A closer look at distributions – examples drawn from Dill

Boltzmann

$$S = k \, \ell n \, W$$

Coin tosses

which sequence is more probable?

H H H H

H T H H

Equally prob $\frac{1}{16}$

which is more probable 4H or 3H, 1T (independent of sequence)?

The latter 1/16 *vs.* 1/4

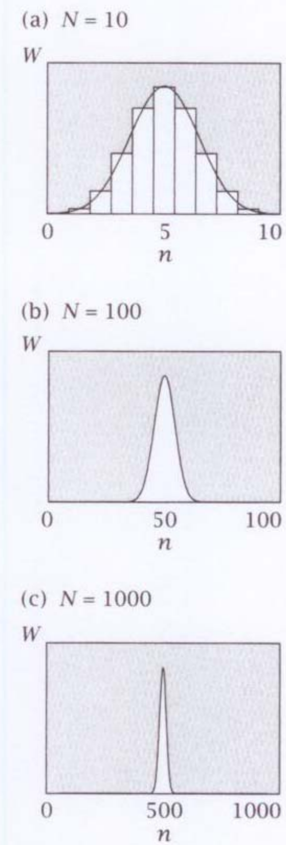


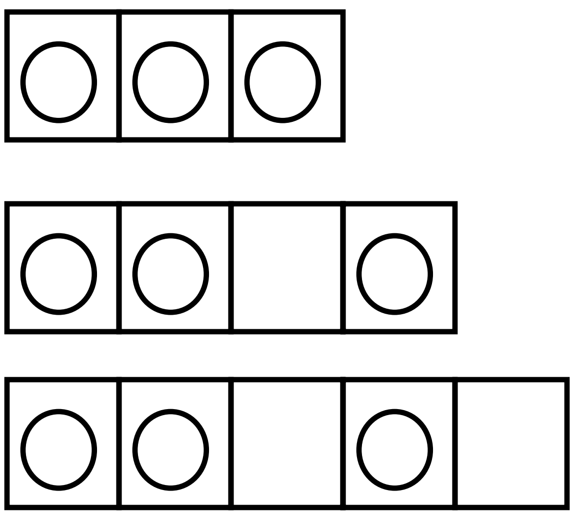
Figure 2.6 The multiplicity function W of the number of heads n narrows as the total number of trials N increases.

coin flips $\frac{N!}{n!(N-n)!}$

1
1 1
1 2 1
1 3 3 1
1 4 6 4 1

binomial distribution $\rightarrow$ Gaussian for large N

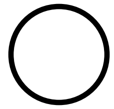
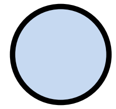
for large *N*, *n** $\rightarrow$ *max prob = N/2* (50% heads, 50% tails)



	Vol.	W
A	3	1
B	4	4
C	5	10

prob. that particles are bunched up in *B* = ½. In *C,* it is only 3/10 $\Rightarrow$ Multiplicity is maximized by spreading out over "cells"

