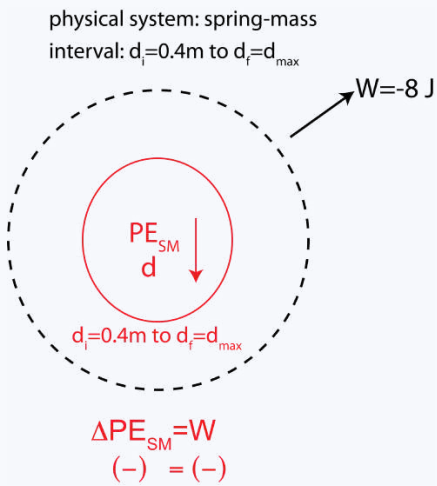
$$\frac{1}{2}k(x_f^2 - x_i^2) + \frac{1}{2}m(v_f^2 - v_i^2) = 0$$

Plugging in values into the equation:

$$\frac{1}{2}(120N/m)(0 - 0.4^2m^2) + \frac{1}{2}(1.5kg)(v_{max}^2 - 0) = 0$$

and solving for v_f, we get $v_f = 3.58m/s$.

b) In 4 oscillations the spring-mass will loose 8 Joules. Let's choose an interval from initial maximum displacement of 0.4m to the final maximum displacement after 4 oscillations. Since the speed is zero when the displacement is maximum, there will be no change in kinetic energy over this interval. The Energy-Interaction Diagram for this process is shown below:



The equation can be rewritten as:

$$\frac{1}{2}k(d_f^2 - d_i^2) = W$$

Plugging in values into the equation:

$$\frac{1}{2}(120N/m)(d_{max}^2 - 0.4^2m^2) = -8J$$

Solving for d_{max}, we find the maximum displacement after 4 oscillations to be 0.16m.

Vertical Spring-Mass Systems

A spring with a mass hanging down acts exactly like a horizontal spring, except that the end of the spring has a different equilibrium position. For a vertically hanging spring-mass there are two forces acting on the mass as it oscillates: the force from the spring pulling up or pushing down, and the force from the Earth always pulling down. Let us take a closer look why the horizontal and vertical spring-mass systems can still be treated identically.

For the vertical spring (as for the horizontal one), the force with which a spring-mass pulls back when stretched (or pushes back when compressed) is proportional to the amount of stretch from the equilibrium determined with the mass attached (provided the spring is not stretched too far). For a vertical spring, we will usually write the restoring force using the symbol "y" instead of with an "x", but this is just a convention:

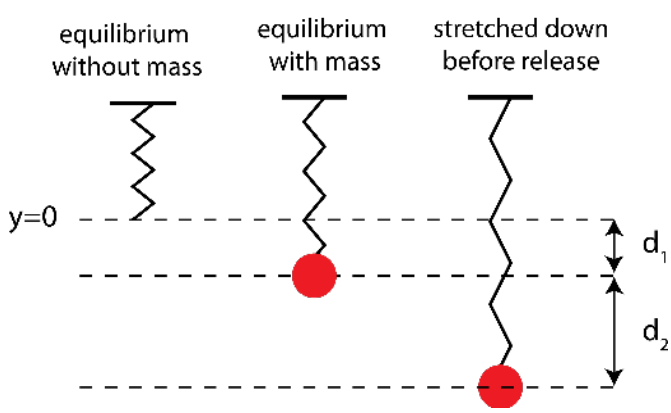
$$F = -ky \tag{2.5.4}$$

Similarly to the horizontally attached spring in Example 2.5.1, let us analyze a situation of finding the maximum speed of the mass at equilibrium. In the example, we found the following general equation for an interval when the mass is released from maximum displacement to its equilibrium position, assuming thermal dissipation is negligible:

$$\frac{1}{2}kx_{max}^2 = \frac{1}{2}mv_{max}^2 \tag{2.5.5}$$

Let us now see what we get for a vertical spring given the same interval. We will start by measuring the potential energy of this system from (*y=0*) in the figure below, the equilibrium position of the spring without the mass attached.

Figure 2.5.3: Vertical spring-mass system.

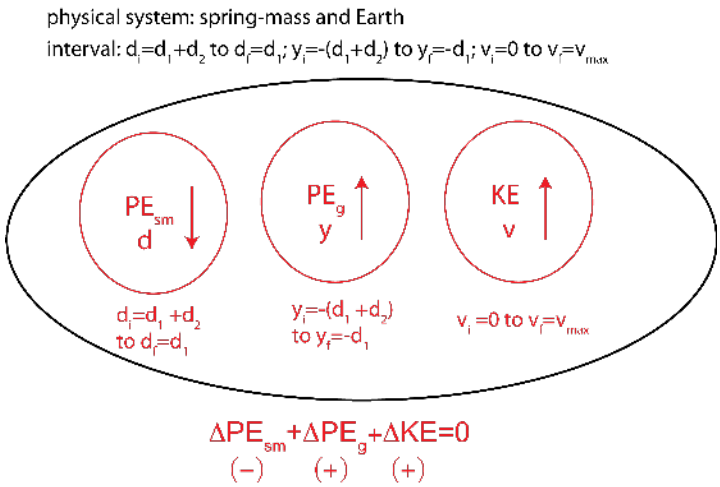


When the mass is initially attached it stretches by a distance d_1 to a new spring-mass equilibrium. At this position the spring-mass is not moving, so the forces acting on it must be balanced. That is, the gravitation force must be equal and opposite to the spring-mass restoring force:

$$mg = kd_1 \tag{2.5.6}$$

The spring-mass is then stretched another distance d_2, released, and allowed to oscillate. Recall, all the vertical heights used in calculating PE_g are measured from the y=0 defined in Figure 2.5.3. Thus, the values of *y* for the equilibrium and stretched positions (center and right configurations in the figure) will be negative. The Energy-Interaction Diagram for calculating the maximum speed when the spring-mass returns back to equilibrium after release is shown in the figure below.

Figure 2.5.4: Energy-Interaction diagram for a vertical spring-mass system.



Expanding the equation from the Energy-Interaction diagram and plugging in the variables for the energy indicators:

$$\frac{1}{2}k(d_f^2-d_i^2)+mg(y_f-y_i)+\frac{1}{2}m(v_f^2-v_i^2)=0 \tag{2.5.7}$$

$$\frac{1}{2}k(d_1^2-(d_1+d_2)^2)+mg(-d_1+d_1+d_2)+\frac{1}{2}m(v_{max}^2-0)=0 \tag{2.5.8}$$

Simplifying:

$$-\frac{1}{2}kd_2^2-kd_1d_2+mgd_2+\frac{1}{2}mv_{max}^2=0 \tag{2.5.9}$$

Using Equation 2.5.6 for d_1, the equation simplifies further to:

$$-\frac{1}{2}kd_2^2+\frac{1}{2}mv_{max}^2=0 \tag{2.5.10}$$

The above equation is identical to the horizontal spring-mass result in Equation 2.5.5, as long as the displacement for the vertical spring-mass is measured from the new equilibrium position once the mass is attached to the spring.

Alert

The result above shows that when a spring-mass is vertically attached the effect of the gravitation force is automatically taken into account, as long as the new equilibrium position is defined at the position of the spring with the mass attached. Using the new equilibrium position the potential energy of the spring-mass is described by the behavior of the spring-mass oscillator only. Imagine if the spring-mass system was far in outer space away from gravity, mounted on a wall of a spaceship. The spring-mass would still oscillate, but the orientation of "horizontal" vs. "vertical" would lose its meaning.

Contributors

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2.6: Plotting Energies

This page is a draft and is under active development.

Another Way to State Conservation of Energy

So far we have dealt only with changes in energy, since those are the important quantities for understanding the *Energy-Interaction Model*. In other words, what matters between two instances in time is how the energy of the system changed. However, sometimes it is useful to not only focus on two particular moments in time, but rather analyze energy over all instances in time. Recall, the energy-conservation equation for a closed system:

$$\Delta E_{tot} = 0 \tag{2.6.1}$$

This equation can be rewritten as:

$$E_{tot,final} = E_{tot,initial} \tag{2.6.2}$$

Since "initial" and "final" can refer to any instant in time as long as the system stays closed, the above equation implies that the total energy is constant over the entire interval:

$$E_{tot} = \text{constant} \tag{2.6.3}$$

Kinetic and Gravitational Potential Energy

Lets us return to the example depicted Figure 2.4.3 of a ball thrown upward. If we focus on the interval of the ball's path from the moment it was thrown upward to the moment it reached its maximum height, we can assume that the total energy is constant, as long as air friction is neglected:

$$E_{tot} = KE + PE_g = \text{constant} \tag{2.6.4}$$

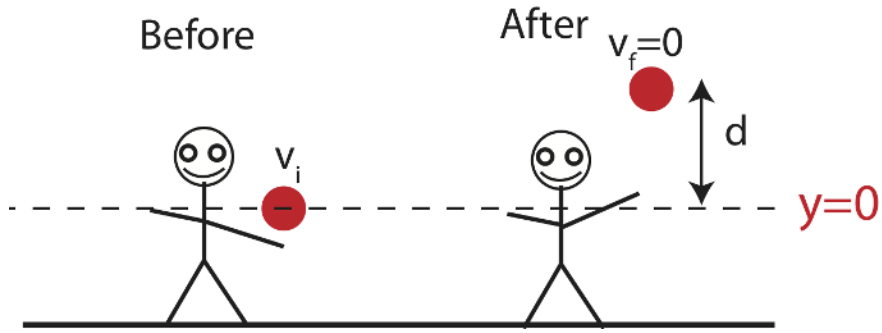
which can be written as

$$E_{tot} = \frac{1}{2}mv^2 + mgy = \text{constant} \tag{2.6.5}$$

This equation will hold for all values of *y* for which the ball/Earth system is closed. For example, if the ball falls back down and hits the ground, or if you catch the ball on its way down, the system would no longer be considered closed, since the ball/Earth would interact with another object (the floor or your hand). Also, the value of *y* cannot exceed the maximum height of the ball.

Equation 2.6.5 is informative, but it is often instructive to represent physical behavior graphically. We would like to make a plot of *KE* and *PEg* as a function of height. In order to make this plot we need to define a physical location that represents the origin of *y* (where is y=0?). Since we want to plot the interval from the moment the ball is thrown to its maximum height, the logical location of the origin is the location of the ball right after it is thrown, as shown in the figure below.

Figure 2.6.1: Setting the origin of *y* for the ball thrown upward.

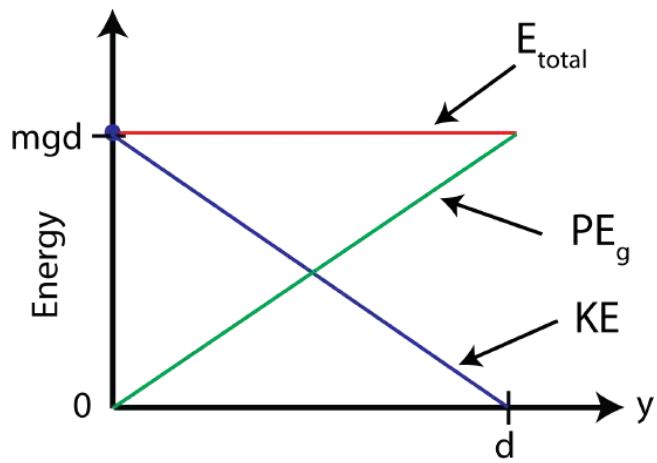


The gravitational potential energy in this interval will vary linearly with *y*, from $PE_g = 0$ at y=0 to $PE_g = mgd$ at y=d. Next, we can find the total energy. We know that at the maximum height the speed of the ball will go to zero. Thus, $KE = 0$ when y=d, and:

$$E_{tot} = PE_g + KE = mgd \tag{2.6.6}$$

Once we know the total energy in one location, we know it everywhere when the system is closed, since the result above tells us that $E_{tot} = \text{constant}$. To find how *KE* changes with height we can then use, $KE = E_{tot} - PE_g = mgd - mgy$. This equation tells us that KE will vary from $KE = mdg$ at y=0 to $KE = 0$ at y=d. The plot describing these results is shown below.

Figure 2.6.1: Energy plots of for a ball thrown upward



Note, that our choice of "zero" was just a convenient choice, which resulted in the particular plot of PE_g and E_{tot} shown in the figure. (Kinetic energy does not depend on the choice of the origin, since its indicator is speed.) There was nothing physical about this choice, we could have as well chosen the maximum height, the ground, or the center of the Earth as "zero" height. The different choices would result in different values of potential energy, and thus different total energy values. It is even possible to have negative values of PE_g and E_{tot} as we saw in the vertical spring example in the previous section. Potential energy depends on location of the system, thus, it will depend on the choice of origin. However, regardless on where you choose to define zero, the changes in energies for a given interval will always be the same. The physical meaning is contained in the relative position between two points in space.

Alert

Although initially it might seem very counterintuitive to your understanding of energy, there is nothing unphysical about a system having **negative** energy. It is very important to think about energy as a property of the system that **changes** when there is an interaction that happens. The potential energy of the system depends on position. In order to assign a value for position an origin needs to be defined. Since the definition of the origin is arbitrary, the values of potential energy will be arbitrary as well. What does stay the same is how that potential energy changes. When you lift an object 1m up from the ground, the change in height will be 1m whether you lifted it from y=0 to y=1m or from y=-1m to y=0m.

Example 2.6.1

A 2kg meteorite enters Earth's atmosphere. At an altitude of 1000 meters it is traveling at terminal velocity (constant speed) of 100 m/s. The total energy of the meteorite/earth/air system is 35KJ during an interval from when the meteorite is 1000 meters

high to right before it hits the ground. Plot all the energies involved: total energy, kinetic energy, gravitational potential energy, and thermal energy as a function of height from y=0 meters (defined to be the ground) to y=1000m in the air.

Solution

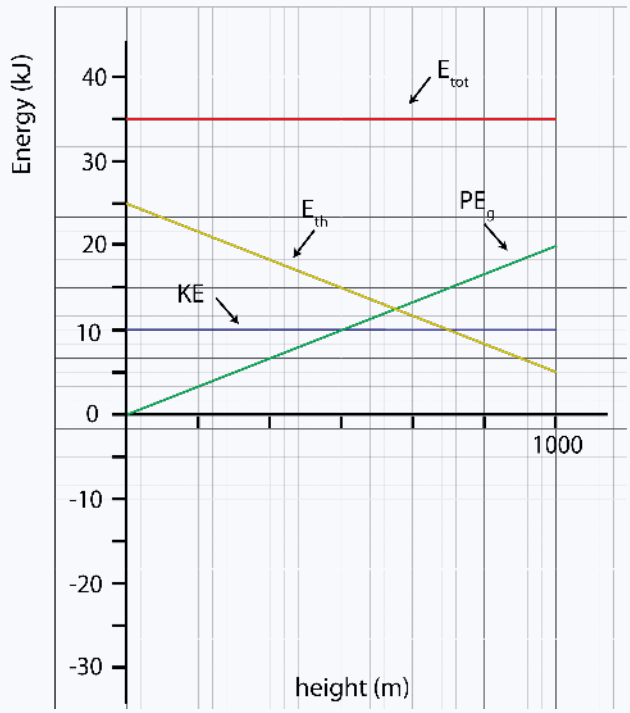
Since the meteorite is falling (PE_g is decreasing) but the speed is staying constant, there must be friction present to account for loss of mechanical energy. This is friction of the meteorite and air, air friction. The total energy of this system is:

$$E_{tot} = PE_g + KE + E_{th}$$

At 1000m: $E_{tot} = 35kJ$, $KE = \frac{1}{2}mv^2 = \frac{1}{2}(2kg)(100)^2 = 10kJ$, $PE_g = mgy = (2kg)(9.8m/s^2)(1000m) = 19.6kJ$, *and* $E_{th} = E_{tot} - KE - PE_g = 4.6kJ$

At 0m: $E_{tot} = 35kJ$, $KE = 10kJ$, $PE_g = 0kJ$, *and* $E_{th} = 25kJ$

The plot below shows all energies in this interval.



Spring-Mass Systems: a Universal Motion

Most physical systems that vibrate back and forth do so like a hanging spring-mass, particularly when the amplitude of vibration is not too large. Because this motion is so common and so important in understanding a lot of physics, it is worth looking at it a little closer.

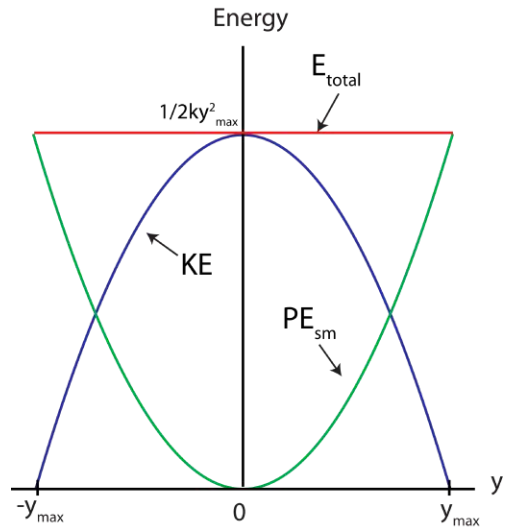
As we saw in the previous section, the maximum value of the PE_{sm} of the spring-mass system occurs when the mass is at its extreme positions (maximum displacement from equilibrium), and its speed is zero. Conversely, the *KE* of the spring-mass system is a maximum when the mass is at its equilibrium position (y=0). When the system is closed in the absence of friction, $\Delta E_{tot} = \Delta KE + \Delta PE_{sm} = 0$, or equivalently E_{tot} is a constant. Looking at E_{tot} at any particular time in its cycle of vibration, the energy is still going to be equal to the same total value. Written symbolically (we chose "y" to represent a vertical spring-mass, but the choice of variable is arbitrary):

$$E_{tot} = PE_{sm} + KE = \frac{1}{2}ky^2 + \frac{1}{2}mv^2 = \text{constant} = PE_{max} = KE_{max} \tag{2.6.7}$$

Since the dependence of PE_{sm} on displacement *y* is quadratic, the function will be parabolic. The total energy is the energy when the spring is at its maximum displacement, $E_{tot} = \frac{1}{2}ky_{max}^2$. The kinetic energy as a function of *y* is the difference between the

maximum energy, *Etot* and PE_{sm}, $KE = E_{tot} - PE_{sm}$. The graph below shows the kinetic energy *KE* and potential energy PE_{sm} of a spring-mass system as a function of the position from equilibrium, *y*.

Figure 2.6.2: Energy plots of for a spring-mass system



Although we cannot show it without investigating the time behavior of the motion of the mass, it turns out that the *time-average* (that is, the average over time) of PE_{sm} and *KE* are the same, and are consequently both equal to one-half the total energy:

$$\text{avg } KE_{spring-mass} = \text{ avg } PE_{sm} = \frac{1}{2} E_{total} \tag{2.6.8}$$

The fact that the time-average potential and kinetic energies are the same has a profound implication for the model of matter that we are about to develop in Chapter 3. This result is true only for a potential energy that depends on the square of the variable. It is precisely the fact that the potential energy is *quadratic* with respect to position that makes a spring-mass system so special, so universal, and so important.

The lowest point on the PE_{sm} curve is frequently called the potential energy minimum. Why is the value of the position variable for which the potential energy is a minimum significant? Consider what happens as energy is removed from a system which is oscillating about the equilibrium value of its position (e.g., a real spring-mass system, because of friction, gradually transfers mechanical energy to thermal energy). The amplitude (maximum extent) of the oscillations decreases until eventually, when all mechanical energy has been transferred to thermal systems, the system comes to rest at the equilibrium position, the position of the potential minimum.

Now consider *any* physical system that oscillates and which will settle down to a stable position as energy is transferred to thermal systems. That stable equilibrium position represents the physical state where potential energy is smallest. (All of the *PE* and *KE* have been transferred to thermal systems.) The potential energy must increase as y increases (either positively or negatively) away from zero, the equilibrium position. Now nature seems to prefer smooth changes of things like potential energies. The simplest smooth mathematical function that increases for both positive and negative y is y^2. When we look at real physical systems, it turns out that sufficiently close to the minimum, the potential energy always "looks parabolic"! This is a result with far reaching consequences. It implies that ***any oscillating system behaves just like our simple spring-mass system, at least for small amplitudes of oscillation!*** What's important is not that the spring-mass system is so special itself; it is, rather, that the behavior of the spring-mass system represents a *truly universal behavior of any oscillating system and* oscillating systems are found everywhere in nature. We will use this property in Chapter 3 when we model the real atoms of liquids and solids as "oscillating masses and springs".

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2.7: Force and Potential Energy

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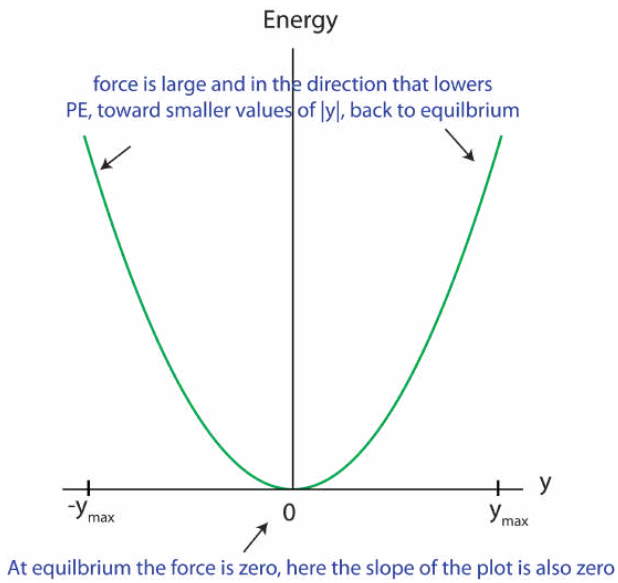
Spring-Mass Force

There is a deep connection between force and potential energy. This relationship has a useful graphical representation that will help us better understand the spring-mass potential energy and, in Chapter 3, the potential energy associated with the bonding between atoms.

