Agenda: Kinetics and Transport in Multiparticle Systems

Dynamics of interacting multi-particle systems

- Interaction energies
  Dissipation & randomization via multiple scattering

- Probabilistic evolution
  Random walk and binomial distribution
  Diffusion/Fokker-Planck processes (Master Equation)
  Fluctuating (Langevin) dissipative forces
  Maxwell-Boltzmann equilibrium energy distributions

- Kinetics of dilute gases
  Fundamental "Ideal Gas" laws, Equation of state (EoS)
  Work and heat transfer
    - Flow of heat and radiation
    - Laws of thermodynamics, thermodynamic ensembles

Reading Assignments
Weeks 3 &4
LN III.1-III.3:

Kondepudi Ch. 1,3,7
Additional Material

McQuarrie & Simon
Ch. 3.1 -3.4

Math Chapter(s)
MC E

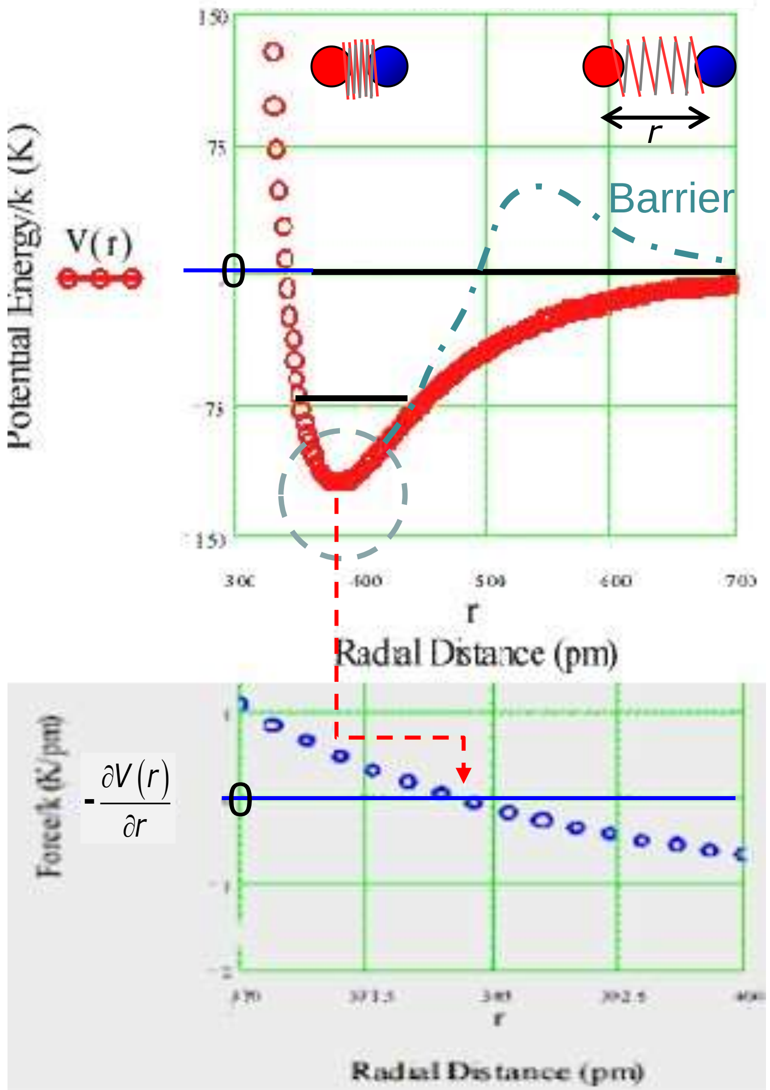
Motivation: Practical Importance of Transport Phenomena

Dissipation (friction, viscosity) and Equilibrium Phenomena, understanding equilibrium=stationary states of matter. Analytical tool for basic physics & technology, e.g., material science.

