

# 1 Einstein Solid

Name \_\_\_\_\_

Section \_\_\_\_\_

Date \_\_\_\_\_

## Objective

To develop a quantum-mechanical model of an elemental solid (*e.g.* aluminum) and introduce the ideas of statistical mechanics.

## Overview of the Model

One of the earliest successful applications of quantum mechanics was done by Albert Einstein in 1907 when he developed a model of an elemental solid (*i.e.* one that consists of a single element from the periodic table like aluminum, lead, *etc.*). We start by assuming that each atom in the solid is bound in a square lattice with each of six neighbors (see Figure 1). Each bond is treated as a simple spring so the mechanical energy for a single atom is

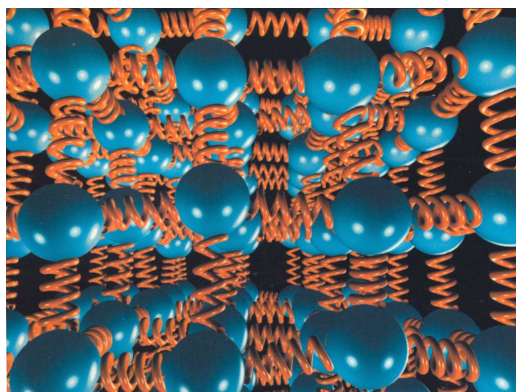


Fig. 1 Einstein solid.

$$E = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}k(x^2 + y^2 + z^2) \quad (1)$$

where  $k$  is the spring constant of the bond, the coordinates  $x$ ,  $y$ , and  $z$  are relative to the equilibrium position of the atom and  $v_x$ ,  $v_y$ , and  $v_z$  are the components of the velocity. Einstein used an idea pioneered by Max Planck in 1901 and guessed the energy in the solid came in discrete pieces or quanta that were all the same size. Adding or removing these quanta heated or cooled the solid. Many years later the quantum mechanical energy  $E$  for a mass on a spring was found to be

$$E = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega \quad (2)$$

where  $\hbar$  is Planck's constant,  $\omega$  is related to the spring constant  $k$  of the bond mentioned above, and  $n_x$ ,  $n_y$ , and  $n_z$  represent the number of quanta associated with each degree of freedom of the spring. The degrees of freedom here correspond to the three possible directions each atom can vibrate. The size of each energy quantum is  $\epsilon = \hbar\omega$ . The total number of energy quanta in the solid is labeled  $q_A$  so the internal energy is  $E_{int} = q_A\epsilon$ . We then assume that all microstates of the solid have an equal probability of being populated. A microstate is a specific arrangement of the quanta on the atoms in the solid.

## Activity 1: The Statistics of Matter

Before you embark on building the model of the Einstein solid consider some ideas from your previous study of gases. You will make some predictions here about the statistical nature of matter that you can refer back to later on in this unit.

(a) Consider a gas in a container. Would it violate Newton's Laws or any other physical law if all the particles in the gas collided in such a way that all of the gas particles ended up in the bottom half of the container leaving the top half empty?

(b) Is such a scenario likely? Explain.

(c) If you started out with all the gas in the bottom half of the container how likely is it to stay there?

The questions you answered above are addressing the notion of irreversibility. Many processes in nature appear to proceed in one ‘direction’ only. When you add milk to coffee it disperses throughout the coffee. After it is dispersed, the milk never re-concentrates into a blob of milk in the middle of the coffee. These processes go from a more orderly configuration (a concentrated drop of milk) to a disordered state (milk spread throughout the liquid). The reverse never happens. We will return to this notion again in this laboratory.

**Activity 2: Calculating the Multiplicity of Some ‘Solids’**

(a) You will first calculate the configurations of the quanta (the microstates) for a VERY simple solid consisting of a single atom! The number of atoms for solid  $A$  is  $N_A = 1$  so there are three degrees of freedom  $N_a = 3$  because there is one degree of freedom for each spatial direction. The atom’s vibration can be decomposed into three components, one for each direction. Let the ‘solid’ contain two quanta of energy so  $q_A = 2$ . Make a table with the headings  $n_1$ ,  $n_2$ , and  $n_3$  and in each row enter one arrangement of the two quanta. This is a microstate. Make a table with all of the possible microstates. The multiplicity  $\Omega_A$  of the system is the number of all possible microstates. What is your multiplicity? Record it here.

(b) You can calculate the multiplicity  $\Omega_A$  using the expression

$$\Omega(N_A, q_A) = \frac{(q_A + 3N_A - 1)!}{q_A!(3N_A - 1)!} \quad (3)$$

Make the calculation for  $N_A = 1$  and  $q_A = 2$ . Does this agree with your result in part 2.a?

(c) Now do the same thing for a different ‘solid’. This time for solid  $B$ , let  $N_B = 2$  (two whole atoms!) and  $q_B = 1$ . How many degrees of freedom does solid  $B$  have? Make a table analogous to the one in part 2.a on the same sheet as before. What is the multiplicity of solid  $B$ ? Record it here. Use the expression in Activity 2.b to check your calculation.

**Activity 3: Putting the ‘Solids’ Together**

When two solids are brought together heat/energy can flow between the two objects. For the model of the Einstein solid you are building this corresponds to energy quanta ( $\hbar\omega$ ) moving from atom to atom and occupying different microstates of the combined system.

