Physical Principles in Biology
Biology 3550
Spring 2024

Lecture 18:

Thermal Motion of Molecules

Wednesday, 21 February 2024

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Announcements

- Problem Set 3:
  - Due 11:59 PM, Monday, 26 February.
  - Download problems from Canvas.
  - Upload work to Gradescope.
  - Show your work!
- Quiz 3:
  - Friday, 23 February
  - 25 min, second half of class
- No office hours on Thursday, 22 February
- Review Session
  - 5:15 PM, Thursday, 22 February
  - HEB 2002
  - Come with questions!

Kinetic Energy

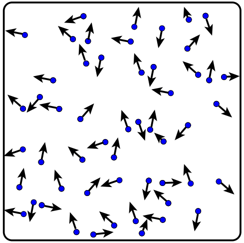
- A object of mass, m, moving with velocity, v, in the x-direction has kinetic energy in that direction of:

$$E_{\mathrm{k},x} = mv_x^2/2$$

- What does this mean?
  - The energy required to accelerate the mass, m, from rest to velocity, v_x.
  - Also the energy released during the deceleration of the mass from velocity, v_x, to rest.
  - Kinetic energy does not depend on the rate of acceleration or deceleration, only the final velocity.

Kinetic Energy of Molecules

- Temperature is the measure of kinetic energy of molecules.
- How do we measure temperature?
- Pressure of a gas is due to the collision of molecules against container walls.



$$PV = nRT$$

P = pressure, V = volume, n = number of moles, T = temperature,
R = gas constant.

Clicker Question #1

$$PV = nRT$$

What are the units of the gas constant?

A) $\text{pascal} \cdot \text{L} \cdot \text{K}^{-1}\text{mol}^{-1}$

B) $\text{kg} \cdot \text{m}^2\text{s}^{-2}\text{K}^{-1}\text{mol}^{-1}$

C) $\text{m}^3\text{bar} \cdot \text{K}^{-1}\text{mol}^{-1}$

D) $\text{JK}^{-1}\text{mol}^{-1}$

E) $\text{L} \cdot \text{atm} \cdot \text{K}^{-1}\text{mol}^{-1}$

All of the above!

Units of the Gas Constant

- From the ideal gas law: $$R = \frac{PV}{nT}$$
- In SI basic units:

  Pressure, force per unit area: $\mathrm{kg} \cdot \mathrm{m} \cdot \mathrm{s}^{-2} \div \mathrm{m}^2 = \mathrm{kg} \cdot \mathrm{m}^{-1}\mathrm{s}^{-2} = \mathrm{Pa}$

  Volume: m^3

  Gas constant: $\dfrac{\mathrm{kg} \cdot \mathrm{m}^{-1} \cdot \mathrm{s}^{-2} \times \mathrm{m}^3}{\mathrm{K} \cdot \mathrm{mol}} = \mathrm{kg} \cdot \mathrm{m}^2\mathrm{s}^{-2}\mathrm{K}^{-1}\mathrm{mol}^{-1}$
- Joule (unit of energy) = Nm = $\mathrm{kg} \cdot \mathrm{m}^2\mathrm{s}^{-2}$
- The gas constant expressed in energy units:

  $$R \approx 8.314\,\mathrm{JK}^{-1}\mathrm{mol}^{-1} \approx 1.987\,\mathrm{cal} \cdot \mathrm{K}^{-1}\mathrm{mol}^{-1}$$
- The kinetic energy of one mole of molecules at temperature T is proportional to RT.

Kinetic Energy of Molecules

- The Boltzmann constant, k, the "gas constant per molecule":

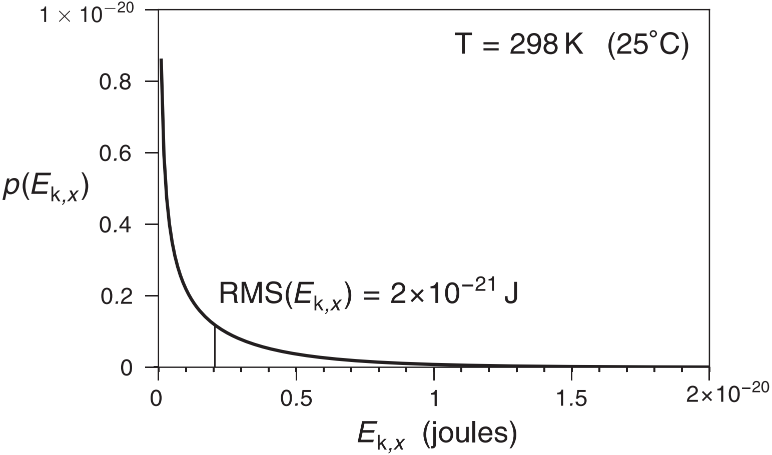
$$
\begin{aligned}
k = R/N_{\mathrm{A}} &= 8.314\,\mathrm{JK^{-1}mol^{-1}} \div 6.02 \times 10^{23}\,\mathrm{molecule/mol} \\
&= 1.38 \times 10^{-23}\,\mathrm{JK^{-1}}
\end{aligned}
$$

- Molecules at a given temperature do not have unique velocities or kinetic energies.
- Molecules have a broad distribution of energies, with RMS average translational kinetic energy in each direction (x, y or z):

$$\mathrm{RMS}(E_{\mathrm{k},x}) = kT/2$$

- Translational kinetic energy does *not* depend on mass or structure.
- In context of molecular motion, "$E_{\mathrm{k},x}$" will imply RMS value.

