A macroscopic system contains a LARGE number of particles, not all of which have the same set of microscopic properties.

To give a macroscopic system’s state requires a distribution function, \( F \), that describes the “amounts” of properties, either macroscopic or microscopic, as a function of independent variables.

The equilibrium state is described by a unique distribution function for each property.

A Gaussian distribution function, \( F \), of the two co-ordinates \( x \) and \( y \).

Particles in a Box

- Example distribution function for particles in a box, showing two regions.
- Left side has more particles than the right.
  - This particular distribution can be considered bimodal.
  - Real distribution functions are more complex functions of position.
- Equilibrium particle distribution under no outside constraints.
  - Particle density is uniform (i.e. a constant, independent of position).

Two equilibrium distributions

- Two other simple equilibrium distributions:
  - Thermal equilibrium
    - No external constraints
    - Temperature is independent of position
  - Mechanical equilibrium
    - No external constraints
    - Pressure is independent of position
- Not all equilibrium distributions are constants, independent of the variable.
Boltzmann’s distribution: the speed distribution at equilibrium

- An equilibrium distribution that depends on the variable
- Boltzmann distribution of speeds
  - Only kinetic energy
  - Compromise between minimal energy and maximal entropy
  - Normalized
- Depends on speed \( v \), mass \( m \), and temperature \( T \)

\[
F_v(v) = \frac{m}{2\pi kT} \exp\left(\frac{mv^2}{2kT}\right)
\]

\[
F_v(v) = 4\pi \left(\frac{m}{2\pi kT}\right)^{1/2} v^2 \exp\left(\frac{-mv^2}{2kT}\right)
\]

\[
\int F_v(v) dv = 1
\]

\[
\int F_v(v) dv = 1
\]

Calculating average molecular properties

- Averages are integrals of properties weighted by the distribution function
  - Integral must be carried out over all possible values of the independent variable
- Examples
  - Average speed in one dimension
  - Average speed in three dimensions
  - Average temperature at thermal equilibrium
    - For a constant distribution, the average is the single value of the temperature, \( T \)

\[
f_{\text{ave}} = \int f(v) F_v(v) dv
\]

\[
\nu_{\text{ave}} = \int v F_v(v) dv
\]

\[
\nu_{\text{ave}} = \int v^2 F_v(v) dv
\]

\[
\tau_{\text{ave}} = \int (\int F_v(v) dv) F_v(v) dv
\]

\[
\tau_{\text{ave}} = \int (\int F_v(v) dv) F_v(v) dv
\]

\[
\tau_{\text{ave}} = \int (\int F_v(v) dv) F_v(v) dv
\]

\[
\tau_{\text{ave}} = \frac{1}{T^2} \int (\int F_v(v) dv) F_v(v) dv
\]

Flux

- A distribution changes because of transfer of a quantity (e.g., molecules or heat) from one place to another.
- Change is quantified by a parameter called the flux, \( J \), the net amount of a quantity transferred across a plane per unit area in unit time.
- Flux may not be uniform across a macroscopic system: \( J(x) \) = constant
- A nonzero flux is required for a system to go from a nonequilibrium distribution to an equilibrium distribution.

\[
J(x) = \frac{1}{A} \frac{dN}{dt}
\]

Gradients of distributions

- Nonequilibrium systems evolve towards equilibrium
- Spatial distributions of properties, e.g. temperature, are time-dependent in nonequilibrium systems
- An important descriptor is the gradient of a distribution
  - A measure of how the distribution changes from one position to the next
  - In equilibrium systems for which a property (like temperature) is uniform, the gradient at every point is zero.
  - Not all equilibrium distributions are uniform.

\[
G(x_0) = \frac{dF}{dx} \bigg|_{x_0}
\]
Linear response

To determine how a system evolves, one must specify how the flux depends on the system's parameters. It is said to provide a linear response.

In the linear-response regime, the flux is proportional to and opposite in sign to the gradient of the property.