(a) Now bring your solids  $A$  and  $B$  ‘together’ into a single system. What is  $N_{AB}$  the total number of atoms? What is the number of degrees of freedom of the combined system?

(b) What is the total number of energy quanta  $q_{AB}$  for the combined system?

(c) What is the total multiplicity  $\Omega_{AB}$  for the combined system with  $q_A = 2$  and  $q_B = 1$ ? This is the initial macrostate of the system. A macrostate is a configuration of the system defined here by the total number of atoms and quanta in each solid. In this case the macrostate is defined by  $N_A = 1$ ,  $q_A = 2$ ,  $N_B = 2$ , and  $q_B = 1$ .

(d) Now take the energy quantum in solid  $B$  and put it in solid  $A$ , *i.e.*, let heat flow from solid  $B$  into solid  $A$ . This is now a macrostate where  $q_A = 3$  and  $q_B = 0$ . What is the new multiplicity  $\Omega_A$  for solid  $A$  and the multiplicity  $\Omega_B$  for solid  $B$ ?

(e) What is the multiplicity  $\Omega_{AB}$  for the combined system (solids  $A$  and  $B$ )?

(f) Remember that a macrostate is defined by the combination of  $N_A$ ,  $N_B$ ,  $q_A$ , and  $q_B$ . Which macrostate had the greatest multiplicity,  $(q_A = 2, q_B = 1)$  or  $(q_A = 3, q_B = 0)$  (remember that  $N_A$  and  $N_B$  are the same in each configuration so we don’t list those parameters here)?

(g) If the energy quanta can move from atom to atom which macrostate  $(q_A = 2, q_B = 1)$  or  $(q_A = 3, q_B = 0)$  is most probable? Why?

(h) If you started out in the  $(q_A = 3, q_B = 0)$  macrostate is it more likely that you will remain in that macrostate or evolve to the  $(q_A = 2, q_B = 1)$  macrostate? Why?

What you have discovered is a version of the irreversibility mentioned earlier. One macrostate  $(q_A = 2, q_B = 1)$  is preferred over the other because it has more microstates than the other. This result depends critically on your assumption that all states are equally populated.

#### Activity 4: Using *StatMech* For More Complex Cases

You should have found in the previous activity that the  $(q_A = 2, q_B = 1)$  macrostate was more likely to occur and the process proposed in part 3.d is relatively unlikely. In other words, it is more likely for energy to be

spread evenly throughout the system. This is good news because it means the statistical picture we are painting is consistent with reality. Remember what happens to the blob of milk in the coffee.

(a) You should realize that making the sorts of calculations you did in Activity 3 above would become rather painful for say  $N_A = 300$  atoms. In order to push the model further you will use a software packaged called *StatMech* to perform the same calculations. To run the program go to the Physics Applications menu and click on *StatMech*. You should see a window like the one below. The top of the window has several entry boxes

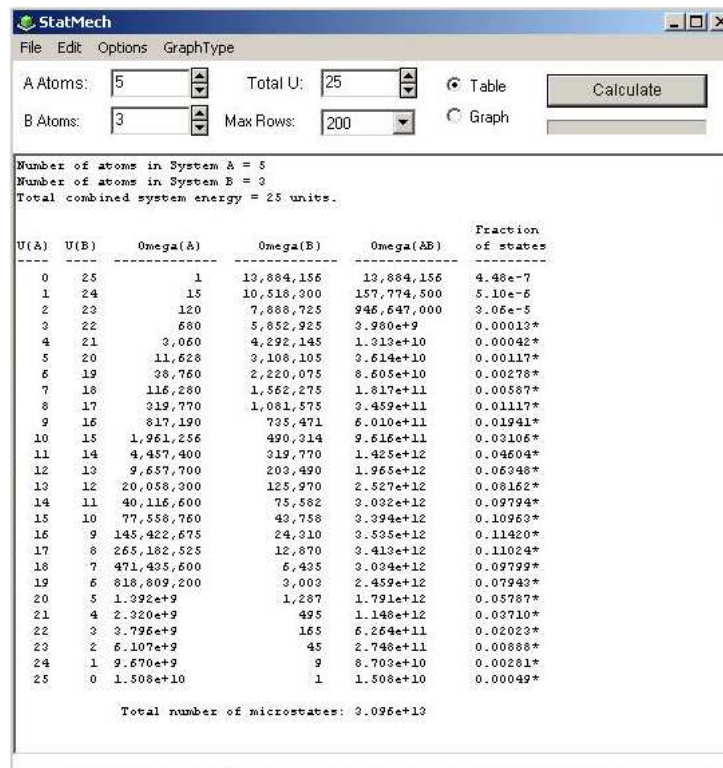


Figure 2: The *StatMech* window showing the table of multiplicities for each microstate. Each row corresponds to a different value of  $q_A$ .

where you can set the number of atoms ( $N_A$  and  $N_B$ ) and the total number of energy quanta in the system  $U$ . The parameter  $U$  is the total internal energy  $_{int}$  in the system in units of  $\epsilon = \hbar\omega$ . It is equivalent to the sum  $q_{AB} = q_A + q_B$ . You can also set the number of rows of microstates to print out or choose to view a graph instead of the table. To test the operation of *StatMech* redo the calculations of the microstates that you did in Activity 3. Make sure your results in Activity 3 agree with the output of *StatMech*. You will also see there are other macrostates that were ignored in Activity 3 for simplicity.

