BIOPHYSICS, PHYSICAL METHODS OF ANALYSIS

Lecture 2

Molecular Physics. Thermodynamics.

Plan of the Lecture

1. Types of thermodynamical systems.

2. Laws of thermodynamics.

3. The ideal gas.

4. Classical vs. statistical thermodynamics .

5. Real gases.

6. Thermodynamic potentials.

Purpose of the lecture is

➡ **to obtain the practical skills of using the laws of molecular physics and thermodynamics in studying chemical and biological sciences.**

Thermodynamics

Originally developed as a 19thC theory of steam engines, thermo (heat) dynamics (power or capacity) i.e. power created by heat. Sadi Carnot (1824) *Reflections on the Motive Power of Fire.*

Scope of thermodynamics is now 'almost everything':

- heat engines, heat pumps and refrigerators (cyclic processes)
- the arrow of time
- chemistry, incl. biochemistry: photosynthesis, haemoglobin, ATP
- hurricanes, plate tectonics, magnetisation & demagnetisation
- life processes e.g. ecosystems

Different types of system

open system   closed system   isolated system
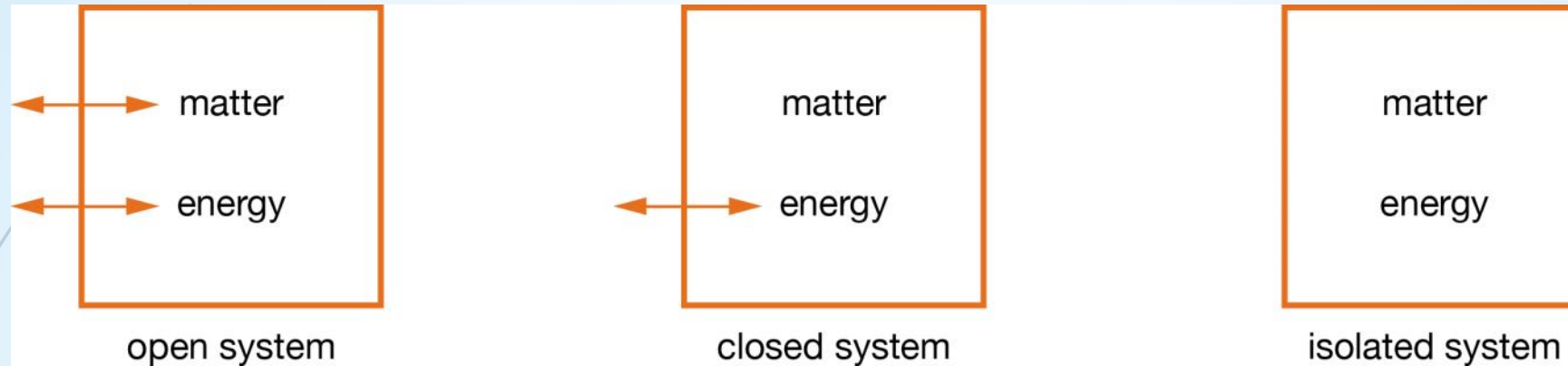
- Heat can be transferred in a number of different ways:
  - **Conduction**: transfer of heat via molecular collisions. Usually the dominant mechanism for heat transfer in metals.
  - **Convection**: transfer of heat of mass movement of molecules. Usually the dominant mechanism of heat transfer in liquids and gases.
  - **Radiation**: transfer of heat using electromagnetic radiation (e.g. light).

1st law

- The first law of thermodynamics is an extension of the law of conservation of energy

- The transfer of energy from a system to its surroundings, as a result of a temperature difference, is called **heat** (thermal transfer).

- The change in internal energy of a system is equal to the heat added to the system minus the work done by the system

$$\Delta U = Q - W$$

2nd law

- It is not possible to completely change heat into work with no other change taking place.

- Heat flows naturally from a hot object to a cold object; heat will not flow spontaneously from a cold object to a hot object.

- During any process the universe moves toward more probably states--states with more entropy. (**S** is a measure of the disorder of its matter and energy.)

