Entropy *versus* Disorder

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Purpose

Qualitatively evaluate the visual and entropic states of a confined system of macroscopic particles during a spontaneous process as a model of molecular and atomic systems.

Learning Objectives

- Learn the definitions of microstate and macrostate, and be able to differentiate them.
- Learn the definitions of entropy and spontaneity.
- Learn how spontaneity and changes in entropy relate to free energy changes and chemical processes. Apply this knowledge within the special circumstances of the lab apparatus.
- Understand the extent of the relationship between entropy and disorder.
- Understand why changes in entropy favor different macrostates.

Laboratory Skills

- Calculate the molar density of the model system.
- Understand the difference between local and global density.
- Understand the difference between correlation, causation, and coincidence.
- State and test a hypothesis.

Equipment

- Clear, rigid container with removable lid and fixed volume
- One or more sets of small, nondeformable, polyhedral particles of sufficient quantity to fill clear container
- One 10 cm (or greater) metric ruler per lab group.

Before you begin

Turn to the "Discussion questions" section at the end of this lab handout and write the definition of "entropy" to the best of your current knowledge. This question will only be considered for completeness and not for the level of accuracy in your current understanding and written description. Do this before reading any of the remainder of this document.

Background

What is entropy?

Entropy is often conflated with disorder. The second law of thermodynamics states that the entropy change in the universe during any process is ≥ 0. Sometimes this law is incorrectly stated as "the disorder in the universe is always increasing." But this is incorrect, because the word "entropy" does not carry any implication about order or disorder. While it is often true that increases in entropy are *correlated* to increases in disorder, no physical law guarantees such a correlation. This lab exercise will teach you the correct definition of entropy and will demonstrate that entropy is not the same as disorder.

What is the definition of entropy then? To understand entropy properly, let us first introduce the closely related concept of states of a system.[1] We can describe any chemical system in terms of its macrostate(s) and microstate(s). A macrostate is a description of the *macroscopic* variables of the system, such as its temperature, pressure, volume, etc.[2] A single microstate is defined by the way the total energy of a system is distributed among each of the forms of kinetic and potential energy contained in the substance. Finally, entropy is a quantification of the number of microstates states (a.k.a. "energy states") available to a system. In other words, entropy is the number of unique ways the energy can be distributed among all the particles in the system. Since energy is quantized[3] and every real system is composed of a finite number of atoms, then the number of energetic states the system can adopt is also finite. Maxwell Boltzmann provided the mathematical definition of entropy as:

$$S = k_B \cdot \ln(W) \qquad \text{(eq.1)}$$

in which S is the entropy, k_B is the Boltzmann constant, and W is the number of available microstates. The term "*available* microstates" is central to the idea of entropy because, a system is only in one microstate at a time. "Available microstates" refers to all those microstates which would produce the same macrostate. As a simple example, a macrostate for a system comprised

[1] "System" is a broad term that can refer to any collection of physical particles. Chemists are most interested in systems comprised of atoms and/or molecules.

[2] These examples— temperature, pressure, and volume— are called macroscopic variables because their concepts are only meaningful at a macroscopic level, in a sense. Temperature is related to the average kinetic energy per particle in a system, and therefore it does not make sense to discuss the temperature of a single particle. Similarly, atoms and molecules are quantum particles with no definite size or volume; we can only meaningfully discuss the volume of a macroscopic collection of particles, such as a block of metal or a cylinder of gas.

[3] "Energy is quantized" refers to the fact that energy only exists in discrete quantities. That is, objects can not have an arbitrary, fractional amount of energy, but only an integer number of energy's smallest units.

two standard dice might be "a total value of seven;" the available microstates would then be all those combinations of individual die values that sum to seven.

In practice, we are usually interested in the value of entropy or change in entropy so that we can calculate a change in free energy for some valuable process. Theoretically, one could accurately calculate the entropy of any substance if the number of available microstates was known. Similarly, calculating a change in entropy would require knowing the number of available microstates at two different points during a process. Unfortunately, for any macroscopic system (e.g. a glass of water, a piece of lumber, a metal paper weight, etc.), the number of microstates is astronomically large, and impractical to try to compute.[4] In this lab, however, we will exploit the known thermodynamic conditions of a special system which will permit qualitative assessments of entropy and entropy changes without having to quantify the value of entropy. At the same time, we will observe any visible changes in disorder to assess the relationship (or lack thereof) between entropy and disorder.

