(3) What is average number of molecules in each part?

$$\langle N_1 \rangle = pN = \left(\frac{V_1}{V}\right) N$$

$$\langle N_2 \rangle = (1-p) N = \left(\frac{V_2}{V}\right) N$$

(4) What are the relative flucuations of the number of molecules in each part?

$$\frac{\sigma_1}{\langle N_1 \rangle} = \frac{\sqrt{Np(1-p)}}{\langle N_1 \rangle} = \frac{\sqrt{N(V_1/V)(V_2/V)}}{(V_1/V)\, N} = \frac{\sqrt{(V_2/V)}}{\sqrt{(V_1/V)}\sqrt{N}} = \sqrt{\frac{V_2}{V_1}}\, \frac{1}{\sqrt{N}}$$

$$\frac{\sigma_2}{\langle N_2 \rangle} = \frac{\sqrt{N(V_2/V)(V_1/V)}}{(V_2/V)\, N} = \sqrt{\frac{V_1}{V_2}}\, \frac{1}{\sqrt{N}}$$

We will see that the fact that relative flucuations scale as $1/\sqrt{N}$ is quite a generic result

More generally, for the binomial distribution:

$$\frac{\sigma}{\langle N \rangle} = \frac{\sqrt{Np(1-p)}}{Np} = \left(\frac{1-p}{p}\right)^{1/2} \frac{1}{\sqrt{N}}$$

this is exactly 1 if $p = 1/2$

Aside: Stirling's approximation

We will frequently need to evaluate $\log N!$ for $N \gg 1$, and thus the following approximation is quite useful:

$$\boxed{\log N! \approx N \log N - N + \frac{1}{2} \log 2\pi N}$$

Note: the 1st two terms are $\mathcal{O}(N)$ but the 3rd is $\mathcal{O}(\log N)$ and thus we can sometimes use the weaker approximation: $\log N! \approx N \log N - N$

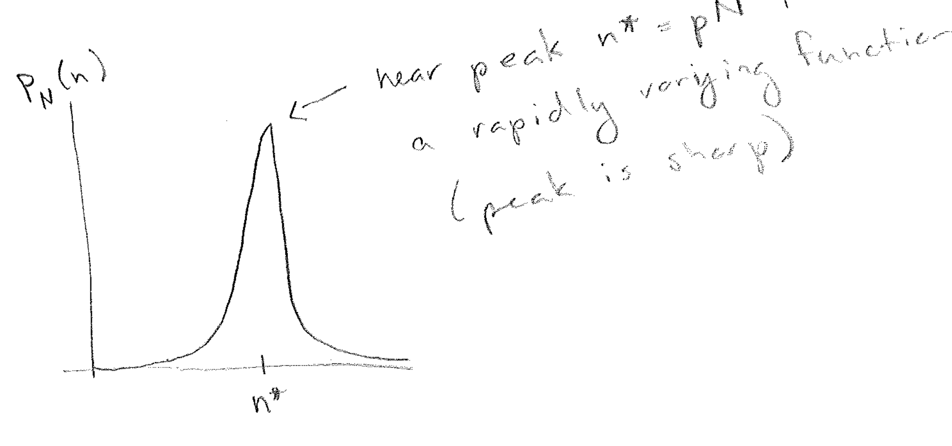
Binomial distribution for large N

(applet demo 3.2)

- We have often discussed how statistical mechanics is necessary due to the fact that N is very large.
- We just saw that as N grows large, it begins to look more and more like a gaussian

Now we will show this a bit more rigorously, that is we will find the continous function $p(n)$

that approximates the discrete binomial distribution as $N \to \infty$

(1) 

→ we don't want to approximate $P_N(n)$ directly, instead use $\log P_N(n)$; we expect its Taylor series to converge because it is much more slowly varying

Expand $\log[P_N(n)]$ about $n = n^*$

$$\log P_N(n) = \log P_N(n=n^*) + (n-n^*) \left.\frac{d \log P_N(n)}{dn}\right|_{n=n^*}$$
$$+ \frac{1}{2}(n-n^*)^2 \left.\frac{d^2 \log P_N(n)}{dn^2}\right|_{n=n^*} + \dots$$

⇒ $\log P_N(n)$ is monotonic function of $P_N(n)$

since $P_N(n^*)$ is maximum, so is $\log P_N(n^*)$

$$\Rightarrow \quad \left.\frac{d \log P_N(n)}{dn}\right|_{n=n^*} = 0$$

$$\left.\frac{d^2 \log P_n(n)}{dn^2}\right|_{n=n^*} < 0$$

(2) Assume that terms $\mathcal{O}(n^3)$ and greater can be neglected, and define

$$\log A \equiv \log[P_N(n^*)]$$

$$B \equiv - \left.\frac{d^2 \log[P_N(n)]}{dn^2}\right|_{n=n^*}$$

Then, $\log[P_N(n)] \approx \log A + \frac{1}{2}(n-n^*)^2(-B)$

OR

$$P_N(n) \approx A e^{-\frac{1}{2}B(n-n^*)^2}$$

So, we just need to find A & B and we are done. We can do this by going back to the definition of $P_N(n)$,