Laws of Thermodynamics

- Zeroth Law: If object A is in thermal equilibrium with object B, and if object B is in thermal equilibrium with object C, then objects A and C are also in equilibrium. This is sort of a "transitive property of heat."

- First Law: Energy is always conserved. It can change forms: kinetic, potential, internal etc., but the total energy is a constant.

- Second Law: During any natural process the total amount of *entropy* in the universe always increases. Entropy can be defined informally as a measure of the randomness or disorder in a system.

- Third Law: Absolute Zero is unattainable.

Classical vs Statistical

- Classical thermodynamics concerns the relationships between bulk properties of matter. Nothing is examined at the atomic or molecular level.

All of thermodynamics can be expressed in terms of four quantities: Temperature (T), Internal Energy (U), Entropy (S), Heat (Q)

- Statistical thermodynamics seeks to explain those bulk properties in terms of constituent atoms. The statistical part treats the aggregation of atoms, not the behavior of any individual atom.

Temperature scales. One step on the Kelvin scale is the same as one step on the Celsius scale. These scales are off by 273.15 K, so: *K = C + 273.15*

Room temperature is around 293 kelvins, which is 20 °C

Process Terminology

$$\Delta U = Q - W$$

- Adiabatic – no heat transferred (Q=0)
- Isothermal – constant temperature (for ideal gases, if $\Delta T=0$, $\Delta U = 0$, therefore, $Q = W$)
- Isobaric – constant pressure (ΔU, W, and Q are generally non-zero, but calculating the work done by an ideal gas is $W = P \cdot \Delta V$)
- Isochoric – constant volume (when the volume of a system doesn't change, it will do no work on its surroundings. $W = 0$, $\Delta U = Q$)

An ideal gas (kinetic theory)

• huge number of point molecules (occupy negligible volume) in continual random <u>motion</u> (and so 'kinetic')

• colliding elastically with each other and with container walls

• no forces between the molecules, except in collision

An ideal gas (kinetic theory)

- time in collisions very small compared to time between collisions

- distance travelled between collisions ('mean free path') depends on gas density

- average speed of molecules depends on gas temperature

- in a gas composed of different molecules, the average molecular E_k is the same for all, so those with larger mass have smaller speed

Avogadro's Number

One mole is the number of atoms in a 12 g sample of carbon-12. The number of atoms or molecules in a mole is called *Avogadro's Number*, N_A.

$$N_A = 6.02 \times 10^{23} \ mol^{-1} \qquad \text{(Avogadro's number),}$$

If n is the number of moles contained in a sample of any substance, N is the number of molecules, M_{sam} is the mass of the sample, m is the molecular mass, and M is the molar mass, then

$$n = \frac{N}{N_A}. \qquad M = mN_A. \qquad n = \frac{M_{sam}}{M} = \frac{M_{sam}}{mN_A}.$$

Ideal Gases

The equation of state of a rarefied gas is found to be

$$pV = nRT \quad \text{(ideal gas law),} \qquad R = 8.31 \text{ J/mol} \cdot \text{K.}$$

Here p is the pressure, n is the number of moles of gas present, and T is its temperature in kelvins.
R is the gas constant that has the same value for all gases.
Or equivalently,

$$pV = NkT \quad \text{(ideal gas law).}$$

Here, k is the Boltzmann constant, and N the number of molecules.

$$k = \frac{R}{N_A} = \frac{8.31 \text{ J/mol} \cdot \text{K}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 1.38 \times 10^{-23} \text{ J/K.}$$

The internal energy.

- We have assumed that the internal energy U of a monatomic gas is equal to $(3/2)kT$.

- It turns out that each degree of freedom carried an internal energy of $(1/2)kT$.

- Predictions for a diatomic molecule:
  - Linear motion: 3 degrees of freedom.
  - Rotational motion: 2 degrees of freedom.
  - Vibrational motion: 2 degrees of freedom.

