CHAPTER 15

Entropy and Statistics

Thermodynamic systems are collections of huge numbers of atoms or molecules. How these atoms or molecules behave statistically determines the disorder in the system. In other words, the second law of thermodynamics is based on the statistics of systems with extremely large numbers of atoms or molecules.

As an analogy, suppose we take four identical coins, number them, and toss them. We could report the outcome in two different ways: either by specifying the outcome of each coin toss individually (e.g., coin 1 is heads, coin 2 is tails, coin 3 is heads, and coin 4 is heads), or just by reporting the overall outcome as the number of heads.

Specifying the outcome of each coin toss individually is analogous to describing the **microstate** of a thermodynamic system. A microstate specifies the state of each constituent particle. For instance, in a monatomic ideal gas with N atoms, a microstate is specified by the position and velocity of each of the N atoms. As the atoms move about and collide, the system changes from one microstate to another. The total number of heads for coin tossing is analogous to a **macrostate** of a thermodynamic system. A macrostate of an ideal gas is determined by the values of the macroscopic state variables (the pressure, volume, temperature, and internal energy).

In the four-coin model, each of the microstates is equally likely to occur on any toss. Each of the coins has equal probability of landing heads or tails. Since each of 4 coins has 2 possible outcomes, there are $2^4 = 16$ different but equally probable microstates. There are only five macrostates: the number of heads can range from zero to four. The macrostates are *not* equally likely. A good guess would be that 2 heads is much more likely than 4 heads. To find the probability of a macrostate, we count up the number of microstates corresponding to that macrostate and divide by the total number of microstates for all the possible macrostates. From Table 15.3, the probability of the most likely macrostate (2 heads) is $6/16 = 0.375$. The probability of 4 heads is only $1/16 = 0.0625$.

$$\text{probability of macrostate} = \frac{\text{number of microstates corresponding to the macrostate}}{\text{total number of microstates for all possible macrostates}}$$

PHYSICS AT HOME

Repeatedly toss a collection of 10 identical coins. After each toss, count and record the number of heads. After a large number of tosses, are your results similar to the results of a statistical analysis (see Fig. 15.20)? Why are your results not exactly the same?

Table 15.3 Possible Results of Tossing Four Coins

Macrostate	Microstates	Number of Microstates	Probability of Macrostate
4 heads	HHHH	1	$\frac{1}{16}$
3 heads	HHHT HHTH HTHH THHH	4	$\frac{4}{16}$
2 heads	HHTT HTHT HTTH THHT THTH TTHH	6	$\frac{6}{16}$
1 head	HTTT THTT TTHT TTTH	4	$\frac{4}{16}$
0 heads	TTTT	1	$\frac{1}{16}$
	Total number of microstates = 16		

Unlike our four-coin model, thermodynamic systems have huge numbers of particles (for instance, there are 6×10^{23} particles in one mole). What happens to the coin-tossing problem if the number of coins gets large? In Fig. 15.20, we have graphed the number of microstates for the various macrostates for systems with $N = 4$ coins, 10 coins, 100 coins, and 1 mole of coins. The horizontal axes for the four graphs specify the macrostate as the *fractional* number of heads, which ranges from 0 to 1. The probability of obtaining any macrostate is proportional to the number of microstates since the microstates are equally likely.

Notice what happens to the probability peak: as N gets large, the probability of obtaining a macrostate having a number of heads significantly different (say, more than 0.01%) from $\frac{1}{2}N$ gets smaller and smaller. With 4, 10, or 100 coins, it is possible to toss the coins and observe a decrease in entropy—that is, the observed macrostate after the toss can be one that is less probable than the macrostate before the toss. What if there were 6×10^{23} coins? The probability of getting anything more than 0.01% away from 3×10^{23} heads is so small that we can call it zero—it is impossible.

This kind of statistical analysis is the basis for the second law of thermodynamics. The entropy S of a macrostate is proportional to the number of microstates Ω that correspond to that macrostate:

$$S = k \ln \Omega \qquad (15\text{-}22)$$

where k is Boltzrnann's constant.

The relationship between S and Ω has to be logarithmic because entropy is additive: if system 1 has entropy S_1 and system 2 has entropy S_2, then the total entropy is $S_1 + S_2$. However, the number of microstates is *multiplicative*. Think of dice: if die 1 has 6 microstates and die 2 also has 6, the total number of microstates is not 12, but $6 \times 6 = 36$. The entropy is additive since $\ln 6 + \ln 6 = \ln 36$.

Entropy never decreases because the macrostate with the highest entropy is the one with the greatest number of microstates, and thus the highest probability. (Recall that since the microstates are equally likely, the probability of a macrostate is proportional to Ω.) The probability peak is so sharp and narrow in thermodynamic systems that the probability of finding a macrostate not in that peak is effectively zero. The equilibrium macrostate is the one with the largest number of microstates. Since the macrostate with the highest probability has the highest entropy, a system will always evolve toward the highest entropy.