Distribution of Molecular Kinetic Energies



$$p(E_{k,x}) = \frac{1}{\sqrt{\pi E_{k,x} kT}} e^{-E_{k,x}/(kT)}$$

Clicker Question #2

How fast does a small molecule move at room temperature (between collisions)?

A) 10^{-4} m/s

B) 10^{-2} m/s

C) 1 m/s

D) 10^{2} m/s

E) 10^{4} m/s

All answers count for now.

Velocities of Molecules

- Kinetic energy of a molecule, in x-direction: $\mathrm{RMS}(E_{\mathrm{k},x}) = kT/2$
- Kinetic energy of any object: $E_{\mathrm{k},x} = mv_x^2/2$
- Solving for v:

$$mv_x^2/2 = kT/2$$

$$v_x^2 = kT/m$$

$$v_x = \sqrt{kT/m}$$

(also an RMS value)

- Velocity increases with $\sqrt{T}$ and decreases with $\sqrt{m}$.
- Energy does not depend on molecular mass, but velocity does.

Velocity of an N_2 Molecule at Room Temperature

- Mass

$$m = 28\,\mathrm{g/mol} \div 6.02 \times 10^{23}\,\mathrm{molecules/mol}$$

$$= 4.65 \times 10^{-23}\,\mathrm{g} = 4.65 \times 10^{-26}\,\mathrm{kg}$$

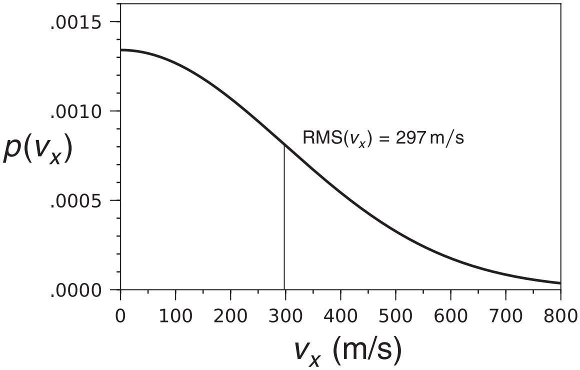
- Temperature = 25°C= 298 K
- Velocity:

$$\mathrm{RMS}(v_x) = \sqrt{kT/m}$$

$$= \sqrt{1.38 \times 10^{-23}\,\mathrm{kg \cdot m^2 s^{-2} K^{-1}} \times 298\,\mathrm{K}/4.65 \times 10^{-26}\,\mathrm{kg}}$$

$$\approx 300\,\mathrm{m/s} \quad (1,000\,\mathrm{km/hr})$$

Distribution of N_2 Velocities in a Gas at 298 K



- The Maxwell-Boltzmann distribution

$$p(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mv_x^2/(2kT)}$$

(assumes ideal gas behavior)

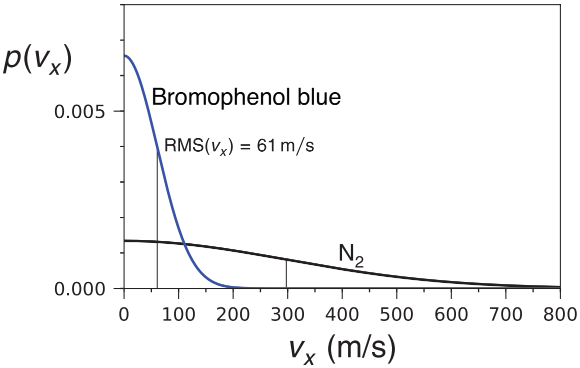
Diffusion of Bromophenol Blue Revisited

- From diffusion experiment: $D = 2 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s}$
- Definition of the diffusion coefficient: $D = \frac{\delta_x^2}{2\tau}$.
- δ_x/τ = velocity, which we can calculate now!
  - $v_x = \sqrt{kT/m}$
  - Molar mass = 670 g/mol
    Molecular mass = 1.11×10^{-24} kg

$$v_x = \sqrt{1.38 \times 10^{-23}\,\mathrm{kg} \cdot \mathrm{m}^2\mathrm{s}^{-2}\mathrm{K}^{-1} \times 298\,\mathrm{K}/1.1 \times 10^{-24}\,\mathrm{kg}}$$

$$= 61\,\mathrm{m}/\mathrm{s}$$

Distribution of Velocities at 298 K



- Average (RMS) kinetic energies of molecules are the same.
- Based on ideal gas behavior.
- Distribution is similar in liquids.