Graphed below is the potential energy of a spring-mass system vs. deformation amount of the spring. As was explained earlier, this is a second degree, or parabolic relationship. Marked on the figure are the positions where the force exerted by the spring has the greatest and the least values.

Figure 2.7.1: spring-mass forces at different displacements from equilibrium



If pulled or pushed to some value of the position *y*, we know intuitively that the spring will try to snap back to its original shape -- that is, that it will tend to return to zero deformation. We also know that it takes more force to deform the spring as you go further from equilibrium. How can we confirm our intuitions from the graph? Mathematically, we have already described this type of force using Hooke's Law: $F = -kx$. Now let us go backward and see what we can learn about force directly from potential energy.

Force and Potential Energy Connection

We see from our understanding of behavior of the spring and from Figure 2.7.1 that the force is largest away from equilibrium, which is where the slope of the PE_{sm} plot is the largest as well. The force also points toward decreasing potential energy, or toward smaller values of |y|. At equilibrium the slope of the plot is zero, which is where there is also no force acting on the spring-mass. This clear connection we are seeing between the slope of PE_{sm} vs. y plot and magnitude of force, and the direction of force pointing toward decreasing $PE_{sm,}$ turns out to be universal. Mathematically these relationships are written as:

$$F_x = -\frac{dPE}{dx} \tag{2.7.1}$$

The subscript "x" refers to the component of the force vector pointing in the "x" direction. For a one-dimensional force, such as the force of gravity which always points down toward the -y direction, or the spring-mass force which always points in the -|x| direction, you may drop the subscript. This is a general result that is true for the force associated with any potential energy.

The derivative of a function f(x), $\frac{df}{dx}$, at some values of *x* represents the slope of the f(x) vs x plot at the particular values of *x*. Thus, graphically Equation 2.7.1 means that if we have potential energy vs. position plot, the force is the negative of the *slope* of the function at some point:

$$F = -(slope) \tag{2.7.2}$$

Disregarding the minus sign for a moment, this tells us that the steeper the slope of a PE curve plotted against its position variable, the greater the magnitude of the force. The restoring force of the spring (or anything that oscillates) will be zero when the slope is zero, which occurs at the equilibrium point, i.e., where the object comes to rest when it stops vibrating.

The minus sign means that if the slope is positive, the force is toward the negative direction (-x), and visa versa. This should make sense, because it says that the force will try to push the object back to lower potential. If it were the other way around, springs would stretch themselves out spontaneously and planets would fly away from each other! For example, looking back at Figure 2.7.1, we see that the slope of the plot on the positive side of *y* (spring is stretched) is positive, which will give us a negative force. Recalling that force is a vector, so the negative sign for a one-dimensional force tells us that it points toward the negative direction. If the spring is stretched (y>0), this result tell us that the force point in the (-y) direction, thus toward lower values of y (and lower values of PE_{sm}) back to equilibrium. On the other side of the plot when the spring is compressed, slope is negative, giving us a force pointing toward +y direction, which is where the equilibrium is and toward lower values of PE_{sm}. This is consistent with behavior of the spring which pulls back when stretched and pushes back when compressed.

To summarize, we learned two very important points here:

- *magnitude of force is equal to the magnitude of the slope of potential energy as a function of position graph.*
- *force points in the direction of decreasing potential energy.*

We can quantitatively show just how correct this relationships is. If we take our spring-mass potential energy function, then the force is:

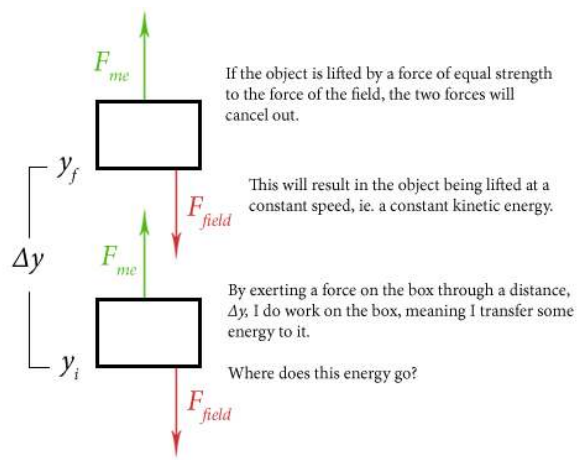
$$F_y = -\frac{PE}{dy} = -\frac{d}{dy}(\frac{1}{2}ky^2) = -ky \tag{2.7.3}$$

The final result is Hooke's Law, the first equation introduced in our discussion of springs! Now that you're convinced that this relationship is real, let's see if we can understand why.

Using What We Know

It all boils down to the concepts of work and energy conservation, we have been using in the Energy-Interaction Model. To see this, consider the following situation (pictured below). Imagine a box is lifted through a force *field (*we use a general word "field" here to refer to a force that can be defined everywhere in space), like lifting an object against gravity. Imagine also that the force is constant and pointing downwards at all points in space.

Figure 2.7.2: forces that result in a change of potential energy.



As described in the figure above, the box is being lifted at a constant kinetic energy. The work cannot be going to kinetic energy, but it is being transferred to potential energy. The amount of work I do on the object is given by the force I exert times the distance I moved it:

$$W = F_{me}\Delta y \tag{2.7.4}$$

The "object" exerting F_{field} is part of the physical system, since it is interacting with the object that was moved resulting in a change of potential energy. Thus, the force only I exert (outside "object") contributes to the amount of potential energy the object

gains. We can therefore replace the amount of work done by me with the amount of potential gained, $W = \Delta PE$. Solving for F_{me}, we get:

$$F_{me} = \frac{\Delta PE}{\Delta y} \tag{2.7.5}$$

However, what we wish to know is not the force I exerted, but the force the field exerted, since it is exactly that force between two objects (box and Earth in this example) that defines the potential energy between them. Since the box is moving at constant speed the forces must be balanced. Thus, the force the field exerts is equal and opposite the force I exert:

$$F_{field} = -\frac{\Delta PE}{\Delta y} \tag{2.7.6}$$

To derive this result, we used constant force field (gravity near the surface of the Earth). But this applies even to changing forces. As Δ's become sufficiently small $\frac{\Delta PE}{\Delta y}$ becomes a derivative, $\frac{dPE}{dy}$, which is precisely the slope of potential energy as a function of y.

Everything we say here about the relation of force to potential energy is strictly true when the force depends on only one spatial dimension. That is, we consider the spring to move in only one direction in space or gravity only pointing down. It the force depends on movement in two or three dimensions, then technically the force is the negative of the *gradient* of the potential:

$$\vec{F} = -\vec{\nabla} PE \tag{2.7.7}$$

The *gradient operator* ∇ is short-hand for writing:

$$F_x = -\frac{dPE}{dx}; \quad F_y = -\frac{dPE}{dy}; \quad F_z = -\frac{dPE}{dz} \tag{2.7.8}$$

where x, y, and z are variables for the three spatial dimensions. This is analogous to releasing a ball on a smooth hillside; the ball starts to roll in the direction of the steepest slope of the hill. In two or three dimensions, the force is the derivative of the potential in the direction of “steepest slope".

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2.8: Looking Back and Ahead

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We now have quite a few different forms of energy: thermal, bond, kinetic, gravitational potential, and spring (or elastic) potential energy. A given physical situation could involve any number of these. Energy can be transferred among physical systems either as heat (when there is a temperature difference between two objects) or as work (when one object exerts a force on another object that acts through a distance). There are yet other forms of energy that involve electrical interactions, magnetic interactions, and a more general form of the gravitational energy.

It turns out that gravitational potential and spring potential energies we discussed in this Chapter are examples of one of the two fundamental *types* of energy, the type that depends on the *positions* of objects. An energy that depends only on the relative positions of objects, and not on their past history (the path they took) or on their speeds, is called a potential energy. “Positional energy” is a more descriptive word, but for historical reasons, these are labeled *potential energy*. The second fundamental type of energy depends only on the speeds of particles (objects). This kind of energy is called energy of motion or *kinetic energy*.

All of the various kinds of energy fit into one of the two fundamental types. For example, chemical bonds involve the electric potential energies that depend on the locations of the electrons of the atoms as well as their kinetic energies as they whirl around the nucleus. Thermal energy is a combination of the kinetic and potential energies of individual atoms due to their random motions. Bond energy is a potential energy due to the force individual atoms exert on each other. The elastic energy of a spring is a potential energy because it depends only on the positions of the elements of the spring, not on their speeds. When an object rotates, it has energy due to its rotational motion, rotational kinetic energy.

One energy is as good as any other, almost. On a ***microscopic*** scale, energy is energy and any kind can be turned into any other kind. But on a ***macroscopic*** scale, where lots of particles (atoms and molecules) are involved, it turns out that all kinds of energy can be turned into thermal energy, but there are restrictions on turning thermal energy back into other kinds. We can convert some, but not all thermal energy to other forms. (We delve into the mysteries of entropy and the second law of thermodynamics in Chapter 4.)

By treating thermal interactions and mechanical interactions on an equal footing, we can approach realistic situations without having to automatically assume friction or air resistance is negligible. By now you should be very comfortable with the Energy-Interaction model. When we encounter new “kinds” of energy, it won’t be a “big deal”. We simply add them to our repertoire of energies that might change in any particular interaction.

Now we are in a position to delve into particle models of matter. Our goal is to be able to understand, in a general or universal way, as many of the properties of matter as we can. As we do this, we will also make a much more direct connection to thermodynamic concepts you have worked with in chemistry courses.

Even as we extend and perfect our Energy-Interaction model, we recognize that many questions are beyond its reach. For example, our before-and-after approach cannot tell us, “How long did it take an object to fall?”. Questions like this involve the dynamics (the details) of interactions. We will spend more time in Physics 7B and accompanying courses understanding the dynamics of rigid objects. This is fundamentally the relation of force to motion known as Newton’s Laws. Using Newton’s laws and kinematics to describe the details of interactions, we can answer questions that are unanswerable using the before-and-after approach. But for right now, we stick to an energy approach and avoid, as much as possible, the details of interactions.

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CHAPTER OVERVIEW

3: Applying Particle Models to Matter

> This page is a draft and is under active development.

3.1: Where we are headed
3.2: Intro Particle Model of Matter
3.3: Particle Model of Bond Energy
3.4: Particle Model of Thermal Energy
3.5: Looking Back and Ahead

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3.1: Where we are headed

Introducing Particle Models to Matter

As previously noted, we are pursuing two goals in Physics 7A. On the one hand, we want to get a solid understanding of energy and how we can use this understanding to get answers and make predictions about interesting phenomena. In Chapter 2 we got through the basics of introducing work and potential energy and applied these concepts to mostly macroscopic phenomena. Now to achieve the second goal of 7A, in Chapter 3, we turn to the development of particle models of matter. We would like to be able to answer questions such as: Why do things melt and/or vaporize at different temperatures? What determines heat capacities of different substances? What aspects of these thermal properties are common to many substances and which are unique to particular substances? What common things can we say about all kinds of chemical bonding? Some of the most important ideas in our particle models of matter are related to the behavior of the spring-mass motion introduced in Chapter 2. We extend these ideas to understand the motion of atoms using a model that has at its core the idea that atoms and molecules in liquids and solids act like they oscillate exactly the way the spring-mass system oscillates. The relation between force and potential energy allows us to really make sense of the forces that act between atoms and molecules in terms of their equilibrium spacing and to understand the differences between solids, liquids, and gases in a much more fundamental way.

With start with a famous quote by Nobel laureate in physics, Richard P. Feynman, from the first chapter of an introductory physics book he wrote for Cal Tech students back in the late 50's, claiming that the *Particle Model of Matter* is *the most* important or powerful model in science. Here is what he said:

> *"If, in some cataclysm, all of scientific knowledge were to be destroyed, and only* ***one sentence*** *passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the* ***atomic hypothesis*** *(or the atomic fact, or whatever you wish to call it) that* ***all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*** *In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied." -The Feynman Lectures on Physics, Volume I, page 1-2*

Your job over the next couple of weeks is to use "*a little imagination*" and apply "*a little thinking*" to the content of this powerful statement.

In This Chapter

The heart of the content in Chapter 3 is the development of a full understanding of the details contained in the Feynman quote. You already have a lot of useful ideas about this model. Much of it you have studied in chemistry. Keep consciously trying to integrate this new material with things you already know. It will take mental effort, but the understanding you gain will help your see chemical and biological concepts in a new light.

One of the areas in which our particle model of matter really shines is in explaining the experimentally observed thermal properties of matter, e.g., the values and trends of the specific heats of many substances in the gas, liquid, and solid phases. One of the interesting things about science is that it is in trying to resolve discrepancies as we push ahead and make breakthroughs. One of the discrepancies we will meet as we look at specific heats is that values for gases as well as solids are often lower than we would predict, especially at lower temperatures, but tend to rise to the predicted values as the temperature rises. The changes we need to incorporate in our model are due to the quantum mechanical nature of matter on a microscopic scale. We introduce some quantum ideas here and will continue to return to them throughout the course. Of course, you already know a lot about some of the central notions of quantum mechanics from your study of chemistry. For example, you have encountered the notion of orbital, or quantized energy levels for the electrons swirling about the nuclei of atoms. When you get to the discussion in this *chapter* on how quantum mechanics alters things, you should definitely connect it to what you already know about quantization.

The particulate nature of matter provides a model that allows explanations of a large range of phenomena that simply cannot be explained without invoking this fundamental idea regarding what matter is. In this chapter much of the focus will be simply

developing a basic particle model, *Intro Particle Model of Matter*, sufficiently far so that, with a *Particle Model of Bond Energy* and a *Particle Model of Thermal Energy* it will be possible to develop explanations for many of the empirically determined thermal properties of matter encountered in Chapter 1. Specifically, how do we make sense of the range of thermal and bond energies we encountered in Chapter 1? In addition to the sampling of heat capacity data and heats of fusion and vaporization presented in Chapter 1, we would expect our models to provide us with the capability of explaining the heat capacity values, both at constant pressure and at constant volume for a large range of substances.

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3.2: Intro Particle Model of Matter

Overview

In the *Intro Particle Model of Matter* we focus primarily on the interaction between two neutrally charged atoms or molecules. We make extensive use of the relation of force to potential energy in order to describe the force between two atomic sized particles. In the next two models will use the basic ideas established here to help us develop a much deeper understanding of both bond energy and thermal energy, as we will make the transition from the microscopic atomic level to the macroscopic perspective.

The Particle Model of Matter that we introduce here is the familiar picture of matter as composed of atoms and molecules. Our particle model for ordinary matter is simple and universal. It is not restricted to a particular kind of matter, but encompasses all ordinary matter. That is what makes this model so useful. Of course, being very general, it cannot predict many of the details that depend on the "particulars", but it can predict many of the *universal* properties.

A Very Important Interaction

Repeating the quote by the famous Nobel laureate in physics, Richard P. Feynman:

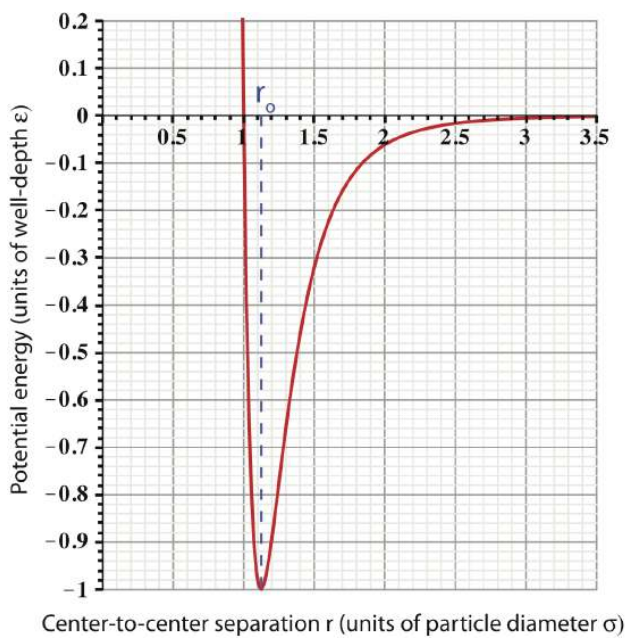
> *"if, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generations of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis (or the atomic fact, or whatever you wish to call it) that* ***all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another.*** *In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied."* -The Feynman Lectures on Physics, Volume I, page 1.

We will now go on to represent the words highlighted in red in terms of a potential energy between two subatomic particles.

Lennard-Jones Potential

We will spend the rest of this section understanding the meaning of Feynman's statement. Graphically, the key points in Feynman's statement that describe the way neutral particles interact are represented in the figure below which we will set out to understand. The relationship illustrated in the figure was developed by John Lennard Jones in 1924, known as the *Lennard-Jones potential* (sometimes abbreviated as the LJ potential). More generally, this is known as the *pair-wise potential*, since it describes an interaction between a pair of particles.

Figure 3.3.1: Pair-wise Potential between neutrally charged subatomic particles (modeled by the Lennard-Jones potential).



Let us define some important characteristics seen in this plot:

- *Particle*: we use the general word "particle" to refer to a microscopic constituent of matter, since the Lennard-Jones potential models interactions between either neutral atoms or neutral molecules.
- *Center-to-center separation*: we consistently refer to the distance between particles as being the center-to-center separation, rather than the distance between their surfaces. Usually we will use the symbol *r* to indicate this separation distance.
- *Particle diameter*: is the diameter for a particular atom or molecule, for which we use the symbol σ. It is useful to represent the particle seperation *r* in units of diameter, since this allows a universal scale. However, if the particle separation was shown in terms of units of length instead, such as nanometers (1nm=10^{-9}m), the plot would provide more information about the types of atoms or molecules that are interacting.
- *Equilibrium separation*: there is a “special” separation for which we use the symbol r_o. This separation is "special" since it is when the inter-particle force is zero. Looking at the figure above, we see that the slope of the PE plot goes to zero at $r = r_o$, which tells us force is zero (recall the discussion in Section 2.7). In terms of particle diameter, $r_o = 1.12\sigma$, an important fact that you should commit to memory.
- *Well-depth*: the value of the potential energy at the equilibrium separation is know as the *well-depth* of the LJ potential, symbolically represented by ε. This is the value of the minimum potential energy, $PE_{LJ}(r = r_o) = -\varepsilon$. The units of ε are joules, since potential energy must have units of energy.

Algebraically the Lennard-Jones potential is written as:

$$PE_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3.2.1}$$

Although, the subscripts "12" and "6" may seem strange, this form of the potential most accurately represent neutral interacting subatomic particles. If you plug this equation into a graphic calculator, you should find a shape seen in Figure 3.3.1.

Forces Between Neutral Particles

Let us return to the relationship between force and potential energy developed in Section 2.7 in order to help us understand the forces involved between particles whose interaction is described by the Lennard-Jones potential. Since the LJ potential is described in terms of particles separation *r*, it is useful to rewrite the force-potential energy relationship as:

$$F_r = -\frac{dPE}{dr} \tag{3.2.2}$$

Atomic sized particles exert forces on each other in the same way that large-scale objects do. These forces can be *attractive* or *repulsive*. The Lennard-Jones potential has similarities to the spring-mass system. A mass hanging on a spring hangs at a particular “separation” from the point at which the spring is supported. This is the favored or the equilibrium position. If the mass finds itself closer to the point of support, the “spring force” pushes it away, back toward the equilibrium position. Conversely, if it finds itself too far form the support, the spring force pulls it back toward the equilibrium position. The exact same thing happens with two atomic sized particles. However, unlike the spring-mass potential which is parabolic, the LJ potential only appear to be parabolic near equilibrium separation r_o, but becomes steeper for values less than r_o and flattens out for values larger than r_o.

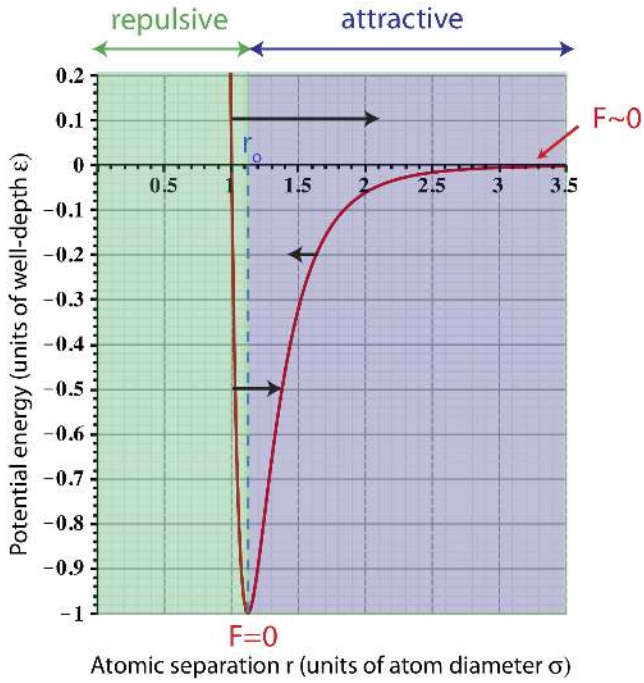
Feynman's statement claims that for small separations, $r < r_o$, the force is repulsive: *"repelling upon being squeezed into one another"*. The force relationship in Equation 3.2.2 states that when the slope of the PE plot is negative (as in the $r < r_o$ region), the force, F_r will be positive, which means it points in the direction of positive or increasing particle separation, *r*. In other words, the force points in the direction that increases separation pushing the particles apart as they are squeezed together, thus the force is *repulsive*, as Feynman claims.

