Homework set 3-solution

Problems:

2.1, 2.2, 2.5, 2.6, 2.8, 2.15, 2.28, 2.31, 2.33, 2.35

Problem 2.1. (Flipping four coins.)

(a) Here are all the possible outcomes, 16 in total:

TTTT	TTHH	THHH
	THTH	HTHH
TTTH	THHT	HHTH
TTHT	HTTH	HHHT
THTT	HTHT	
HTTT	HHTT	HHHH

(b) The macrostates are:

$$\begin{aligned}
&0 \text{ heads}, \ \Omega = 1, \text{ probability} = 1/16\\
&1 \text{ head}, \ \ \Omega = 4, \text{ probability} = 4/16\\
&2 \text{ heads}, \ \Omega = 6, \text{ probability} = 6/16\\
&3 \text{ heads}, \ \Omega = 4, \text{ probability} = 4/16\\
&4 \text{ heads}, \ \Omega = 1, \text{ probability} = 1/16
\end{aligned}$$

(c) For $N = 4$ and $n = 0$, equation 2.6 gives $\Omega = 4!/(0! \cdot 4!) = 1$, since $0! = 1$. For $n = 1$, we have $\Omega = 4!/(1! \cdot 3!) = 24/6 = 4$. For $n = 2$, $\Omega = 4!/(2! \cdot 2!) = 24/4 = 6$. For $n = 3$ the formula predicts the same result as for $n = 1$, namely 4. And for $n = 4$ it's again 1, the same as for $n = 0$.

Problem 2.2. (Flipping 20 coins.)

(a) Each coin has two possible states, and the coins are independent, so the total number of microstates is $2^{20} = 1048576$, or a little over a million.

(b) The sequence given corresponds to just one particular microstate. If the coins are fair every microstate is equally probable, so the probability of any one of them, including this, is $1/2^{20}$ or a little less than one in a million. (And yet, amazingly, I got exactly that sequence, on the first try, when I was writing the problem!)

(c) The number of ways of getting exactly 8 heads is

$$\binom{20}{8} = \frac{20 \cdot 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13}{8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1} = 125970.$$

So the probability of getting exactly 8 heads is $125970/1048576 = 12.0\%$.

Problem 2.5. (Microstates of a small Einstein solid.) To represent each microstate I'll use a sequence of digits, for the number of energy units in the first, second, and third oscillators, respectively.

(a) $N = 3,\ q = 4$:

400	310	031	220	211
040	301	103	202	121
004	130	013	022	112

I count 15 microstates. And according to the formula, there should be

$$\binom{4+3-1}{4} = \frac{6!}{4!\,2!} = \frac{6\cdot 5}{2} = 15.$$

(b) $N = 3,\ q = 5$:

500	410	041	320	032	311	221
050	401	104	302	203	131	212
005	140	014	230	023	113	122

I count 21 microstates. And according to the formula, there should be

$$\binom{5+3-1}{5} = \frac{7!}{5!\,2!} = \frac{7\cdot 6}{2} = 21.$$

(c) $N = 3,\ q = 6$:

600	501	015	042	141	033	132
060	150	420	204	114	321	213
006	051	402	024	330	312	123
510	105	240	411	303	231	222

I count 28 microstates. And according to the formula, there should be

$$\binom{6+3-1}{6} = \frac{8!}{6!\,2!} = \frac{8\cdot 7}{2} = 28.$$

(d) $N = 4,\ q = 2$:

2000	0020	1100	1001	0101
0200	0002	1010	0110	0011

I count 10 microstates. And according to the formula, there should be

$$\binom{2+4-1}{2} = \frac{5!}{2!\,3!} = \frac{5\cdot 4}{2} = 10.$$

(e) $N = 4,\ q = 3$:

3000	2100	0210	0021	1110
0300	2010	0201	1002	1101
0030	2001	1020	0102	1011
0003	1200	0120	0012	0111

I count 20 microstates. And according to the formula, there should be

$$\binom{3+4-1}{3} = \frac{6!}{3!\,3!} = \frac{6\cdot 5\cdot 4}{3\cdot 2} = 20.$$