- The number of degrees of freedom excited depend on the temperature.
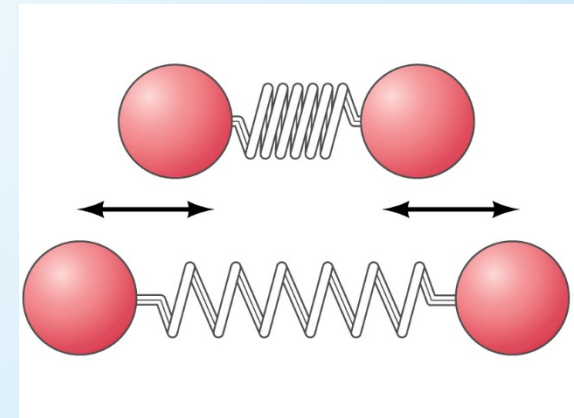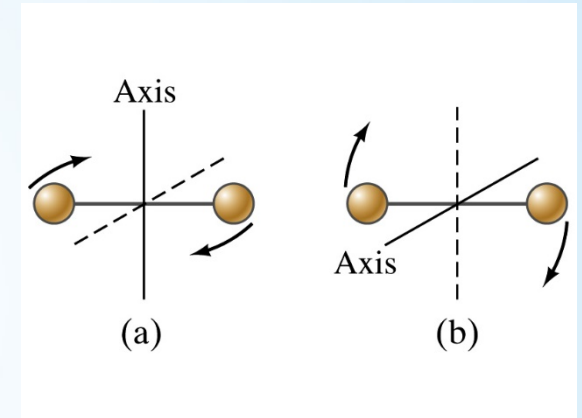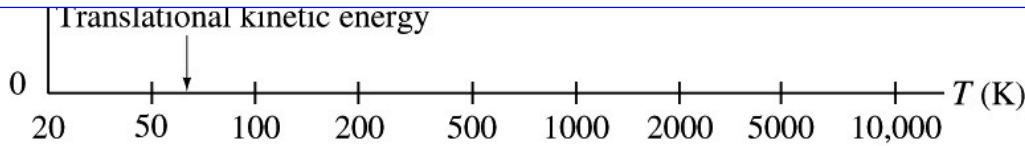
Heat Capacity of Ideal Gas

- C_V = heat capacity at constant volume $C_V = 3/2\ R$

- C_P = heat capacity at constant pressure $C_P = 5/2\ R$

- For constant volume $Q = nC_V\Delta T = \Delta U$

- The universal gas constant $R = 8.314$ J/mol·K

- recall the ideal gas equations $pV = NkT$ and $pV = \frac{7}{2}nRT$

- recall the mean E_k of a gas molecule, $E = \frac{3}{2}kT$
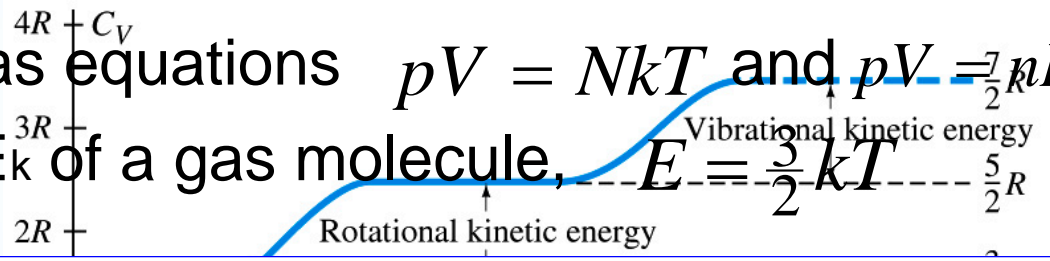
Using C_v to measure the degrees of freedom.

