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

   $$(x + x^2 + x^3 + x^4 + x^5 + x^6)^3. \tag{1}$$

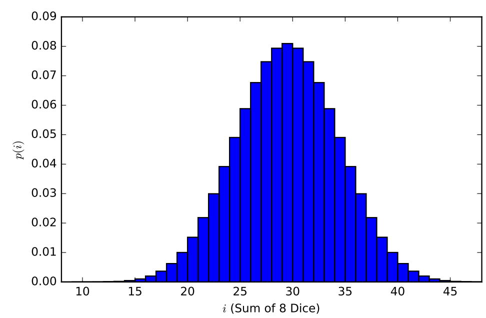
   Programs such as Mathematica (available for free to BU students) and websites such as Wolfram Alpha can be very useful for this type of thing.

   $$\begin{aligned}(x + x^2 + x^3 + x^4 + x^5 + x^6)^3 = \\ &x^{18} + 3x^{17} + 6x^{16} + 10x^{15} + 15x^{14} + 21x^{13} + 25x^{12} + 27x^{11} \\ &+ 27x^{10} + 25x^9 + 21x^8 + 15x^7 + 10x^6 + 6x^5 + 3x^4 + x^3\end{aligned}$$

   So $N(3,13) = 21$.

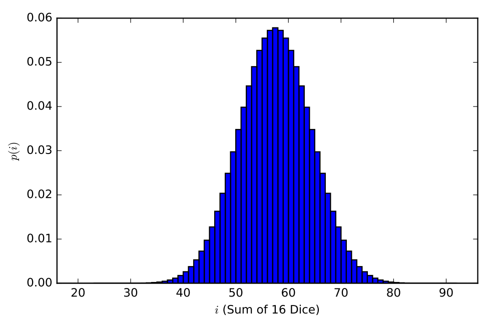
   (b) Now that we've shown how to find $N(d,s)$, back to the original question. What is the ratio $N(8,28)/N(8,18)$? Note, the sums 28 and 18 are the most likely and halfway between the minimum and the most likely, respectively.

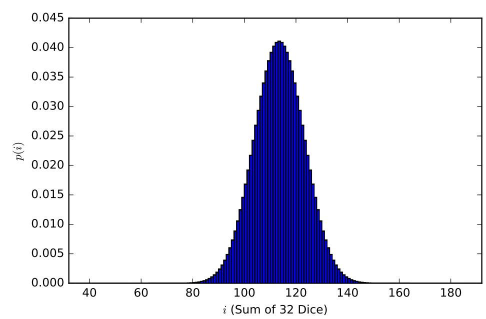
   $N(8,28) = 135954$ and $N(8,18) = 16808$ so $N(8,28)/N(8,18) = \frac{67977}{8404} = 8.08865$



   (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.

   $N(16,56) = 163112472594$ and $N(16,36) = 2065764520$. Then $N(16,56)/N(16,36) = \frac{81556236297}{1032882260} = 78.9599$. That's nearly an order of magnitude more!





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_i, for this initial system.

   The total system W_i will be equal to the product of W_l and W_r for the left and right sides respectively: $W_i = W_l \times W_r$. Trivially, because it is just empty, $W_r = 1$.

   The left side is a greater than that though (assuming $N < M$). However, this is just figuring out how to arrange N particles in the M sites or similarly how to get N heads on M flips of a coin. As we've discussed, this is just $W_l = \binom{M}{N} = \frac{M!}{N!(M-N)!}$.

   Therefore, $W_i = \frac{M!}{N!(M-N)!}$.