- Brownian particle motion on surfaces & in space: gases, liquids, and solids, incl. organic materials
  Biology, Medicine, Semiconductor industry,
- Diffusion and mixing of gases
  in gases like air→ practical applications, smell, toxic gases, Climate CO_2 atmosphere, DAC CO_2, transport in gaseous plasmas
- Diffusion of gases in liquids (glasses, plastics)
  gas in liquids: acidification of ocean water, environment, climate
  DAC CO_2
- Diffusion & permeation of gases in solids: chemical industry, reactors
  Hydrogen economy, nuclear energy, fusion reactors, isotopic separation
- Diffusion of liquids in liquids
  Mixing industrial fluids, pollution of rivers, lakes, ground water
- Diffusion of liquids in solid matrices
  Chemical industry, contamination of toxic waste in soil, corrosion

Atomic Potential Interacting Energies

Lennard-Jones Potential



Multi-Particle Systems : ≥6·*N* dof

Lennard-Jones potential: Attractive (< 0) at intermediate & large distances, repulsive (≫0) at small distances

Potential

$$V(r) = 4\varepsilon \cdot \left[+ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} + \cdots\cdots \right]$$

depth   rep. & attr. ranges   Reaction/dissociation barrier

Force

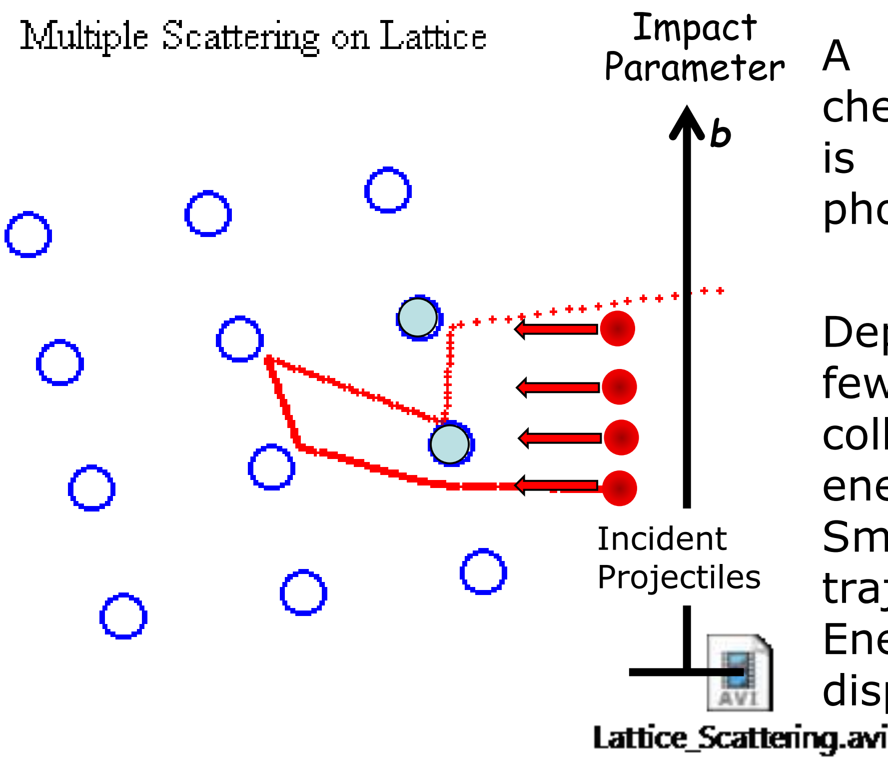
$$F(r) = -\frac{dV}{dr} =$$

$$\approx \frac{24\varepsilon}{\sigma} \cdot \left[2\left(\frac{\sigma}{r}\right)^{13} - \left(\frac{\sigma}{r}\right)^{7} \right]$$

Work = Kinetic Energy Gain/Loss = ΔV

$$\Delta K_{r_a \to r_b} = -\int_{r_a}^{r_b} \frac{dV}{dr} \cdot dr = V(r_a) - V(r_b)$$

