Fundamental 5

Entropy

What is the microscopic perspective of thermal equilibrium?

Pre-Activity Questions

1. Review F.4 Heat. In general, what is the observed direction of heat transfer for two subsystems in contact at different temperatures and what defines the equilibrium state?

2. Review F.2 Counting Configurations. Consider a sequence of nine objects. Each object is either a line or a dot. Determine the number of possible permutations of a series of three lines and six dots. What is the probability of the sequence: • | •• | | •••?

3. Review the rules for logarithms and identify an alternative way of representing each of the following: a) $\ln x + \ln y$ b) $\ln x - \ln y$ c) $y \ln x$

4. What is $\ln 1$ =?

Model 1 Microscopic energy models

According to Quantum Mechanics, the energy of atoms and molecules is ***quantized***, *i.e.*, only distinct energy levels or states are allowed. The figure below shows two equivalent representations of a system of four particles.

Figure 1: (a) an *energy system* where each dot represents a particle and lines indicate the energy of the particle (b) a *line/dot system* where each dot represents one unit of energy and lines differentiate particles. Reading left to right on either diagram, there is one energy unit for the first particle, two units of energy for the second particle, no energy for the third particle, and 3 units of energy for the fourth particle.

Critical Thinking Questions

1. Total energy in ε for the system in Model 1 is 6ε. Explain how you could determine this by looking at...

   a) The energy level diagram

   b) The line/dot diagram

2. In the line/dot representation, explain how only three lines can represent four particle "bins". (Note that two lines can represent three bins, etc.)

3. Calculate the total multiplicity (configurations) for Model 1 where six units of energy can be distributed among four particles.

4. In the same manner as Figure 1 sketch an energy system and corresponding line/dot representation for four particles with a total of zero energy. What is the multiplicity for this configuration?

5. Draw a representation of the sytem that results when one unit of energy is added to this lowest energy configuration. What is the multiplicity for this new system?

6. As the energy of the system increases, what is the effect on the multiplicity or number ways to distribute this energy? Present your team's justification.

Model 2 Microscopic spontaneity

Consider an isolated system of N = 4 particles divided into two subsystems isolated from the surroundings and separated by a partition. Each subsystem has 2 identical particles that can have any integer unit of energy from 0ε to 6ε, depending on the total energy of the subsystem. Assume subsystem "A" has a total energy of 5ε and subsystem "B" has a total energy of 1ε.

Critical Thinking Questions

7. Individually (without the help of your group mates), draw an energy diagram representing subsystem A. (You will compare answers in the next question.)

8. Compare your answer to CTQ 7 with the other members of your team and determine whether or not there are multiple "correct" answers. If there are, determine the multiplicity and show your calculation.

9. Draw an energy diagram representing subsystem B. Are there multiple "correct" answers. If so, how many?

10. Write an equation for W_{tot} in terms of W_{A} and W_{B} (the multiplicities of subsystem A and subsystem B, respectively), and confirm that the value in this case is $W_{\text{tot}} = 12$.

11. Suppose you are interested in defining an extensive function of multiplicity $f(W)$ such that the total would be equal to the sum of each individual contribution: $f(W_{\text{tot}}) = f(W_{\text{A}}) + f(W_{\text{B}})$. Which of the following relationships would work? Present your team's justification.

a) $f = W$
b) $f = W^2$
c) $f = \exp W$
d) $f = \ln W$
e) $f = \log W$

Model 3 Entropy

The number of different configurations or multiplicity plays an important role in predicting the tendency or driving force of a system towards a new state. Ludwig Boltzmann recognized the significance of this microscopic quantity and proposed the following relationship

$$S = \mathrm{k} \ln W \tag{F5.1}$$

defining entropy S, a macroscopic quantity in terms of the microscopic multiplicity, W, in terms of a proportionality constant known as the Boltzmann constant, k.

Critical Thinking Questions

12. According to Eq. F5.1, what must be the minimum value of S? (Assume k is a positive constant.) Record your team's justification.

13. Assume W_{A} , W_{B}, and W_{tot}, are the multiplicities of subsystem A, subsystem B, and the total system respectively.

   a) Identify the individual entropies, S_{A}, S_{B}, and S_{tot} based on F5.1.

   b) Rewrite the expression for S_{tot}, replacing W_{tot} in terms of W_{A} and W_{B}.

   c) Based on the relationships above, is entropy, S, an extensive property (*e.g.* $S_{\mathrm{tot}} = S_{\mathrm{A}} + S_{\mathrm{B}}$)? Provide justification for your team's answer. (Hint: Look back at the pre-activity.)

14. Determine the entropies of each subsystem in Model 2 and the entropy of the total system. (To make the math very simple, we will let k = 1 for now.)

15. Suppose the two systems described in Model 2 are brought into thermal contact such that energy can transfer from one subsystem to the other but the particles cannot.

a) Since each subsystem has the same number of particles, prior to contact, which would you predict to have a higher temperature based on the energies of each subsystem?

b) Would you predict the direction of heat transfer to subsystem A or B? Why?

c) Predict the energy of each subsystem A and B when thermal equilibrium is reached. Explain.

Model 4 Driving force

The following table summarizes all possible ways that 6 units of energy can be distributed among the two subsystems described in Model 2. Note: The column labeled E_A gives the energy of subsystem A.

E_A	S_A	S_B	S_{tot}
6	1.95	0	1.95
5	1.79	0.69	2.48
4	1.61	1.10	2.71
3	1.39	1.39	2.78
2			
1	0.69	1.79	2.48
0	0	1.95	1.95

Critical Thinking Questions

16. How you can tell that $E_B = 6$ for the bottom row of the table, even though there is no column labeled E_B.

17. Which row in the table can be used to confirm your answer to CTQ 14? (If your answer does not agree with this row, go back and check your work.)

18. If subsystem A has 2 units of energy:

a) how many units of energy will subsystem B have? __________

b) calculate S_A, S_B, and S_{tot} fill in each of the missing entries in the table. Clearly justify how each quantity is determined.

19. For each of the following, indicate the resulting change (increase/decrease/same) in the energy of subsystem A and total entropy as the system approaches equilibrium. (Recall CTQ 15)

a) If $E_A = 5$, the energy will __________ and S_{tot} will __________

b) If $E_A = 2$, the energy will __________ and S_{tot} will __________

c) If $E_A = 3$, the energy will __________ and S_{tot} will __________

20. Sketch a plot of S_{tot} as a function of E_A, and mark the point where the derivative of S_{tot}, $dS_{tot} = 0$.

a) What is the significance of this point where $dS_{tot} = 0$?

b) What is happening when $dS_{tot} > 0$?

21. In general, what happens to the total entropy as a system moves towards equilibrium?

22. What is the driving force for energy tranfer in this system?

Exercises

1. Consider the system in Model 2.

   a) Draw a similar sketch of a system with three particles in each subsystem.

   b) Assume that eight (8) total units of energy are distributed between both subsystems. Draw one possible labeled energy system and corresponding line dot representation of the energy system for

      i) $E_A = 2$

      ii) $E_A = 3$

   c) Calculate S_A, S_B, and S_{tot} for the cases where

      i) $E_A = 2$

      ii) $E_A = 3$

   d) Make and fill in a table similar to the table in Model 4.

   e) Construct a graph of S_{tot} as a function of E_A .