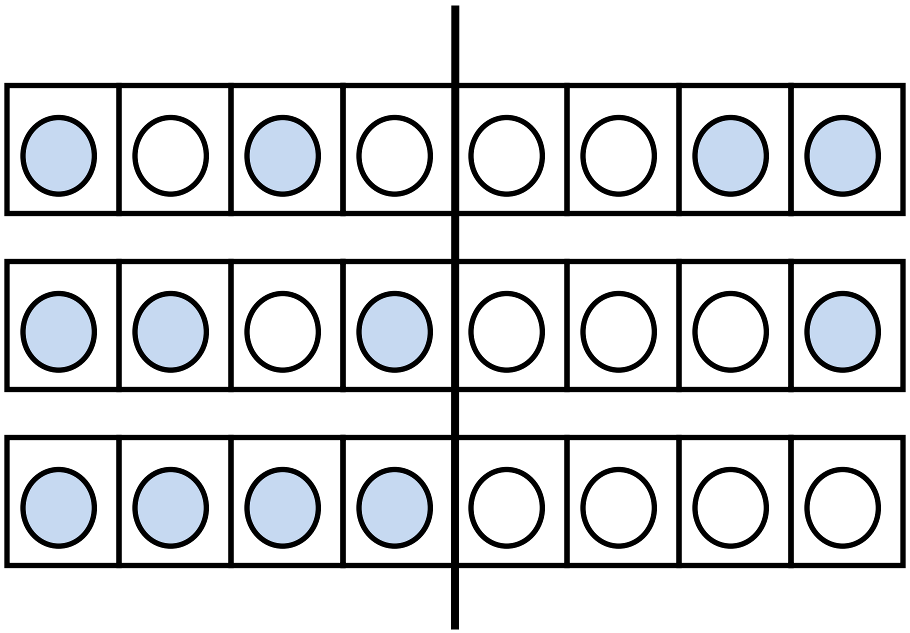
< basis for the force we call pressure>

Now consider two types of particles  and 

A

B

C



$$W = \frac{4!}{2!2!}\frac{4!}{2!2!} = 36$$

ways 2 on left,
2 on right

$$W = \frac{4!}{3!1!}\frac{4!}{3!1!} = 16$$

3 on left,
1 on right

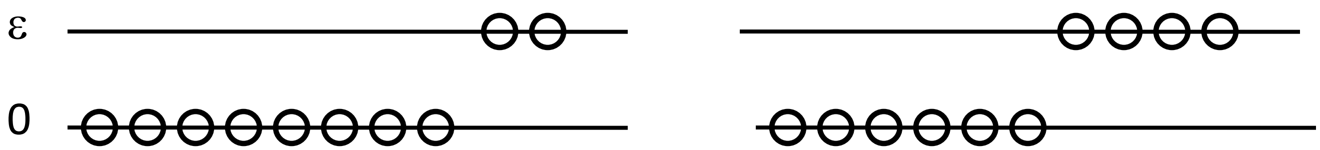
$$W = 1$$

consistent with what we know of diffusion of particles

chemical potential is the force for mixing (again, no interactions are needed)

We have also seen that the # of arrangements grows with > *E*

Why does heat flow?



$A,\ E_A = 2\varepsilon$ $\qquad$ $B,\ E_B = 4\varepsilon$

$$w_A = \frac{10!}{8!2!} = 45 \qquad w_B = \frac{10!}{6!4!} = 210$$

Bring *A* and *B* into thermal contact.

If no exchange of energy $w_A w_b = 45x210 = 9450$ arrangements

suppose energy is exchanged so $E_A = E_B$

$$w_{A+B} = \left(\frac{10!}{7!3!}\right)^2 = 14400$$ ⟵ more arrangements

⇒ energy will flow

$$\frac{20!}{14!6!} = 38760$$

All arrangements with fixed $E_A + E_B$

heat flows to achieve max # of arrangements not to equalize the energy (although it accomplishes that in above example).

In general, $E_A \neq E_B$ after equilibration

Consider

A 10 particles $E_A = 2$

B 4 particles $E_B = 2$

$$W_A W_B = \frac{10!}{8!2!}\frac{4!}{2!2!} = 270$$

Now suppose B transfers energy to A s.t. $E_A = 3, \quad E_B = 1$

$$W_A W_B = \frac{10!}{7!3!}\frac{4!}{3!1!} = \frac{10 \cdot 9 \cdot 8}{6} \cdot 4 = 480$$

temperature is the driving force for energy flow

$$n! \approx \sqrt{2\pi n}\left(\frac{n}{e}\right)^n$$

$$\ell n\ n! \approx \frac{1}{2}\ell n 2\pi n + \left(n + \frac{1}{2}\right)\ell n\ n - n$$

$$\ell n\ n! \approx n \ell n\ n - n \quad \text{for } n >> 10$$

$$n! \approx \left(\frac{n}{e}\right)^n$$

Stirling's
Approx.

1D random walk ("drunken walker")

Each step has unit length in either *+x* or *–x*

total of *N* steps

m in *+x* and *(N – m)* in *–x* direction

$$P(m,N)=\left(\frac{1}{2}\right)^N \frac{N!}{m!(N-m)!},$$

*Define: m** is most probable endpoint

$$\ell n P(m)=\ell n P(m^*)+\left(\frac{d\ \ell n\,P}{dm}\right)_{m^*}(m-m^*)+\frac{1}{2}\left(\frac{d^2\ell n P}{dm^2}\right)_{m^*}(m-m^*)^2+\ldots$$

Taylor series about m*

$$\left.\frac{d\,\ell n P}{dm}\right|_{m^*}=-1-\ell n(m^*)+\ell n(N-m^*)+1$$

$$\Rightarrow m^*=N/2$$

max of *P*
when *m = m**
so 1st deriv
vanishes

$$\left.\frac{d^2 \ell n P}{dm^2}\right|_{m^*} = -\frac{4}{N}$$

$$P = P^* e^{-2(m-m^*)^2/N}$$ ⟵ Gaussian distrib.

$$P(x) = \frac{1}{\sqrt{2\pi N}} e^{-x^2/2N}$$ In distance space

x = m - (N-m) = 2m – N

m = N/2; x** = 0

$$\left\langle x^2 \right\rangle = N$$

$$\sqrt{x^2} = \sqrt{N}$$

Note: if walker was directed (one direction only) this would be *N*.