Energy Transfer & Dissipation in Multiple Interactions



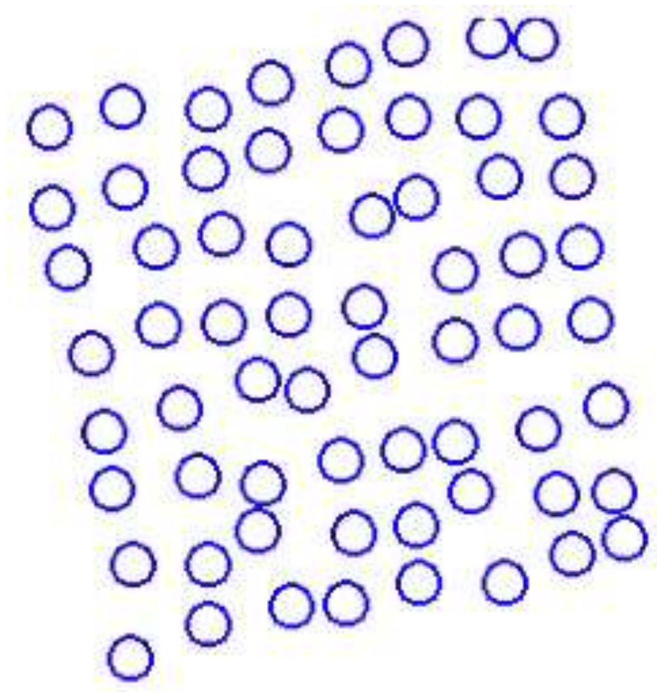
A stationary lattice of massive (M), chemically bound atoms or ions at rest is hit by fast projectiles, particles or photons ($m \ll M$).

Depending on how and where the first few lattice particles are hit, a few collisions and their momentum and energy transfer change drastically. Small changes in b cause very different trajectories (chaotic dynamics). Energetic disturbance travels and disperses through lattice.

Scattered projectiles leave the lattice at very different final speeds and directions, depending on the initial conditions (impact parameter)

Collisions with unbound **gas** particles are even "more random" than collisions with a periodic solid-sate lattice structure.

Randomization via Multiple Interactions



Lattice_Scattering.avi

A stationary lattice of massive (M), chemically bound atoms or ions at rest is hit by fast projectiles, particles or photons ($m \ll M$).

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Binary Random Walk *(RW)*

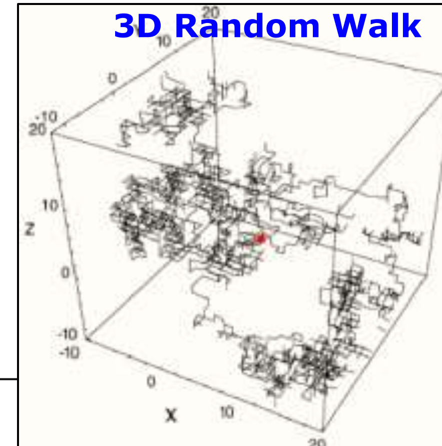
Configuration (state) space of a system is approximated by a ***1*-dimensional** lattice of equal cells $\Delta x = \Delta m = \pm 1$. (Simple to extend to *3*-D and *n*-D)

Scenario: 2 discrete properties for discrete t-evolution (Yor N; L or R; ….)

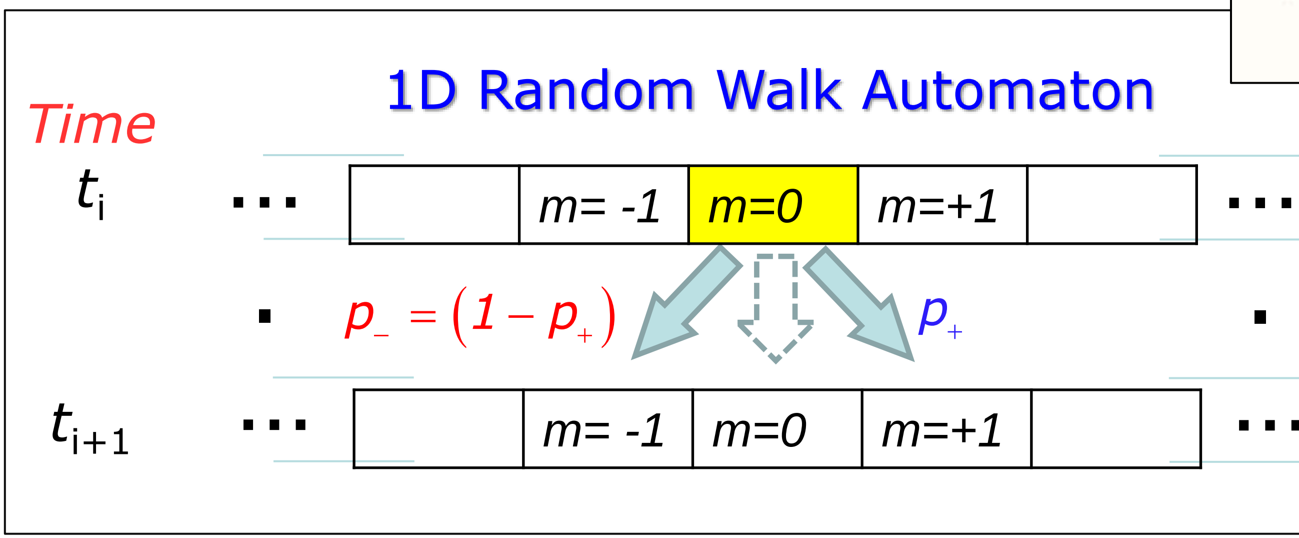
Time $t_i \rightarrow t_{i+1}$ transition rule: each cell $m \rightarrow m \pm 1$.