Another part of Feynman's statement states that for slightly larger separations the force becomes attractive,*"attracting each other when they are a little distance apart"*. In the region for separations slightly larger than equilibrium, $r > r_o$, the slope in Figure 3.3.1 becomes positive, thus the the force becomes negative. This means that the force points toward the -r direction, or toward decreasing particle separation, implying the force is pulling the particles together or is *attractive*.

We also observe that as the particle separation gets larger, $r \gtrsim 3\sigma$, the slope of the PE plot goes to zero, thus, the force goes to zero as well. Since the force goes to zero at rather small separations (only 3 diameters apart!), this pair-wise interaction is known as *short-range*.

The figure below summarizes the forces between particles for different values of separation.

Figure 3.3.2: Forces between two neutral particles.



There are two force arrows drawn on the plot that represent repulsive (pointing to the right toward larger r's) forces at different values of separation. At very small values of r, the force is larger (longer arrow) since the slope of the plots gets steeper (Equation 3.2.2 tells us that the magnitude of force increases with the magnitude of the slope). This short distance repulsion tells us that particles cannot overlap or be squeezed into each other. The deeper explanation of this behavior is quantum mechanical and comes from the Pauli-exclusion principle, which we will not cover in this course. As the separation gets slightly bigger, the slope decreases, so the force becomes less repulsive, as shown by a shorter arrow on the graph. (Note, the relative arrow lengths are not drawn to scale.) A force arrow pointing to the left (shorter than the other two due to smaller slope) is shown to represent a separation when the force is attractive.

The fact that the force goes from being repulsive at small distances to attractive at large ones, implies that there is some particular separation which particles seem to prefer. Mathematically, in order for the slope of any plot to go from negative to positive, the potential energy must have an extremum point, such as a minimum or a maximum. This is represented by the potential minimum at the equilibrium separation r_o, where the slope, and thus the force, goes to zero, as marked on the plot.

Alert

As seen on the plot the Lennard-Jones potential energy is zero at a separation of one diameter. It is tempting to assign some importance to this separation since the potential energy goes from being positive to negative as the particles move further apart. However, the physical characteristics of the interacting system is described by the slopes of the potential energy, giving us the directions and magnitudes of forces at different separations. In other words, if we shifted the entire plot up, it would still describe the same type of interaction since the slopes would not change. But shifting the plot upward would change where the graph crosses the x-axis. Thus, this location happens to have zero potential energy only due to the convention of choosing the potential energy to go to zero at far separations, and has no physical significance. This is similar to choosing the origin in order to define the "zero" of gravitational potential energy.

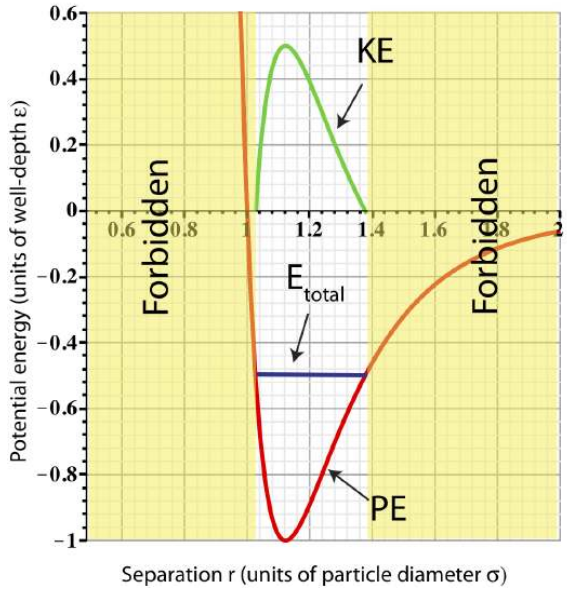
Bound and Unbound States

So far we have discussed the pair-wise *potential energy* between two interacting neutral particles. We also noted that the behavior of particles interacting with the LJ potential is very similar to the spring-mass system, at least for separation close to equilibrium, which does appear parabolic (like PE_{sm}) near r_o. When the spring-mass system is displaced from equilibrium and released, it starts to oscillate speeding up at equilibrium, slowing down, and then stopping at the points of maximum displacement before turning around. Thus, the spring-mass transfers its energy between potential and kinetic while keeping the total energy constant, as long as friction is negligable. Similar ideas can be applied to two particles interacting with the LJ potential.

Picture a two-particles motionless and at their equilibrium separation. There are no forces acting on the particles, thus they will remain motionless with zero kinetic energy. At r_o: $E_{tot} = PE + KE = PE(r_o) = -\varepsilon$. This is analogous to a spring-mass system at rest and at its equilibrium position. What happens when energy is added to the two-particle system? In the spring-mass system we add energy as work by stretching (or compressing) a spring. Analogously, energy can be added to the two-particle system by pulling the particles apart or pushing them together away from their equilibrium separation.

We know that for the spring the end result is oscillating behavior. Let us look at an example of adding 0.5ε of energy to the two-particle system. Since the initial energy at equilibrium was $-\varepsilon$, adding this amount of energy results in $E_{tot} = -0.5\varepsilon$. This total energy is plotted in the figure below.

Figure 3.3.3: Total Energy representing bound particles.



The figure shows us that adding 0.5ε of energy is equivalent of separating the two particles from r_o to $1.4r_o$ or squeezing them to $1.03r_o$ (look at the values of *r* where E_{total} intercepts PE). Let us assume the particles where pushed apart to $1.4r_o$ and "released". At this separation the particles experience an attractive force pushing them back to equilibrium. (Equivalently, when a spring-mass is stretched, the restoring force points back to equilibrium.) As the particles return to equilibrium, their potential energy will decrease, while kinetic energy increases. Since PE_{LJ} is minimum at r_o, the particles will be moving the fastest at this separation. As they move past equilibrium to separations smaller than r_o, they will start feeling a repulsive force and will gain PE and loose KE. Kinetic energy will go to zero at the minimum separation, $r_{min} \sim 1.03r_o$, at which point the particles will start moving apart. This behavior will continue in this oscillatory manner (as for the spring-mass) as long as there is no source of energy loss. The plot for KE as a function of particle separation is shown in Figure 3.3.3.

Any separation smaller than r_{min} is not allowed (marked "forbidden" on the plot). At the minimum separation the total energy equals to the potential energy. At separations smaller then r_{min} the potential becomes greater than the E_{tot}. In order to obey conservation of energy, $E_{tot} = PE_{LJ} + KE$, that would imply that $KE < 0$ when $r < r_{min}$, since $PE_{LJ} > E_{tot}$. Kinetic energy cannot be negative since it is proportional to speed squared, $KE = \frac{1}{2}mv^2$. Thus, having a separation smaller than r_{min} is not physical, and thus, forbidden. Using the same arguments, any separation larger than r_{max} results is $KE < 0$, and therefore, is forbidden.

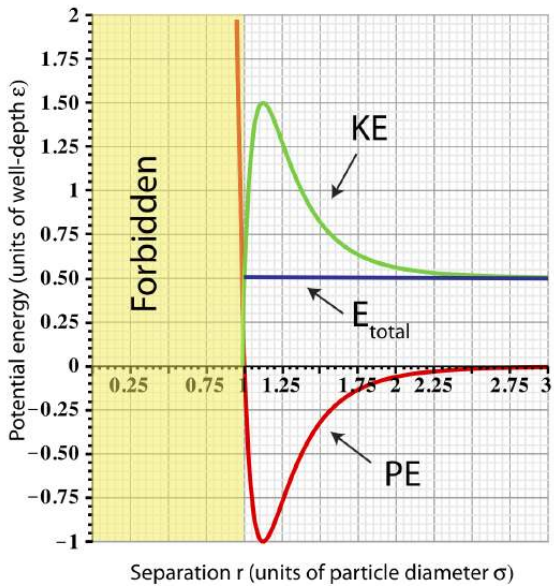
When the particles oscillate back and forth about their equilibrium separation, we call them *bound* to each other, since they cannot move independently of each other. As we add more energy to the system, the E_{tot} line will move up and the distance between r_{min} and r_{max} will increase, thus the particles will oscillates with a greater ranges and a faster speed at equilibrium.

A summary of *bound* particle characteristics:

- *Total energy*: $E_{tot} = PE_{LJ} + KE$. For the particle to be bound $E_{tot} < 0$.
- *Minimum separation*: r_{min} is the smallest allowed separation for a given value of E_{tot}.
- *Maximum separation*: r_{max} is the largest allowed separation for a given value of E_{tot}.

As the total energy approaches zero, the total energy plot no longer intersects the potential energy on the right. Let us look at an example of $E_{tot} = 0.5\varepsilon$ as shown in the figure below. In this case, since $E_{tot} > PE$ for separations of $r > r_{min}$, kinetic energy will always stay positive at these separations. This implies that the two particles will move apart at large separations where they are no longer interacting since the force goes to zero for $r \gtrsim 3\sigma$. Once the two particles are far apart, there is no force acting to bring them back together. They become independent of each other, and, thus, we call them *unbound*.

Figure 3.3.4: Total Energy representing unbound particles.

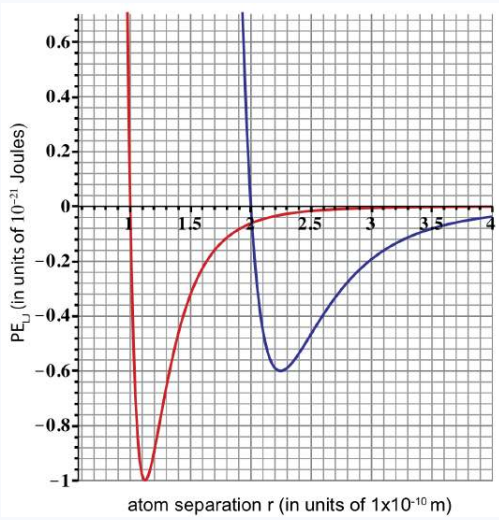


A summary of *unbound* particle characteristics:

- *Total energy*: $E_{tot} = PE_{LJ} + KE$. For the particle to be unbound $E_{tot} \geq 0$.
- *Minimum separation*: r_{min} is the smallest allowed separation for a given value of E_{tot}.
- *Maximum separation*: the is no limit on maximum separation since $KE \geq 0$ for all values of $r \geq r_{min}$.

Example 3.2.1

UC Davis scientists discover two new atoms, Aggieum (*Ai*) and Cyclerium (*Cy*). The plot below shows Lennard-Jones potential energies for Ai-Ai and Cy-Cy atoms.



a) The diameter of Cy is twice the diameter of *Ai*. Determine the diameter of both from the given plot. Label the two curves as either Ai-Ai or Cy-Cy potential energy.

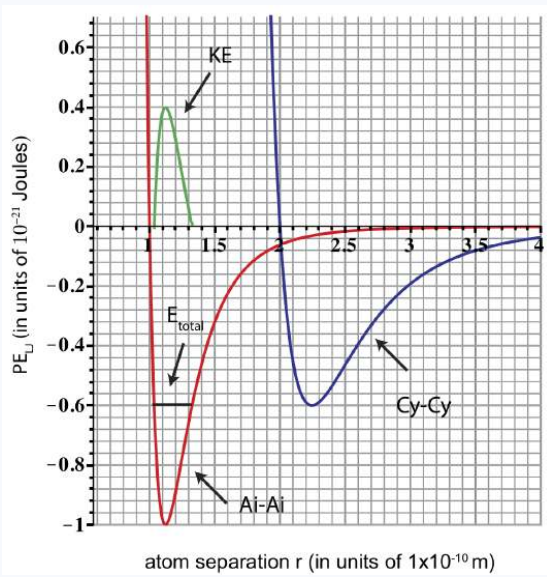
b) A pair of atoms is oscillating with a $E_{tot} = -0.6 \times 10^{-21}$ Joules. Determine which pair (Ai-Ai or Cy-Cy) is oscillating and plot the corresponding E_{tot} and KE.

c) For the result in b), is the pair bound or unbound? If bound, how much more energy do you need to add in order to break the bond between the two atoms.

Solution

a) Diameter of Ai is $1x10^{-10}$ m, and diameter of Cy is $2x10^{-10}$m. Atom diameter is found from the Lennard-Jones potential when PE intercepts the x-axis.

b) Only the Ai-Ai pair will be oscillating with $E_{tot} = -0.6 \times 10^{-21}$ Joules. Cy-Cy pair at this energy will be stationary and at equilibrium (E_{tot} intercepts PE at one point). We obtain the plot for KE as shown in the figure below, by using E_{tot} = KE + PE. E_{tot} is constant due to conservation of energy.



c) When $E_{tot} = -0.6 \times 10^{-21}$ Joules the atoms oscillate between r_{min} and r_{max} as shown in the plot, thus they are bound. You need to add 0.6×10^{-21} joules of energy to reach E_{tot}=0, at which point the atoms become unbound.

From Two to Many Particles

When there are *many* particles, the phase (solid, liquid, or gas) of those particles depends on their total energy. At sufficiently high total energy, the particles are unbound and in the gas phase. At sufficiently low energy the particles are in the liquid or solid phase and are bound. The average particle-particle separation in the bound state is approximately equal to the separation corresponding to the minimum of the pair-wise potential energy. In the unbound state it is much greater than the separation corresponding to the minimum PE.

The *macroscopic* size of matter, whether it is in a solid, liquid or gas phase, is due to the simultaneous interactions of something like ~10^{23} pair-wise interactions if we have a mole of the substance. Our task in the next two sections will be to go from the two-particle *microscopic* description summarized in this section to the *macroscopic* sizes of matter. These ideas are far from simple. Initially, try to imagine a solid at very low temperatures (KE is nearly zero). Each particle "wants" to be at the right distance with respect to all of its neighbors. If there is a way for the system to "get rid" of its energy (by giving it to some colder system, for example), it will continue to settle down and reduce its thermal energy. Eventually, all the random motion comes to a stop (if we can keep cooling the sample) and the particles find their "magic" places, each near the "bottom" of the $PE_{pair\text{-}wise}$ with each of their neighbors.

Now, imagine we start adding energy to the sample. All the particles begin acting like little spring-masses, oscillating back and forth around their equilibrium positions. Eventually they move sufficiently far, so that some "jump" out of where they are "supposed to be". Particles at or near the surface might even leave the sample if their vibrations get vigorous enough. Picturing

what happens when a substance melts, i.e., turns from a solid to a liquid, is difficult, even for the experts. Don't worry about picturing that transition. But you can imagine continuing to add energy until all the particles, even 10^{23} particles, have sufficient energy to separate far apart from each other, causing them to be in the gas phase. So, what is the bottom line here at this point in our making sense of all this? Without getting into a lot of detail, it should make sense to you that at some sufficiently low temperature, everything will be a solid and at some sufficiently high temperature, everything should be a gas. That is plenty for right now.

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3.3: Particle Model of Bond Energy

Overview

In this section we develop the *Particle Model of Bond Energy*. We start with the idea of adding enough energy to break a bond between two subatomic particles interacting with a Lennard-Jones potential. We then proceed to thinking about how much energy is needed to break bonds between multiple particles. At the end of this section, we come up with an approximation that will allow us to easily estimate the bond energy of a macroscopic substance and compare to experimentally determined values of enthalpy we saw in Chapter 1.

Microscopic Bond Energy

In the previous section we modeled two neutrally interacting atoms or molecules with a pair-wise Lennard-Jones potential. Since this potential energy closely mimics the behavior of the spring-mass system (at least near equilibrium), we can think of two interacting particles as being connected by a spring as shown in the figure below. Unlike a "standard" spring, the spring connecting two particles gets very stiff when the particles are very close together (the slope of PE_{LJ} is very steep for $r < r_o$), weak as particles move apart (slope decreases for $r > r_o$, until the spring "breaks apart" for larger separations of $r \gtrsim 3r_o$. The figure also shows the equilibrium separation, r_o, between two such atoms. Since $r_o = 1.12\sigma$ the two atoms are nearly touching as pictured. (Recall, we measure particle separation using center-to-center distances, so two touching atoms would have a separation of σ).

Figure 3.4.1: Two interacting neutral atoms.

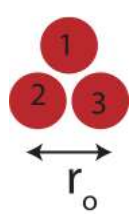
To calculate the energy required to break a bond, let us assume that the two atoms are motionless at equilibrium separation of r_o. The initial total energy of these atoms is then $E_{\text{tot,initial}} = PE(r_o) = -\varepsilon$. We discussed in the previous section that as long as E_{tot} is less than zero the particles remain bound. When E_{tot} becomes greater than zero the two particles become unbound and are very far apart, $r \gg r_o$. If we assume that the atoms remain motionless (KE=0) after enough energy is added to break the bond, the total final energy will be zero since at large separations $PE_{LJ}(r \gg r_o) \sim 0$. The amount of energy required to break the bond between two atoms that are initially at equilibrium is:

$$\Delta E = E_f - E_i = 0 - (-\varepsilon) = \varepsilon \tag{3.3.1}$$

We can think of this quantity as the change of bond energy of the two particle system initially at equilibrium. As we discussed in Chapter 1 energy is required to break bonds, thus the change in bond energy has to be positive when a bonds are broken, such as for a phase transition from liquid to gas. We see the same result here on a microscopic scale.

Since we want to transition to a macroscopic scale, let us start adding atoms to our physical system. Below is a illustration of three atoms, all at equilibrium separations.

Figure 3.4.2: Three interacting neutral atoms.



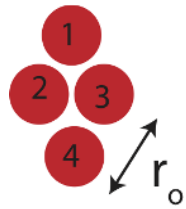
If we want to know the energy required to break up the three atom structure, we need to consider the three bonds present: 1-2, 1-3, and 2-3. Since, all three pairs are separated by r_o, the initial energy of these motionless atoms is simply the sum of the potential energies of the three pairs:

$$E_{\text{tot,initial}} = PE_{12}(r_o) + PE_{13}(r_o) + PE_{23}(r_o) = -3\varepsilon \tag{3.3.2}$$

As before, the energy of the system when all three atoms are unbound or at far separations is zero, $E_{\text{total,final}} = 0$, so the energy required to break this structure is $\Delta E = +3\varepsilon$.

For now, we will stick to *two-dimensional* structures for simplicity. Let us consider a structure of four atoms keeping them as close as possible to each other, as shown below.

Figure 3.4.3: Four interacting neutral atoms.



As before we need to break all the bonds present for this structure to become unbound. For the four atom structure there are 6 bonds: 1-2, 1-3, 1-4, 2-3, 2-4, and 3-4. However, it is no longer possible to arrange four atoms in two-dimensions so all of them are at the r_o separation. From the figure above we can see that atoms 1 and 4 are not separated by r_o. We can use Pythagorean theorem to find the distance between atoms 1 and 4:

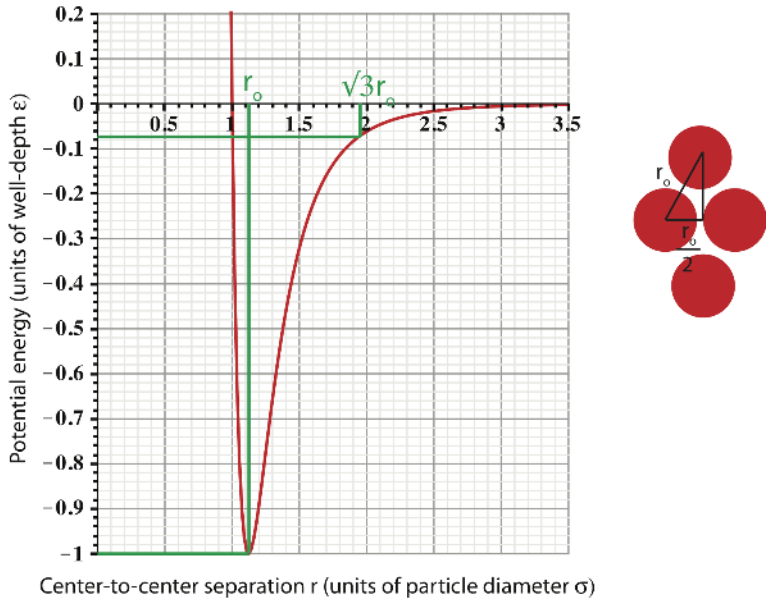
$$r_{14} = 2\sqrt{(r_o)^2 - \left(\frac{r_o}{2}\right)^2} = \sqrt{3}r_o \tag{3.3.3}$$

See Figure 3.4.4 below for the geometry of calculating this distance. We call atoms that are separated by the shortest possible distance, *nearest neighbors*, sometimes abbreviated as *nn*. The pairs that have the next possible shortest distance in a given configuration are known as the *next-to-nearest neighbors*, sometimes abbreviated as *nnn*. In the four-atom example pairs 1-2, 1-3, 2-3, 2-4, and 3-4 are *nearest neighbors*, and pair 1-4 are *next-to-nearest neighbors*.