The proportionality defines the transport coefficient, $\alpha$, for the process.

- For electrical systems, the coefficient is called the conductance.
- For systems involving approach to thermal equilibrium, the coefficient is called thermal conductivity.
- For systems involving movement of particles, the coefficient is called the diffusion coefficient.

The size of a transport coefficient gives a measure of how efficiently transport occurs.

Nonlinear response occurs when the flux is strongly coupled to the parameters of the system.

- Systems may display time dependences that are unusual or unexpected under these conditions.

\[ J_N = -\alpha_n \frac{dN}{dx} \]
\[ J_T = -\alpha_T \frac{dT}{dx} \]

Fick’s first law and the diffusion coefficient

- In a three-dimensional system, not all molecules that are nominally traveling in the $x$ direction reach the plane.
- Molecules have off-axis components.
- Correct by multiplying the previously derived quantity by $2/3$, the fraction that will reach the plane.
- By comparison to Fick’s law, one has an equation for the diffusion coefficient of an ideal gas in terms of kinetic-theory parameters.
- Fick’s first law is generally applicable to a wide variety of substances and phases.
- The kinetic-theory representation of the diffusion coefficient is only appropriate to the gas phase.

\[ J > = -\frac{2}{3}D \frac{dG}{dx} \]
\[ < J > = -DG \]

\[ D = \frac{kV_{mol} \lambda}{3} \]

Determination of net flux of molecules across a plane

- Count number of molecules in a volume on the left whose distance to the plane allows them to reach the plane in a time, $t$.
- Only half of the molecules on the left are moving towards the plane.
- The number of molecules on the right who will reach the plane in the same time is the same, except that the speed is negative.
- The net flux, $J$, through the plane is the difference of these two.
- Averaging over the speed distribution gives the total flux.

\[ J = \frac{\int_{0}^{\infty} N d\nu G_v J \cdot d\nu \cdot \delta \nu}{\int_{0}^{\infty} N d\nu G_v \cdot d\nu \cdot \delta \nu} \]

Gas-phase diffusion

- Diffusion coefficient can be calculated from gas-kinetic parameters

\[ D = \frac{k V_{mol} \lambda}{3} \]

where $k = 1/3$ or $1/2$ from simple kinetic theory

$1/16$ from accurate theory

<table>
<thead>
<tr>
<th>Noble Gas</th>
<th>Diffusion Coefficient (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neon</td>
<td>$1.32 \times 10^{-5}$</td>
</tr>
<tr>
<td>Argon</td>
<td>$1.45 \times 10^{-5}$</td>
</tr>
<tr>
<td>Krypton</td>
<td>$6.50 \times 10^{-6}$</td>
</tr>
<tr>
<td>Xenon</td>
<td>$6.35 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Time-dependent changes of concentration

- Can measure concentration and concentration gradients as a function of time.
- Need an expression for the time-dependence of concentration.
- Fick's second law

\[ \frac{\partial N}{\partial t} = D \left( \frac{\partial^2 N}{\partial x^2} \right) \]

Solution of Fick's second law

- The solution of Fick's second law depends on the boundary conditions.
- For diffusion from a plane that is populated with \( N_0 \) molecules, the solution is a Gaussian that broadens as a function of time.
- In the limit of infinite time, the result is a constant density of molecules across the sample space.

Solution of Fick's second law:

\[ N(x,t) = \frac{N_0}{2\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \]

Another solution of Fick's equation

- An infinitely long tube
- Initial condition:
  - All molecules to the left of the tube
  - Like sugar water diffusing into pure water in a pipe
- Two ways to measure diffusion:
  - Monitor time dependence of concentration at one position
  - Monitor position dependence of concentration at one time

Concentration profiles as a function of time: \( N(t) = N_0 e^{-\frac{t}{2Dt}} \)

Typical diffusion coefficients

- "Sizes" of quantities are important to remember.
- Diffusion coefficients of gases are larger than diffusion coefficients of liquids.
- Heavier molecules often have smaller diffusion coefficients, if the two molecules are in the same phase.