Time evolution of CA modeled in discrete time steps→generations.

Evolution @ probabilistic rule: probabilities $\boldsymbol{p_-}$ and $\boldsymbol{p_+}$ with $p_- + p_+ = 1$



Initial cell @ $\boldsymbol{m}(t_1) = 0$ → Consider ***RW*** "trajectory" $p_- = p_+ = 1/2$;
N = total number of steps, with $\boldsymbol{N_+}$ to the right, $\boldsymbol{N_-}$ steps to the left.



Question: How to change procedure to admit m=0→m=0?

Deterministic vs. Probabilistic Propagation Protocols

Deterministic Sim

Equations of Motion
Initial Cond's

$$\ddot{x} = f(x)$$
$$x_0, \dot{x}_0$$

$$x_{i+1} = x_i + \dot{x} \cdot \Delta t$$

$$i + 1 \rightarrow i$$

Probabilistic Sim

Propagation Rules *P(i)=0,1*
Initial Cond's

$$x_{i+1} = x_i + \begin{cases} -P(i)\,\Delta x \\ \left(1 - P(i)\right)\Delta x \end{cases}$$
$$x_0$$

$$P(i) = ?$$

0

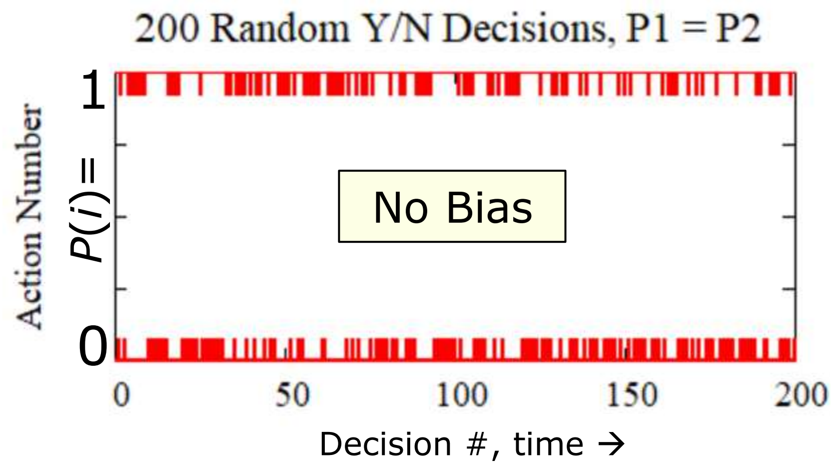
$$x_{i+1} = x_i + \Delta x$$

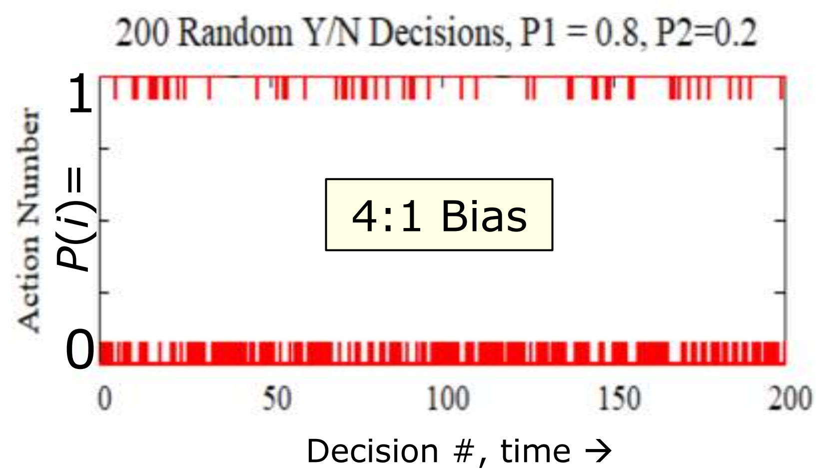
1

$$x_{i+1} = x_i - \Delta x$$

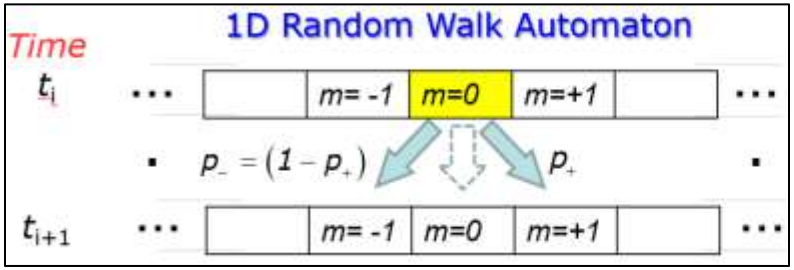
