Convergence to Most Probable Macrostate

In class we did the example of three particles (A, B, and C) which could have energy levels of 0, 1, 2, or 3 units, with a total energy of 3 units. We identified three possible **macrostates** with, 1) one particle having 3 units of energy, and the other two having zero, 2) one particle having 2 units, one having 1, and the last having zero, and 3) all particles having 1 unit of energy. We found that there were 3 microstates for the 1st macrostate, 6 for the second, and 1 for the third, resulting in macrostate probabilities of 0.3, 0.6, and 0.1.

Let's extend this problem to the limit of large number of particles. We have the same energy levels (0, 1, 2, 3), and the same total energy (3 units), but now we have N particles, where $N > 3$.

We'll have the same essential macrostates, with the additional caveat that we have a lot more particles with zero energy.

Macrostate 1: One particle has 3 units of energy, and all others have zero.

Macrostate 2: One particle has 2 units of energy, one has 1, and all others have zero.

Macrostate 3: Three different particles have one unit of energy.

Let's calculate the number of ways each macrostate can happen for N total particles. That is, let's calculate the number of microstates for each macrostate for a given N.

Macrostate 1: We have N particles, and only one can have energy, so we have N microstates.

Macrostate 2: One particle gets 2 units of energy. There are N particles that can have the 2 units. Once the particle with 2 units is selected, there are (N-1) remaining choices for the particle with 1 unit, so the total number of microstates is N(N-1).

Macrostate 3: Now three particles get energy. Following the reasoning above, there are N choices for the first one to get 1 unit, N-1 for the second particle to get 1 unit, and N-2 for third one. But we've overcounted again here, since the ordering (who gets the first and who gets the last, etc.) doesn't matter. For each set of 3 particles with one unit of energy, we've overcounted by 3! or 6, so the total number of microstates is N(N-1)(N-2)/6.

So the total number of microstates is:

$$\Omega = \Omega_1 + \Omega_2 + \Omega_3 = N + N(N-1) + \frac{N(N-1)(N-2)}{6} \qquad (1)$$

and the fraction in each macrostate is simply Ω_i/Ω. You can verify our results from class by substituting $N = 3$ into the expression above. The calculations for increasing N are shown in the attached spreadsheet. At $N = 3$, our starting condition, Macrostate 3, the evenly distributed energy case, is least probable, but its probability rapidly increases with N while the probability of Macrostate 2 decreases, and that of Macrostate 1 decreases most rapidly. By one million particles, the fraction of microstates in the most probable macrostate is already 99.9994% of the total. For real systems at $N > 10^{20}$ microstates not in the most probable microstate will account for of the order of 10^{-20} of the total - a truly negligible amount.

	Number of microstates				Fraction of total microstates		
N	Ω_1	Ω_2	Ω_3	Ω_{TOT}	f_1	f_2	f_3
3	3	6	1	10	0.300	0.600	0.100
4	4	12	4	20	0.200	0.600	0.200
5	5	20	10	35	0.143	0.571	0.286
10	10	90	120	220	0.045	0.409	0.545
100	100	9900	161700	171700	0.001	0.058	0.942
1000	1000	9.99E+05	1.66E+08	1.67E+08	5.98E-06	0.00598	0.99402
10000	10000	1.00E+08	1.67E+11	1.67E+11	6.00E-08	6.00E-04	0.99940
100000	1.00E+05	1.00E+10	1.67E+14	1.67E+14	6.00E-10	6.00E-05	0.99994
1.00E+06	1.00E+06	1.00E+12	1.67E+17	1.67E+17	6.00E-12	6.00E-06	0.999994
1.00E+09	1.00E+09	1.00E+18	1.67E+26	1.67E+26	6.00E-18	6.00E-09	0.99999999
1.00E+12	1.00E+12	1.00E+24	1.67E+35	1.67E+35	6.00E-24	6.00E-12	1