<table>
<thead>
<tr>
<th>Gas (°C)</th>
<th>D (m²s⁻¹)</th>
<th>Liquid (25°C)</th>
<th>D (m²s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>1.5x10⁻⁴</td>
<td>H₂O</td>
<td>2.4x10⁻⁸</td>
</tr>
<tr>
<td>O₂</td>
<td>1.9x10⁻⁵</td>
<td>CH₃OH</td>
<td>2.3x10⁻⁸</td>
</tr>
<tr>
<td>N₂</td>
<td>1.5x10⁻⁵</td>
<td>C₆H₆</td>
<td>2.2x10⁻⁹</td>
</tr>
<tr>
<td>CO₂</td>
<td>1.0x10⁻⁵</td>
<td>Hg</td>
<td>1.7x10⁻⁹</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>0.9x10⁻⁹</td>
<td>C₆H₁₂OH</td>
<td>1.0x10⁻⁹</td>
</tr>
<tr>
<td>Xe</td>
<td>0.5x10⁻⁹</td>
<td>C₆H₁₂OH</td>
<td>0.8x10⁻⁹</td>
</tr>
</tbody>
</table>
Diffusion coefficients of proteins

Proteins tend to have smaller diffusion coefficients than small molecules in liquids.

Example diffusion coefficients at 20°C:

<table>
<thead>
<tr>
<th>Protein</th>
<th>D (m² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alcohol dehydrogenase</td>
<td>4.7×10⁻¹¹</td>
</tr>
<tr>
<td>Cytochrome C</td>
<td>1.3×10⁻¹¹</td>
</tr>
<tr>
<td>Ferritin</td>
<td>10.2×10⁻¹¹</td>
</tr>
<tr>
<td>Glutathione</td>
<td>3.8×10⁻¹¹</td>
</tr>
<tr>
<td>Hemoglobin A</td>
<td>4.5×10⁻¹¹</td>
</tr>
<tr>
<td>Insulin</td>
<td>5.4×10⁻¹¹</td>
</tr>
<tr>
<td>Lipoprotein, HD</td>
<td>4.9×10⁻¹¹</td>
</tr>
<tr>
<td>Myoglobin</td>
<td>9.4×10⁻¹¹</td>
</tr>
<tr>
<td>Pepsin</td>
<td>9.7×10⁻¹¹</td>
</tr>
<tr>
<td>Pyruvate kinase</td>
<td>4.8×10⁻¹¹</td>
</tr>
<tr>
<td>α-Lactalbumin</td>
<td>10.8×10⁻¹¹</td>
</tr>
<tr>
<td>β-Lactoglobulin</td>
<td>2.4×10⁻¹¹</td>
</tr>
<tr>
<td>β-Lactalbumin</td>
<td>13×10⁻¹¹</td>
</tr>
<tr>
<td>Cytochrome C</td>
<td>10.6×10⁻¹¹</td>
</tr>
<tr>
<td>β-Lactoglobulin</td>
<td>4.7×10⁻¹¹</td>
</tr>
</tbody>
</table>

Summary

Calculations with distribution functions give average values of quantities such as speed.

Nonequilibrium distributions evolve to equilibrium distributions.

Inhomogeneous distribution of molecules evolves to a homogeneous distribution.

Fick’s laws govern the return to the equilibrium mass distribution.

Diffusion coefficients are expressible in terms of kinetic-theory parameters.

It allows estimation of the diffusion coefficient of a gas that is nearly ideal.

It can determine parameters like molecular diameter from diffusion measurement.

Diffusion occurs in other phases:

- Diffusion in liquids
  - Self-diffusion
  - Interdiffusion between two different liquids
  - Diffusion of molecules in solids (often very, very slow)

Sizes of diffusion coefficients:

- Fast diffusion for gases (D = 10⁻⁵ m² s⁻¹)
- Diffusion of liquids (D = 10⁻⁹ m² s⁻¹)