As for the three-atom case, the initial total energy is the sum of all the pair-wise potential energies. Except for the four-atom system, there is now one pair whose potential energy is no longer evaluated at r_o, but rather at $\sqrt{3}r_o$. To break the 1-4 bond will require *less* energy since its initial energy is no longer the minimum potential energy of $-\varepsilon$. Figure 3.4.4 graphically illustrates the value of $PE_{LJ}(\sqrt{3}r_o)$. Since the x-axis is in units of σ, the separation needs to be converted to these units. Using $r_o = 1.12\sigma$, the separation between atoms 1 and 4 is $r = \sqrt{3}r_o = 1.94\sigma$ as marked on the plot. If we read the value directly from the plot we get $PE_{LJ}(\sqrt{3}r_o) \sim -0.07\varepsilon$. A more accurate method would be to plug in this separation into the Lennard-Jones Equation 3.2.1 directly:

$$PE_{LJ}(r = 1.94\sigma) = 4\varepsilon\left[\left(\frac{\sigma}{1.94\sigma}\right)^{12} - \left(\frac{\sigma}{1.94\sigma}\right)^{6}\right] = -0.074\varepsilon \tag{3.3.4}$$

Figure 3.4.4: Finding equilibrium energy for a four-atom structure.



The initial total energy of the four-atom two-dimensional system is given by:

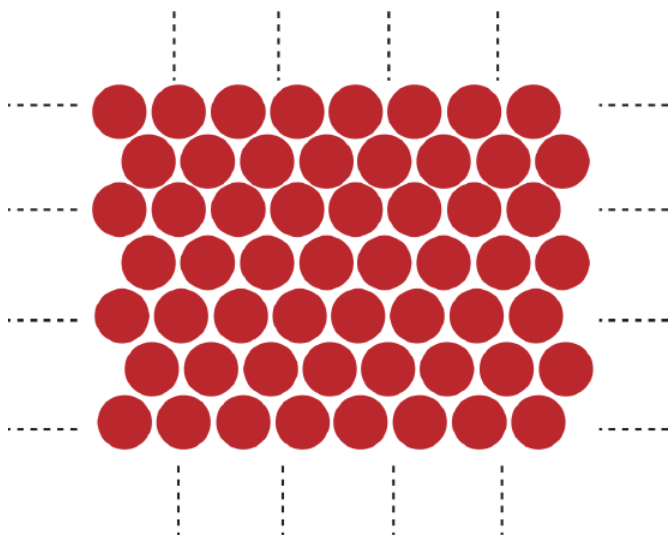
$$\begin{aligned} E_{\text{tot,initial}} &= PE_{12}(r_o) + PE_{13}(r_o) + PE_{23}(r_o) + PE_{24}(r_o) + PE_{34}(r_o) + PE_{14}(\sqrt{3}r_o) \\ &= -5\varepsilon - 0.074\varepsilon \simeq -5.07\varepsilon \end{aligned} \tag{3.3.5}$$

The three systems we analyzed so far in 2D (two-atom, three-atom, and four-atom) are all still considered microscopic since they consist only of a few atoms. Next, we want to see how to extend this analysis for a macroscopic (on the order of one mole, $\sim 10^{23}$ number of particles) system.

Macroscopic Bond Energy

As we continue to add atoms to our two-dimensional structure we come up with the following picture:

Figure 3.4.5: Macroscopic 2D atom structure.



The dashed lines indicate that the atoms continue indefinitely. In order to calculate the amount of energy required to break up this structure we would need to consider **all** the pairs that are present in this structure. We saw when calculating the energy required to break just a few atoms, we set the initial energy of the structure when all atoms are motionless at equilibrium. When we added enough energy to break up all the bonds in a structure, while keeping the kinetic energy of the particles zero, we found that the final energy was always zero, since the pair-wise potential energy goes to zero when the particles are far apart.

Since the system is now macroscopic we can start drawing connections between the pair-wise potential that binds *microscopic* particles together to the change of bond energy we discussed in Chapter 1 during a phase transition for a *macroscopic* pure substance. We can write the change in bond energy as:

$$\Delta E_{bond} = E_{bond,final} - E_{bond,initial} \tag{3.3.6}$$

Comparing the above equation to our analysis of microscopic structure we see that $E_{bond,initial}$ (such as the bond energy of a solid or liquid) corresponds to $E_{total,initial}$, while $E_{bond,final}$ (bond energy of a gas where particles are no longer interacting) is $E_{total,final}$ which is zero. We define the *bond energy* in the *Particle Model of Bond Energy* of a substance as the sum of *all* of the pair-wise potential energies of the particles comprising the substance, calculated when all of the particles are at their equilibrium positions corresponding to a particular physical and chemical state:

$$E_{bond} = \sum_{all-pairs} PE_{LJ}(\text{evaluated at equilibrium separations}) \tag{3.3.7}$$

In solid and liquid phases there is a bond energy associated with the attractive part of all the pair-wise potential energies acting between pairs of particles. Energy must be added to separate the particles sufficiently far apart, thus breaking the bonds. Since the maximum value of the bond energy occurs when the particles are widely separated, and because of the way the pair-wise potential is defined, the bond energy of liquids and solids must be less than zero; that is, the bond energy is negative. Energy required to break the bonds or the change in bond energy is simply the magnitude of the bond energy and is always a positive number, even though the bond energy is negative.

Alert

By convention, all pair-wise potentials are defined to be zero when the particles are separated sufficiently so that the force acting between the particles is zero and negative when the particles are bound. Therefore, the *bond energy* of any condensed substance (solid of liquid) is *always negative*. The maximum value of the bond energy is zero when the particles that comprised the substance are all completely separated to large distances. This is sometimes hard to get our minds around. But it simply has to do with our choice of where to set the zero potential energy as we discussed in the previous section as well as in our discussion of setting the origin for the gravitational potential energy. What matters is that that the **change in bond energy** when bonds are broken is positive, which is the case here since we start with a negative bond energy and end up with zero bond energy.

If we attempt to calculated the bond energy as defined in Equation 3.3.7 for the 2D structure in Figure 3.4.5, we can see that very quickly that this calculation becomes extremely overwhelming due to the number of pairs involved. It is certainly not possible to do without a computer. Before relying on computers to do our work, physicists often prefer to understand nature by simplifying things, even if it means making some assumptions, as long as they are reasonable. We saw for a four-atom system that the energy required to break next-to-nearest neighbor pair was 0.07ε, which significantly less then the energy of ε required to break a nearest neighbor pair.

Thus, let us approximate the bond energy Equation 3.3.7 by only considering nearest neighbor pairs separated by r_o. Since the value of the pair-wise potential for a nearest neighbor pair is the potential minimum, $PE_{LJ}(r_o) = -\varepsilon$, this approximation results in:

$$E_{bond} \approx -(\text{total number of nn pairs}) \times \varepsilon \tag{3.3.8}$$

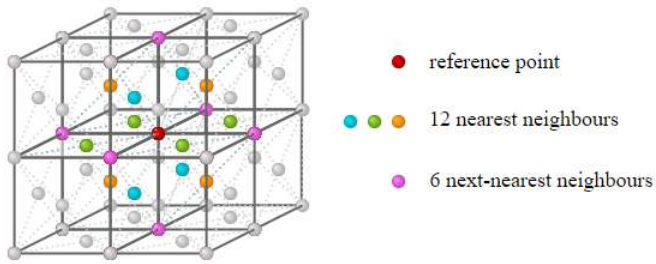
If we revisit to our 2D structure in Figure 3.4.5 we can easily apply this approximation without having to reply on a computer. The only task is to calculate the total number of nearest neighbors. If we focus on some central atom in the figure, we count that it has 6 nearest neighbors. This is true for any atom in the structure, except for the ones at the very edge. However, we we want to focus on one mole, $N_A = 6.02 \times 10^{23}$, of atoms, so the majority of atoms will not be at the edge. Thus, we will neglect edge effects. You might be tempted to say the the total number of nearest neighbors (neglecting edge effects) is just 6 times the number of atoms. To see why this is not correct, let us return to the three atoms in Figure 3.4.2. Of course, here we can just count the pairs directly (there are three!), but if we applied the described method we would say that each atom has 2 neighbors, there are 3 atoms, thus 6 neighbors. This is double of the actual number of bonds! Thus, taking *double counting* into account, the total number of nearest-neighbor pairs, N_{nn}, for a general structure of N atoms:

Misplaced '#'

In the real world, at least more common everyday substances that we analyzed in Chapter 1, such as water, lead, and gold, are three-dimensional in nature. The number of neighboring atoms and their distances will depend on a particular structure that a

substance form when in the solid phase. An example of a common one, known a the face-centered cubic (fcc) structure has 12 nearest neighbors as shown in the figure below.

Figure 3.4.6: Nearest neighbors of a 3D fcc structure.



Applying Equations 3.3.8 and ??? for one mole of a "standard" solid, the bond energy is:

$$E_{bond} \approx -6N_A \times \varepsilon \tag{3.3.9}$$

Do we need to worry about interactions between atoms or molecules that are not nearest neighbors? A little bit, depending on how accurate we want our numerical predictions to be. Looking back at the pair-wise potential energy curve, we see that the slope is not fully horizontal when the particles are located two diameters from each other. There are a lot of nearby neighbors that are within two diameters of each other, so these non-nearest neighbors will still be attracting each other a little bit and will make a contribution to the bond energy, but typically significantly less than the nearest neighbors. This approximation, however, will tend to underestimate the *bond energy*. The underestimation comes in because we have not added in the contributions of the many neighbor pairs that are in the one to two diameter separation range.

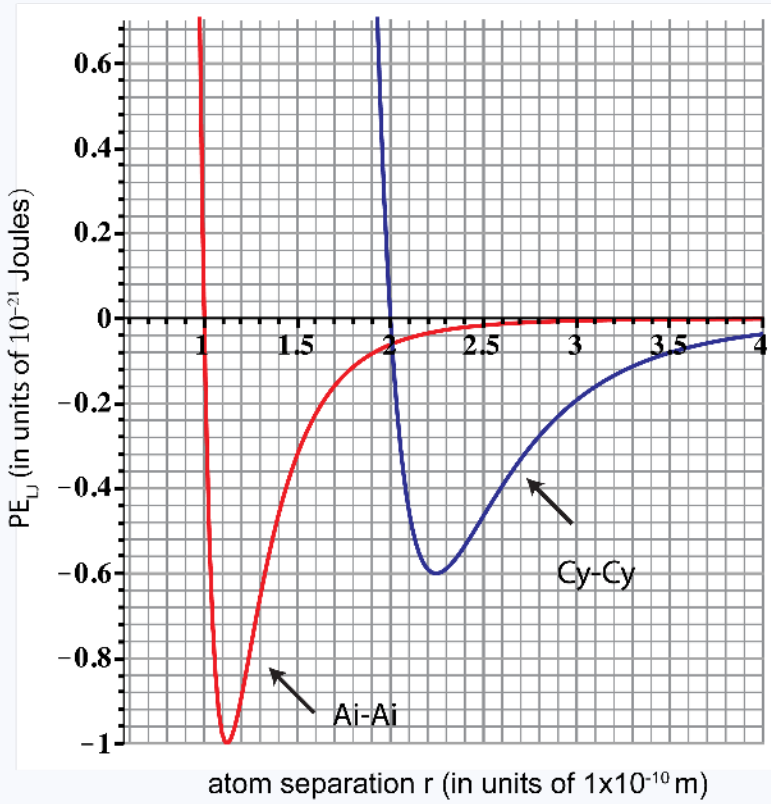
This definition of bond energy avoids the issue of the thermal energy possibly changing, because the calculation is carried out at essentially zero Kelvin (all particles are in their equilibrium positions as they would be at absolute zero, if the phase actually existed at absolute zero) in both the bound state as well as when the particles are separated. We take this to be our technical definition of bond energy. An equivalent definition would be to say that the energy required to separate the particles is carried out so that the thermal energy is the same after the separation as before the separation. We will incorporate thermal energy into our model in the next section.

The empirically determined heats of melting and heats of vaporization are reasonable *approximations* to the *changes* in bond energy at the respective physical phase changes. There are a few tricky aspects associated with directly relating bond energies to heats involved in phase changes. We will see our *Particle Model of Thermal Energy* that there are changes in the thermal energy at a phase change as well as in the bond energy. The empirically determined ΔH's that we used in the bond energy *system* in Chapter 1, however, do incorporate any changes of energy in thermal energy at a phase change. Thus, the ΔH's are not precisely a measure of the particle model bond energy change. For the most part we will ignore this until we have sufficient background to make sense of it. There are also several other rather subtle effects that we will ignore until we are ready to make sense of them in Chapter 4. We have also assume that the structure goes from a solid phase (all particles at equilibrium) to a gas phase (all particles unbound), completely ignoring what happens during the solid to liquid phase transition. For now we will make the approximation that connects the microscopic and the macroscopic definitions of bond energy:

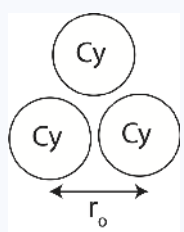
$$\Delta E_{bond} \approx |\Delta m \Delta H| \tag{3.3.10}$$

Example 3.3.1

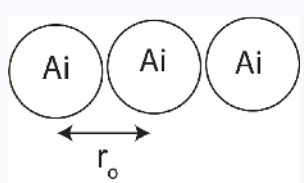
UC Davis scientists continue to conduct experiment on the two new atoms, Aggieum (*Ai*) and Cyclerium (*Cy*). The plot below shows Lennard-Jones potential energies for Ai-Ai and Cy-Cy atoms.



a) Calculate E_{bond} for the configuration shown below. Include all pair-wise interactions.



b) Calculate E_{bond} for another configuration shown below. Include all pair-wise interactions.



c) If the configuration in b) was instead a linear chain of 1 mole of A_i atoms, calculate the bond energy including only nearest-neighbor interactions. Include the effect of atoms at the edges. Do edge effects make a significant contribution to bond energy?

Solution

a) There are 3 nearest neighbor bonds. For C_y, $PE(r_o) = -0.6 \times 10^{-21} J$. Therefore:

$$E_{bond} = -3 \times PE(r_o) = 3 \times (-0.6 \times 10^{-21}) = -1.8 \times 10^{-21} J \tag{3.3.11}$$

b) There are 2 nearest neighbor bonds. For A_i, $PE(r_o) = -1.0 \times 10^{-21} J$. There is also one next-to-nearest neighbor bond at:

$$r = 2r_o = 2 \times 1.12\sigma = 2.24\sigma = 2.24 \times 10^{-10} m \tag{3.3.12}$$

It is possible to read $PE(r = 2.24 \times 10^{-10} m)$ from the plot, but it is more accurate to plug this values into the Lennard-Jones equation:

$$PE_{LJ}(r = 2.24\sigma) = 4\varepsilon\left[\left(\frac{\sigma}{2.24\sigma}\right)^{12} - \left(\frac{\sigma}{2.24\sigma}\right)^{6}\right] = -0.031\varepsilon \tag{3.3.13}$$

Thus:

$$E_{bond} = -2 \times (1 \times 10^{-21} J) - 0.031 \times 10^{-21} J = -2.031 \times 10^{-21} J \tag{3.3.14}$$

c) Each atom has 2 nearest neighbors in a linear chain. The total number of nn for one mole is $\frac{N_A}{2} \times 2 = N_A$. However, there are two extra bonds we are counting at the two edges. But the edges are not double counted, so we need to subtract one bond. If we account for this, $N_{nn} = N_A - 1$ and the bond energy becomes:

$$E_{bond} \approx -(1 \times 10^{-21} J) \times (N_A - 1) = -602 J \tag{3.3.15}$$

Since $N_A \gg 1$, edge effect are truly negligible, which is typically the case for a macroscopic structure.

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3.4: Particle Model of Thermal Energy

Overview

In the previous section we modeled the macroscopic definition of bond energy from Chapter 1 with the microscopic perspective of neutral subatomic particles interacting with a pair-wise potential. In this section we will attempt to make the same connection for thermal energy. In Chapter 1 for pure substances in the temperature range where the Three-Phase Model is valid we said that the total energy of a system is given by:

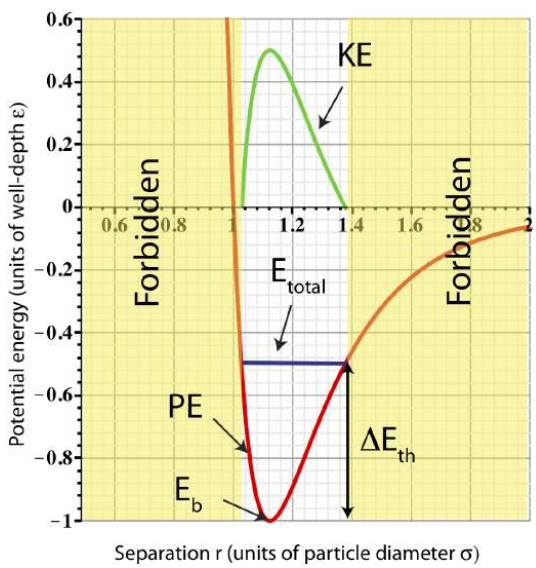
$$E_{tot} = E_b + E_{th} \tag{3.4.1}$$

In the microscopic description of particles interacting with the Lennard-Jones potential the total energy of a system is:

$$E_{tot} = PE_{tot} + KE_{tot} \tag{3.4.2}$$

The subscript "tot" refers to the sum of kinetic and potential energies over all particles. Although, we will focus on just two particles for now, for generality, we add the "tot" subscript so the equations can be applied to many-particles systems, as well. In the previous section we said that macroscopic bond energy can be modeled as the sum of pair-wise *potential energies* between all pairs at their equilibrium configurations (at zero temperature). Your instinct might tell you that thermal energy should be represented in terms of the sum over all the *kinetic energies* of the particles. But careful! If we add some energy to the two-particle system without breaking the bond, the bond energy does not change, so only thermal energy changes. And as we discussed in Section 3.2, when energy is added to the system the particles begin to vibrate about equilibrium. As energy is added to the system increasing thermal energy only, the range of fluctuations increasing, which increases both the average potential and kinetic energy, as can be viewed on the figure below.

Figure 3.5.1: Total Energy in a two-particle system.



Thus, thermal energy is related to potential energy, as well as kinetic. When energy is added, it is not possible to increase kinetic energy without increasing potential energy. As in the spring-mass system when you add potential energy by stretching the spring further, you will also increase the kinetic energy as the spring will oscillate faster on average. In Section 2.6 we discussed that averaged over time the kinetic and potential energies are the same for a spring-mass system, and as a result half of the total energy. Since the Lennard-Jones potential mimics the spring-mass potential at least for small oscillations, we will assume that this interaction when averaged over time will also result in $KE_{avg} = PE_{avg}$. When energy is added without breaking bonds all the energy goes into thermal energy which is equally split between kinetic and potential energy:

$$KE_{tot} = \frac{E_{th}}{2} \tag{3.4.3}$$

The potential energy that contributes to the other half of thermal energy has to do with the random vibrations, but there is also the part of potential energy that is equal to bond energy at zero temperature before energy was added:

$$E_{th}$$

$$PE_{tot} = \frac{E_{th}}{2} + E_b \tag{3.4.4}$$

To check the validity of these equations add them together to get:

$$KE_{tot} + PE_{tot} = E_{th} + E_b \tag{3.4.5}$$

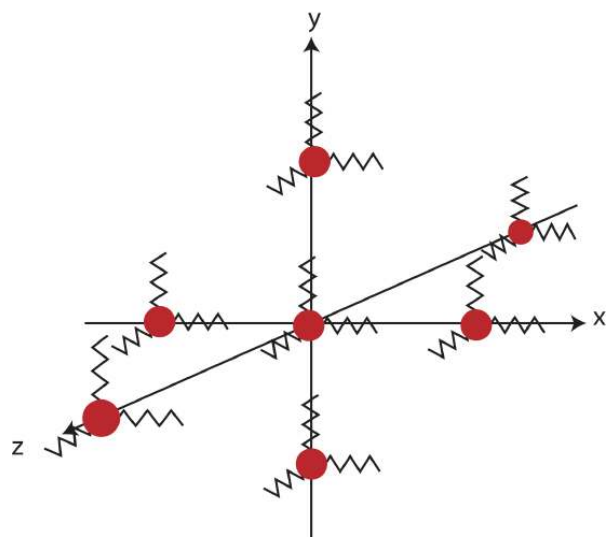
which is precisely the two definitions of total energy given in Equations 3.4.1 and 3.4.2, making the connection between the microscopic and the macroscopic descriptions of total energy.

We saw here that as thermal energy increases the particles start to vibrate about their equilibrium. Thus, thermal energy has to do with the random fluctuations of the particles, while bond energy has to do with their equilibrium configurations. We also discussed the idea of added energy being split evenly between kinetic and potential energies, which will bring us to the idea of *Equipartition of Energy* below.

Particle Model of Thermal Energy

In the *Particle Model of Thermal Energy* we describe thermal energy of a macroscopic solid of liquid in terms of random fluctuations of subatomic particles which vibrate in the three spacial dimensions. Since most vibrating systems can be described by a spring like potential, we will model these oscillating particles as a masses held in place by three perpendicular springs, one for each independent spacial dimension, as depicted in the figure below.

Figure 3.5.1: Model of thermal energy with particles attached to springs.



In order to make sense of how thermal energy can be formulated from these random fluctuations, we would like to know how many ways does each of these particles can “have energy” and how is the total energy distributed among these different "ways"? To answer this within the constraints of our model, we start with the fact that a spring-mass system has a kinetic and a potential energy. Because of the randomness or disorder of thermal motions of the microscopic spring-masses in all three spacial directions, it is plausible that on average, each spring would have the same average KE and PE, as would any other spring. The potential and kinetic energies that are associated with those oscillations can *each* be divided into three independent terms, each one corresponding to one of the three independent spatial dimensions. Therefore, *each* particle in a liquid or solid has *at least* these *six* independent ways it can "have energy".