Diffusion of Bromophenol Blue Revisited

- $D = \delta_x^2/(2\tau) = 2 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s}$
- Express D in terms of velocity:

$$D = v_x \delta_x / 2$$

- $v_x = \delta_x/\tau = 61\,\mathrm{m/s}$
- Solve for δ_x

$$\delta_x = 2D/v_x = 2 \times 2 \times 10^{-10}\,\mathrm{m}^2/\mathrm{s} \div 61\,\mathrm{m/s}$$
$$= 6.5 \times 10^{-12}\,\mathrm{m}$$

Diffusion of Bromophenol Blue Revisited

- From the previous slide

$$\delta_x = v_x \cdot \tau = 6.5 \times 10^{-12}\,\mathrm{m}$$

- Solve for τ

$$v_x = \delta_x / \tau$$

$$\tau = \delta_x / v_x = 6.5 \times 10^{-12}\,\mathrm{m} \div 61\,\mathrm{m/s}$$

$$= 10^{-13}\,\mathrm{s} = 0.1\,\mathrm{ps}$$

- VERY short distances and times!

Clicker Question #3

A "typical" protein molecule in water: $D = 1 \times 10^{-11}\,\mathrm{m^2/s}$ and $v_x = 6\,\mathrm{m/s}$

What is the RMS step length, δ_x, as the molecule diffuses via a random walk?

A) $1\times10^{-13}\,\mathrm{m}$

B) $3\times10^{-13}\,\mathrm{m}$

C) $1\times10^{-12}\,\mathrm{m}$

D) $3\times10^{-12}\,\mathrm{m}$

E) $1\times10^{-11}\,\mathrm{m}$

$$D = \frac{\delta_x^2}{2\tau}$$

$$\delta_x = \frac{2D}{v_x} = \frac{2 \times 1 \times 10^{-11}\,\mathrm{m^2/s}}{6\,\mathrm{m/s}} = 3.3 \times 10^{-12}\,\mathrm{m}$$

Clicker Question #4

A "typical" protein molecule in water: $D = 1 \times 10^{-11}\ \mathrm{m^2/s}$ and $v_x = 6\ \mathrm{m/s}$.

What is the RMS average time between direction changes, τ, as the molecule diffuses via a random walk?

A) 5×10^{-14} s

B) 5×10^{-13} s

C) 5×10^{-12} s

D) 5×10^{-11} s

E) 5×10^{-10} m

$$D = \frac{\delta_x^2}{2\tau}$$

$$\tau = \frac{\delta_x}{v_x} = \frac{3.3 \times 10^{-12}\ \mathrm{m}}{6\ \mathrm{m/s}} = 5.5 \times 10^{-13}\ \mathrm{s}$$

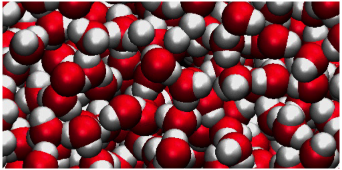
A Small Molecule Versus a Big One

	Bromophenol blue	Protein
Molar mass	670 g/mol	60,000 g/mol
Velocity	60 m/s	6 m/s
D	$2 \times 10^{-10}\ \mathrm{m}^2/\mathrm{s}$	$1 \times 10^{-11}\ \mathrm{m}^2/\mathrm{s}$
δ_x	6×10^{-12} m	3×10^{-12} m
τ	1×10^{-13} s	5×10^{-13} s

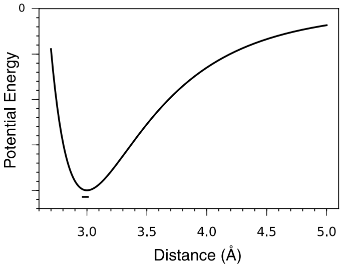
- How do we think about the numbers on a molecular scale?
- Have to think about liquids.

The Nature of Liquids

- Molecules are very densely packed
- Motions of molecules are limited by the "energy barriers" surrounding them.
- Other molecules in a solution are similarly constrained.
- Molecules move only very short distances before they change direction.
- The larger the molecule is, the less freedom it has and the more slowly it moves.



From a simulation of liquid water.



RMS Distance of Diffusion

- Random walk along one direction: $\langle x^2 \rangle = n\delta_x^2$
- For diffusion:

$$D = \frac{\delta_x^2}{2\tau}$$

$$\delta_x^2 = 2D\tau$$

$$n = t/\tau$$

$$\langle x^2 \rangle = n\delta_x^2 = \frac{t}{\tau} 2D\tau = 2Dt$$

$$\mathrm{RMS}(x) = \sqrt{2Dt}$$

- For bromophenol blue (and molecules of similar size):

$$\mathrm{RMS}(x) = \sqrt{t/s} \times 2 \times 10^{-5}\,\mathrm{m}$$

RMS Distance of Diffusion for a Small Molecule