   (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 ($\ln x! = x \ln x - x$), calculate the entropy S_i of the initial state described above.

$$\begin{aligned}
S_i &= k_B \ln W_i \\
&= k_B \ln \left(\frac{M!}{N!(M-N)!} \right) \\
&= k_B \left(\ln M! - \ln N! - \ln(M-N)! \right) \\
&= k_B \left(M \ln M - M - N \ln N + N - (M-N)\ln(M-N) + M - N \right) \\
&= k_B \left(M \left(\ln M - \ln(M-N) \right) - N \left(\ln N - \ln(M-N) \right) \right) \\
&= k_B \left(M \ln \frac{M}{M-N} - N \ln \frac{N}{M-N} \right) \\
&= k_B \left(-M \ln \left(1 - \frac{N}{M} \right) + N \ln \left(\frac{M}{N} - 1 \right) \right) \qquad (2)
\end{aligned}$$

   Note, there are many ways this could be simplified, but I think this is one of the cleanest looking.

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

   Here, we can note that the only thing that changes in S_f from S_i is the size of the box which is now $2M$. Therefore,

$$S_f = k_B \left(-2M \ln \left(1 - \frac{N}{2M} \right) + N \ln \left(\frac{2M}{N} - 1 \right) \right) \qquad (3)$$

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

   $\Delta S = S_f - S_i$ so using eqs. (2) and (3) and using the approximation $M \gg N$,

$$\begin{aligned}
\Delta S &= k_B \left(-2M \ln(1) + N \ln \left(\frac{2M}{N} \right) \right) - k_B \left(-M \ln(1) + N \ln \left(\frac{M}{N} \right) \right) \\
&= k_B N \ln 2
\end{aligned}$$

   Interestingly, ΔS does not depend on the system size (as long as $M \gg N$), but it is linearly dependent on the number of particles and logarithmically dependent on the change in volume.

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?

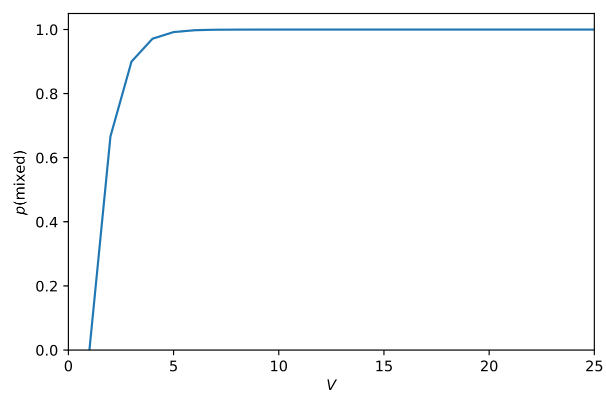
   For $V = 1$, there is no unmixed state, so the probability of being unmixed is 1. For $V = 2$, there are two states that are unmixed, but four that are mixed: probability of unmixed is $\frac{2}{3}$. At least for these two examples, the larger system has a larger probability of being unmixed.

   (b) Now think about the general case of V sites. Show (mathematically) how they are unlikely to demix assuming no interparticle interactions.

   Looking at multiplicity, there are only two ways for the system to be unmixed: all black on the left and white on the right or the opposite. However, there are $\binom{2V}{V} - 2$ ways for the particles to be arranged mixed. So as we saw above, as long as $V \geq 1$, being mixed is much more likely:

$$\begin{aligned} p(\text{mixed}) &= \frac{\binom{2V}{V} - 2}{\binom{2V}{V}} \\ &= 1 - \frac{2}{\binom{2V}{V}} \end{aligned}$$

   Even for fairly small values of V (i.e., not even needing to get to macroscopic-size systems), the probability of completely unmixing randomly becomes extremely small as can be see below:



   (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?

   Everything described above is due to entropic contributions: there is more “randomness” to being mixed whereas an unmixed state is very ordered.

   For an enthalpic contribution to unmixing, there would need to be some sort of interparticle interactions. For example, if white particles “preferred” being next to white particles, that would contribute an enthalpic force towards unmixing that could possibly overcome the entropic energy of being mixed.

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

$$W(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n} \tag{4}$$

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?

See solution to problem set 1, posted soon.

n^* will be the same for $W(n)$ and $\ln W(n)$.