The important point to remember here, is that regardless of the actual kind of chemical bonding (types of bonds and the geometrical configuration of the bonds) the thermal energy due to the oscillation of the atoms or molecules (treated as rigid particles) is modeled as if they are connected by three independent springs, corresponding to the three independent spatial dimensions in a 3-D universe.

Unbound atoms in the gas phase have other ways to have energy, they can move around freely in space. If the gas is made up of molecules, the individual molecules can also rotate and vibrate. There is a name, or label, for “way to have energy", which we call a *mode*, also sometimes referred to as a *degree of freedom*.

Equipartition of Energy

When we discussed a two-particle system, we argued that it is reasonable to assume that half of the thermal energy goes to kinetic and the other half to potential when averaged over time. From the particle model perspective when a macroscopic system reaches thermal equilibrium the energy associated with random fluctuations (the motions of particles about their equilibrium positions in a solid or liquid or their random motions when in the gas phase) is *uniformly distributed throughout the entire sample*. That is, there will be about as much energy associated with the random energies of a small piece of the sample as in any other same size small piece. This is known as *Equipartition of Energy*. It is similar to what we would say about temperature, if we wait for a sufficiently long time, the temperature will become uniform throughout the sample. There would seem to be a direct connection between temperature and the disordered random motion associated with thermal energy.

Using tools of statistical mechanics (which is beyond the scope of this course) it can be shown that each type of energy that a substance can have, or each *mode*, has this amount of thermal energy:

$$E_{\text{thermal}}(\text{per mode}) = \frac{1}{2}k_BT \tag{3.4.6}$$

where $k_B = 1.38 \times 10^{-23} J/K$ is the *Boltzmann constant* and T is temperature. This expression provides a connection between a macroscopic concept of *temperature* and a microscopic idea of a *mode*. In words the above equation means that *temperature is a measure of the average energy in an active mode when the sample is in thermal equilibrium*. To calculate the total thermal energy, we need to multiple the $\frac{1}{2}k_BT$ factor for the thermal energy per mode by the total number of modes in our sample. The total number of modes is the total number of particles *N* times the number of modes per particle. Thus, total thermal energy can be written as

$$E_{\text{thermal}} = (\#\text{ modes per particle}) \times \frac{1}{2}k_BT \tag{3.4.7}$$

Our next task to to count the number of modes per particle for different types of substances.

Counting Modes

When we asked how many ways does *each spring* in a solid can have energy, the answer was two, one kinetic and one potential. We will refer to these modes as the *vibrational kinetic energy*, KE_{vib}, and *vibrational potential energy*, PE_{vib} modes. To answer how many ways does *each particle* in a solid have to have energy, we saw that there are three springs and two modes per spring, so a solid must be six number of modes, 3 KE_{vib} modes and 3 PE_{vib}. *Equipartition of Energy* tells us that each one of these modes will have the same amount of energy of $\frac{1}{2}k_BT$ at thermal equilibrium. One mole of a solid will have $6N_A$ number of modes, resulting in a total thermal energy of:

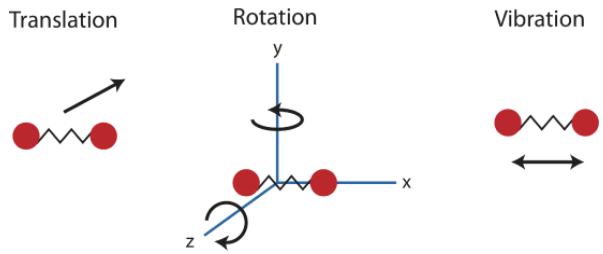
$$E_{\text{thermal}} = 3N_Ak_BT \tag{3.4.8}$$

How many modes do different gases have? In a simple *monatomic gas*, composed of single atoms, such as He or Ne gases, *aka* Noble gases, the atoms are no longer interacting with a pair-wise potential since their average separations are $r \sim 10\sigma$. Therefore, the atoms cannot be modeled with springs since they are not vibrating around some equilibrium. Rather the atoms are moving around freely in three-dimensions. We refer to this type of motion as *translational kinetic energy*, KE_{trans}. Since there are three dimensions, each atom in a monatomic gas will have 3 modes. We can find the average speed of a gas particle by considering that *each* of the three KE_{trans} modes has $\frac{1}{2}k_BT$ of thermal energy. Thus:

$$KE_{avg} = \frac{1}{2}mv_{avg}^2 = \frac{3}{2}k_BT \tag{3.4.9}$$

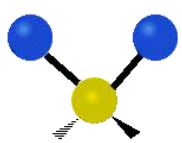
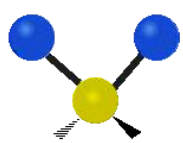
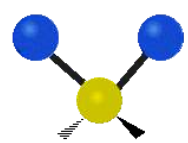
In a *diatomic gas*, composed of two-atom molecules, such as H_2 or O_2, there are still no *inter-molecular* (between molecules) interactions, but there are now *intra-molecular* (between the atoms within a molecule) interactions to consider. We can model the bond between the two atoms in a molecule as a spring, allowing the two atoms to vibrate relative to each other. Thus, each molecule will have one vibrational kinetic and potential energy mode. In addition, as for the monatomic gas, the molecule as a whole is free to move in space, since it is not interacting with other molecules. Thus each molecule has 3 translational kinetic energy modes. Another way this molecule can have kinetic energy is through rotations. The figure below depicts all the possible *rotational modes* of a diatomic molecule. The energy associate with rotations is known as *rotational kinetic energy*, KE_{rot}. For a diatomic molecule only two rotational modes are energetically allowed (for quantum mechanical reasons we will not address here). As shown in the figure these are rotations about the y- and z- axes. One way to think about this is that only rotations that change the orientation of the molecule or are not symmetric, are energetically allowed. Thus, since rotating the molecule about the x- axis is symmetric, this rotation is not allowed. For a diatomic gas we have found a total of 7 modes: 3 *KEtrans*, 2 KE_{rot}, 1 *KEvib*, and 1 P*Evib*.

Figure 3.5.2: Modes in a diatomic molecule.



Generally, a *polyatomic gas* is composed of molecules having *N* number of atoms. A molecule is *linear*, when all atoms are arranged in a straight line, such as all diatomic molecules. Other examples of linear molecules are CO_2 and C_2H_2. All linear molecules have 3 KE_{trans} modes and 2 KE_{rot}. *Non-linear* molecules, such as H_2O, are not symmetric can rotate around all 3 axes, thus have 3 KE_{rot} modes. Counting the number of vibrational modes directly can get tricky. Below is a depiction of all the possible vibrational modes in a *non-linear triatomic molecule*.

Figure 3.5.3: Possible vibrational modes in a non-linear triatomic molecule.

Symmetric Stretching	Asymmetric Stretching	Scissoring (bending)
		

However, without thinking about the geometry of all the possible vibrations, we can count the number of vibrational modes indirectly. If we treat each atom in a polyatomic molecule independently, we conclude that the molecule has *3N* kinetic energy modes, 3 for each atoms. We know that a non-linear molecule will have 3 KE_{trans} and 3 *KErot*. To add up to *3N total kinetic energy modes*, $3N = 3 + 3 + (KE_{vib})$, we find that there must be *(3N-6)* KE_{vib} modes. For each kinetic vibrational mode there has to be a potential vibrational mode, so there are also *3N-6* PE_{vib} modes. Thus, the total number of possible modes in a non-linear polyatomic molecule is:

$$\begin{aligned} &\text{total number of modes} \\ &= 3(KE_{trans}) + 3(KE_{rot}) + (3N-6)(KE_{vib}) + (3N-6)(PE_{vib}) = 6N-6 \end{aligned} \tag{3.4.10}$$

Similar analysis can be done for a non-linear molecules. A summary of the number of modes for all the types of substances is shown in the table below.

Table 3.5.1: Number of Modes for Different Substances in 3D.

Type of Substance	Translational Modes	Rotational Modes	Vibrational Modes	Total Modes per particle
Solid	0	0	6	6
Monatomic Gas	3	0	0	3
Linear Polyatomic Gas (N atoms)	3	2	6N-10	6N-5
Non-linear Polyatomic Gas (N atoms)	3	3	6N-12	6N-6

Sometimes, however, some of the modes do not "get excited" due to the quantization of energy levels. At low temperatures, the quantum splitting between energy levels is larger than thermal energy, and the mode cannot be activated. When this happens, we say that mode is *frozen out*. *Frozen modes* cannot share thermal energy among other modes. *Active modes* are the only ones that share the thermal energy equally among themselves. Rotational modes typically have lower energy than vibrational modes. Thus, vibrational modes are frozen out for typical temperatures, but rotational modes can also become inactive when the temperature is low enough. Translational modes are always active, as long as the temperature is above zero Kelvin.

Example 3.4.1

1) You perform various experiments to determine properties of an unknown substance. In one experiment, you place 10 moles of a solid and 12 moles of the unknown substance in separate insulated and sealed containers. You find that when you add the same amount of energy to each container, you measure the same temperature change. Assume there are no phase changes for either substance. Determine whether the unknown substance is a solid, monatomic gas, diatomic gas with frozen vibrational modes, or a diamotic gas with active vibrational modes.

2) In another experiment you combine 2 moles of a solid with 3 moles of a diatomic gas with vibrational modes frozen in an insulated contained. The two substances are initially at different temperatures. As the two substances reach thermal equilibrium, which one will have a larger magnitude of a temperature change?

Solution

1) In the Particle Model of Thermal Energy the change in thermal energy is given as:

Misplaced '#'

Since $\Delta E_{\text{thermal}}$ is the same for the same ΔT for both substances, the total number of modes must be the same for both substances. The total number modes is the number of particles times the number of modes per particle, so for the solid we get:

Misplaced '#'

For the unknown substance:

Misplaced '#'

resulting in (# modes per particle) = 5, which is true for a diatomic gas with frozen vibrational modes.

2) Since the two substances are a closed system, $\Delta E_{\text{thermal}}$ gained by one substance must equal be $\Delta E_{\text{thermal}}$ lost by the other:

Misplaced '#'

From equation above, the substance with less total # of modes will have a larger temperature change. The solid has $2N_A \times 6 = 12N_A$ total number of modes, and the diatomic gas with vibrational modes frozen out has $3N_A \times 5 = 15N_A$ total number of modes. Thus, the solid will have a larger temperature change.

Heat Capacity at Constant Volume

Let us now make the connection between the definition of macroscopic thermal energy from Chapter 1 and the microscopic description presented here. Specifically, we would like to develop an understanding of heat capacity from Chapter 1 in terms of microscopic parameters. But we need to be careful that we are actually comparing the same things. We know that if a force acts through a distance, work will be done by one physical object on another. When we make a heat capacity measurement, we do not want the sample doing work on the atmosphere or the container it is in. Therefore, we specify that the sample be kept at constant volume during the heat capacity measurement. The important point here is that we have a way to directly measure the change in the thermal energy by measuring the heat capacity of a sample at constant volume, ensuring all the heat we put into the sample goes to changing its thermal energy and not doing some work by expanding the container or pushing against the air in the room. From the Energy-Interaction Model when no work is being done and only temperature is changing we have $\Delta E_{tot} = \Delta E_{th} = Q$. When the change in thermal energy is due solely to the addition or removal of energy as heat, the constant volume heat capacity, designated with subscript "v", C_V, is given by the rate of change of thermal energy with respect to temperature. This is precisely how we defined thermal energy in Equation 1.2.6 in Chapter 1:

$$\Delta E_{thermal} = C_V \Delta T \tag{3.4.11}$$

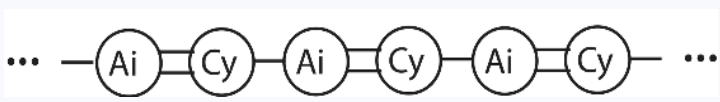
except now we add the "V" subscript for accuracy. The expression above is the macroscopic definition of thermal energy at constant volume. Let us compare the above equation with Equation 3.4.7 described in the Particle Model of Thermal Energy. Setting the two equations equal to each other, using the gas constant $R = N_A k_B = 8.314 \frac{J}{Kmol}$, and solving for molar heat capacity $c_{v,mol}$ ($C_V = c_{v,mol}$ for one mole or N_A number of particles), we get:

Misplaced '#'

We have simple expression above that connects the idea of heat capacity that can be experimentally measured in a lab using macroscopic substances with the microscopic idea of each particle in a substance having an energy mode. We will check the validity of this model next, when we look at some data patterns.

Example 3.4.1

UC Davis scientists construct the following one-dimensional solid structure from their newly discovered atoms, Aggieum (*Ai*) and Cyclerium (*Cy*):



The total number of atoms is $4N_A$. The double lines represent strong Ai-Cy bonds, where the single lines are weaker AiCy-AiCy bonds. Each particle is free to move in one-dimension only.

a) Calculate the heat capacity C_v for the substance in the diagram.

b) You add enough energy to break all weaker bonds. The resulting gas particles are free to move in three-dimensions. Calculate the heat capacity C_v for this substance assuming all modes are active.

c) You add some more energy, and notice that at T=500K all of the stronger bonds are broken as well. If the mass of Ai is nine times the mass of Cy, calculate the ratio of their speeds at T=500K.

d) You take two moles of the substance in part a) and one mole of the substance in part b) and place them together in an insulated container. Compare the magnitudes of the changes in thermal energy of the two substances as they come to thermal equilibrium. Assume there is no change in bond energy in the interval you are analyzing.

Solution

a) Since each atom in this solid can only move in one-dimension, there are 2 modes per atom, one PE and one KE. Heat capacity:

Misplaced '#'

b) After the weak bonds are broken the AiCy molecules are no longer interacting, so we have a diatomic gas. If all modes are active, there are 7 modes per molecule. Since there are $4N_A$ total atoms, there will be $2N_A$ AiCy molecules. Heat capacity:

R

$$C_v = nc_{v,mol} = 2 \times 7 \times \frac{R}{2} = 58.2 J/K$$

c) Ai and Cy atoms are at the same temperature, thus they'll have the same $KE = \frac{3}{2}k_BT = \frac{1}{2}mv^2$. *Setting the two kinetic energies equal to each other:*

$$\frac{1}{2}m_{Ai}v_{Ai}^2 = \frac{1}{2}m_{Cy}v_{Cy}^2$$

$$\frac{v_{Cy}^2}{v_{Ai}^2} = \frac{m_{Ai}}{m_{Cy}} = 9$$

$$\frac{v_{Cy}}{v_{Ai}} = 3$$

Thus, Cy atoms are on average moving three times faster than Ai atoms.

d) Only the idea of energy conservation is needed to answer this question. They are in an insulated container:

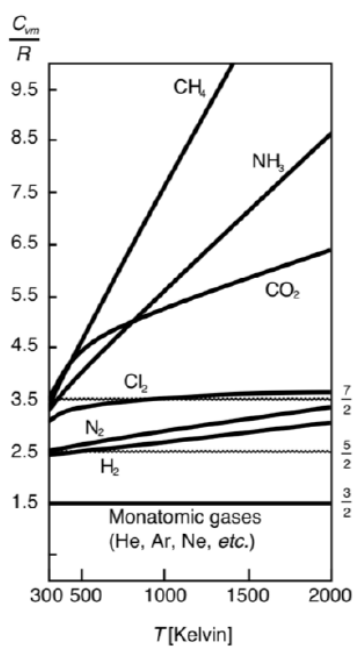
$$\Delta E_{th,a} + \Delta E_{th,b} = 0$$

Thus, both will have the same magnitude of change in thermal energy.

Data Patterns

The figure below shows the constant volume molar heat capacity, scaled with gas constant, for several gases from room temperature up to several thousand kelvin. Since Misplaced '#', the plot is showing us how the number of modes per particle changes with temperature. The monatomic gases have the lowest molar constant volume heat capacity of $\frac{3}{2}R$, and the values are independent of temperature. Diatomic gases seem to have higher values starting at about $\frac{5}{2}R$, while polyatomic gases have significantly larger values, but also a much more pronounced temperature dependence. This data tells us that not all modes are active at all temperature. As we previously discussed at lower temperature some modes get *frozen out* when there is not enough energy to overcome the quantum energy gap to excite a particular mode. For example, we see that around room temperature diatomic molecules have 5 modes, instead of the possible 7 modes, implying that the two vibrational modes are inactive. This data shows an average over one mole of particles, this is why the number of modes changes smoothly (rather than by integer count) as modes become activated in an increasing number of particles as temperature increases.

Figure 3.5.4: Heat Capacity as a function for temperature for various gases.



The table below shows heat capacity patterns that are seen in different gases. Each type of gas, e.g., monatomic, has similar values of specific heats, and the values are ordered from smaller to larger as we go from monatomic to diatomic to triatomic, as implied by

Equation ???. We will analyze in the next chapter why the specific heats of gases measured at constant pressure are greater than at constant volume, as well as the similar difference between C_{mp} and C_{mv} for all gases.

Table 3.2.1: Molar values of both Cp and Cv for monatomic, diatomic, and triatomic gases at room temperature.

gas	C_{mp}	C_{mv}	$\frac{C_{mv}}{R}$	$C_{mp} - C_{mv}$	$\frac{(C_{mp}-C_{mv})}{R}$
Monatomic					
He	20.79	12.52	1.51	8.27	0.99
Ne	20.79	12.68	1.52	8.11	0.98
Ar	20.79	12.45	1.50	8.34	1.00
Li	20.79	12.45	1.50	8.34	1.00
Xi	20.79	12.52	1.51	8.27	0.99
Diatomic					
N_2	29.12	20.80	2.50	8.32	1.00
H_2	28.82	20.44	2.46	8.38	1.01
O_2	29.37	20.98	2.52	8.39	1.01
CO	29.04	20.74	2.49	8.30	1.00
Triatomic					
CO_2	36.62	28.17	3.39	8.45	1.02
N_2O	36.90	28.39	3.41	8.51	1.02
H_2S	36.12	27.36	3.29	8.76	1.05

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3.5: Looking Back and Ahead

The concepts of bond energy and thermal energy are very useful in models that help us make sense of the particulate nature of matter. However, the quantities that are actually measured, although closely related to these ideas, are not quite the same. That is, the ΔH's we encountered in Chapter 1 and the bond energy we used there based on these ΔH's are not precisely the same as the bond energy defined in terms of the pair-wise interactions. However, it is rather tricky to understand precisely how they are related. Until then, we will accept that when making comparisons of the concepts in our models to empirical data, we are making some approximations, which will always be pointed out.

These approximations typically allow us to still make numerical comparisons to within 10-20 percent of the best we can do with extremely complicated models. From a modeling perspective, this is initially a price well worth paying in order to have a model sufficiently simple and broadly applicable to enable us to develop a meaningful understanding of a great deal of the "how and why" matter behaves the way it does from a particulate perspective. The models we develop in this chapter apply, in the sense that they allow us to make sense of phenomena and get pretty close when making numerical predictions, to a *very wide range of phenomena* without getting bogged down in so many details that we never get anywhere in our understanding. Thermodynamics is the "science" of understanding the subtleties and the details of precisely determined empirical data. In Chapter 4 we will get a brief introduction and a taste of the power it provides, but at a cost of the loss of the simplicity of the models in Chapter 3.

At this point we have developed the energy-interaction approach rather completely. There are still some "kinds" of energy we have not encountered, but when we do, we know what to do: treat it as another type of energy. We know how to approach physical systems that involve changes in macroscopic mechanical energies as well as changes in internal energies. We have a systematic way of "dealing with" friction as the transfer of energy to thermal systems. We have also refined our model of matter to a point where we can understand most of the thermal properties it exhibits. For certain thermal properties, we can make very definite numerical predictions with our model.

With our model of matter and understanding of energy and energy conservation, we now can actually understand many of the fundamental concepts that underlie much of thermal physics, thermochemistry and the properties of gases, liquids, and solids. We have also developed a much more sophisticated understanding of temperature. We have made a solid connection of the macroscopic concept of temperature that we measure with a thermometer to our extended microscopic model of matter.

Up to this point we have tried to avoid getting into the messy details of the interactions of matter. What is remarkable, is how much we have accomplished with this approach. There are, however, many questions that we cannot answer without getting involved in the details. An example is how do we determine the strength of bonds (or spring force constant). It turns out that the spring constants are directly related to the frequency of vibration of the particles themselves. Infrared spectroscopy is one way to determine these frequencies and thus the spring constants. This is an important question that we definitely want to explore. But before we can proceed, we need to go back and spend some time developing the general connection between unbalanced force and change in motion. In Physics 7B, we will do this, and can then come back to the question of oscillation frequency of our oscillators.

In the meantime, we will use our model of matter and energy interaction approach, along with some new constructs and relationships to explore other interesting physical phenomena using a very powerful approach to understanding interactions of a chemical and biological nature: the thermodynamic model.

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CHAPTER OVERVIEW

4: Models of Thermodynamics

This page is a draft and is under active development.

4.1: Where We Are Headed
4.2: Work and Pressure
4.3: Ideal Gas Model
4.4: Intro Model of Thermodynamics
4.5: Thermodynamics processes
4.6: Second Law of Thermodynamics
4.7: Looking Back and Ahead

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4.1: Where We Are Headed

We continue our pursuit of an energy conservation approach, which looks at the state of a system before an interaction and then looks at the state of the system after the interaction, trying to avoid the messy details that occur in between. With our understanding of heat, work, thermal energy and heat capacities in terms or our particle model of matter, we are in a position to make explicit connections to the traditional field of thermodynamics. Thermodynamics is a very practical discipline. Scientists from all fields (chemistry, physics, biology, earth sciences, environmental sciences) find thermodynamics to be a very useful approach to determining values of physical variables. Our goal is to demystify thermodynamics as much as we can. In particular, we make direct connection to our particulate models of matter and our *Energy-Interaction Model.* The connection of entropy and energy to particulate models of matter helps to make thermodynamics much less mysterious to most of us. We can more readily see why so many things in nature "are they way they are" in terms of our models.