Derivation of the model.

The model system we will use in this lab includes a collection of hard, polyhedral particles to simulate atoms or molecules and a rigid container to ensure a constant volume. By shaking the container, we will simulate the constant random motion of real particles. The thermodynamic conditions in this system are special because they allow us to confidently conclude that any visible changes in the system are a direct result of changes in the system's entropy. The remainder of this section shows how this conclusion is derived.

You should have already learned elsewhere the definition for a change in the Gibbs free energy:

$$\Delta G = \Delta H - T\Delta S \qquad \text{(eq.2)}$$

in which T is the temperature (which is held constant), S is the entropy as defined above, and H is the enthalpy. If the definition of the change of enthalpy (ΔH) is applied to eq.2, we obtain the expanded form:

$$\Delta G = \Delta U + P\Delta V - T\Delta S \qquad \text{(eq.3)}$$

in which P is the external pressure, V is the volume, and U is the internal energy. The term "internal energy" includes the kinetic and potential energy of the system's constituents, but excludes any additional energy due to external forces (e.g. gravity, a magnetic field, etc.). It is important to note that free energy can be defined for any system and that a change in free energy can occur during any *process* and is not limited to chemical reactions. Therefore, eq.3 is also applicable to the model system we will use in this procedure. Any changes in the Gibbs free energy of the model system are also governed by eq.3.

As stated above, our model system uses a rigid container such that its volume can not change. This implies that $\Delta V = 0$ in this special case. Since the particles in our system are non-

[4] Entropy values in a thermodynamic data table are relatively small numbers because of the effect of the natural logarithm and multiplication by k_B, which is a very tiny number.

deformable and have no apparent attractions or repulsions to one another,[5] the system's internal energy, U, will be defined only by the particle's kinetic energy in this special case. In addition, eq.3 requires that the temperature, T, is constant during the process. Since a system's temperature is defined by the average kinetic energy of its particles, eq.3 implies that there is no change in the average kinetic energy per particle during the process. Given this reasoning, eq.3 is reduced to:

$$\Delta G = -T\Delta S \qquad \text{(eq.4)}$$

Notice what eq.4 implies: for any special system that obeys our assumptions, a change in free energy is just the opposite of the change in entropy, multiplied by a constant (T)! Furthermore, we know that spontaneous processes are those for which the change in free energy is less than 0:

$$\Delta G_{\text{spontaneous}} < 0 \qquad \text{(eq.5)}$$

So, a positive ΔS, implying $S_f > S_i$, corresponds to a negative ΔG. This is to say, *if a spontaneous process occurs in the special environment outlined above, that process is guaranteed to have resulted from an increase in entropy.*

This lab experiment uses a physical realization of the model system just derived to study entropy and investigate its relationship with disorder.

[5] While all particles with mass exert a gravitational force on one another, these forces are so small that they are totally ignorable at the scale and level of precision we are interested.

Procedure

1. Read this entire "Procedure" section before continuing. After reading the procedure, turn to the "Discussion questions" section at the end and answer questions 2 and 3.

2. You should complete all steps of this procedure with at least two sets of particles, or as directed by your lab instructor. Record the particle types you will use here.

3. Fill the container with one of the sets of hard polyhedra. Do not attempt to stack or organize the particles in any way as you fill the container, but leave them exactly as they entered the container. Pouring the particles from a plastic bag into the container helps with this goal. Fill the container as much as possible while still being able to fully close the lid. It is ok if you have to press moderately on the lid to get it to close or if you have to hold it closed; but the lid can not be bent or lifted in any place. Seal the lid onto the container using ordinary rubber bands or special, large silicone bands provided.

4. With the lid firmly in place, gently rotate the filled container in order to view this initial arrangement of the particles. Do you see any patterns or visual order? Do all the particles look random and disorganized? Take a photo of one side of the filled container to include in the Observations section below. Alternatively, sketch the view of one side of the container if cell phones are not allowed in your lab. (Tips: Only draw in 2D and approximate particles simply as circles, squares, triangles, etc.) This is the initial configuration or "state" of the system.

5. While keeping the lid firmly sealed on the container, shake the whole system vigorously and consistently to simulate the particles having a constant temperature. Note that, in order to eliminate any appreciable effect of gravity, you must rotate the container in all directions while shaking. Shake the container for at least 10 seconds, listening for any changes in the pattern of sound.