(b) Now run *StatMech* for the case where  $N_A = 10$ ,  $N_B = 20$ ,  $U = 500$ . What is the value of  $q_A$  for the most probable microstate? Record it here. Click on the button at the top of the *StatMech* window and choose graph. You will see a graph of the table and it should look something like Figure 3. The vertical axis is the probability of a particular macrostate divided by the maximum probability of any macrostate. The horizontal axis is  $U_A/U_{TOT}$  where  $U_A$  is the energy of solid A in units of  $\epsilon$  (equivalent to  $q_A$ ) and  $U_{TOT}$  is the total internal energy of the solid in units of  $\epsilon$  (equivalent to the total number of quanta  $q_{AB}$ ). What is the value of  $U_A/U_{TOT}$  for the most probable state? How is this value related to the value of  $q_A$  for the most probable microstate? Also, explain in words what this plot is showing you.

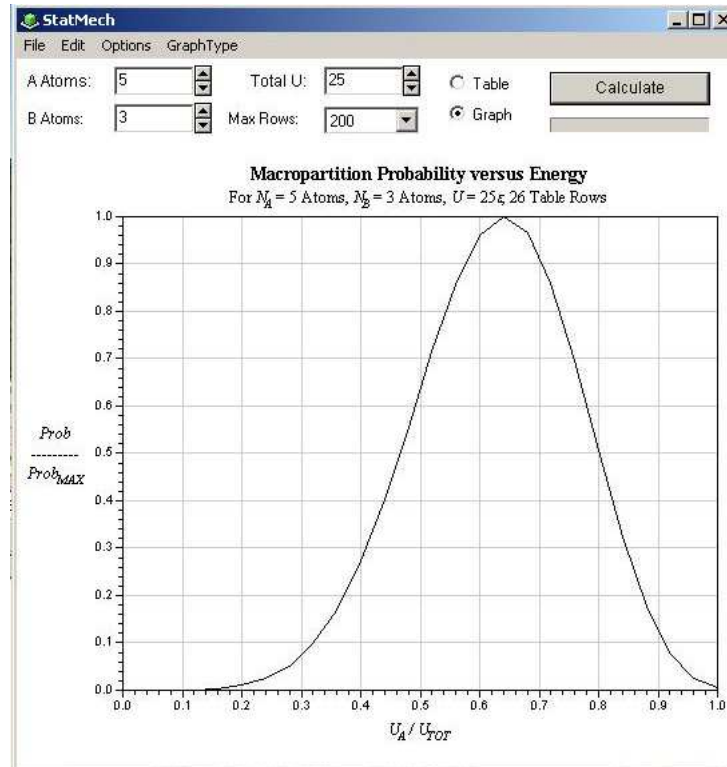


Figure 3: The StatMech window showing a graph of the multiplicities as a function of  $E_A/E_{int}$  where  $E_A = q_A \hbar \omega$  and  $E_{int} = q_{AB} \hbar \omega = (q_A + q_B) \hbar \omega$ .

(c) How wide is the distribution of microstates? Measure this number by estimating the full-width-half-maximum (FWHM) from your graph. Do this by finding the largest value on the vertical axis, divide it by two, and find the two points on either side of the peak where the distribution is equal to that half-maximum. Take the difference between these two points and this is the FWHM. Record your result here.

(d) Now repeat steps 4.b-c with  $U = 100,000$  and  $N_A$  and  $N_B$  at their last values. What is the most probable value of  $U_A/U_{TOT}$  and the FWHM? How have things changed.

(e) Keeping  $U = 100,000$  now repeat steps 3.b-c, but this time double the values of  $N_A$  and  $N_B$ . Record the most probable microstate and the FWHM. Repeat this doubling of the number of atoms in each solid while keeping  $U$  fixed at least 3-4 times. Record the most probable microstate and the FWHM each time along with  $N_A$  and  $N_B$ .

(f) How does the value of  $q_A$  for the most probable microstate change as the number of atoms increases?

(g) How does the FWHM change as the number of atoms increases?

### Activity 5: Irreversibility

You will now use the results from the previous Activity to delve into some of the implications of the statistical mechanics of the Einstein solid.

(a) As the number of atoms increases, what happens to the probability for finding the system in a microstate different from the most probable microstate? Use the results of your calculations to explain your answer.

(b) When the system is in a microstate far from the most probable one, what is the most likely thing to happen as energy or heat flows around the system?

(c) For the last calculation what is the probability of the state with the minimum value of  $q_A$ ? In other words what is the probability that all of the quanta would end up all in solid  $A$ ? What is the probability of the most probable state?

(d) Go back to the questions in Activity 1 and look at your answers. Do they still appear to be correct? A situation where all of the gas particles end up in one part of the container is a macrostate of the system analogous to the situation in Activity 5.c where all of the quanta end up in one of the solids and not the other. Answer those questions in Activity 1 again in terms of microstates, macrostates, and probability.

The behavior you are seeing here is for an Einstein solid, but is actually typical for most macroscopic systems. These systems have a large number of atoms or molecules with a variety of different energy states available. They evolve to the most probable macrostate and there is essentially no chance to occupy a state far from the most probable one. When two materials are first put in thermal contact they may be far from the most probable macrostate, but they equilibrate at that most probable one (where the temperatures are equal) and never go back. This is the irreversibility.

