

Name and section: _____

1. In class we discussed how a large number of coin flips will make the distribution much more strongly peaked than a smaller number of coin flips. Is the same true for the sums of dice rolls?

- (a) How many ways can you roll a sum of 13 with three dice? Let's call this $N(3, 13)$. Likely the easiest way to do this is to recognize that $N(3, 13)$ is the coefficient of x^{13} in the expansion of

$$(x + x^2 + x^3 + x^4 + x^5 + x^6)^3. \quad (1)$$

Programs such as Mathematica (available for free to BU students) and websites such as Wolfram Alpha can be very useful for this type of thing.

- (b) Now that we've shown how to find $N(d, s)$, back to the original question. What is the ratio $N(8, 28)/N(8, 18)$? Note, the sums 28 and 18 are the most likely and halfway between the minimum and the most likely, respectively.

- (c) What is the ratio $N(16, 56)/N(16, 36)$? Note again that these are the most likely and halfway to the most likely.

2. Consider two identical regions of space initially separated by a removable wall. Suppose the left region is represented by M lattice sites and the right region is represented by an additional M sites. Initially, with the separating wall in place, the left region contains N particles, while the right region contains no particles.

(a) Write down an expression for the total number of configurations, W , for this system.

(b) If the entropy, S , of the system is related to W by $S = k_B \ln W$, where k_B is the Boltzmann constant, using Stirling's approximation, calculate the entropy S_i of the initial state described above.

(c) Now the wall is removed and the system equilibrates to its final state where its entropy is S_f . Calculate S_f .

(d) Compute the change in entropy ΔS . Simplify ΔS by assuming the ideal gas limit $M \gg N$ so that $1 - N/M \approx 1$

3. Suppose that you have $2V$ black particles and $2V$ white particles in $4V$ lattice sites. There are $2V$ lattice sites on the left and $2V$ lattice sites on the right, separated by a permeable wall. The total volume is fixed. Show that perfect de-mixing (all white on one side, all black on the other) becomes increasingly improbable as V increases. (Hint: refer to Example 2.3 in the book.)
- (a) If it helps, start by thinking about the cases you can easily draw all the possibilities ($V = 1$ and $V = 2$, for example). Which is more likely to be unmixed?
- (b) Now think about the general case of V sites. Show (mathematically) how they are unlikely to demix assuming no interparticle interactions.
- (c) Starting to think about *enthalpic* versus *entropic* contributions to the driving forces, which driving force makes demixing unlikely? How might the other force contribute to demixing?

4. Find the value $n = n^*$ that causes the function

$$W(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \quad (2)$$

to be a maximum, for constants p and N . Use Stirling's approximation, $x! \approx (x/e)^x$. Note that it is easier to find the value of n that maximizes $\ln W$ than the value that maximizes W . Will the value of n^* will be the same?