(f) If $N = 1$, then all the energy must belong to the one and only oscillator, so there's only one microstate, which we would denote simple "q". And according to the formula, the multiplicity should be

$$\binom{q+1-1}{q} = \frac{q!}{q!} = 1.$$

(g) If $q = 1$, then there's only one unit of energy to distribute among the N oscillators, so the allowed states would be $1000\cdots$, $0100\cdots$, $0010\cdots$, and so on up to $\cdots 0001$. There are N places to put the unit of energy, so the number of possible microstates is N. And indeed, according to the formula,

$$\Omega(N,1) = \binom{1+N-1}{1} = \frac{N!}{1!\,(N-1)!} = N.$$

Problem 2.6. For $N = 30$ and $q = 30$, the number of microstates should be

$$\Omega(30,30) = \binom{30+30-1}{30} = \frac{59!}{(30!)(29!)} = 5.91\times 10^{16}.$$

Problem 2.8. (Two small Einstein solids.)

(a) Of the 20 units of energy, anywhere from 0 to 20 could be in solid A. Each possibility from 0 to 20 defines a different macrostate, so there are 21 macrostates in total.

(b) The combined system has 20 oscillators and 20 units of energy, so the total number of microstates is

$$\Omega(20,20) = \binom{20+20-1}{20} = \frac{39!}{(20!)(19!)} = 6.89\times 10^{10}.$$

(c) For the macrostate with all the energy in solid A, the multiplicity of solid A is

$$\Omega(10,20) = \binom{20+10-1}{20} = \frac{29!}{(20!)(9!)} = 1.00\times 10^{7},$$

while the multiplicity of solid B is 1. Assuming that the system is in equilibrium, all microstates are equally probable, so the probability of this macrostate is

$$\text{Probability} = \frac{\Omega(\text{this state})}{\Omega(\text{total})} = \frac{1.00\times 10^{7}}{6.89\times 10^{10}} = 1.45\times 10^{-4}.$$

(d) For the macrostate with half the energy in each solid, the multiplicity of the combined system is

$$\Omega = \Omega_A \Omega_B = \binom{10+10-1}{10}\binom{10+10-1}{10} = \left(\frac{19!}{(10!)(9!)}\right)^2 = 8.534 \times 10^9,$$

so the probability (in equilibrium) is

$$\text{Probability} = \frac{8.53 \times 10^9}{6.89 \times 10^{10}} = 0.124.$$

(e) The probability of the energy being evenly distributed is greater than that of all the energy being in A by a factor of nearly 1000. So if this system started out with all (or nearly all) of the energy in one solid or the other, then we could be pretty sure that it would evolve toward a state with energy more evenly distributed. And if it started out with the energy evenly distributed, we could be pretty sure that at some later time we wouldn't find all the energy on one side or the other—this would happen less than one time in a thousand. So the evolution from the unlikely state to the likely one is sortof irreversible, but not exactly since the process does occasionally happen in reverse.

Problem 2.15. According to my calculator, $50! = 3.0414 \times 10^{64}$. Stirling's approximation, however, gives

$$50! \approx 50^{50} e^{-50} \sqrt{2\pi \cdot 50} = 3.0363 \times 10^{64},$$

off by about 0.2%. The natural logarithm of 50! is 148.5, while the simplified form of Stirling's approximation gives

$$\ln 50! \approx 50 \ln 50 - 50 = 145.6,$$

off by about 2%.

Problem 2.28. There are 52 possible cards that could be on top, and for each of these choices there are 51 possibilities for the next card, then 50 for the next, and so on down to 1 choice for the bottom card. So the total number of arrangements is just $52! = 8.06 \times 10^{67}$. If all arrangements are accessible, then the entropy is

$$\frac{S}{k} = \ln 52! = 156; \qquad S = 156k = 2.16 \times 10^{-21}\ \text{J/K}.$$

This is then the amount of entropy created by shuffling the cards, and it's *tiny* compared to the entropy associated with thermal motions, which is typically a large number (proportional to the number of particles) in fundamental units and a number of order 1 when multiplied by Boltzmann's constant.