Molar Specific Heat at Constant Volume

The temperature increase is done without changing the volume.
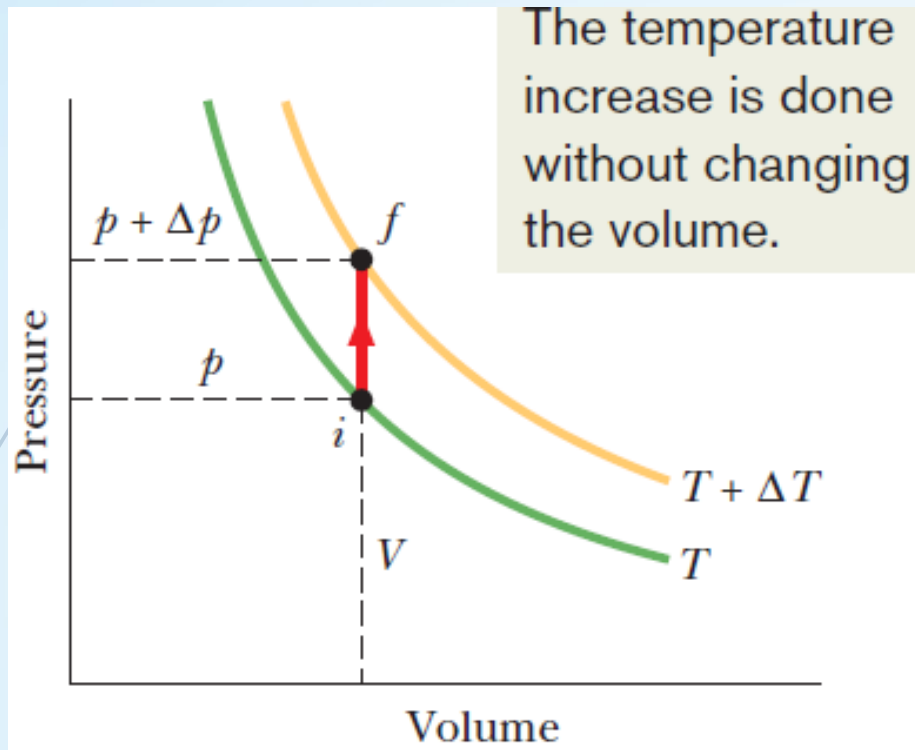
$$Q = nC_V \Delta T \qquad \text{(constant volume)},$$

where C_V is a constant called **the molar specific heat at constant volume**.

But, $\Delta E_{int} = Q - W.$

Therefore, $\Delta E_{int} = nC_V \Delta T - W.$

With the volume held constant, the gas cannot expand and thus cannot do any work.
Therefore,

$$C_V = \frac{\Delta E_{int}}{n \, \Delta T}$$

$$\Delta E_{int} = \tfrac{3}{2} nR \, \Delta T. \longrightarrow C_V = \tfrac{3}{2} R = 12.5 \text{ J/mol} \cdot \text{K} \qquad \text{(monatomic gas)}.$$

When a confined ideal gas undergoes temperature change T, the resulting change in its internal energy is

$$\Delta E_{int} = nC_V \Delta T \qquad \text{(ideal gas, any process)}.$$

A change in the internal energy E_{int} of a confined ideal gas depends on only the change in the temperature, not on what type of process produces the change.