We will actually spend very little time, relatively, on thermodynamics. We can't expect to become experts in such a short time. But what we do hope is that you will develop some understanding of how traditional thermodynamics relates to what we have been doing. Perhaps, when you run across thermodynamics later in your studies or work, it won't seem so mysterious. The idea of entropy and its connection to statistical arguments should make the second law of thermodynamics much more understandable. The ideas expressed in the second law are very general. They apply to all systems composed of many particles. That takes in just about everything, since essentially everything is made up of little particles.

Kinds of Questions and Explanations

First kind of Question

- Why is thermodynamics such a useful tool throughout all the sciences?
- Why does almost everything you look up in a chemistry or biochemistry reference have a "ΔH" associated with it? And why is it so often negative?
- What the heck is "entropy," anyway? Does the 2nd law of Thermo have anything to do with the perpetual state of my desk? My hectic life?
- Why does Gibbs Energy seem to be such an important idea? And what is it that is "free" about it anyway."

The kinds of questions listed above will be the focus of much of our short and intense involvement with our *Intro Model of Thermodynamics*. Combined with the *Intro Statistical Model of Thermodynamics*, you should be able to feel pretty comfortable regarding your answers to these types of questions. But in addition, you should also be able to make a lot of sense and construct convincing explanations for questions like those in the second category below.

Second kind of Question

- What are the differences when water evaporates from your skin on a warm summer day in California and from the surface of a pot of nearly boiling water in an open pot on the stove?
- What is the temperature of the water vapor as it leaves either surface? Which evaporation process, if either, produces more cooling?
- Which "ΔH" is different, if either, in the two cases? Give a numerical prediction for the difference.

We won't have time to practice constructing answers to too many of these second kinds of questions, but in your own work in advanced science courses and making sense of research papers you are likely to get ample opportunities, provided you get a good foundation with some of the basic underlying ideas. That is the learning outcome we are aiming far.

Phenomena and Data Patterns

Although thermodynamics can be applied to physical systems as large as galaxies and even our entire universe, it really comes into its natural power when we have questions and need answers about what is going on *internally* in rather controlled environments. This might be in a biochemistry lab or in the cells in the human body. Thermodynamics (and the additional insight and understanding obtained from a statistical approach to entropy and Gibbs energy) connect the real world of empirical data with an extremely powerful approach to analysis that enables scientists to get answers to questions and make numerical predictions when it would seem that it is impossible to get the necessary data to do so. That is, often our questions are of a nature that we would normally believe that the only way they could be answered would by doing specific experiments directly on the phenomenon in question. Frequently, however, these experiments are either impossible to do directly or they are extremely difficult/expensive/illegal, etc. But here is where thermodynamics comes to the rescue.

How does this work? Well, the simple short answer is that for most physical systems, there might be tens, maybe even close to a hundred various physical parameters that characterize that physical system and distinguish it from a similar physical system. But, (here is the short answer) *all of these parameters are not independent of each other*! Thermodynamics is the *tool* that tells us how to determine the values of the ones we *can't directly measure* (and which no one else has measured and tabulated either) from values of parameters that have been measured and tabulated. At first it seems almost like magic. And to an "outsider" to the field, it is very analogous to magic, in the sense that you know there must "be a trick," but you can't imagine what it is. When you are reading and making judgments on scientific papers, you don't want to be like the "jaw-dropped-open in amazement" spectator, but rather "the insider," who at least knows where the "trick" is occurring, even if you don't have the skill to perform it yourself.

A tremendous amount of data has been collected and tabulated on the seemingly infinite variety of biochemical compounds and interactions among these compounds. Thermodynamics is the tool that lets you get maximum benefit from all the work so many thousands of scientists have done on so many different physical systems. So, in a sense, the data patterns of thermodynamics are mostly all of the data that has ever been collected and tabulated on the properties of every imaginable kind of substance or composite material.

In this chapter, we don't really even scratch the surface. With more and more data becoming accessible on-line, "doing thermodynamics" is getting easier every day. Don't forget its power when you need it.

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4.2: Work and Pressure

Work revisited

We introduced work in Chapter 2 for a total force acting on an object over some displacement of the object:

$$W = \int_A^B \vec{F}_{net} \cdot \vec{ds} \tag{4.2.1}$$

There are several special cases that are worth noting. First, when the force is constant and is parallel to the displacement x, the above equation simplifies to:

$$W = Fx \tag{4.2.2}$$

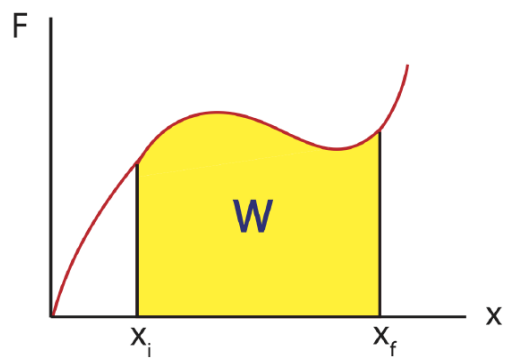
The next simplest case is when the force is a linear function of x. For example, $F(x) = kx$ for a spring. In this case, work then becomes:

$$W = k \int_{x_i}^{x_f} x dx = \frac{1}{2} k(x_f^2 - x_i^2) \tag{4.2.3}$$

Graphical Interpretation of Work

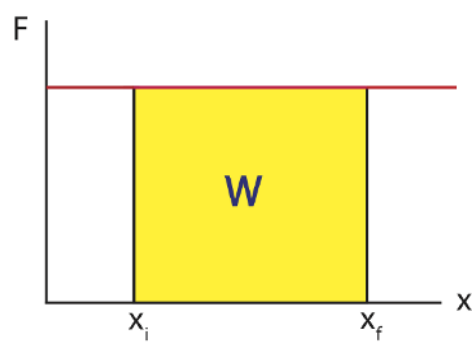
If a force $F(x)$ is plotted as a function of x, there is a very simple interpretation of the definite integral in the above equation: the work, W, is simply the area under the $F(x)$ curve. This should come as no surprise to anyone who has studied integrals. The figure below illustrates a force that varies with position (red curve), and the area in the yellow region is the work done over the interval x_i to x_f.

Figure 4.3.1: Work for a variable force.



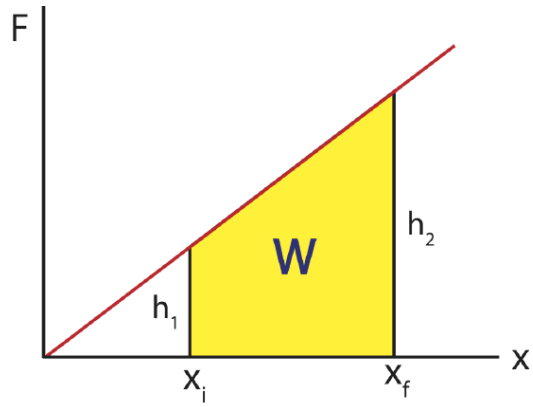
Examining the aforementioned special cases in this graphical way reveal the simplicity and utility of the graphical approach. The graph of a constant force is a horizontal line as shown below. The region under a line is a rectangle, whose area is simply $W = F\Delta x = F(x_f - x_i)$.

Figure 4.3.2: Work for a constant force.



A linear force describes the behavior of simple springs and sometimes pendulums, and is the basis for the simple harmonic oscillator, a widely applicable model. To find the work done graphically, we must compute the area of the yellow region below, which in this case is a trapezoid. There is an area formula for a trapezoid, which is $A = \frac{h_1 + h_2}{2} b$, where the base $b = x_f - x_i$. Or you can treat this area as a sum of the areas of a rectangle $A_1 = h_1 b$ and a triangle $A_2 = \frac{1}{2}(h_2 - h_1)b$. Adding the two areas results in the exact equation for an area of a trapezoid.

Figure 4.3.3: Work for a linear force.



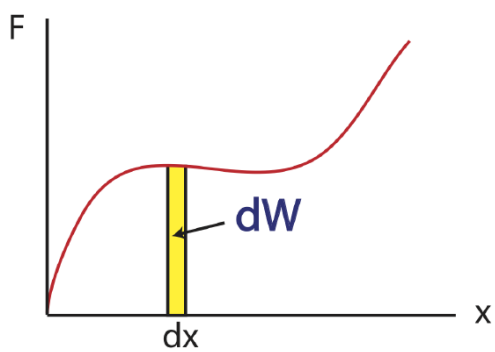
Calculating work directly from the graph, remember that the functional form of force is $F(x) = kx$, thus h_1 is $F(x_i) = kx_i$, and h_2 is $F(x_f) = kx_f$. Then we have:

$$W = \frac{h_1 + h_2}{2} b = \frac{kx_i + kx_f}{2}(x_f - x_i) = \frac{k}{2}(x_f + x_i)(x_f - x_i) = \frac{k}{2}(x_f^2 - x_i^2) \tag{4.2.4}$$

This is identical to Equation 4.2.3 for work done by a linear force that we obtain above by performing direct integration.

Rather than the integral expression for work, it is often convenient to use a differential expression. That is, we want to talk about the small increment of work corresponding to the product of the parallel component of force and the differential increment of distance, dx.

Figure 4.3.4: Work for a differential increment of distance

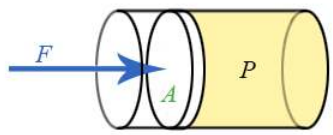


This expression for the incremental work, $dW = F(x)dx$, fits nicely with the graphical representation of work and the graphical interpretation of the definite integral. If you do not remember this from your calculus class, you might want to go back and review it over the next couple of weeks. (The graphical interpretations of derivatives and integrals are two of the those important concepts that you should take away from calculus, i.e., things you remember for the rest of your life.)

Work Done on a Fluid

We now have a general expressions for work in terms of forces and distances moved. But when you push on a fluid (i.e., a liquid or a gas), it is more useful to describe this force in terms of *pressure*. The force exerted on a fluid by an object of cross-sectional area A is proportional to the pressure P and area A and is directed in a direction perpendicular to A. This is illustrated in the figure below.

Figure 4.3.5: Animation of pressure on a fluid.



The force pushing the movable piston to the right is equal to the force the fluid contained in the cylinder exerts on the piston to the left. The magnitude of this force is not a definition of pressure, but simply the relation of force to pressure:

$$P = \frac{F}{A} \tag{4.2.5}$$

The dimensionality of pressure is force per area, which is also energy per volume:

$$\text{Pressure} = \frac{\text{Force}}{\text{length}^2} = \frac{\text{Energy}}{\text{length}^3} = \frac{\text{Energy}}{\text{volume}}$$

The units of pressure in SI are the Pascal (Pa):

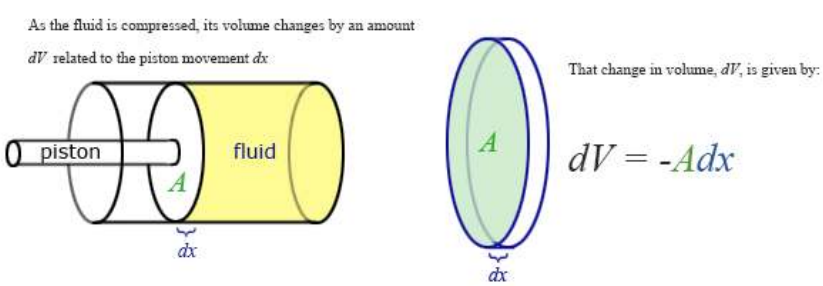
$$\text{Pressure} = \frac{N}{m^2} = \frac{J}{m^3} = \text{Pascal}$$

Some useful conversions involving pressure are:

$$1.0atm = 1.01 \times 10^5 Pa = 14.7 \frac{lb}{in^2} (psi)$$

Our previous expressions for work were in terms of the linear distance, a product of force and displacement. However, when dealing with fluids, it is useful to make a change of variables from x to V. For the case of a piston, the relation between the differentials dV and dx is illustrated in the figure below.

Figure 4.3.5: Animation of work done on a fluid



Note: The reason for the minus sign in front of dV is because the volume gets smaller as "x" increases.

To extend the definition of work to fluids using V and dV rather than x and dx, use $dV = -Adx$ to make the change of variables. Substitute $\frac{-dV}{A}$ for dx and use the relationship between force, pressure, and area to substitute $F(x)$ for $P(V)A$, and the integral becomes:

$$W = -\int_{V_i}^{V_f} P(V)dV \tag{4.2.6}$$

This is the expression for the work done on a fluid when it is compressed from a volume V_i to a volume V_f. The minus sign in front of the integral ensures that when the fluid is being compressed (dV is negative), work comes out positive, since work is being done

on the system. If instead of being compressed, the volume expands, the work done on the fluid will be negative since dV is positive, since the fluid does positive work on some other physical system or work is being done *by the system*.

In a special case is when work being done is at constant pressure, work simplifies to:

$$W = -P\Delta V \tag{4.2.7}$$

Since the area under a F(x) vs. x plot gave us work done, the area under a P(V) vs. V plot will give us the work done on or by the gas. We will explore this idea in greater detail in Section 4.4.

Contributors

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4.3: Ideal Gas Model

Ideal Gas Law

The *Ideal Gas Law* is a good approximation for the behavior of most gases. The word "ideal" refers to the following assumption about the gas:

- the gas is made-up of a large number of particles whose motion is random.
- the gas particles are negligibly small compared to the the volume the gas occupies.
- there is no intermolecular forces between the particles.
- the there is no energy loss due to particle collisions.

Given the assumption described above, there is an important relationship between the pressure, temperature, volume, and number of particles in an ideal gas:

$$PV = Nk_BT \tag{4.3.1}$$

or

$$PV = nRT \tag{4.3.2}$$

where n is the number of moles, while N is the actual number of gas molecules. The number of moles is defined as:

$$n = \frac{N}{N_A} \tag{4.3.3}$$

where N_A is Avogadro's constant. The Boltzmann's constant is k_B is:

$$k_B = \frac{R}{N_A} = 1.381 \times 10^{-23}\ \frac{J}{K} \tag{4.3.4}$$

an the gas constant R is:

$$R = 8.314 \frac{J}{mol \cdot K} \tag{4.3.5}$$

The *Ideal Gas Law* states that pressure and volume are not uniquely related, but depend on the temperature. Therefore, the work done when compressing a gas will depend on how temperature changes as the pressure and volume change. That is, it takes different amounts of work to compress a gas, depending on how the temperature varies during the compression, as heat is or is not allowed to enter the system. Pressure vs. Volume plots (PV diagrams) introduced in the next section and a new way of stating conservation of energy will allow us to determine the contributions of work and heat to changes in systems.

The Ideal Gas connects the *microscopic* way of thinking about gases to the *macroscopic* way of thinking about gases. The temperature term forms a bridge between the particle model of thermal energy and macroscopic thermodynamics. Temperature connects directly to the meaning of thermal energy through the fundamental relationship of temperature as a measure of the random thermal motion in any energy mode at thermal equilibrium, while at the same time, temperature is seen to be directly proportional to the pressure of a gas.

Heat Capacity for an Ideal Gas

In Section 3.4 we defined heat capacity at a constant volume. Most chemical reactions or biological processes occur in open containers, where the gas is allowed to expand or compress, keeping the pressure constant. The assumption for heat capacity at constant volume was that no work was being done on or by the system. Based on the definition in the previous section, $W = -\int PdV$, we can now see that when the volume is not changing $dV = 0$, there is no work being done. In an experiment where the container is open, we can no longer make that assumption.

Using energy conservation we know that, $\Delta E_{tot} = Q + W$. There are no intermolecular interaction in an ideal gas, thus, there are no changes in bond energy and only thermal energy can change during an interaction, $\Delta E_{tot} = \Delta E_{th}$. Going back to the definition of heat capacity, $C = Q/\Delta T$, and plugging in for Q, heat capacity can be written as:

$$C = \frac{\Delta E_{th} - W}{\Delta T} \tag{4.3.6}$$

In Equation 3.4.10 we defined heat capacity at constant volume at $C_V = \Delta E_{th}/\Delta T$. Thus, we can write the above equation as:

$$C = C_V - \frac{W}{\Delta T} \tag{4.3.7}$$

For constant pressure the integral equation for work simplifies to $W = -P\Delta V$, and using the Ideal Gas Law Equation 4.3.2 the above equation simplifies to:

$$C_P = C_V + nR \tag{4.3.8}$$

where the subscript "P" refers to heat capacity at constant pressure.

For one mole the expression for the molar heat capacity at constant pressure for an ideal gas becomes:

$$c_{pm} = c_{vm} + R \tag{4.3.9}$$

For an ideal gas, the molar heat capacity at constant pressure is larger than at constant volume by exactly the value *R*. This is true for any ideal gas, whether monatomic, diatomic, or polyatomic, because the Ideal Gas Law does not depend on *intramolecular* motions and interactions. Looking back at Table 3.2.1 of experimentally determined heat capacities, we see indeed that the molar heat capacity measured at constant pressure is larger than the constant volume heat capacity by R. Our model of matter does indeed work pretty well for gases!

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4.4: Intro Model of Thermodynamics

First Law of Thermodynamics

The *First Law of Thermodynamics* is our Energy-Interaction Model applied to systems where only the *internal* energies are changing. The 1st law states that: *the change in internal energy is equal to the energy added or removed as heat and/or work.* Symbolically, using U to refer to internal energy, the 1st Law is given by a familiar equation:

$$\Delta U = Q + W \tag{4.4.1}$$

where, generally, $\Delta U = \Delta E_{bond} + \Delta E_{thermal} + \Delta E_{atomic} + \Delta E_{nuclear}$ and is called the *change in internal energy*. Atomic and nuclear energies includes changes in the atomic states of atoms that are not involved in chemical bonds. In normal chemical reactions and phase changes, there are no changes in atomic or nuclear energies, so the last two terms are zero for the types of physical systems we study in this course. This equation is always true as long as we interpret ΔU to include ***all*** changes of energy associated with the ***physical system***, and we mean by Q and W the addition of energy as heat or as work **to** the system when Q and/or W are positive or a removal of energy **from** the system as heat or as work when Q and/or W are negative.

Thermodynamic State

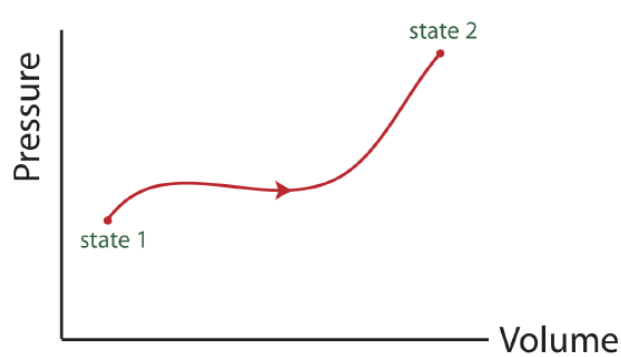
One aspect of thermodynamics that we will study is the evolution of systems from one state to another. To understand this we need to be able to describe the initial and final states, known as a *thermodynamic states*, and to describe the *process* for getting from one to the other. In describing individual states, we can use certain variables that have unique values for that thermodynamic state. These variables are called *state variables*. For example, an ideal gas in a particular state is described by state variables pressure, P, volume, V, temperature, T, and internal energy, U. State variables do not depend on the *process* or how the system evolved to that state. Work, W, and heat, Q, are not state variables, since they depend on the process between two states. As a system changes, due to heat or work being added or removed, the values of these state variables will change. When we discuss how one state variable depends on other state variables, we can refer to that state variable as a *state function*. Relationships between these variables are expressed in *equations of state*. For example, in the previous section we introduced one equation of state – the ideal gas equation, $PV = nRT$.

State Diagrams

Previously we used Energy-Interaction diagrams as a useful representational tool for analyzing energy conservation for specific phenomenon. To describe changes in state variables as a system undergoes change, we can use a different representational tool: *state diagrams*. A state diagram is a graph of one state variable plotted as a function of another state variable for a particular process. Because it is frequently the case that two state variables completely determine the state of the system, a two dimensional state diagram can be a very useful and sufficient representational tool.

Often, the pressure, P, and volume, V, are chosen to be the two representative state variables in a state diagram. Another useful pair is entropy and temperature, that will be introduced later in this chapter. One reason the two-variable state diagram is such a useful representation, is because it is possible to easily follow the path a system takes as it undergoes the process from some initial to some final state. By path, we mean the continuous line of intermediate states that a system passes through, as it moves from an initial to a final state. The *PV diagram* below shows one of the infinite number of possible paths connecting *state 1* with *state 2*.

Figure 4.4.1: PV state diagram.



A PV diagram needs to contain information about:

- initial and final states.
- the path connecting initial and final states.
- the direction of the path.

We will find many uses for PV diagrams, especially for understanding the energy exchanges that take place as thermodynamic systems undergo a change. One of the most important things we have already seen is that the *area under a PV-curve* represents the work done on or by the system during a volume change. This work, in turn, is directly related to heat transfer and changes in the internal energy of the system.

It makes no sense to try to represent a state of a system on state diagram, unless the system is in equilibrium. The state variables, which are macroscopic variables, must have unique values that are the same throughout the system, which can only be measured once the system is in equilibrium. Likewise, it makes no sense to talk about a particular path along a state diagram unless all the intermediate states are equilibrium states as well. This is not to say that a real physical system cannot go from one state, say *state 1* in the example above to *state 2* and not follow a set of intermediate states that are equilibrium states. In fact, most processes do not follow a path that continuously moves along a set of equilibrium states. It is just that we cannot show the path if it does not pass through a series of equilibrium states. The end points, however, are well defined, regardless of how the system gets from the initial to the final equilibrium state. The system can start in an equilibrium state and end up in an equilibrium state and never be in an equilibrium state along the way.