### Activity 6: Homework Problems (E - exercise, P - problem)

1. (E) Consider the following 'gas'. It consists of four atoms in a cubical box. At any instant, there is a 50% chance of each atom being in the left half of the box ( $L$ ) or the right half ( $R$ ). Make a table showing all the microstates of this system. (Hint: There are 16.) How many macrostates are there? How many microstates are in each macrostate?

2. (E) Show that for  $N$  gas atoms in a box, the number of possible microstates is  $2^N$  when microstates are defined by whether a given molecule is in the left half of the box or the right half of the box. The volumes of each half are equal.
3. (E) Imagine that we have an ideal gas consisting of 15 molecules. We can flip the signs of each of the three velocity components of a given molecule without changing its overall energy (and thus without changing the gas's macrostate). How many possible patterns of sign choices are there?
4. (E) Calculate the multiplicity of an Einstein solid with  $N = 1$  and  $E_{int} = 6\epsilon$  by directly listing and counting the microstates. Check your work by using equation 3.
5. (E) Calculate the multiplicity of an Einstein solid with  $N = 1$  and  $E_{int} = 5\epsilon$  by directly listing and counting the microstates. Check your work by using equation 3.
6. (E) Use equation 3 to calculate the multiplicity of an Einstein solid with  $N = 4$  and  $E_{int} = 10\epsilon$ .
7. (E) Use equation 3 to calculate the multiplicity of an Einstein solid with  $N = 3$  and  $E_{int} = 15\epsilon$ .
8. (E) How many times more likely is that the combined system of solids described in the table below will be found in macropartition 3:3 than in macropartition 0:6, if the fundamental assumption is true?
9. (E) How many times more likely is it that the combined system of solids describe in the table below will not be found in macropartition 3:3 than it is to be found in macropartition 0:6, if the fundamental assumption is true?

Macropartition	$E_A$	$E_B$	$\Omega_A$	$\Omega_B$	$\Omega_{AB}$
0:6	0	6	1	28	28
1:5	1	5	3	21	63
2:4	2	4	6	15	90
3:3	3	3	10	10	100
4:2	4	2	15	6	90
5:1	5	1	21	3	63
6:0	6	9	28	1	28
Total=					462

Table 1: Possible macropartitions for  $N_A = 1$ ,  $N_B = 1$ ,  $E_{int} = 6\epsilon$ .

10. (E) Consider the system consisting of a pair of Einstein solids in thermal contact. A certain macropartition has a multiplicity of  $3.7 \times 10^{1024}$ , while the total number of microstates available to the system in all macropartitions is  $5.9 \times 10^{1042}$ . If we look at the system at a given instant of time, what is the probability that we will find it to be in our certain macropartition?
11. (E) Consider the system consisting of a pair of Einstein solids in thermal contact. A certain macropartition has a multiplicity of  $1.2 \times 10^{346}$ , while the total number of microstates available to the system in all macropartitions is  $5.9 \times 10^{362}$ . If we look at the system at a given instant of time, what is the probability that we will find it to be in our certain macropartition?
12. (E) Consider the system consisting of a pair of Einstein solids in thermal contact. Imagine that it is initially in a macropartition that has a multiplicity of  $8.8 \times 10^{123}$ . The adjacent macrostate closer to the equilibrium macrostate has a multiplicity of  $4.2 \times 10^{1234}$ . If we look at the system a short later, how many times more likely is it to have moved to the second macropartition than to have stayed with the first?