6. As you continued to shake the system, did the sound change? If there was a noticeable change, briefly describe the change in tone, loudness, etc. If you did not notice any change in the sound, simply record "No change."

7. When you stop shaking the system, make sure the lid is facing upward before releasing your grip (rubber band(s) should still be around the container). Gently rotate the container to investigate this final state without disturbing the particle arrangement. Just as in step 3, look at each face of the container for any visible patterns or organization of the particles.[6] If you do not see any visible difference in the particles' configuration between steps 3 and 6, repeat steps 4 and 5 twice more (for a total of three trials).

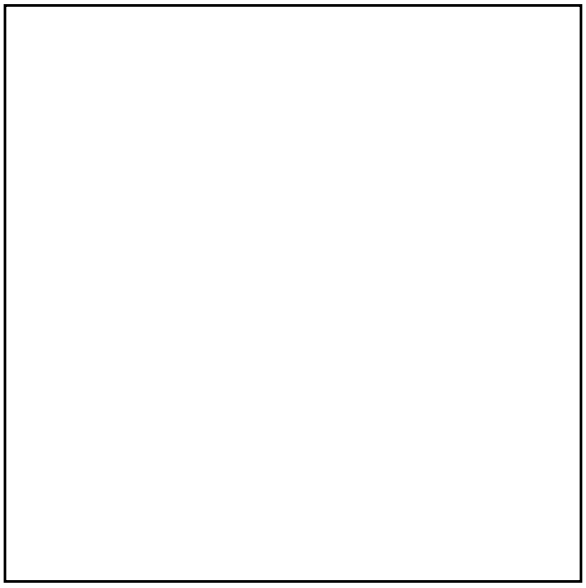
8. After completing all necessary trials of steps 4-6, accept the current configuration as the "final configuration." Photograph/sketch what you see when viewing one or more faces of the container. Write a brief description of any changes you observed (Hint: possible observations include such phrases as, "no change," or, "initial configuration showed no obvious order, while final configuration appeared arranged in stacks or a square grid," or, "Particles initially appeared arranged like ____, but transitioned into a ____ arrangement." But you are not limited to these response examples!)

[6] If you have already learned about "crystal packing," it may be helpful to recall the common patterns such as simple cubic, body-centered cubic, and face-centered cubic. If these terms are unfamiliar to you, ignore this footnote.

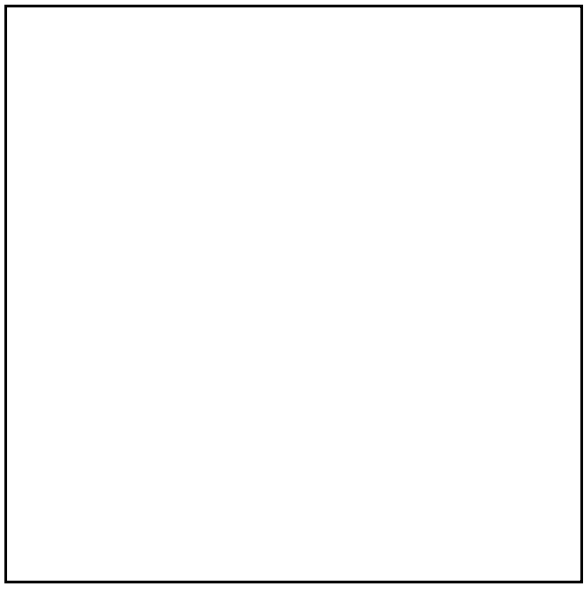
Observations

In the blanks provided, list the polyhedral shape you are working with. If drawing your own sketches, these boxes represent one side of your container already drawn for you.