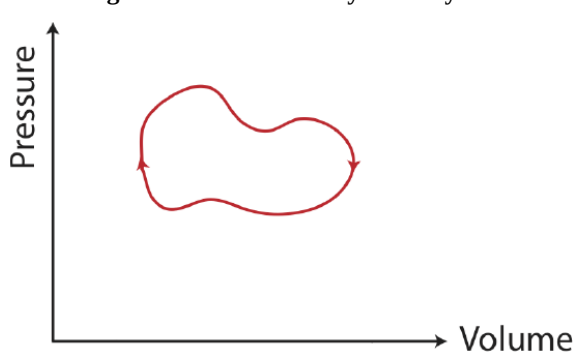
Types of Problems

There are typically **three quantities** for a particular process that we can calculate from a PV diagram alone:

1. W: work can be obtained directly from the PV diagram by either doing an integral or calculating an area under a curve. The sign of work can be found by considering the direction of the process indicated on the PV diagram. From definition of work in Equation 4.2.6, if the volume increased during a process work is negative, if the volume decreases work is positive, and if the volume stays constant work is zero.
2. ΔU: when there is no change in bond energy, change in internal energy is equal to the change in thermal energy, which can be calculated using $\Delta E_{th} = \frac{1}{2}(\text{total } \# \text{ modes})k_B\Delta T$. Initial and final temperatures can be calculated from the PV diagram using the Ideal Gas Law: $PV = nRT$. Also, information about the total number of particles and the type of gas is needed in order to calculate the total number of modes.
3. Q: the heat entering or leaving the system can be found indirectly from the PV diagram by calculating W and ΔU first as described in 1. and 2., and then using the 1st Law of Thermodynamics: $Q = \Delta U - W$.

There is a special type of process known as a *thermodynamic cycle*, which returns a system to its original state. An example of a PV diagram for a cycle is shown in the figure below.

Figure 4.4.2: A thermodynamic cycle.

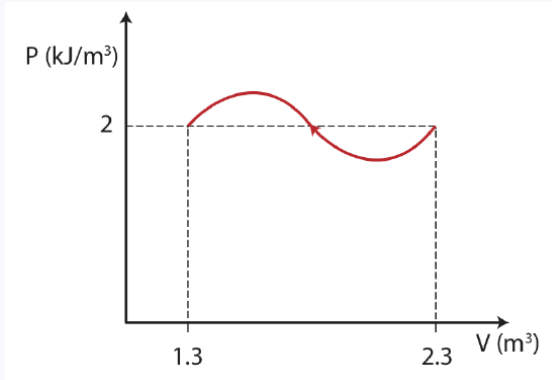


For a cycle:

1. W: when the cycle is clockwise work is negative, and when its counterclockwise work is positive.
2. ΔU: the internal energy is a state variable, thus, it is path independent. Since the system returns to its original state, there is no change in internal energy.
3. Q: since the change in internal energy is zero for a cycle, $Q = -W$.

Example 4.4.1

The thermodynamic process below is described by a PV diagram for 1 mole of an *ideal monatomic gas* that does not change phase. During this process, 5kJ of heat is removed from the system.



a) Calculate the final temperature of the gas.

b) What is the change in internal energy for the process?

c) Calculate the work in the process. Is the work being done by the system or on the system?

Solution

a) Here will use the Ideal gas law and solve for the final temperature:

$$T_f = \frac{PV}{nR} = \frac{(2\times 10^3 J/m^3)(1.3m^3)}{(1mole)(8.314J/Kmol)} = 312.7K$$

b) Since the system does not undergo a phase change, the change in internal energy is equal to the change in thermal energy. The change in thermal energy is:

$$\Delta E_{th} = \frac{1}{2}(\text{total } \# \text{ modes})k_B\Delta T$$

To find ΔT, we need to find the initial temperature as well:

$$T_i = \frac{PV}{nR} = \frac{(2\times 10^3 J/m^3)(2.3m^3)}{(1mole)(8.314J/Kmol)} = 553K$$

For one mole of a monatomic gas: $\text{total } \# \text{ modes} = (1N_A)(3\text{modes/particle}) = 3N_A$. *Using* $R = k_B N_A$ *we get:*

$$\Delta E_{th} = \frac{1}{2}(3)(8.314J/Kmol)(312.7K - 553K) = -3KJ$$

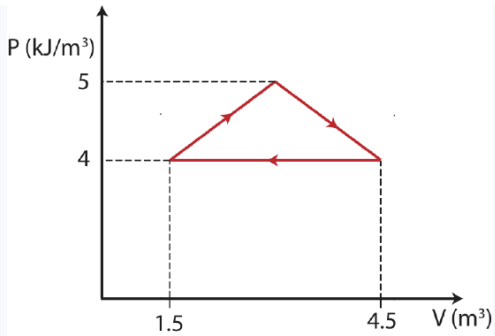
c) Using 1st law:

$$W = \Delta U - Q = -3KJ + 5kJ = 2kJ$$

The positive work obtained from the calculation above tells us that work is being done on the system. We can also see this directly from the diagram, since the volume is decreasing in this process work is positive.

Example 4.4.2

The thermodynamic cycle below (making a shape of an isosceles triangle) is described by a PV diagram for 1 mole of an *ideal monatomic gas* that does not change phase.



Find the total change in internal energy, the work done, and the heat for this thermodynamics cycle.

Solution

In a cycle the start and end states are the same, thus there is no change in the values of state variables. Since $\Delta T = 0$, the total change in internal energy is zero as well, $\Delta U = 0$. This simplifies the 1st law to

$$W = -Q$$

The sign of work is negative since the cycle is clockwise. We can find work by finding the area inside the cycle:

$$W = -\frac{1}{2}(1 \times 10^3 J/m^3)(4.5m^3 - 1.5m^3) = -1.5kJ$$

Therefore, the heat added is 1.5 kJ.

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4.5: Thermodynamics processes

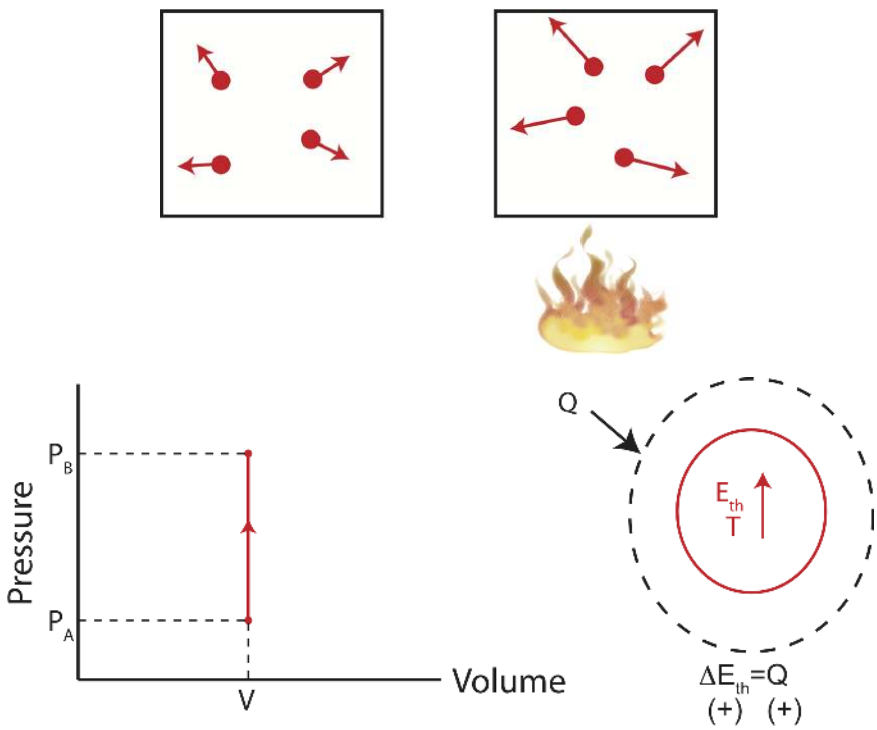
Isochoric

When the volume of a system remains constant during a thermodynamic process, the process is called *isochoric*. Consider a sealed container with a gas at equilibrium. If the sealed container is then heated, the gas particles will start moving around faster, exerting a greater pressure on the wall of the container. Setting the initial and According to Ideal Gas law, when the initial and final volumes are the same, we get the following relationship:

$$\frac{T_i}{P_i} = \frac{T_f}{P_f} \tag{4.5.1}$$

Since the volume stays constant, no work is being done and only the heat entering the system contributes to the change in internal energy. A physical example of this process is illustrated below, in addition to the PV diagram and the Energy-Interaction diagram that describes this particular process.

Figure 4.4.3: Example of an Isochoric Process.



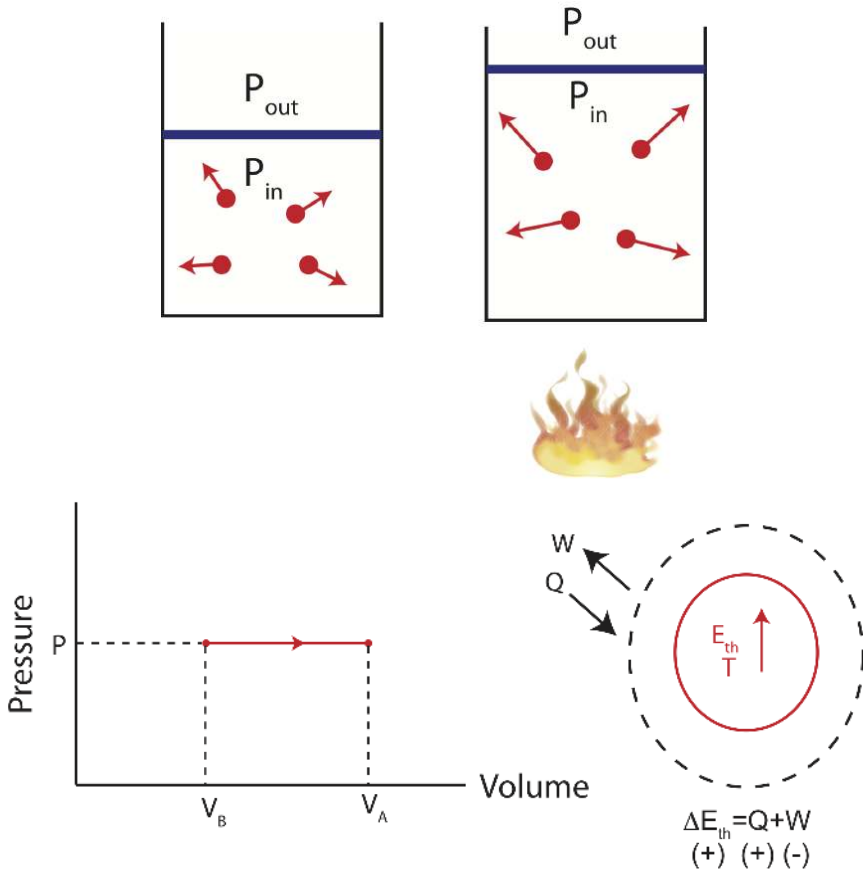
Using both the 1st Law and the Ideal Gas Law for an isochoric process, we find that heat depend on the change in pressure as:

$$Q = \Delta E_{th} = (\text{total \# of modes})\frac{1}{2}k_B\Delta T = \frac{1}{2}(\text{\# of modes per particle})V\Delta P \tag{4.5.2}$$

Isobaric

Now imagine a different experimental set-up where the container has a movable piston or negligible mass and friction allowing the volume to change as the gas is either cooled or heated. As illustrated below when the gas is heated, the speed of the gas particles increases. This creates a larger pressure inside the container compared to the outside. The gas particles inside the container do work on the piston expanding the gas until the pressure outside and inside is the same, and the gas reaches equilibrium. Although, the particles are moving faster the volume is also larger, making it possible to have the same pressure as in its initial state. When the pressure of a system remains constant during a thermodynamic process, the process is called *isobaric*. And illustration of such process is shown below.

Figure 4.4.4: Example of an Isobaric Process.



The corresponding PV diagram and the Energy-Interaction Diagram is also shown. Since the volume is increasing in this example, the work done is negative (the gas is doing work in the environment as it expands).

At constant pressure, calculating work is straightforward, since it is just an area of a rectangle, $W = -P\Delta V$. Therefore, the change in internal energy for an isobaric process is:

$$\Delta U = Q - P\Delta V \tag{4.5.3}$$

Recall from above that we can define a new *state variable* as long as it depends on other state variable by some *state function*. *Enthalpy* is defined as:

$$H = U + PV \tag{4.5.4}$$

Note, that the three variables *U*, *P*, and *V* that define *H* are all state variable.

Why would a function equal to the internal energy plus the product of the two state variables pressure and volume be useful? As with energy, it is the *changes* in H that occur during a process that are important. Changes in enthalpy are most useful under certain conditions: specifically, situations in which ***pressure is held constant***. Chemists and biologists conduct many of their experiments (any reaction carried out in a container open to the atmosphere) under constant pressure.

The following derivation shows why enthalpy is a convenient variable when considering changes occurring under constant pressure:

$$\Delta H = \Delta U + P\Delta V + V\Delta P \tag{4.5.5}$$

The last term is zero when the pressure is constant.

For ΔU we can substitute the expression for internal energy in Equation 4.5.3 we obtained from the first law of thermodynamics. This gives us

$$\Delta H = Q - P\Delta V + P\Delta V = Q \tag{4.5.6}$$

So at constant pressure, the enthalpy change during a reaction is simply equal to the heat entering the system. Likewise, if a phase change is allowed to occur at constant pressure, the heats of melting and vaporization are simply equal to the ***changes in enthalpy***. So now we finally see why heats of fusion and vaporization are often listed as changes in enthalpies. When you measure the energies transferred as heat during a phase change at constant pressure, you are directly measuring the change in the state function H. A negative ΔH means heat is transferred out, and the reaction is exothermic. A positive ΔH means heat is transferred in and the reaction is endothermic:

$$\Delta H < 0: \ exothermic \tag{4.5.7}$$

$$\Delta H > 0: \ endothermic \tag{4.5.8}$$

It is because $\Delta H = Q$ for the conditions so common in chemistry and biochemistry, and technology in general, that enthalpy is so useful. Most measurements are carried out at constant pressure, and for many systems, the only work involved comes from compressing or expanding a gas.

Example 4.5.3

Two moles of an *ideal diatomic gas* with vibrational modes frozen undergoes an isobaric process that results in a $2.5 \times 10^{-3} m^3$ change in volume and 500 Joules of work done on the gas. No phase change occurs during this process. Determine whether heat is zero, positive, or negative and if non-zero find its magnitude.

Solution

Since work is being done on the gas, work is positive, and the change in volume must be negative. When the volume decreases at constant pressure, the temperature must decrease as well according to the Ideal Gas Law:

$$\frac{T_i}{V_i} = \frac{T_f}{V_f}$$

A decrease in temperature implies a decrease in internal energy. Since work is positive, in order to have $\Delta U < 0$, the heat must be negative according to $\Delta U = Q + W$. To find heat, we first need to calculate the change in internal energy, $Q = \Delta U - W$. Since there is not phase change $\Delta U = \Delta E_{th}$. Thermal energy is proportional to change in temperature, which we can calculate from the ideal gas law:

$$\Delta T = \frac{P\Delta V}{nR}. \tag{4.5.9}$$

The quantity \(P\Delta V\=-W=-500 J), using the definition of work at constant pressure.

A diatomic gas with frozen vibrational modes will have 5 active modes (3 translational and 2 rotational kinetic energy modes). Using the equation for thermal energy:

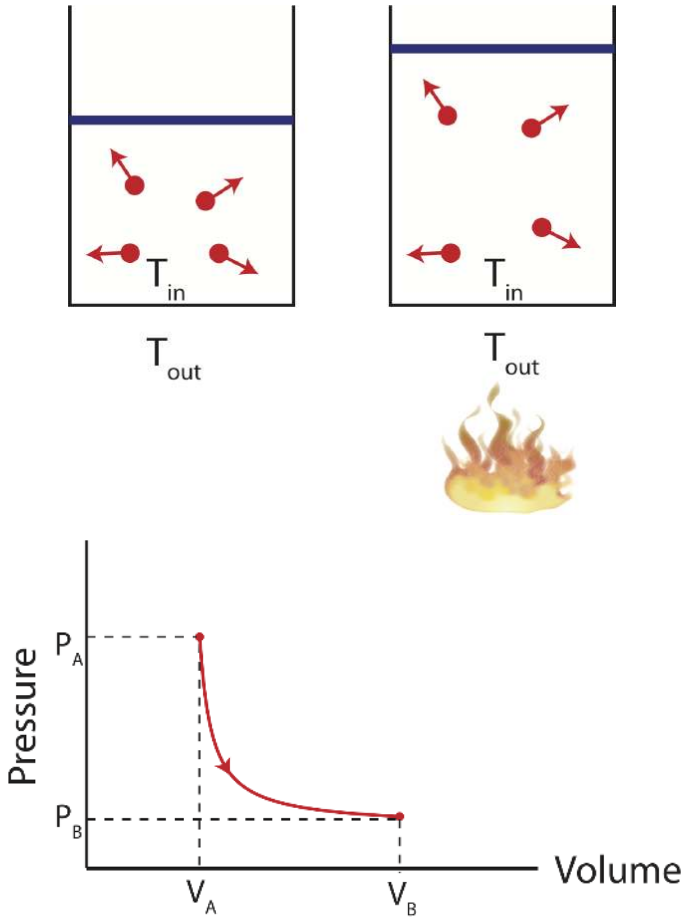
$$\Delta E_{th} = (\text{total \# modes})\frac{1}{2}k_B\Delta T = 2N_A \times 5 \times \frac{1}{2}k_B\frac{-500J}{2R} = -1250J$$

Solving for $Q = -1250J - 500J = -1750J$.

Isothermal

Consider a container in thermal equilibrium with a large reservoir which is kept at a constant temperature. If the system is in contact with a large temperature reservoir and the process occurs slowly, the system is always staying in equilibrium with its environment, keeping the temperature constant. In the figure below this implies that the temperature inside the container, T_{in}, will always equal to the temperature of the environment, T_{out}. This process is called *isothermal*. All the heat the enters the system which is free, the heat added will go into the work being done by the gas at it expands. Since the temperature of the gas does not change, the increasing volume will result in decreasing pressure, as seen on the figure below. Every point on the PV diagram is at the same temperature.

Figure 4.4.5: Example of an Isothermal Process.



For an isothermal process, you can no longer simply calculate the area under the curve, so taking an integral is necessary:

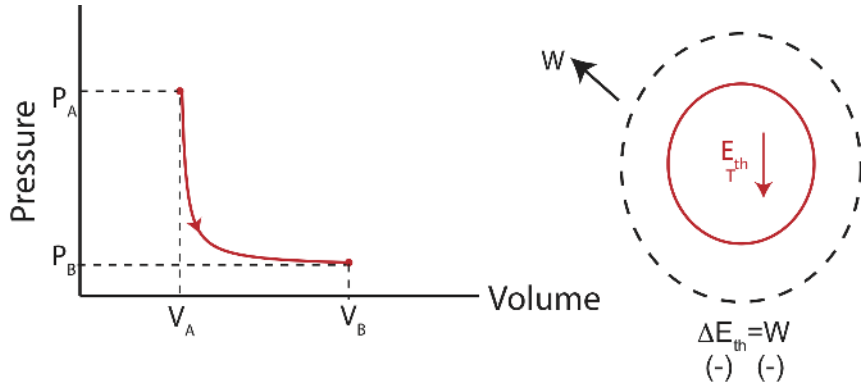
$$W = -\int_{V_A}^{V_B} PdV = -\int_{V_A}^{V_B} \left(\frac{nRT}{V}\right) dV = -nRT \int_{V_A}^{V_B} \frac{dV}{V} = nRT \ln\left(\frac{V_A}{V_B}\right) \tag{4.5.10}$$

There are many examples of isothermal processes that occur in systems that are built to regulate temperature. For example, in living cells temperature fluctuations are not desirable, so chemical reaction in cells occur isothermally. Also, many machines designed to keep the temperature constant, such as refrigerators or heat pumps, follow isothermal processes.

Adiabatic

Adiabatic processes cause an change in internal energy without transfer of heat, but purely through work. An example of a PV diagram and an Energy-Interaction diagram is shown below.

Figure 4.4.6: Example of an Adiabatic Process.



Adiabatic processes typically occur very quickly, such that the system has not time to exchange heat with its environment. Every time you open a carbonated beverage, the pressured gas quickly expands causing the temperature to drop. This *adiabatic cooling* cause the water vapor in the gas to condense, creating a small cloud. Another example in nature of an adiabatic process is the cooling of air in the mountains. As wind brings air over a mountain range, the lower pressure cause the air to expand, and thus cooling it. The cooling air often results in water vapor condensation creating clouds, causing it to rain. If there is a prevailing wind direction, this explains why on some mountain ranges there is more vegetation on only one side. By the time the cloud gets to the other side of the mountain, it has used up all of its moisture. Although, no processes are truly adiabatic (since they depend of an either perfectly insulated system or a process of a very quick time scale), often, it is a good approximation.