13. (E) Consider the system consisting of a pair of Einstein solids in thermal contact. Imagine that it is initially in a macropartition that has a multiplicity of  $7.6 \times 10^{3235}$ . The adjacent macropartition closer to the equilibrium macropartition has a multiplicity of  $4.1 \times 10^{3278}$ . If we look at the system a short time later, how many times more likely is it to have moved to the second macropartition than to have stayed with the first?
14. (P) Suppose you put 100 pennies in a cup, shake it up, and toss them all into the air. (a) After landing, how many different head-tail arrangements (microstates) are possible for the hundred pennies? (b) What is the probability of finding exactly 50 heads? (c) 49 heads? (d) 1 head?
15. (P) You ask your roommate to clean up a mess he or she made in your room. Your roommate refuses, because cleaning up the mess would violate the second law of thermodynamics, and campus security's record of your roommate's legal violation is already excessive. Gently but firmly explain why complying will not put your roommate at risk of such an infraction.
16. (P) The classic statement of Murphy's law reads, 'If something can go wrong, it will.' Explain how this is really a consequence of the second law of thermodynamics. (Hint: What is the entropy of 'wrong' in a given context compared to the entropy of 'right'?)
17. (P) Run the *StatMech* program to answer the questions below.
  - (a) For two Einstein solids in contact with  $N_A = N_B = 100$  and  $E_{int} = 200\epsilon$  answer the following questions. (1) How many times more likely is the system to be found in the center macropartition than in the extreme macropartition where  $E_A = 0$  and  $E_B = 200\epsilon$  (2) What is the range of values that  $E_A$  is likely to have more than 99.98% of the time? (3) if  $E_A$  were initially to have the extreme value 0, how many times more likely is it to move to the next macropartition nearer the center than to remain in the extreme one?
  - (b) Answer the same question as in (a) for a run where you scale everything up by a factor of 10, so that  $N_A = N_B = 1000$  and  $E_{int} = 2000\epsilon$ .
  - (c) Answer the same question as in (a) for a run where  $N_A = N_B = 1000$  and  $E_{int} = 200\epsilon$ . Comment on the effect that increasing just the size of the system by a factor of 10 has on these answers.
  - (d) Answer the same question as in (a) for a run where  $N_A = N_B = 100$  and  $E_{int} = 2000\epsilon$ . Comment on the effect that increasing just the energy available to the system by a factor of 10 has on these answers.
18. (P) Consider two Einstein solids in thermal contact. The solids have different values of  $N$  but are identical in all other respects. It is plausible, since every atom in the combined system is identical, that in equilibrium the energy will be distributed among the solids in such a way that the average energy per atom is the same. Use *StatMech* to test this hypothesis in the situation where  $E_{int} = 1000\epsilon$  and  $N_A$  and  $N_B$  have various different values such that  $N_A + N_B = 1000$ . (Set Max Rows to 1000 so that you can see every macropartition).
  - (a) Is it true in most cases that in the most probable macropartition the solids have energies such that the average energy per atom in each is the same? Is it strictly true in every case? Answer these questions by discussing the values  $N_A$  and  $N_B$  you tested, and whether the actual most probable macropartition is the same as that predicted by the hypothesis.
  - (b) In any case where the hypothesis does not work, does increasing both  $N_A$  and  $N_B$  by a factor of 10 or 100 (but leaving  $U$  alone) yield a result more or less consistent with the hypothesis?
  - (c) Speculate as to the value of this hypothesis in the large- $N$  limit.
19. (P) For the following questions, you will find that using *StatMech* is by far the fastest way to calculate the multiplicity.
  - (a) What is the entropy of an Einstein solid with 5 atoms and an energy of  $15\epsilon$ ? Express your answer as a multiple of  $k_b$ .



- (b) What is the entropy of an Einstein solid with 50 atoms and an energy of  $100\epsilon$ ? Express your answer as a multiple of  $k_b$ .
20. (P) A certain macropartition of two Einstein solids has an entropy of  $305.2k_b$ . The next macropartition closer to the most probable one has an entropy of  $335.5k_b$ . If the system is initially in the first macropartition and we check it again later, how many times more likely is it to have moved to the other than to have stayed in the first?
21. (P) My calculator cannot display  $e^x$  for  $x > 230$ . One can calculate  $e^x$  for larger values of  $x$  as follows. Define  $y$  such that  $x = y \ln 10$ . This means that  $e^x = e^{y \ln 10} = (e^{\ln 10})^y = 10^y = 10^{x \ln 10}$ . Note that we can calculate 10 raised to a non-integer power (for example,  $103.46$ ) as follows:  $10^{3.46} = 10^{3+0.46} = 10^3(10^{0.46}) = 2.9 \times 10^3$ . Use these techniques to solve the following problem. The entropy of the most probable macropartition for a certain system of Einstein solids is  $6025.3k_b$ , while the entropy of an extreme macropartition is only  $5755.4k_b$ . What is the probability of finding the system at a given time in the extreme macropartition compared to that of finding it in the most probable macropartition?
22. (P) In principle, the entropy of a isolated system decreases a little bit whenever random processes cause its macropartition to fluctuate away from the most probable macropartition. We can certainly see this with small systems. But is this really a possibility for a typical macroscopic system? Imagine that we can measure the entropy of a system of two solids to within 2 parts in 1 billion. This means that we could just barely distinguish a system that has an entropy of  $4.99999999 \text{ J/K}$  (eight 9s!) from one that has  $5.00000000 \text{ J/K}$ . (This is a reasonable entropy for a macroscopic system).
- (a) Imagine that the entropy of the equilibrium macropartition is  $5.00000000 \text{ J/K}$ . Show that the approximate probability that at any given time later we will find the system in a macropartition with entropy  $4.99999999 \text{ J/K}$  (*i.e.*, with an entropy that is only barely measurably smaller) is about 10315,000,000,000,000 times smaller than the probability we will still find it to have entropy  $5.00000000 \text{ J/K}$ . (Hint: See problem 17.)
- (b) Defend the statement that the entropy of an isolated system in thermal equilibrium never decreases.

## 2 Entropy and Temperature

Name \_\_\_\_\_

Section \_\_\_\_\_

Date \_\_\_\_\_

### Objective

To explore the connection between the fundamental definition of entropy and temperature.

### Overview

Recall our definition of the entropy of a system

$$S = k_B \ln \Omega \quad (4)$$

where  $k_B$  is Boltzmann's constant and  $\Omega$  is the multiplicity or number of microstates. A microstate is defined by a particular arrangement of energy quanta among the atoms. A macrostate is defined by the total number of energy quanta  $q$  and the number of atoms  $N$ . We are building a model of an elemental solid (*e.g.*, like aluminum) where the total internal energy in the solid  $E_{int}$  is described by

$$E_{int} = q\hbar\omega \quad (5)$$

where  $\hbar$  is Planck's constant divided by  $2\pi$  and  $\omega$  is a constant that characterizes the strength of the bonds between the atoms. The parameter  $q$  is the total number of quanta in the system and is a constant. These quanta are statistically distributed over the  $N$  atoms of the solid so all possible states of the system are equally likely and the multiplicity  $\Omega$  is

$$\Omega = \frac{(q + 3N - 1)!}{q!(3N - 1)!} \quad (6)$$

This model of an elemental solid is called an Einstein solid.