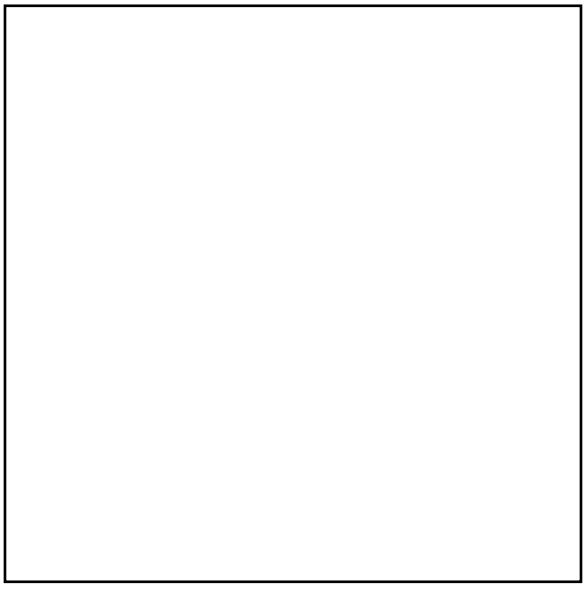
Initial configuration, _____



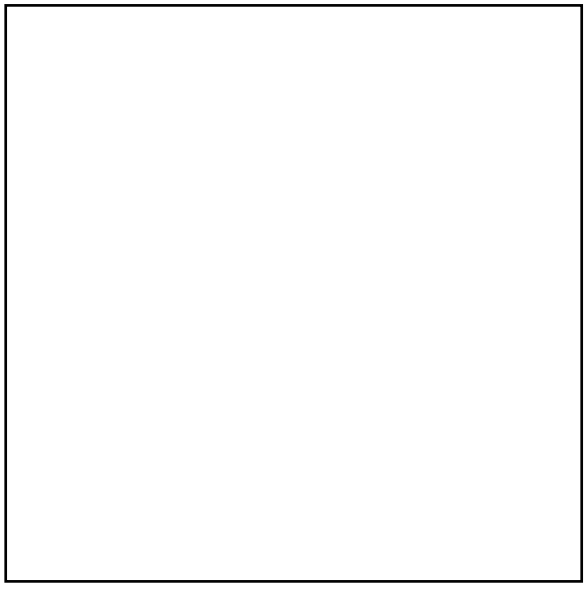
Initial configuration, _____



Final configuration, _____



Final configuration, _____



Discussion questions

1. Write the definition of entropy as you currently understand the term.

2. Thinking of the lab apparatus as a physical "system," can you give an example of a microstate and macrostate of this system? (Hint: your answers may assume any one of the particle shapes available for the experiment.)

3. Based on your understanding of the procedure and the definition of entropy, construct a hypothesis about the relationship between entropy (or entropy changes) and disorder. (Hint: make an educated guess about what the initial and final states of the system will look like. From these guesses, construct a hypothesis in the form of:
"Disorder [is/is not] [always/never/sometimes] [the same as/caused by/correlated to/only sometimes coincident with] [entropy/±changes in entropy]")

4. List any special constraints were present in, or assumptions made about, the special model system. (Hint: review the derivation of the model.)

5. Consider a 2 L cylinder of Ar gas (which is approximately and ideal gas) at STP.
    a. How many moles of Ar are in the cylinder?

    b. If Ar atoms are assumed to be spheres with a radius of 188 pm, what is the total volume of atoms in the cylinder, in L?

6. Was there any change in volume during the experiment? Defend your answer in light of your answer to the previous question.

7. Describe any visible differences in the initial and final states of the physical model system.

8. What implication(s), if any, does the derivation of the model have upon the interpretation of your observations? Can you confidently make any comparative statement(s) about the entropy of the initial and/or final states of the system?

9. What is the definition of entropy? Is entropy the same thing as disorder? Explain your findings and whether your hypothesis was proven or disproven.

10. Can you explain your observation(s) in terms of the definition of entropy? In other words, how can your understanding of entropy be used to explain the observed process?

11. In many real-life scenarios, a process resulting in a positive change in entropy will also have a corresponding increase of spatial disorder. Can you think of any reasons why this could frequently be the case? (Hint: consider what effect removing assumptions about this special model system might have on its behavior.) Why is entropy often confused with disorder?

12. At what length scale is the lab apparatus a realistic model of a microscopic system?

a. Calculate the molarity of pure water at STP.

b. Calculate the approximate volume of a single water molecule in solution at STP.

c. The density of Al and Pb are 2.70 g/mL and 11.35 g/mL, respectively. Calculate the approximate volume of a single Al and Pb atom.

d. What would the clear container's edge length have to be (in nm) to make the lab apparatus an accurate scale model of a metal? What is the scale factor of the lab model? (Hint, assume that your particles are somewhere between the size of Al and Pb atoms.)