Molar Specific Heat at Constant Pressure

The temperature increase is done without changing the pressure.
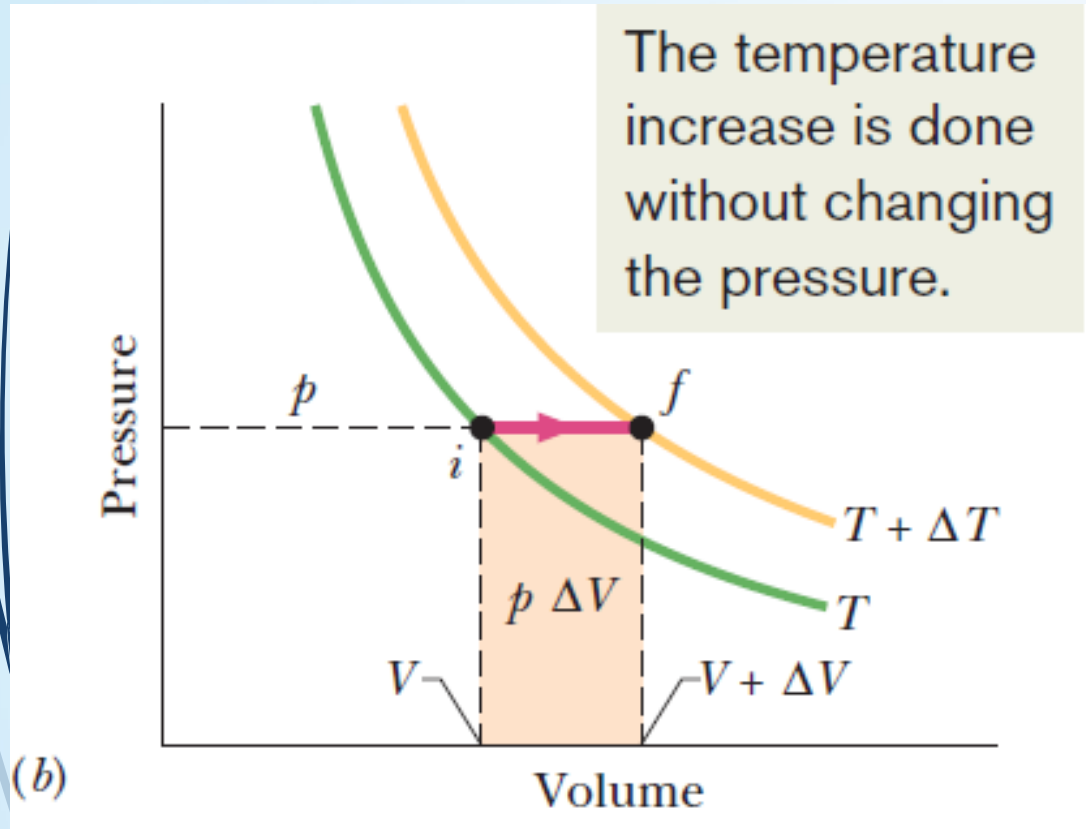
$$Q = nC_p\,\Delta T \qquad \text{(constant pressure)},$$

where C_p is a constant called **the molar specific heat at constant pressure.**
This C_p is greater than the molar specific heat at constant volume C_V, since for the same internal energy change, more heat is needed to provide work.

$$\Delta E_{int} = Q - W.$$

$$W = p\,\Delta V = nR\,\Delta T.$$

$$\Delta E_{int} = nC_V\Delta T$$

$$C_V = C_p - R \quad \Rightarrow \quad C_p = C_V + R.$$

The total pressure of a mixture of gases equals the sum of the pressures that each would exert if it were present alone

$$P_T = P_1 + P_2 + P_3 + \ldots P_n$$

REAL GASES

1. Molecules have volume

2. Molecules have attractive forces (intermolecular)

Van der Waals Equation of State

$$P = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2$$

Thermodynamic potentials

Potential	Variables
U (S,V,N)	**S, V, N**
H (S,P,N)	**S, P, N**
F (T,V,N)	**V, T, N**
G (T,P,N)	**P, T, N**

$$dU(S,V,N) = T\,dS - P\,dV + \mu\,dN$$

$$dH(S,P,N) = T\,dS + V\,dP + \mu\,dN$$

$$dF(T,V,N) = -S\,dT - P\,dV + \mu\,dN$$

$$dG(T,P,N) = -S\,dT + V\,dP + \mu\,dN$$

$$\text{Maxwell relation:} \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}, \; \cdots$$

Internal energy: $U = TS - PV + \mu N \Rightarrow S\,dT - V\,dP + N\,d\mu = 0$

Enthalpy: $H = U + PV = TS + \mu N$

Helmholtz Free energy: $F = U - TS = -PV + \mu N$

Gibbs Free energy: $G = U - TS + PV = N\mu$

Grand Free energy: $\Phi = U - TS - \mu N = -PV$ (Pr. 5.23)

First order phase transformation

❏ In a first order transformation the product phase is very different from the parent phase in some way (e.g. in solidification the crystal is ordered while the liquid is not).

❏ Exhibit a discontinuity in the first derivative of the free energy with a thermodynamic variable. The various solid/liquid/gas transitions are classified as first-order transitions because they involve a discontinuous change in density (which is the first derivative of the free energy with respect to chemical potential.)

❏ Similarly, the entropy of the parent and product phases are very different (liquid has high entropy while the solid has low entropy) and a plot of S vs T curve will show a discontinuity.

Second order phase transformation

❏ NO discontinuous changes in entropy, enthalpy & specific volume.

❏ NO latent heat of transformation.

❏ High specific heat at the transition temperature.