We want to find a connection between the entropy defined in Equation 1 and the temperature. Recall how temperature is usually defined relative to some properties of matter like the freezing and boiling points of water. You are developing the microscopic picture of entropy, but it won't be successful until you can connect it to the observed behavior of bulk matter and our familiar notions of temperature.

### Activity 1: The Entropy of Einstein Solids in Thermal Equilibrium

(a) To start connecting the entropy to the temperature you have to study the behavior of the entropy as the energy changes. To do this we will study two Einstein solids ( $A$  and  $B$ ) in thermal equilibrium with each other. Their total internal energy will be

$$E_{int} = q_{AB}\hbar\omega = (q_A + q_B)\hbar\omega \quad (7)$$

where  $q_A$  and  $q_B$  are the numbers of energy quanta in each solid and  $q_{AB}$  is their sum.

Use the program *StatMech* (see the **Physics Applications** menu) for the configuration where you choose  $N_A > 100$ ,  $N_B > 80$  and  $U > 400$ . The label  $U$  in the *StatMech* window refers the total number of energy quanta in the system in units of  $\hbar\omega$  and is equivalent to  $q_{AB}$  here. An example of the output of *StatMech* is shown in Figure 1. The first two columns in the lower panel of Figure 1 represent  $U(A)$  and  $U(B)$ , the energies in each individual solid (again in units of  $\hbar\omega$ ) and are equivalent to  $q_A$  and  $q_B$ . After you perform the calculation with *StatMech* scan quickly down the column labeled 'Omega(AB)'. If any of the exponents you see exceed the value 307, then run the calculation again with smaller inputs until no exponent exceeds 307. This limitation is a restriction on MicroSoft *Excel* that you will use later to make plots. Record your values of  $N_A$ ,  $N_B$ , and  $U$ .

(b) Now generate plots of  $S_{AB} = S_A + S_B$ ,  $S_A$ , and  $S_B$  from the *StatMech* table. You can do this with *Excel*, but there are some intermediate steps necessary. Start Microsoft *Word* first. Next, go to the *StatMech* window, highlight the table, copy it (see the **Edit** menu on the *StatMech* window), and paste it into the *Word* document. In *Word* edit out all the commas (',') and asterisks (\*) in the file (use the **Replace** option under the **Edit** menu).

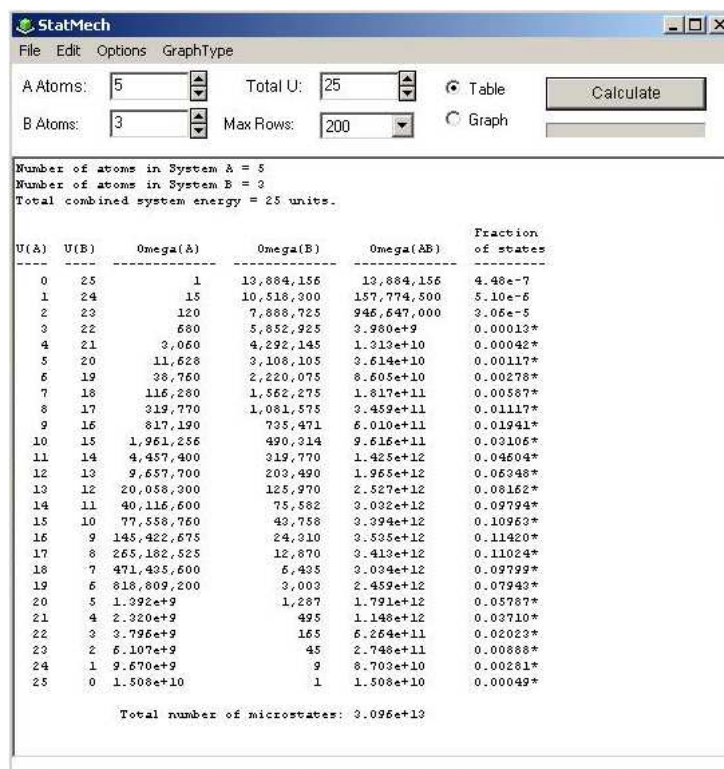


Figure 4: The StatMech window showing the table of multiplicities for each microstate. Each row corresponds to a different value of  $q_A$ .

Save the Word file, but save it as a plain text ('.txt') file. You can now open the file in *Excel*. When you open the file, *Excel* pops up a Text Import Wizard that will guide you through the format of the input file. The defaults usually seem to work. Use *Excel* to calculate and plot on one graph  $S_{AB}$ ,  $S_A$ , and  $S_B$  as a function of  $q_A$ . Print out your plot and attach it to this unit.

(c) What is  $q_A$  for the most probable macrostate? What mathematical condition can you impose on the total entropy  $S_{AB}$  to determine the most probable macrostate? How do you think the temperatures of solids  $A$  and  $B$  are related at the most probable microstate?

(d) How are the slopes of  $S_A$  and  $S_B$  related to one another at the most probable microstate?