Problem 2.31. Starting from equation 2.40 for the multiplicity, we have for the entropy of an ideal gas

$$\begin{aligned}\frac{S}{k} &= \ln\left(\frac{1}{N!}\frac{V^N}{h^{3N}}\frac{\pi^{3N/2}}{(3N/2)!}(2mU)^{3N/2}\right) = \ln V^N + \ln\left(\frac{2\pi mU}{h^2}\right)^{3N/2} - \ln N! - \ln[(3N/2)!] \\ &= N\ln V + N\ln\left(\frac{2\pi mU}{h^2}\right)^{3/2} - N\ln N + N - \frac{3N}{2}\ln\left(\frac{3N}{2}\right) + \frac{3N}{2} \\ &= N\left[\ln\frac{V}{N} + \ln\left(\frac{2\pi mU}{h^2}\right)^{3/2} - \ln\left(\frac{3N}{2}\right)^{3/2} + \frac{5}{2}\right] = N\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right) + \frac{5}{2}\right].\end{aligned}$$

In the second line I've used Stirling's approximation twice, in the form of equation 2.16 which omits the merely "large" factor of $\sqrt{2\pi N}$. The final expression is the Sackur-Tetrode result, equation 2.49.

Problem 2.33. For argon at room temperature and atmospheric pressure, the volume per molecule is

$$\frac{V}{N} = \frac{kT}{P} = \frac{(1.38\times10^{-23}\ \text{J/K})(300\ \text{K})}{10^5\ \text{N/m}^2} = 4.14\times10^{-26}\ \text{m}^3,$$

while the energy per molecule is

$$\frac{U}{N} = \frac{3}{2}kT = \frac{3}{2}(1.38\times10^{-23}\ \text{J/K})(300\ \text{K}) = 6.21\times10^{-21}\ \text{J}.$$

The mass of an argon atom is 40 u or 6.64×10^{-26} kg, so the argument of the logarithm in the Sackur-Tetrode equation is

$$\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2} = (4.14\times10^{-26}\ \text{m}^3)\left(\frac{4\pi(6.64\times10^{-26}\ \text{kg})(6.21\times10^{-21}\ \text{J})}{3(6.63\times10^{-34}\ \text{J}\cdot\text{s})^2}\right)^{3/2} = 1.02\times10^7.$$

The entropy of a mole of argon under these conditions is therefore

$$S = R[\ln(1.02\times10^7) + \tfrac{5}{2}] = R[18.64] = 155\ \text{J/K}.$$

The only relevant difference between argon and helium in this calculation is the larger mass of the argon atom, which increases the argument of the logarithm by a factor of $(40/4)^{3/2} = 31.6$. The reason why m matters is because for a given energy, a molecule with more mass has more momentum, resulting in a larger "hypersphere" of allowed momentum states for the gas and hence a larger multiplicity.

Problem 2.35. Writing 5/2 as $\ln e^{5/2}$, the Sackur-Tetrode equation becomes

$$S = Nk \ln\left[\frac{V}{N} e^{5/2} \left(\frac{4\pi m U}{3Nh^2}\right)^{3/2}\right].$$

We want to know when this quantity is negative, that is, when the argument of the logarithm is less than 1. So set it equal to 1 and use the equipartition theorem to write U in terms of T:

$$1 = \frac{V}{N} e^{5/2} \left(\frac{4\pi m U}{3Nh^2}\right)^{3/2} = \frac{V}{N} e^{5/2} \left(\frac{2\pi m k T}{h^2}\right)^{3/2}.$$

Solving for T gives

$$T = \left(\frac{N}{V}\right)^{2/3} \frac{h^2}{2\pi e^{5/3} m k}.$$

We're to assume that N/V is the same as at room temperature (T_0) and atmospheric pressure (P_0), so we can use the ideal gas law to write it as P_0/kT_0, then plug in $P_0 = 10^5$ Pa and $T_0 = 300$ K. The mass of a helium atom is 4 u, where 1 u $= 1.66 \times 10^{-27}$ kg. Plugging in all these numbers, I get $T \approx 0.01$ K. Below this temperature, the methods of Chapter 7 become necessary.