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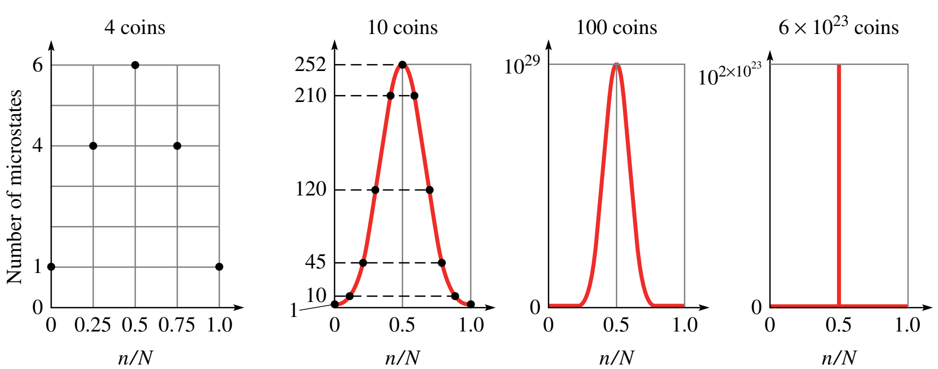

Figure 15.20 Graphs of the number of microstates versus n/N ($n = 0, 1, \ldots, N$), where n = number of heads for $N = 4$ coins, 10 coins, 100 coins, 6×10^{23} coins.

Example 15.11

Increased Number of Microstates in Free Expansion

Refer to the free expansion of an ideal gas (Example 15.9). How does the number of microstates change when the volume of the gas (containing N molecules) is doubled?

Strategy Since in Example 15.9 we found the entropy change for this process, we can now use the entropy change to find how the number of microstates changes. Since the relationship between S and Ω is logarithmic, an increase in S will tell us by what *factor* Ω increases.

Solution The entropy change for n moles was found to be

$$\Delta S = -nR \ln \tfrac{1}{2} = nR \ln 2$$

Since $nR = Nk$, the entropy increase can be written in terms of N:

$$\Delta S = Nk \ln 2$$

If Ω_i and Ω_f are the initial and final number of microstates, then

$$\Delta S = k \ln \Omega_f - k \ln \Omega_i = k\,(\ln \Omega_f - \ln \Omega_i) = k \ln \frac{\Omega_f}{\Omega_i}$$

Equating these last two expressions for ΔS, we find

$$N \ln 2 = \ln \frac{\Omega_f}{\Omega_i}$$

Since $\ln 2^N = N \ln 2$,

$$\frac{\Omega_f}{\Omega_i} = 2^N$$

Discussion To get an idea of how large the increase in the number of microstates is, let $N = N_A$ (1 mol of gas). To write the number $2N$ in ordinary base 10 notation, we would need 2×10^{23} *digits.*

The temperature is the same before and after, so the number of velocity states, rotational states, and vibrational states before and after is the same. But each molecule has twice as much volume in which it can be found, so the number of microstates is multiplied by 2 for each molecule, or by $2N$ overall.

Practice Problem 15.11 Change in Entropy for 10 Coins

What is the change in entropy (expressed as a multiple of the Boltzmann constant) if a box of 10 coins starts with 8 heads showing and then is shaken until 4 heads are showing? [*Hint:* See Fig. 15.20.]

Problems

81. Suppose there are four balls in a box; three balls are yellow and one is blue. The blue ball is marked with the number 1. The yellow balls are numbered 2, 3, and 4. You are blindfolded and choose two balls from the box, removing them one at a time. (a) List all possible combinations of choosing two balls such that one is blue and one yellow. (b) What is the number of microstates for the system of one blue and one yellow ball? (c) List all possible combinations of choosing two balls such that both are yellow. (d) What is the number of microstates for the system of two yellow balls? (e) Of the two possible macrostates (blue and yellow, yellow and yellow), is one more probable than the other?

82. Suppose the macrostate of a system of 100 identical coins is specified by the number of heads. What is the entropy of the state with one head (in terms of Boltzmann's constant, k)?

83. For a system composed of two identical dice, let the macrostate be defined by the sum of the numbers showing on the top faces. What is the maximum entropy of this system in units of Boltzmann's constant, k?

✦84. (a) What is the number of ways that five identical coins can be arranged so one of them shows heads? (b) What is the entropy of this state in units of Boltzmann's constant, k? (c) Repeat parts (a) and (b) for five identical coins with two showing heads.

✦85. Two identical dice are thrown. A macrostate is specified by the sum of the two numbers that come up on the dice. (a) How is a microstate specified for this system?

(b) How many different microstates are there? (c) How many different macrostates are there? (d) What is the most probable macrostate? (e) What is the probability of getting this result? (f) What is the probability of rolling "snake eyes" (two 1s)?

✦86. Six identical coins are tossed simultaneously. The macrostate is specified by the number of "heads." (a) What is/are the most probable macrostate(s)? (b) What is/are the least probable macrostate(s)? (c) What is the probability of obtaining the most probable macrostate?

87. If 1.0 g of ice at 0.0°C melts into liquid water at 0.0°C, by what factor has the number of microstates increased?

88. If the number of microstates for a thermodynamic system doubles, how much has the system's entropy increased?

✦89. Four indistinguishable marbles must be placed into two distinguishable boxes. (a) How many microstates are there? (b) How many macrostates? (c) What is the most probable macrostate? (d) What is the entropy of that macrostate? (e) What is the least probable macrostate? (f) What is the entropy of the least probable macrostate?

Ⓒ90. What is the change in entropy when a collection of eight identical coins, arranged to show four heads and four tails, is changed to all eight showing heads? If the entropy of the coins decreases, how can the entropy of the universe increase in this process?

Ⓒ91. List these in order of increasing entropy: (a) 1000 He atoms moving at random velocities with an average speed of 400 m/s; (b) 1000 He atoms all moving at 400 m/s in the same direction; (c) 1000 He atoms all moving at 400 m/s in random directions.

Answers to Practice Problems

15.11 $k \ln \dfrac{210}{45} \approx +1.54k$