$$i + 1 \rightarrow i$$

Binomial Probabilistic Switch





Binary Random Walk (Unbiased)



Equal probabilities per step $p_- = p_+ = 1/2$
Let RW evolve over some time = total number of steps = $N \gg 1$.

Equal probabilities → Averaged over entire history = trajectory:

$$\langle N_- \rangle_N = \langle N_+ \rangle_N \rightarrow \langle m \rangle_N = 0$$

For a given trajectory, what is actual final position $m=m(t_N)$ **after *N* steps** ?

Cannot be answered precisely, since this is not a deterministic process, but …

$$\text{For a given } m = m(t_N) \rightarrow N_- = \frac{1}{2}(N-m) \quad \text{and} \quad N_+ = \frac{1}{2}(N+m)$$

$$\rightarrow \boxed{m = N_+ - N_-} \quad (\textit{can be reached by different trajectories})$$

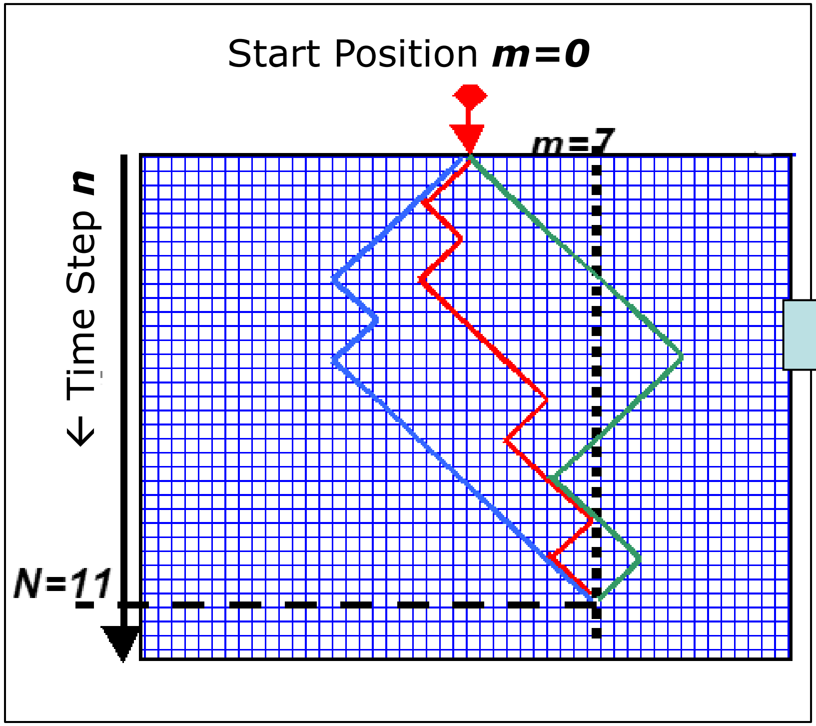
Final position ***m*** (after ***N*** steps) of trajectory is determined by the simple difference in # of left vs. right steps, since $p_- = p_+ = 1/2$. For $p_- \neq p_+$, left and right step numbers must be weighted by corresponding probabilities.

