

## CYL110 2012-2013 Thermodynamics Tutorial 1

1. (a) Write out all the ways (microstates) to distribute 2 quanta of energy to 5 oscillators, grouping these states into distinct configurations. (b) How much more probable is it to find two particles each with one quantum of energy than finding a single particle with both quanta?
2. Suppose you flip four fair coins. (a) Make a list of all the possible outcomes. (b) Make a list of all the different “macrostates” and their probabilities. (c) Compute the multiplicity of each macrostate using the combinatorial formula, and check that these results agree with what you got by brute-force counting.
3. Suppose you flip 20 fair coins. (a) How many possible outcomes (microstates) are there? (b) What is the probability of getting the sequence HTHHTTTHTHHHTHHHTHT (in exactly that order)? (c) What is the probability of getting 12 heads and 8 tails (in any order)?
4. Suppose you flip 50 fair coins. (a) How many possible outcomes (microstates) are there? (b) How many ways are there of getting exactly 25 heads and 25 tails? (c) What is the probability of getting exactly 25 heads and 25 tails? (d) What is the probability of getting exactly 30 heads and 20 tails? (e) What is the probability of getting exactly 40 heads and 10 tails? (f) What is the probability of getting 50 heads and no tails? (g) Plot a graph of the probability of getting  $n$  heads, as a function of  $n$ .
5. This is an illustration of the usefulness of Stirling’s approximation for the factorial. Evaluate  $10!$  by brute force. Use a calculator or some other means to evaluate  $100!$  and  $1000!$ . Estimate the error if you used Stirling’s approximation to evaluate these factorials.
6. Another illustration of Stirling’s approximation. Suppose you flip 1000 coins.
  - (a) What is the probability of getting exactly 500 heads and 500 tails?
  - (b) What is the probability of getting 502 heads and 498 tails?
  - (c) What is the probability of getting 600 heads and 400 tails?
7. For a harmonic oscillator with each of the following values of  $N$  and  $q$ , list all of the possible microstates, count them, and verify the combinatorial formula (a)  $N = 3, q = 4$  (b)  $N = 3, q = 5$  (c)  $N = 3, q = 6$  (d)  $N = 4, q = 2$  (e)  $N = 4, q = 3$  (f)  $N = 1, q = \text{anything}$  (g)  $N = \text{anything}, q = 1$
8. Calculate the multiplicity of a system with 30 oscillators and 30 units of energy. (Do not attempt to list all the microstates.)
9. In a system with energy levels evenly spaced by  $1.5 \times 10^{-19}$  J at 500 K,  $n_0$  is  $1 \times 10^{10}$ . What is  $n_1$ ? What is  $n_1$  at 175 K?
10. The ratio  $n_j/n_i = 0.40$  for a system at 175 K. What is  $\Delta e_{i,j}$  for this system? At 350K?
11. It was determined from spectroscopy that  $n_j/n_i = 0.15$  and  $\Delta e_{i,j} = 7.8 \times 10^{-21}$  J. (a) What is the temperature of the system? (b) If the temperature of the system was found to be 400 K, what would the observed  $n_j/n_i$  be?
12. If configuration A is the Boltzmann distribution, and configuration B is a distribution having energy level populations differing by 0.005% from those of A, what is  $W_B/W_A$  if the system contains (a) 10,000 particles? (b) 0.5 mol particles?

13. For a certain reaction to occur the system has to have an energy of at least  $3.0 \times 10^{-20}$  J above the ground state. (a) What fraction of the particles will have enough energy to react at 100 K? (b) at 500 K?
14. For a certain reaction to occur the system has to have on average an energy 20 kJ per mole of particles. (a) What fraction of the particles will have enough energy to react at 300 K? (b) At what temperature does the system need to be for 2% of the particles to have enough energy to react?
15. Consider a system made up of two subsystems each containing 10 oscillators sharing a total of 20 units of energy. Assume that the subsystems are weakly coupled, so that the exchange of energy between the subsystems is much slower than the exchange of energy among the oscillators within each solid, and that the total energy is fixed.
- How many different configurations (macrostates) are available to this system?
  - How many microstates are available to this system?
  - Assuming that this system is in thermal equilibrium, what is the probability of finding all the energy in the first system?
  - What is the probability of finding exactly half the energy in the first solid?
16. Use Stirling's approximation to show that the multiplicity (number of microstates) of a system composed of  $N$  oscillators with  $q$  quanta of energy (both  $N$  and  $q$  large), is approximately

$$W(N, q) = \frac{\left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N}{\sqrt{\frac{2\pi q(q+N)}{N}}}$$

17. This problem gives an approach to estimating the width of the peak of the multiplicity function for a system of two large subsystems of oscillators. (a) Consider two identical subsystems, each with  $N$  oscillators, in thermal contact with each other. Suppose that the total number of energy units in the combined system is exactly  $2N$ . How many different macrostates (that is, possible values for the total energy in the first solid) are there for this combined system? (b) Find an approximate expression for the total number of microstates for the combined system. (Hint: Treat the combined system as a single system. Do not throw away factors of "large" numbers, since you will eventually be dividing two "very large" numbers that are nearly equal. (c) The most likely macrostate for this system is (of course) the one in which the energy is shared equally between the two solids. Find an approximate expression for the multiplicity of this macrostate. (d) You can get a rough idea of the "sharpness" of the multiplicity function by comparing your answers to parts (b) and (c). Part (c) tells you the height of the peak, while part (b) tells you the total area under the entire graph. As a very crude approximation, pretend that the peak's shape is rectangular. In this case, how wide would it be? Out of all the macrostates, what fraction have reasonably large probabilities? Evaluate this fraction numerically for the case  $N = 10^{23}$ .