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

Now, we take the logarithm of both sides:

$$\log[P_N(n)] = \log N! - \log n! - \log(N-n)! + n\log p + (N-n)\log(1-p)$$

Now, we need to find n^*, so we need to evaluate $\frac{d(\log P_N(n))}{dn}$, which we can do so with help from Stirling's approximation:

$$\frac{d}{dx}(\log x!) \approx \frac{d}{dx}\left(x\log x - x + \frac{1}{2}\log(2\pi x)\right)$$

$$\approx \log x + x\frac{1}{x} - 1 + \frac{1}{2}\cancel{\frac{1}{x}}^{\to 0}$$

large x!

$$\boxed{\frac{d}{dx}(\log x!) \approx \log x}$$

Thus, rewriting

$$\log P_N(n) = \log N! - \log n! - \log(N-n)! + n\log p + N\log(1-p) - n\log(1-p)$$

$$\frac{d\log P_n(n)}{dn} = \frac{d}{dn}(\cancel{\log N!})^{0} - \frac{d}{dn}(\log n!) - \frac{d}{dn}(\log(N-n)!) + \frac{d}{dn}(n\log p)$$

$$+ \frac{d}{dn}(N\cancel{\log(1-p)})^{0} - \frac{d}{dn}(n\log(1-p))$$

$$= \frac{d}{dn}(\log n!) - \frac{d}{dn}(\log(N-n)!) + \log p - \log(1-p)$$

Then we can use the relation we just derived

$$\approx -\log n + \log(N-n) + \log p - \log(1-p)$$

Then, n^* is given by $\frac{d(\log P_N(n^*))}{dn} = 0$, so

$$\log\left(\frac{N-n^*}{n^*}\right) = \log\left(\frac{1-p}{p}\right)$$

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

$$N - n^* - \frac{1-p}{p} n^* = 0$$

$$N = \left(\frac{p+1-p}{p}\right) n^*$$

$$\boxed{n^* = Np}$$

Which is what we expected from binomial distribution, but now we have shown it rigorously. We can now find the 2nd deriviative to get $\mathcal{B}$

Recall : $\frac{d(\log P_N(n))}{dn} \approx -\log n + \log(N-n) + \log p - \log(1-p)$

$$\frac{d^2(\log P_N(n))}{dn} \approx \frac{-1}{n} - \frac{1}{N-n}$$

$$B \equiv -\frac{d^2 \log P_N(n)}{dn^2}\Big|_{n=n^*}$$

$$= -\left(\frac{-1}{Np} - \frac{1}{N-Np}\right)$$

$$= -\left(\frac{-N+Np-Np}{Np(N(1-p))}\right)$$

$$= -\left(\frac{-N}{N^2p(1-p)}\right) = \frac{1}{Np(1-p)} = \frac{1}{\sigma^2}$$ ← variance from binomial distribution

$$\boxed{B = \frac{1}{\sigma^2}}$$

Now, we can find A, $\log A \equiv \log[P_N(n^*)]$

$$\log A = \log N! - \log(Np)! - \log(N(1-p))! + Np\log p + N(1-p)\log(1-p)$$

Now, substitute $\log N! \approx N\log N - N + \frac{1}{2}\log 2\pi N$

$$\approx N\log N - N + \frac{1}{2}\log 2\pi N - pN\log pN + pN - \frac{1}{2}\log 2\pi pN$$
$$- (1-p)N\log(N(1-p)) + (1-p)N - \frac{1}{2}\log 2\pi(1-p)N + Np\log p$$
$$+ N(1-p)\log(1-p)$$

$$\approx N\cancel{\log N} - \cancel{N} - pN\log pN + \cancel{pN} - N\log \cancel{N(1-p)} + pN\log(\cancel{N(1-p)})$$
$$+ \cancel{(1-p)N} + Np\log p + N\log(1-p) - Np\cancel{\log(1-p)}$$
$$+ \frac{1}{2}\log\left(\frac{\cancel{2\pi N}}{2\pi pN\,\cancel{2\pi N}(1-p)}\right)$$

$$\log A \approx \log\left[\left(\frac{1}{2\pi Np(1-p)}\right)^{1/2}\right]$$

$$A = \frac{1}{\sqrt{2\pi\sigma^2}}$$ ← alternitively, could have found through normalization

$$\Rightarrow \boxed{P_N(n) = \frac{1}{\sqrt{2\pi\sigma^2}}\, e^{-(n-\mu)^2/2\sigma^2}}$$

Gaussian!

Note: $\langle n \rangle = \mu$

$\langle (n-\mu)^2 \rangle = \sigma$