Binary Random Walk (on a Lattice)

Equal probabilities per step $p_- = p_+ = 1/2$
Let RW evolve over some time = total number of steps = $N \gg 1$.

How to calculate probability that a random trajectory stating at $\boldsymbol{m=0}$ **@t_0** will end up populating $\boldsymbol{m}(t_N)$?
→ Count # of all trajectories with N steps that lead from $\boldsymbol{m}(t_0)=0$ → $\boldsymbol{m}(t_N)$.

$$\text{Known is (for example) } m = m(t_N) > 0 \;\rightarrow\; m = N_+ - N_-$$



Calculate # possible partitions of N into $\{N_+, N_-\} \triangleq \{N, N_+\}$; $N_- = N - N_+$

Binomial coefficient

$$\binom{N}{N_+} = \frac{N!}{(N_+)! \times (N - N_+)!} = \frac{N!}{(N_+)! \times (N_-)!}$$

Factorial $N! := 1 \times 2 \times 3 \times \cdots \times N$
#permutations of N objects

$$\text{Example}: \binom{N=11}{N_+=7} = \frac{11!}{7!\cdot 4!} = 330 \text{ trajectories}$$

Binomial Probability Distribution

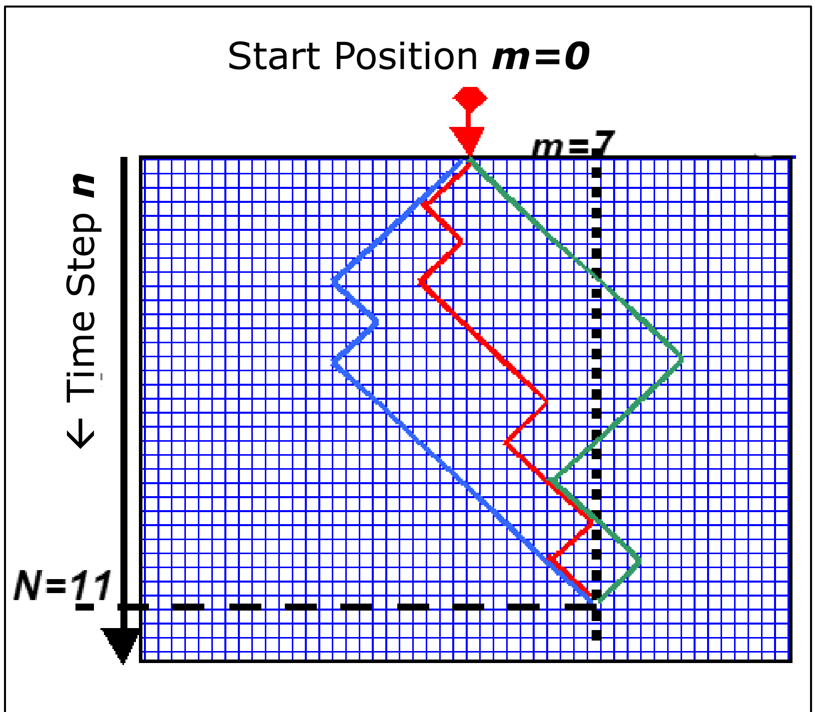
Arbitrary *Lvs.R* (binomial) probabilities $p_-+p_+=1$. RW evolves for $N \gg 1$ steps.

The ***probability*** for a random trajectory to land at position $m = N_+ - N_-$ after N steps in directions with associated individual probabilities $p_-+p_+=1$ is given by the binomial distribution in N_+ (or N_-)

$$P(N,N_+) = \frac{N!}{(N_+)! \cdot (N-N_+)!} \cdot p_+^{N_+} \cdot p_-^{N-N_+} \rightarrow$$

$$P(N,N_+) = \binom{N}{N_+} \cdot p_+^{N_+} \cdot (1-p_+)^{N-N_+}$$

$$P(N,N_-) = \binom{N}{N_-} \cdot p_-^{N_-} \cdot (1-p_-)^{N-N_-}$$



Proper normalization of probability
→ Binomial Theorem

$$\sum_{N_+=0}^{N} P(N,N_+) = \sum_{N_+=0}^{N} \binom{N}{N_+} \cdot p_+^{N_+} \cdot p_-^{N-N_+}$$
$$= (p_+ + p_-)^N = 1$$