(e) How is  $E_A$ , the energy in solid  $A$  related to  $q_A$ ? How is  $E_B$ , the energy in solid  $B$  related to  $q_A$ ? Remember that  $q_{AB}$  is a constant and  $q_{AB} = q_A + q_B$ . Calculate the differentials  $dE_A$  and  $dE_B$  and rewrite the answer in part 1.d in terms of  $dS_A/dE_A$  and  $dS_B/dE_B$ .

### Activity 2: Relating Entropy and Temperature

(a) Using the spreadsheet you generated in Activity 1, calculate  $dS_A/dq_A$  as a function of  $q_A$  and plot it. You can do this to an adequate approximation by doing taking the difference between  $S_A$  at adjacent values/rows of  $q_A$ . Suppose your spreadsheet has the values of  $S_A$  in column  $H$ . The *Excel* syntax for estimating the derivative for the first value of  $q_A$  (the first row) is `'=(H2-H1)/1.0'` where H2 is the value in the second row and H1 is the value in the first row. The numerator of one is redundant, but it shows you are approximating the derivative using the data from points that differ by 1.0 in  $q_A$ . The syntax for  $dS_A/dq_A$  for the second value of  $q_A$  is `'=(H3-H2)/1.0'` and so on. Do the same for  $dS_B/dq_A$  and  $dS_{AB}/dq_A$ . Does the slope of  $S_{AB}$  pass through zero at the correct spot (recall part 1.c)? How are  $dS_A/dq_A$  and  $dS_B/dq_A$  related at the most probable macrostate. Does you plot agree with that result?

(b) If the energy  $E_A$  and  $q_A$  of solid  $A$  increases what should the temperature of solid  $A$  do? If the energy  $E_A$  of solid  $A$  increases what happens to  $dS_A/dq_A$  in your plot? Do the temperature and  $dS_A/dq_A$  change in the same way or in a different way as  $E_A$  increases?

(c) We want to come up with a relationship between temperature and the entropy. From the results above (parts 1.a-e) you should have found

$$\frac{dS_A}{dE_A} = \frac{dS_B}{dE_B} \quad (8)$$

and

$$T_A = T_B \quad (9)$$

for the most probable macrostate. This means there is some function of the temperature  $T$  such that

$$f(T) = \frac{dS}{dE} \quad (10)$$

for each solid that will be equal at equilibrium. We want  $f(T)$  to behave like the temperatures we are accustomed to using. In other words, as the energy in the solid increases  $T$  should increase. Recall part 2.b and the behavior of  $dS/dE$  as  $T$  increases. Try to guess a mathematical form of  $f(T)$  that acts like 'normal' temperatures and one that doesn't. Explain your reasoning.

Solid	$dE/dT$ per mole	Solid	$dE/dT$ per mole
Lead	26.4 J/K – mole	Gold	25.4 J/K – mole
Silver	25.4 J/K – mole	Copper	24.5 J/K – mole
Iron	25.0 J/K – mole	Aluminum	26.4 J/K – mole

Table 2: Heat capacities ( $dE/dT$ ) for several elemental solids.

(d) How would you choose which of the forms you guessed in part 2.c is the correct one?

### Activity 3: Determining $f(T)$ and the Heat Capacity

In the previous Activity you should have found that the mathematical form of  $f(T)$  has to be something like  $1/T^n$  where  $n$  is some positive number. This is necessary because your graphs should show that as the energy  $E_A$  (and the number of quanta  $q_A$ ) of the solid increases  $f(T) = dS/dE$  goes down. To make sure the temperature  $T$  behaves reasonable (and goes up with  $E_A$  and  $q_A$ )  $f(T)$  must be some inverse of function of  $T$ . To decide exactly which function is right requires comparing Equation 7 or some result from it to some data.

Consider Table 1 of heat capacities ( $dE/dT$ ) for several elemental solids for high temperatures. The heat capacities are constant with respect to temperature and are similar in value to one another. These are the data that will help us determine  $f(T)$ . To calculate  $dE/dT$  we must find a relationship between  $E$  and  $T$  for the Einstein solid.

(a) Start with Equations 1 and 7 and the chain rule and show the following.

$$\frac{dS}{dE} = k_B \frac{1}{\Omega} \frac{d\Omega}{dE} \quad (11)$$

(b) Use Equation 2 to show

$$dE = \hbar\omega dq \quad \text{and} \quad \frac{d\Omega}{dE} = \frac{1}{\hbar\omega} \frac{d\Omega}{dq} \quad . \quad (12)$$

(c) Starting with Equations 1 and 3 one can show

$$\frac{d\Omega}{dq} = \frac{3N\hbar\omega}{E}\Omega \quad . \quad (13)$$

Combine this equation (number 10) and the results from 3.a-b to get a relationship for  $dS/dE$  for the Einstein solid in terms of  $N$  and  $E$ . Set that expression equal to  $f(T)$ , and solve for  $E$  the internal energy. It is the derivative of this last equation ( $dE/dT$ ) that will give you the heat capacity. What function of  $f(T)$  will give a result that is independent of temperature when you take the derivative with respect to  $T$  of your expression for the internal energy  $E$ ?

(d) What is the final form of Equation 7 and  $f(T)$ ?

(e) Calculate the mean and standard deviation of the heat capacity of the elemental solids in Table 1. Calculate the heat capacity ( $dE/dT$ ) for the Einstein solid using your results from parts 3.c-d. Is the heat capacity for the Einstein solid consistent with the measured ones?