❏ Have a discontinuity in a second derivative of the free energy. These include the ferromagnetic phase transition in materials such as iron, where the magnetization, which is the first derivative of the free energy with the applied magnetic field strength, increases continuously from zero as the temperature is lowered below the Curie temperature.
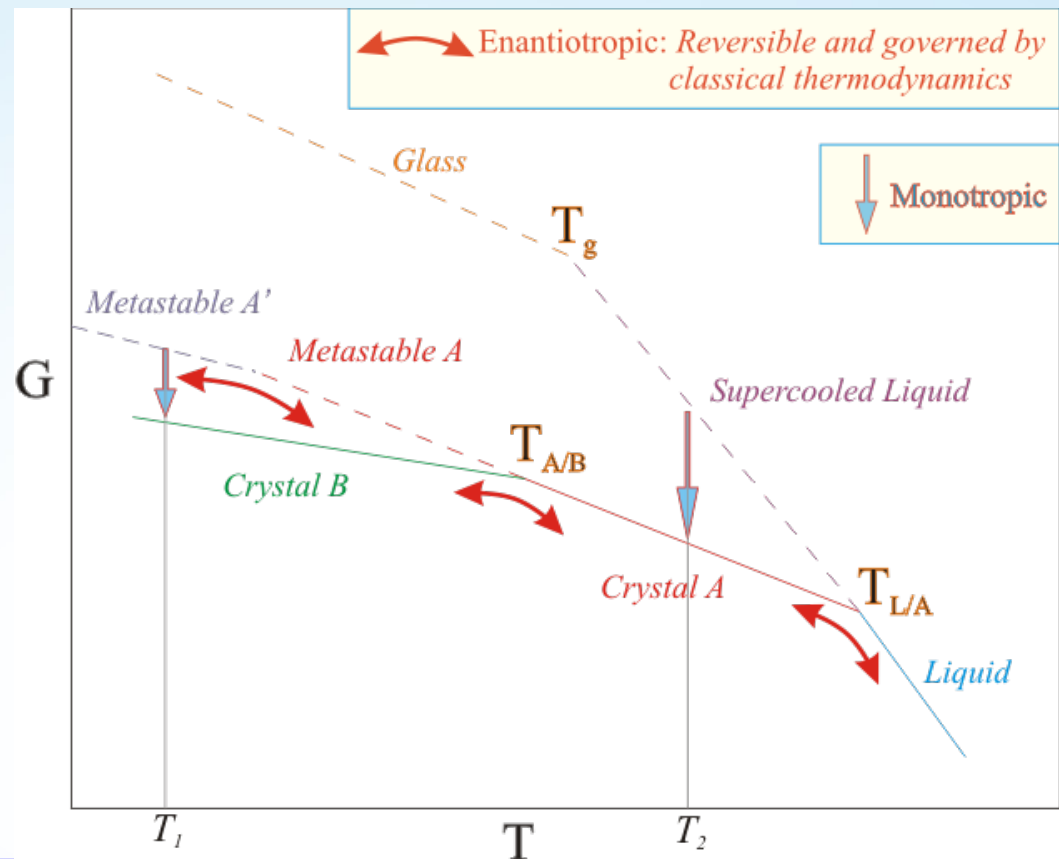
Equilibrium transitions: Reversible and governed by classical thermodynamics

❑ L → A (at the melting point: $T_m = T_{L/A}$)

❑ A → B (at the equilibrium transformation T: $T_{L/A}$)

❑ A → A' (transformation between two metastable phases)

Irreversible (no equilibrium between parent and product phases)

❑ A' (metastable) → B (stable) (at T_1)

❑ Supercooled liquid (metastable) → A (stable) (at T_2)

Clausius-Claperon equation

$$\frac{dP}{dT} = \frac{q}{T(v_2 - v_1)}$$

It determines the change in the pressure of two phases in equilibrium with a change in temperature or in other words the change of pressure with temperature along the phase equilibrium curve. The same formula written in the form

$$\frac{dT}{dP} = \frac{T(v_2 - v_1)}{q}$$

determines the variation of the temperature of the transition from one phase to another (the freezing and boiling points, for example) with pressure.