Expectation Values (& Probability Moments)

Expectation values of m^k*, examples* $k=1$ *(average)* $k=2$ *(variance)*

$$\boxed{\langle m^k\rangle=\sum_{N_+=0}^{N} m^k(N_+)\cdot P(N,N_+)=\sum_{N_+=0}^{N}\binom{N}{N_+}\cdot m^k(N_+)\cdot p_+^{N_+}\cdot p_-^{N-N_+}}$$

constant variable

Express m^k *as a function of* N *and* N_+*, example for* $p_+=p_=1/2$

$$\langle m\rangle=\sum_{N_+=0}^{N}(2N_+-N)\cdot P(N,N_+)=-N+2\cdot\sum_{N_+=0}^{N}N_+\cdot\binom{N}{N_+}\cdot p_+^{N}=0$$

$$\boxed{\langle m\rangle=0}$$

Proof :

$$\underbrace{\sum_{N_+=0}^{N}\frac{N_+\cdot N!}{(N_+)!\cdot(N-N_+)!}}_{\text{First term}=0}p_+^{N}=p_+\cdot N\cdot\sum_{N_+=1}^{N}\frac{(N-1)!}{(N_+-1)!\cdot((N-1)-(N_+-1))!}\cdot p_+^{N-1}=\frac{N}{2}$$

Valid because $\displaystyle\sum_{\bar N_+=0}^{\bar N}\frac{\bar N!}{(\bar N_+)!\cdot(\bar N-\bar N_+)!}\cdot p_+^{\bar N}=1$

Use this method to calculate higher orders, e.g. $\langle N_+^2\rangle$ *etc.*

Expectation Values (& Probability Moments)

Expectation values of m^k, *examples* $k=1$(*average*) $k=2$(*variance*)

$$\boxed{\left\langle m^k \right\rangle = \sum_{N_+=0}^{N} m^k(N_+)\cdot P(N,N_+) = \sum_{N_+=0}^{N} \binom{N}{N_+}\cdot m^k(N_+)\cdot p_+^{N_+}\cdot p_-^{N-N_+}}$$

Similar for variance in m $\left(= \textit{range of final } m(t_N) \textit{ values}\right)$ $\boxed{\textit{Use } m \leftrightarrow N_+}$

$$\underline{\sigma_m^2 = \left\langle m^2 \right\rangle - \left\langle m \right\rangle^2} = \left\langle \left(2N_+ - N\right)^2 \right\rangle - 0 = \left\langle 4N_+^2 - 4N_+N + N^2 \right\rangle = ??$$

Since $p_+ = p_- = 1/2 \rightarrow$ $\boxed{\left\langle N_+ \right\rangle = N/2}$ and $\boxed{\sigma_{N_+}^2 = Np_+p_- = N/4}$

$$\sigma_m^2 = 4\left\langle N_+^2 \right\rangle - 4N\left\langle N_+ \right\rangle + N^2 = 4\left\langle N_+^2 \right\rangle - 8\left\langle N_+ \right\rangle\left\langle N_+ \right\rangle + 4\left\langle N_+ \right\rangle^2 = 4\left(\left\langle N_+^2 \right\rangle - \left\langle N_+ \right\rangle^2\right) = 4\sigma_{N_+}^2$$

$$\boxed{\textit{Variance } \sigma_m^2 = N \quad \textit{Standard Deviation } \sigma_m = \sqrt{N}}$$

Relative spread in asymptotic *m* values decreases with ***N***: $\boxed{\dfrac{\sigma_m}{N} = \dfrac{1}{\sqrt{N}}}$

Determined 2 moments (mean & var.) of the probability distribution
→ What is its shape, e.g.,"normal"? How frequent are rare events?