#### Activity 4: The Second Law of Thermodynamics

(a) Go back to your plots of the entropy as a function of  $q_A$  from part 1.b. Consider two Einstein solids that are brought together at a value of  $q_A$  that is higher than the equilibrium one at the most probable macrostate. Choose a value of  $q_A$  that is halfway between the most probable value and the maximum. Once the two Einstein solids are in contact, how will the system evolve? What happens to  $S_A$  and  $S_B$ ? Do they go up, down, or stay the same? What happens to the total entropy  $S_{AB}$ ? In fact, based on your plot from part 2.b, is there any circumstance where  $S_{AB}$  will not increase?

(c) To vividly see what happens when Einstein solids come in thermal contact, run the program *equilib.exe* available in the **Physics Applications** menu. This program starts with two Einstein solids with all the energy quanta in solid *B*. It simulates the evolution of the two solids as they march toward thermal equilibrium. Click **Evolve** to see the simulation run.

What you should have discovered in the previous part is that the entropy of the combined systems always increases regardless of what configuration the Einstein solids are in when they come in contact. The system always evolves to the most probable, most disordered macrostate where the temperatures will be equal and the entropy is a maximum. The energy quanta are most spread out. This result is stated in several different ways, but the most succinct is simply  $\Delta S > 0$  for an isolated system. The entropy of an isolated system always increases. This is called the Second Law of Thermodynamics.

#### Activity 4: Homework Problems

1. (E) An object's entropy is measured to increase by  $0.1 J/K$  when we add  $35 J$  of energy. What is its approximate temperature? (Assume that the object's temperature does not change much when we add the  $35 J$ .)
2. (E) A certain Einstein solid's entropy changes from  $305.2k_b$  to  $338.1k_b$  when we add 1 unit  $\epsilon$  of energy. What is the value (and units) of  $k_b T/\epsilon$  for this solid? If  $\epsilon = 1.0 eV$ , what is its temperature  $T$ ?
3. (E) Does it make sense to talk about the temperature of a vacuum? If so, how could you measure or calculate it? If not, why not?
4. (E) An Einstein solid in a certain macrostate has a multiplicity of  $3.8 \times 10^{280}$ . What is its entropy (expressed as a multiple of  $k_B$ )?
5. (E) A pair of Einstein solids in a certain macropartition has multiplicities of  $4.2 \times 10^{320}$  and  $8.6 \times 10^{132}$ . What are the entropies of each solid? What is the total entropy of the system in this macropartition? (Express entropies as multiples of  $k_b$ .)
6. (E) Is it really true that the entropy of an isolated system consisting of two Einstein solids never decreases? (Consider a pair of very small solids.) Why is this statement more accurate for large systems than for small systems? Explain in your own words.
7. (P) We have argued on fairly fundamental grounds that  $dS/dE = f(T)$ . In principle, we could define  $f(T)$  to be anything that we like: this would amount to defining temperature and its scale. Still, some definitions would violate deeply embedded preconceptions about the nature of temperature. For example, the simplest definition of temperature would be  $dS/dE = T_{new}$ . Show that this definition
  - (a) Would imply that  $T_{new}$  has units of  $K^{-1}$  and
  - (b) Would imply that heat would flow spontaneously from objects with low  $T_{new}$  to objects with high  $T_{new}$ . This would imply that object with low values of  $T_{new}$  are hot, while objects with high values  $T_{new}$  are cold (we might want to call  $T_{new}$  so defined *coolness* instead of *temperature*). While we could define temperature in this way, it would really fly in the face of convention (if not intuition).
  - (c) If we did define coolness  $T_{new}$  in this way, what ordinary temperature  $T$  would an object with absolutely zero coolness ( $T_{new} = 0$ ) have? What about something that is infinitely cool ( $T_{new} = \infty$ )?
8. (P) Imagine that the entropy of a certain substance as a function of  $N$  and  $E$  is given by the formula  $S = Nk_b \ln E$ . Using the definition of temperature, show that the thermal energy of this substance is related to its temperature by the expression  $E = Nk_b T$ .
9. (P) Imagine that the multiplicity of a certain substance is given by  $\Omega(E, N) = Ne^{\sqrt{NE/\epsilon}}$ , where  $\epsilon$  is some unit of energy. How would the energy of an object made out of this substance depend on its temperature? Would this be a 'normal' substance in our usual sense of temperature.
10. (P) Consider an Einstein solid having  $N = 20$  atoms.

- (a) What is the solids temperature when it has an energy of  $10\epsilon$ , assuming that  $\epsilon = h\omega = 0.02\text{eV}$ ? Calculate this directly from the definition of temperature by finding  $S$  at  $10\epsilon$  and  $11\epsilon$ , computing  $dS/dE \approx [S(11\epsilon) - S(10\epsilon)]/\epsilon$ , and then applying the definition of temperature. (You will find that your work will go faster if you use *StatMech* to tabulate the multiplicities.)
- (b) How does this compare with the result from the formula  $E = 3Nk_bT$  (which is only accurate if  $N$  is large and  $E/3N\epsilon > 1$ )?
- (c) If you have access to *StatMech*, repeat for  $N = 200$  and  $E = 100\epsilon$ . (Hint: If your calculator cannot handle numbers in excess of  $10^{100}$ , use the fact that  $\ln(a \times 10^b) = \ln a + b \ln 10$ ).