Alert

It is easy to confuse the idea of heat and temperature, but they are not the same thing. For an isothermal process, it is possible to add heat to a system, while keeping its temperature constant. Heat is the transfer of energy, and for an isothermal process all the heat that is added to the system goes into work done by the gas. It is also possible for a system to change temperature without any heat transfer, as seen in adiabatic processes. Temperature is an state variable that describes the internal energy (specifically, thermal energy) of the system. Internal energy can change if energy is transferred in or out of the system. But there are two ways to transfer energy, either with heat or work. Thus, work alone can change the temperature of a system.

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4.6: Second Law of Thermodynamics

This page is a draft and is under active development.

Entropy

Up to this point in the course we have focused on conservation of energy which told us how the energy of the system changes when energy is transferred as heat or work in or out of the system, or how energy is transferred from one form to another within the same system. However, there are some physical phenomena that we took as given due to our knowledge of everyday experiences, rather than applying conservation of energy directly. For example, we have always assumed that heat will flow from the hot to the cold system. Imagine the opposite scenario of ice and warm water in an insulated container, where ice gets colder and the liquid gets warmer, each experiencing the same change in magnitude of thermal energy. Even though we know that this does not happen in nature, this process does not violate conservation of energy. Even more dramatically, we do not typically observe thermal energy converting to mechanical energies. Objects do not spontaneously cool off and leap into the air, loosing thermal energy and gaining potential energy. Although the reverse is a common process, in both cases conservation of energy again is not violated, Thus, we need something else to complete our understanding of energy, which we call *entropy*.

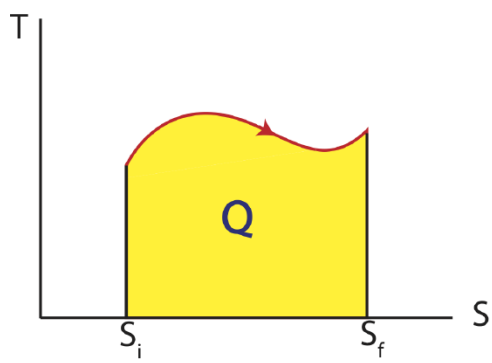
Macroscopic approach:

In the previous sections we defined work in terms of the energy transfer on an ideal gas as the integral of pressure over volume, $W = -\int PdV$. Another form of energy transfer is heat, that we would also like to define in terms of an integral. Energy is transferred as work when there is a pressure difference between the system and its surroundings resulting in a change of volume. Energy is transferred as heat when there is a temperature difference, which then will result in a change of some extensive quantity (a quantity that depends on the size of the system, such as volume). For work this quantity was volume, for heat we call this quantity *entropy*, which is another state function. We arrive at an analogous equation for heat, in terms of an integral of temperature over entropy for a reversible process:

$$Q = \int TdS \tag{4.6.1}$$

Thus, as we analyzed the work done in a process by calculating the area under a curve on a PV diagram, we can equivalently find the heat transfer by looking at the area under a curve on a *TS diagram* as shown below. As for PV diagram, another process that can be depicted on a state diagram must be quasi-static such that every point along the process between an initial and final state define the system as equilibrium.

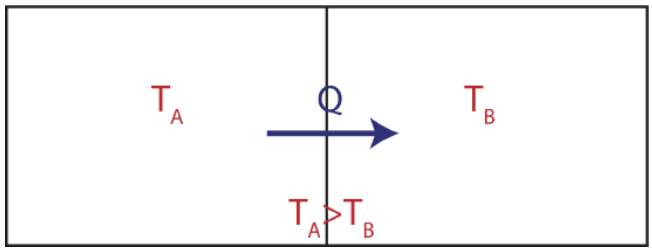
Figure 4.3.1: Temperature vs Entropy, TS Diagram



In the case of heat the sign of the change in entropy is directly related to the sign of heat. Thus, when the entropy of the system is increasing, $\Delta S > 0$, heat is positive, $Q > 0$, and is flowing into the system. When the entropy of the system is decreasing, $\Delta S < 0$, heat is negative, $Q < 0$, and is flowing out the system.

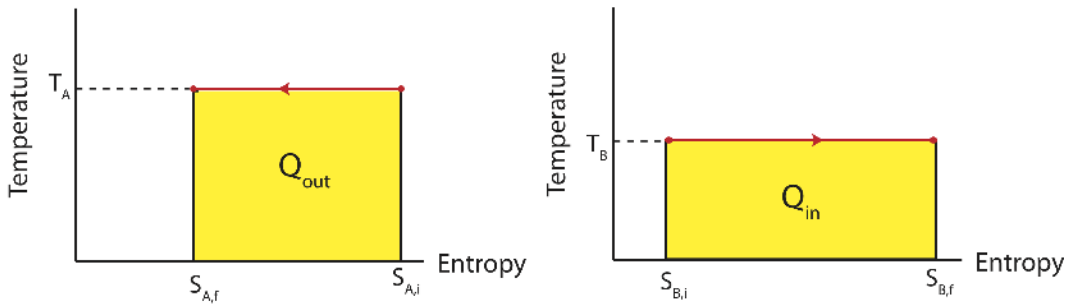
Now let us try to understand what heat that always flows from the hot to the cold system tells us about entropy. Consider two large *thermal reservoirs* exchanging heat. The meaning of a reservoir is that it is large enough to keep its temperature constant, even though heat can flow in and out of it as depicted in the figure below.

Figure 4.3.2: Two Reservoirs Exchanging Heat



If the two reservoirs depicted above define a close system, then the amount of heat that flowing into the colder reservoir at temperature T_B has to equal to the heat that was transferred out of the water reservoir at T_A. If were were to depict this process on two TS diagrams, one for each reservoir, as seen below, the areas under the two curves have to equal since $|Q_{in}| = |Q_{out}|$.

Figure 4.3.3: TS Diagrams for Two Reservoirs Exchanging Heat



The reservoir which is at a higher temperature, T_A will have a higher value on the y-axis with the processes going to the left, since heat is leaving. The lower temperature reservoir, T_B, will have a lower value on the y-axis with the processes flowing to the right since the heat is entering this system. In order for the areas to be equal (the two yellow colored regions), the difference in entropy represented on the x-axis for higher temperature one has to be smaller than the the difference in entropy for the lower temperature one. In other words,

$$|S_{B,f} - S_{B,i}| > |S_{A,f} - S_{A,i}| \tag{4.6.2}$$

Note, the change in entropy that is positive for reservoir B is bigger in magnitude than the change that is negative for reservoir A. Assuming that entropy is additive like volume, $S_{tot} = S_A + S_B$, the total change in entropy for this process is:

$$\Delta S_{tot} = \Delta S_A + \Delta S_B \tag{4.6.3}$$

Assuming the system consisting of reservoir A and B is closed and using the result from equation we arrive at a very important result from Equation 4.6.2, known as the *Second Law of Thermodynamics*:

$$\Delta S_{tot} \geq 0 \tag{4.6.4}$$

The entropy, S, of a closed system can never decrease in any process (the closed system could be a combined open system and the surroundings with which it interacts). If the process is *reversible*, the entropy of the closed system remains constant, $\Delta S = 0$. If the process is *irreversible*, the entropy of the closed system increases, $\Delta S > 0$.

We also arrive at another interpretation of the meaning of temperature. From the start of the course we have thought of temperature so far as a quantity that can be measured with a thermometer which then we defined as the indicator for thermal energy. The new definition comes from the discussion of heat and entropy. Another common form of writing Equation 4.6.1 is:

$$\frac{1}{T} = \frac{\Delta S}{Q} \tag{4.6.5}$$

What the above equation tells us is that the slope of the entropy versus heat graph is the inverse of temperature. The higher the temperature the smaller the slope, since the slope is inversely proportional to temperature. This implies that entropy is changing at a slower rate as heat is transferred at higher temperatures and at a faster rate at lower temperatures. Since heat flows from hot to cold, the positive entropy change of the cold system will be greater in magnitude since it's at a lower temperature than the negative

change of entropy in the warmer system. This again leads us to the Second Law of Thermodynamics assuring that the total change in entropy will always be positive.

Another way to write the equation for the change in entropy for a reversible process is:

$$\Delta S = \int \frac{dQ}{T} \tag{4.6.6}$$

When temperature is constant this simply becomes:

$$\Delta S = \frac{Q}{T} \tag{4.6.7}$$

When temperature is changing implying that there is no change in bond energy, using the definition for heat capacity we get:

$$\Delta S = C \int_{T_i}^{T_f} \frac{dT}{T} = C \ln\left(\frac{T_f}{T_i}\right) \tag{4.6.8}$$

The heat capacity depends on the type of process that is occurring.

Example 4.6.1

You mix some of juice initially at 20°C with 0.2 kg of ice cubes. The ice cubes are initially at -5°C. You leave this in an open cup outside on a cold winter day and forget about it. After the system reached equilibrium, you return to get your juice, you find that 0.15kg of the ice cubes have melted. In this process the environment (cold winter outdoors) gained 100 J/K of entropy. You may treat juice as water.

Constants for water: $c_{ice} = 2.05kJ/(kgK)$, $c_{liq} = 4.18kJ/(kgK)$, $\Delta H_{melt} = 334kJ/kg$.

a. Find the mass of the juice.
b. Find the total change in entropy in this system.
c. Explain why this is an irreversible process and state what the reverse process would be in this scenario.

Solution

a) Since the system reached equilibrium and not all of the ice has melted, this implies that the equilibrium temperature is 0 ^oC. Using the 1st Law of Thermodynamics we know that the change of energy of the ice, ΔE_i, and the juice, ΔE_j, must equal to the heat exchanged with the environment.

$$\Delta E_j + \Delta E_i = Q$$

Since the final temperature is 0 ^oC, the juice just had a change of temperature from 20 ^oC to 0 ^oC, and the ice has a change in temperature from -5 ^oC to 0 ^oC, and then partially melted:

$$m_j c_{liq} \Delta T_j + m_i c_{sol} \Delta T_i + \Delta m_i \Delta H_{melt} = Q$$

We can find Q that left the system for an environment that remains at constant temperature:

$$\Delta S_{env} = \frac{Q}{T}$$

So,

$$Q = \Delta S_{env} T = (100J/K) \times (273K) = 27.3kJ$$

This is the heat that entered the environment, thus -27.3 kJ left the system.

Solving for the mass of the juice from the above equation:

$$m_j = \frac{Q - m_i c_{sol} \Delta T_i - \Delta m_i \Delta H_{melt}}{c_{liq} \Delta T_j} = \frac{-27.3kJ - (0.2kg) \times (2.05kJ/kgK) \times (0+5)K - (0.15kg) \times (334kJ/kg)}{(4.18kJ/kgK) \times (0-20)K} = 0.95kg$$

b) The total change in entropy is the sum of all the changes:

$$\Delta S_{tot} = \Delta S_i + \Delta S_j + \Delta S_{env}$$

For the ice:

$$\Delta S_i = m_i c_s \ln\left(\frac{T_f}{T_i}\right) + \frac{\Delta m_i \Delta H_{melt}}{T_f} = (0.2kg) \times (2.05kJ/kgK) \ln\left(\frac{273}{268}\right) + \frac{(0.15kg) \times (334kJ/kg)}{273} = 0.191kJ/K$$

For the juice:

$$\Delta S_i = m_j c_l \ln\left(\frac{T_f}{T_i}\right) = (0.95kg) \times (4.18kJ/kgK) \ln\left(\frac{273}{293}\right) = -0.281kJ/K$$

Therefore:

$$\Delta S_{tot} = 0.191 - 0.281 + 0.10 = 10J/K$$

c) This process is irreversible because $\Delta S_{tot} \geq 0$. The reverse process would be heat from the outside entering the cup, warming up the juice to 20°C, and freezing and cooling ice to -5°C. This is clearly not a likely event.

Microscopic approach:

Let us start with a brief overview of some simple statistics. The goal here is to understand the idea of equilibrium and to connect it to entropy from a statistical point of view using a model called *Intro to Statistical Model of Thermodynamics*. When describing an equilibrium state of a system, we can fully categorize it by measuring a few state functions, such as temperature, pressure, and volume. From a microscopic point of view these state function can be described by energies of the individual atoms or molecules that made up the system, such as the kinetic energy in three-dimensions of atoms in a monatomic gas. There are multiple ways that individual microscopic particles can have energies but still lead to the same values of state function, T, P, and V of the macroscopic system. It is exactly this multitude of microscopic states that lead to the same macroscopic state is related to entropy.

Let us start with a system which is simple to think about. Imagine you had a large box of an equal number blue and red balls, such that the probabilities of pulling out a blue or a red ball are equal. Every time you pull out a ball, you place it back in the box, so the number of blue and red always stays the same in the box. You want to analyze what is the most likely number of red balls you will have as you pull out more and more balls. Let us start with a simple situation of pulling out a ball two times. All the possible outcomes of our system are called *microstates*. When two balls taken from the box, there are a total of four microstates: RR, RB, BR, and BB, where "R" stands for red and "B" for blue. A *macrostate* is a possible macroscopic outcome that you can have typically described by multiple microstates, such as the number of red balls. In this case there are three possible macrostates: zero red balls, one red ball, and two red balls. We see that the probability of one red ball is the largest, since there are two microstates that describe the macrostate of one red ball. Since there is a total of four microstates, the probability of one red ball is 2/4 or 1/2. More generally, the probability of a macrostate s is the number of microstates of that state, Ω_s divided by the total number of available microstates, Ω_{tot} :

$$P_s = \frac{\Omega_s}{\Omega_{tot}} \tag{4.6.9}$$

We see from this equation that the most probably macrostate is the the one that has the most number of microstates. For an ideal gas, a microstate can be described by the locations of each atom in the gas and their corresponding kinetic energies in each dimension. A macrostate would be a specific temperature and pressure that the gas can have.

A summary of all the macrostates and the corresponding microstates for a *four ball system* is given the table below.

Macrostate	Microstate	Probability
0		$\frac{1}{16}$
1		$\frac{1}{4}$
2		$\frac{3}{8}$
3		$\frac{1}{4}$
4		$\frac{1}{16}$

We see from the four ball example that it is 6 times more likely to pull out 2 red balls than 4 red balls. As the number of balls that you pull out increases, so does the relative probability of half of them being red. For example, by counting microstates, you can calculate that for 100 balls, the probability of getting exactly half of them red is 1×10^{29} times more than the probability of having all of them red. Moreover, having *around* half of them red (e.g. half plus or minus a few balls), is practically certain with near 100% probability. Thus, from the statistical point of view it becomes clear that for a macroscopically large system, there is a macrostate (in this example about half of the balls being red) which is much more likely than any other macrostate.

What does it mean for a system to evolve toward equilibrium? Statistically speaking the system will likely end up in a state which has the greatest number of microstates, since this is the most probable state. By definition we say that, *equilibrium is the macrostate with the greatest number of microstates*. Given enough time, any system will naturally evolve towards equilibrium.

There will always be some constraints limiting the number of microstates of a physical system composed of many particles. Some common examples of constraints are the available volume and total energy. Of course, either of these constraints could be relaxed, by increasing the volume, for example, or adding more energy to the system. But the point is, given whatever constraints actually exist, there is a total number of microstates that the system could find itself in. This total number of *accessible microstates* is usually represented with the uppercase Greek Omega, Ω.

$$S = k_B \ln \Omega \tag{4.6.10}$$

The number of microstates are not additive. We saw that when we pulled out 2 balls from the box, we found 4 number of microstates. For 4 balls, the number became 16, rather than 4+4=8. Thus, it appears that when systems are combined the number of microstates is multiplied:

$$\Omega_{total} = \Omega_1 \times \Omega_2 \tag{4.6.11}$$

This is exactly where the logarithm is helpful, since it turn entropy into an extensive (additive) state function, such as volume. It is clear that volume is extensive, if there was a partition in a container splitting it into individual volumes V1 and V_2, and then the partition was removed, the total volume would just equal to the sum of the individual ones, $V_{tot}=V_1 + V_2$. Entropy has the same extensive behavior which can be shown using properties of logarithmic functions:

$$S_{tot} = S_1 + S_2 = k_B \ln \Omega_1 + k_B \ln \Omega_2 = k_B \ln \Omega_1 \times \Omega_2 = k_B \ln \Omega_{tot} \tag{4.6.12}$$

Since the natural log increases with the number of microstates, entropy will also increase as the number of microstate increases. Since states with the most number of microstates are the most likely ones, entropy will always increase, arriving again at the Second Law of Thermodynamics, $\Delta S \geq 0$ for a closed system.

Example 4.6.2

Two quantum systems are brought into thermal contact allowing them to come to thermal equilibrium. Initially the hotter system has 10 accessible microstates, while the colder one has 4 accessible microstates. At equilibrium each system has the same number of microstates. Find the minimum number of microstates that each system can have at equilibrium.

Solution

The change in entropy of the warmer system, A, is:

$$\Delta S_A = \Delta S_{A,f} - \Delta S_{A,i} = k_B \ln \Omega_f - k_B \ln 10 = k_B \ln \left(\frac{\Omega_f}{10}\right)$$

The change in entropy of the colder system, B, is:

$$\Delta S_B = \Delta S_{B,f} - \Delta S_{B,i} = k_B \ln \Omega_f - k_B \ln 4 = k_B \ln \left(\frac{\Omega_f}{4}\right)$$

The total change in entropy is:

$$\Delta S_{tot} = \Delta S_A + \Delta S_B = k_B \ln \left(\frac{\Omega_f}{10}\right) + k_B \ln \left(\frac{\Omega_f}{4}\right) = k_B \ln \left(\frac{\Omega_f}{10} \times \frac{\Omega_f}{4}\right) = k_B \ln \left(\frac{\Omega_f^2}{40}\right)$$

Second law states that $\Delta S \geq 0$, resulting in

$$\left(\frac{\Omega_f^2}{40}\right) \geq 1$$

or $\Omega_f \geq \sqrt{40}$. Since the number of microstates has to be an integer and $\sqrt{40} = 6.32$, the minimum number of microstates that the equilibrium state must have is 7.

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4.7: Looking Back and Ahead

A fascinating result of the last model is the connection of the thermodynamic state function entropy to notions of probability. The second law of thermodynamics is really nothing more than an expression of the probability of certain configurations occurring in multiparticle systems. In most of the examples you worked out in discussion/lab and in the homework, the number of particles was fairly small. In these small-number-of-particle examples, you could actually calculate probabilities of different configurations of a system. You found that the configurations that were not the most probable still had values that were significant. The system would actually find itself in these less probable configurations some of the time. When we focus on real *macroscopic* samples of matter, the number of particles gets to be the order of Avogadro's number. Now the probability of a system not being in the most probable configuration is vanishingly small. It is because we always deal with systems in everyday experience that have 10^{20} or more particles, that we can make absolute statements like, "heat always flows from a hotter object to a cooler object." It is not that some fundamental law of physics would be violated (conservation of energy, for example) if we sometimes ran across an interaction in which energy was transferred from the cooler to the warmer system as heat. It is just that the probability of this happening is so small, it would never be observed, even if we waited and watched for the entire age of the universe. The probability is just that small!

We also got a taste of what it is like to do some simple thermodynamics. You should have a much better feel now for some of the thermodynamic variables you run across in your chemistry and biology courses. For example, the idea of negative enthalpies of such-and-such should not be so mysterious now. A negative enthalpy change for a reaction (or other interaction/change) means what? Simply that in a constant pressure process, the combination of change of internal energy and PV work is such that heat energy was transferred out of the system, since in such a process, $\Delta H = Q$. The fundamental ideas expressed in the 1st and 2nd laws of thermodynamics are the basis for understanding much of the bio-chemistry that underlies all of the bio-sciences.

An interesting question arises with regard to living systems. Aren't living systems highly ordered systems? Living systems seem to evolve in a direction that contradicts the second law of thermodynamics. They are low entropy, not high entropy configurations. The resolution of this paradox is straight forward. First, it is crucial to remember what the 2nd law actually says. It refers to the change in the ***total*** entropy of all systems that are involved in an interaction (which includes the environment). It says nothing about how a particular system is constrained. It is perfectly OK for some systems to be in low entropy configurations, if there are other systems that increase in entropy and are in high entropy configurations. If we look at living processes what do we find? The low entropy part always interacts with other parts whose entropy increases. For example, a lot of thermal energy is transferred to the environment by living systems.

We can ask, "Can this process go on forever?" The answer is no. As heat energy enters the environment, its entropy continually increases. Simultaneously, sources of low-entropy energy (the sun, for example) are gradually "used up." The energy that was initially in the lower-entropy sun ends up in the higher-entropy environment. This is the one-way fate of our universe. Why? Simply because the probability of ending up in the configuration with the highest number of microstates is so close to unity, that we might as well accept it as a certainty. Too bad other things in life aren't as certain!

In Part 2 of the course, we will continue to use a conservation or before and after approach for two different kinds of phenomena. We will apply our fundamental energy-interaction model to various fluid phenomena, but formulated in such a way to make it useful for this purpose. It turns out that electric circuits behave in many respects the same way as fluids, such as blood flowing around in a human's circulatory system. Yet, all of these phenomena, which seem so different, can be understood using the basic ideas and concepts we have now become fairly familiar with. We use a very similar approach to introduce the basic question Isaac Newton addressed some 300 years ago. Namely, what is the relationship of force to change in motion of an object? It turns out, we can actually make a lot of headway using an approach, *conservation of momentum*, that is very similar to energy conservation. But then, we "have to bite the bullet" and look at the details of the interaction. We want to be able to make sense of the time evolution of physical systems, as well as just knowing their final states. We have to understand what is meant by the simple statement of Newton's 2nd Law and how to use these ideas to relate some common motions to the forces acting on the objects.

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