BE.011/2.772J
Statistical Thermodynamics of Biomolecular Systems
Spring 2004
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Problem Set #2 Solutions
Due: 2/11/04

Dill 2.1, 2.2, 2.3, 2.4, 2.5, 2.6

Problem 1

In this problem we are trying to find the number of ways that we can select 15 sites to contain particles, out of V total sites. Thus, we have two types of sites, those containing particles and those that do not.

a) V = 20 sites

$$W(15,20) = \binom{20}{15} = 15{,}504$$

b) V = 16 sites

$$W(15,16) = \binom{16}{15} = 16$$

c) V = 15 sites

$$W(15,15) = \binom{15}{15} = 1$$

Problem 2

As the problem states, it is likely easier to maximize ln(W) rather than W.

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

$$\ln(W) = \ln\left[\frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}\right]$$

$$\ln(W) = \ln N! - \ln n! - \ln(N-n)! + n\ln p + (N-n)\ln(1-p)$$

If we make the assumption that both N and n are large, we can use Stirling's approximation: $\ln x! = x\ln x - x$

$$\ln(W) \approx N\ln N - N - n\ln n + n - (N-n)\ln(N-n) + (N-n) + n\ln p + (N-n)\ln(1-p)$$

$$\ln(W) \approx N\ln N - n\ln n - (N-n)\ln(N-n) + n\ln p + (N-n)\ln(1-p)$$

Now, we take the derivative.

$$\frac{d}{dn}\ln(W) \approx -\ln n - 1 + \ln(N-n) + 1 + \ln p - \ln(1-p)$$

$$\frac{d}{dn}\ln(W) \approx \ln\frac{N-n}{n} + \ln\frac{p}{1-p}$$

To get the maximum, n^*, set the derivative equal to zero.

$$\frac{d}{dn}\ln(W) = 0 = \ln\frac{N-n^*}{n^*} + \ln\frac{p}{1-p}$$

$$-\ln\frac{N-n^*}{n^*} = \ln\frac{p}{1-p}$$

$$\ln\frac{n^*}{N-n^*} = \ln\frac{p}{1-p}$$

$$\frac{n^*}{N-n^*} = \frac{p}{1-p}$$

$$\Rightarrow n^* = Np$$

Problem 3

In order to find both the maximum and minimum of *V(x)*, we must find the roots of it's derivative.

$$V(x) = \frac{x^3}{3} + \frac{5x^2}{2} - 24x$$

$$\frac{d}{dx}V(x) = x^2 + 5x - 24$$

$$\frac{d}{dx}V(x) = (x-3)(x+8)$$

So now we know the roots are $x = -8, 3$, and we need to figure out which corresponds to a maximum, and which to a minimum. An easy way to do this is using the second derivative test. (Recall, a negative second derivative means the function is concave down, and thus the point corresponds to a maximum, and a positive second derivative means concave up, and thus a minimum.)

$$\left.\frac{d^2}{dx^2}V(x)\right|_{x=-8} = 2(-8) + 5 = -11$$

$$\left.\frac{d^2}{dx^2}V(x)\right|_{x=3} = 2(3) + 5 = 11$$

Thus, we can see that $x = -8$ is a maximum, and $x = 3$ is a minimum.

Problem 4

In this problem we are asked to show that *p(N)/p(2N)* decreases as N increases.

$$p(N) = \binom{4N}{N} 0.5^N 0.5^{3N} = \frac{(4N)!}{N!(3N)!} 0.5^{4N}$$

$$p(2N) = \binom{4N}{2N} 0.5^{2N} 0.5^{2N} = \frac{(4N)!}{(2N)!(2N)!} 0.5^{4N}$$

$$\Rightarrow \frac{p(N)}{p(2N)} = \frac{(2N)!(2N)!}{N!(3N)!} \times \frac{0.5^{4N}}{0.5^{4N}} \times \frac{(4N)!}{(4N)!}$$

$$\frac{p(N)}{p(2N)} = \frac{(2N)!(2N)!}{N!(3N)!}$$

Since we are concerned about how this ratio changes as N increase, let us assume that N is large, and thus we can use Stirling's approximation ($n! \approx \left(\frac{n}{e}\right)^n$).

$$\frac{p(N)}{p(2N)} = \frac{\left(\frac{2N}{e}\right)^{2N}\left(\frac{2N}{e}\right)^{2N}}{\left(\frac{N}{e}\right)^{N}\left(\frac{3N}{e}\right)^{3N}}$$

$$\frac{p(N)}{p(2N)} = \frac{2^{4N} \times N^{4N} \times \left(\frac{1}{e}\right)^{4N}}{3^{3N} \times N^{4N} \times \left(\frac{1}{e}\right)^{4N}}$$

$$\frac{p(N)}{p(2N)} = \left(\frac{2^4}{3^3}\right)^N$$

$$\frac{p(N)}{p(2N)} = \left(\frac{16}{27}\right)^N$$

So we can see that

$$\lim_{N\to\infty} \frac{p(N)}{p(2N)} = \lim_{N\to\infty}\left(\frac{16}{27}\right)^N = 0$$

So the binomial distribution becomes narrower and narrower as N goes to infinity.

Problem 5

In this problem we have *4V* lattice sites, and *2V* white particles and *2V* black particles to fill these sites. The probability of de-mixing is given by the number of ways to arrange all the white particles on one side divided by the total number of possible configurations. For any *V*, there are only *2* ways to achieve perfect de-mixing, all white on the left side (and all black on the right), or all white on the right side (and all black on the left).

$$p(\text{demixing}) = \frac{2}{W_{tot}},$$

$$\text{where } W_{tot} = \binom{4V}{2V} = \frac{(4V)!}{(2V)!(2V)!}$$

$$p(\text{demixing}) = \frac{2(2V)!(2V)!}{(4V)!}$$

Again we can use Stirling's approximation to get

$$p(\text{demixing}) \approx \frac{2({}^{2V}\!/_{e})^{2V}({}^{2V}\!/_{e})^{2V}}{({}^{4V}\!/_{e})^{4V}}$$

$$p(\text{demixing}) \approx \frac{2(2)^{4V}}{(4)^{4V}}$$

$$p(\text{demixing}) \approx 2\left(\frac{1}{2}\right)^{4V}$$

For large V,

$$\lim_{V\to\infty} p(\text{demixing}) \approx 2\lim_{V\to\infty}(0.5)^{4V} = 0$$

Thus, as the number of sites increases, it is increasingly unlikely that the particles will exist in an unmixed state.

Problem 6

The first step is to determine the equilibrium points of the energy function. Again, we find the roots of the derivative.

$$\frac{d}{d\theta}V(\theta) = -\sin(\theta)$$

$$\frac{d}{d\theta}V(\theta) = 0$$

$$\Rightarrow \theta = n\pi, \text{for } n = 0, \pm 1, \pm 2, \ldots$$

The unstable equilibrium points are local maxima, and the stable equilibrium points are local minima. To determine which are maxima and minima, use the second derivative test.

$$\frac{d^2}{d\theta^2}V(\theta) = -\cos(\theta)$$

So for even values of n, the second derivative is negative, corresponding to local maxima. Thus $\theta = n\pi$, for $n = 0, \pm 2, \pm 4\ldots$ are unstable equilibrium points and $\theta = n\pi$, for $n = 1, \pm 3, \pm 5\ldots$ are stable equilibrium points.

Of course, this could be easily done by plotting out the energy function and identifying the maxima and minima. For the energy function in this question, the stable and unstable equilibrium points can be easily obtained.