Random walk in one dimension
- Particle hops from site to site
- Only one step per hop
- Probability of hopping in either direction is \( \frac{1}{2} \) for each step
- Calculate probability that, after \( m \) steps, the particle is at position \( q \)

Mathematics of random walks
- Probability has two factors
  \[ P(q; m) = \left( \frac{1}{2} \right)^m C(n, p) \]
- Number of ways to end up at \( q \) is a combinatorial factor based on the number of positive steps, \( p \), and the number of negative steps, \( n \)
  \[ C(n, p) = \binom{m!}{n!p!(m-n)!} = \frac{m!}{n!(m-n)!} \]

Example random walk
- Movement of He in a given time
  - \( T = 298.15 \) K
  - \( P = 1 \) bar
  - Distance moved
    \[ \Delta x = \sqrt{<x^2> - <x>^2} = \sqrt{m\lambda} = \sqrt{2m\tau} \]
  - Typical flask is of the order of 10 cm in diameter.
  - In one minute, a molecule samples a reasonable fraction of the environment in that flask.

Calculation of averages in a one-dimensional random walk
- Use the probability, \( P \), to get averages of functions of the distance in \( m \) steps
  \[ <f(q)> = \sum_{m=0}^{\infty} P(q; m) f(q) = \left( \frac{1}{2} \right)^m \sum_{m=0}^{\infty} \frac{m!}{(m-q)!((m-q)!)^2} f(q) \]
- Examples:
  \[ <q> = 0 \]
  \[ <q^2> = m \]
  - The average position does not appear to change with number of steps, but the square of the distance traveled does.

Small-step-size, large-step-number random walk
- Treat the distribution function, \( P \), as a continuous function
  \[ P(q; m) = \frac{2}{\sqrt{2\pi m}} \exp\left(-\frac{q^2}{2m}\right) \]
- Technically only correct for either even or odd \( q \), but we "smooth" the probability over many steps
- Gaussian function
- Normalized probability distribution function
### Gaussian functions

- Occur in many different situations where random processes affect the experiment
  
  \[ P(x, \sigma) = \frac{1}{\sqrt{2\pi \sigma}} \exp\left(-\frac{x^2}{2\sigma^2}\right) \]

- Shape is determined by the standard deviation, \( \sigma \)
  
  - Large \( \sigma \), wide function
  - Small \( \sigma \), narrow function

- Random noise is Gaussian

### Diffusion from a point source

- Random movement of molecules is diffusion

- Described by a parameter, \( D \), the diffusion coefficient

- Diffusion in one dimension described by the probability distribution
  
  \[ P(x, t) \, dx = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) \, dx \]

### Gas-phase diffusion

- Diffusion coefficient related to gas-kinetic parameters
  
  \[ D = k \frac{v}{\lambda} \]

  where \( k = 0.5 \) from simple kinetic theory

  \( k = 0.599 \) from more accurate theory

- Measured and calculated gas diffusion coefficients at 273.15 K and 1.01325 bar

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>Calculated Diffusion Coefficient</th>
<th>Experimental Diffusion Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>( 4.35 \times 10^{-5} ) m² s⁻¹</td>
<td>( 4.52 \times 10^{-5} ) m² s⁻¹</td>
</tr>
<tr>
<td>Argon</td>
<td>( 1.54 \times 10^{-5} ) m² s⁻¹</td>
<td>( 1.57 \times 10^{-5} ) m² s⁻¹</td>
</tr>
<tr>
<td>Krypton</td>
<td>( 0.93 \times 10^{-5} ) m² s⁻¹</td>
<td>( 0.93 \times 10^{-5} ) m² s⁻¹</td>
</tr>
<tr>
<td>Xenon</td>
<td>( 0.57 \times 10^{-5} ) m² s⁻¹</td>
<td>( 0.58 \times 10^{-5} ) m² s⁻¹</td>
</tr>
</tbody>
</table>

### Diffusion in three dimensions

- Assume the diffusion in the three dimensions is uncorrelated
  
  \[ P(x, y, z; t) \, dx \, dy \, dz = \frac{1}{(4\piDt)^{3/2}} \exp\left(-\frac{x^2 + y^2 + z^2}{4Dt}\right) \, dx \, dy \, dz \]

  In spherical co-ordinates it simplifies and depends only on \( r \)
  
  \[ P(r, \theta, \phi; t) \, d\Omega = \frac{1}{(4\piDt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right) r^2 \sin \theta \, d\theta \, d\phi \]

### Macroscopic diffusion

- Diffusion eliminates concentration gradients

- Diffusion can be expressed in terms of the changes in concentrations

- Mass flux across an area, \( J \)

- **Fick’s first law** in one dimension: diffusion is “caused” by a concentration gradient
  
  \[ J = -D \frac{\partial c}{\partial x} \]

- **Fick’s second law**: The rate of change of concentration in a volume is determined by the gradient of the flux across its boundaries
  
  \[ \frac{\partial c}{\partial t} = -\frac{\partial J}{\partial x} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) = D \left( \frac{\partial^2 c}{\partial x^2} \right) \]

  In three dimensions
  
  \[ \frac{\partial c}{\partial t} = D \nabla^2 c \]
Solutions of Fick’s equations

- Depends on boundary conditions
- Example: diffusion between two tubular regions, like from sugar water into pure water in a pipe

“Typical” diffusion coefficients

<table>
<thead>
<tr>
<th>Gas (0°C)</th>
<th>D/(10^-4 m²/s)</th>
<th>Liquid (25°C)</th>
<th>D/(10^-9 m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.5</td>
<td>H₂O</td>
<td>2.4</td>
</tr>
<tr>
<td>O₂</td>
<td>0.19</td>
<td>CH₃OH</td>
<td>2.3</td>
</tr>
<tr>
<td>N₂</td>
<td>0.15</td>
<td>C₆H₆</td>
<td>2.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.10</td>
<td>Hg</td>
<td>1.7</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.09</td>
<td>C₃H₇OH</td>
<td>1.0</td>
</tr>
<tr>
<td>Xe</td>
<td>0.05</td>
<td>C₂H₅OH</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Summary

- Random walk is a simple theory of movement
- Diffusion describes the results of random movement of molecules
  - Random-walk derivation
  - Fick’s Laws
  - Diffusion coefficient characterizes the material