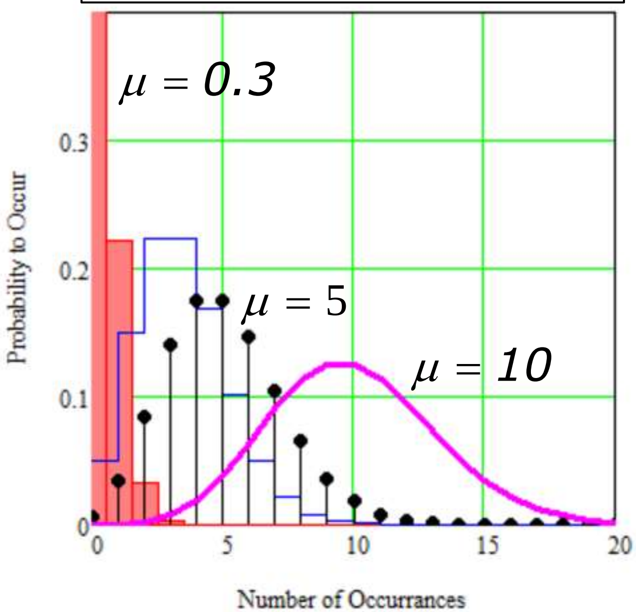
Limit: *Poisson Probability* Distribution

$$P_{binomial}(N,m;p)=\binom{N}{m}p^m(1-p)^{N-m}$$ → $$Lim_{p\to0,N\to\infty}P_{binomial}(N,m)=P_{Poisson}(\mu,m)$$

Probability for observing a number ***m*** of rare events of interest in period Δt, when the average #events per period Δt is known: $\mu = \langle m \rangle = N\cdot p$

Individual ***p***≪1 but ***N***≫1 trials (attempts) → ***N·p >0*** ← determines distribution

Distributions for μ = 0.3-10



Distributions ***P***(m) → Gaussian
p=0.1-0.3 and N~50

$$\boxed{P_{Poisson}(\mu,m)=\frac{\mu^m\cdot e^{-\mu}}{m!}}$$

$$\sigma_m^2 = N\cdot p\cdot(1-p)$$

$$\boxed{\sigma_m^2\approx\mu}$$

$Example: rare\ \#statistical\ decays$ $[\Delta t^{-1}]$

$$p=\frac{\dot N}{N}\ll(1/\Delta t)\to\sigma_m^2\approx\langle m\rangle\ \#counts$$

Observe transition Poisson → Gaussian
"Normal" Can prove rigorously

$$\lim_{\substack{p\to1\\N\gg1}}P_{bin}(N,m,p)=\frac{1}{\sqrt{2\pi\sigma_m^2}}\cdot\exp\left\{-\frac{(x-\langle m\rangle)^2}{2\sigma_m^2}\right\}$$

W. Udo Schröder, 2022

Extensions & Generalizations of RW Model

Associate an actual spatial degree of freedom ***(x)*** with the 1D string of cells ***m***: Step size $\Delta x \sim \Delta m$ → ***x=m·x***. *Results of 1D random Walk back and forth on x, starting from* $x_0 \triangleq m_0$*, is a distribution of positions x along the trajectory:*

Mean position $\boxed{\langle x \rangle = x_0 + \langle m \cdot \Delta x \rangle}$ and *Variance* $\boxed{\sigma_x^2 = \sigma_m^2 \cdot (\Delta x)^2 = N \cdot (\Delta x)^2}$

The trajectory covers a region from x_0 *to* $x_0 + x_{rms}$ *characteristic root-mean-square* x_{rms}

$$\boxed{x_{rms} = \sqrt{\langle x^2 \rangle} = \sqrt{N} \cdot \Delta x}$$

Large numbers $N \gg 1$ of RW steps @ finite probability p , binomial → Gaussian:

$$P_N(m) = \frac{1}{\sqrt{2\pi N}} \cdot \exp\left\{ -\frac{(m - m_0)^2}{2N} \right\} \Rightarrow \boxed{P_N(x) = \frac{1}{\sqrt{2\pi N \cdot (\Delta x)^2}} \cdot \exp\left\{ -\frac{(x - x_0)^2}{2N \cdot (\Delta x)^2} \right\}}$$

1D formalism → 3 or more independent degrees of freedom, e.g., ***x***→{***x, y, z***}
→ simultaneous probability = product of independent probabilities:

$$\boxed{P(x,y,z) = P(x) \cdot P(y) \cdot P(z)}$$