These three areas of study are:

➤ Fluid mechanics

➤ Heat transfer   **Transport processes**

➤ Mass transfer

1. $\dfrac{F_x}{A} = \eta \dfrac{dv_x}{dy}$

2. $\dfrac{1}{A}\dfrac{dQ}{dt} = -\lambda \dfrac{dT}{dy}$

3. $\Phi_y = -D \dfrac{d\underline{\underline{n}}}{dy}$

Momentum Transport – transfer of momentum which occurs in moving media *(viscosity, fluid flow, sedimentation, mixing, filtration)*

Heat Transport – transfer of energy from one region to another *(conduction, drying, evaporation, distillation)*

Mass Transport – transfer of mass of various chemical species from one phase to another distinct phase *(diffusion, distillation, absorption, adsorption, etc.)*
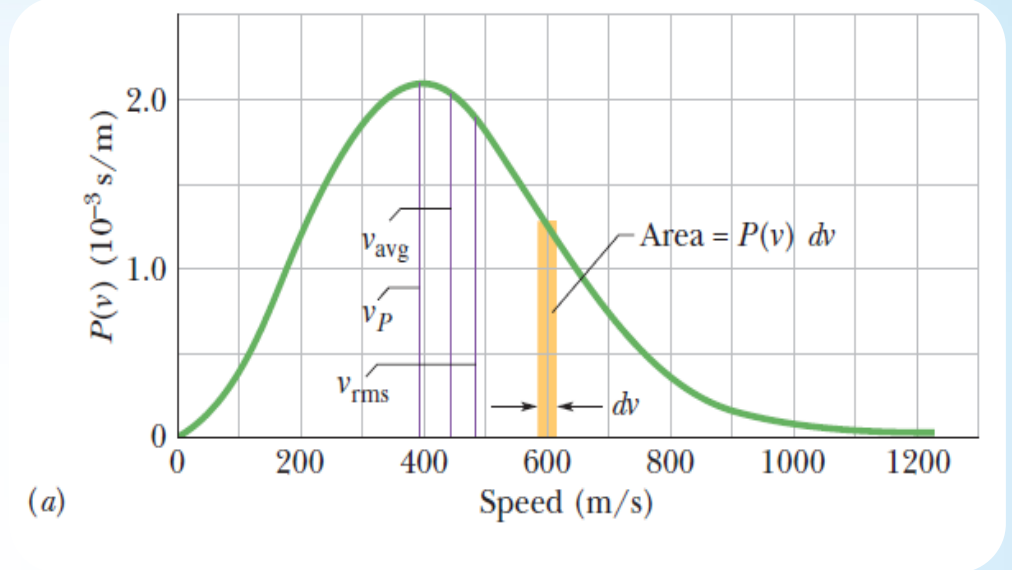
The Distribution of Molecular Speeds

Maxwell's law of speed distribution is:

$$P(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}.$$

$$\int_0^\infty P(v)\, dv = 1.$$

The quantity *P(v)* is a probability distribution function:
For any speed *v*, the product *P(v) dv* is the fraction of molecules with speeds in the interval *dv* centered on speed *v*.

(a)

The Maxwell speed distribution for oxygen molecules at T =300 K. The three characteristic speeds are marked.
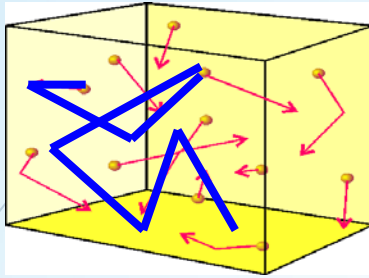
Some Molecular Speeds

$$\bar{v} = \int_0^\infty v f(v)\,dv = \sqrt{\frac{8kT}{\pi m}}$$

$$\overline{v^2} = \int_0^\infty v^2 f(v)\,dv = \frac{3kT}{m}$$

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}}$$

$$v_{max} = \sqrt{\frac{2kT}{m}} \qquad \text{Most Probable}$$

The Mean Free Path of Molecules

Transports energy, momentum, mass – due to random thermal motion of molecules in gases and liquids.

The mean free path _l_ - the average distance traveled by a molecule btw two successive collisions.

An estimate: one molecule is moving with a constant speed **v**, the other molecules are fixed. Model of hard spheres, the radius of molecule **r** ~ 1·10⁻¹⁰ m.
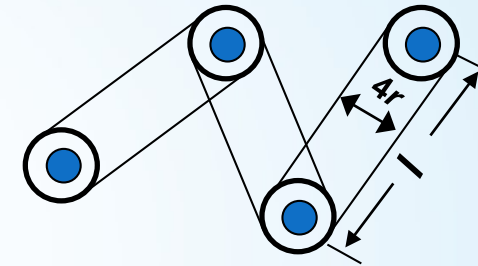
The av. distance traversed by a molecule until the 1st collision is the distance in which the av. # of molecules in this cylinder is 1.

$$\pi (2r)^2 l \times \frac{N}{V} = 1 \implies \boxed{l = \frac{1}{4\pi r^2}\frac{V}{N} = \frac{1}{\sigma n}} \qquad \textbf{\textit{Maxwell:}} \qquad \boxed{l = \frac{1}{\sqrt{2}\,\sigma\, n}}$$

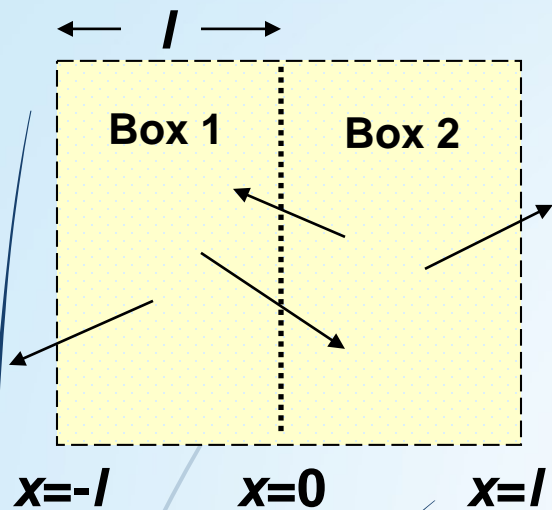**n = N/V**
– the density of molecules

$\sigma = 4\pi r^2$ – collision cross section

The average time interval between successive collisions - **the collision time**:

$$\boxed{\tau = \frac{l}{\overline{v}}}$$

$\overline{v}$ - the most probable speed of a molecule

Transport in Gases (Liquids)

← *l* →

Box 1 | Box 2

x=-l   *x=0*   *x=l*

Each molecule "carries" some quantity φ (mass, kin. energy, etc.), within each box - $\Phi = N\,\varphi = A\,l\,n\,\varphi$. E.g., the flux of the number of molecules across the border per unit area of the border, J_x:

$$J_n \equiv \frac{\Delta N}{A\Delta t} = \frac{1}{6}\bar{v}\left[n(x=-l)-n(x=l)\right] = \frac{1}{6}\bar{v}\left(-2l\frac{\partial n}{\partial x}\right) = -\frac{1}{3}\bar{v}\,l\frac{\partial n}{\partial x} = -D\frac{\partial n}{\partial x}$$
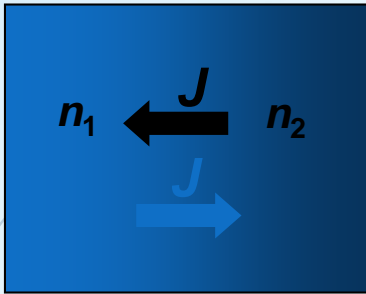
in a 3D case, on average 1/6 of the molecules have a velocity along +*x* or −*x*

the diffusion constant

"-" - if $\partial n/\partial x$ is negative, the flux is in the positive **x** direction (the current flows from high density to low density)

n(x,t) J_x ➡   **x**

In a 3D case, $\boxed{\vec{J}_n = -D\nabla n \quad \vec{J}_U = -K_{th}\nabla T}$

Diffusion

Diffusion – the flow of randomly moving particles caused by variations of the *concentration* of particles. Example: a mixture of two gases, the total concentration **$n = n_1 + n_2$ =const** over the volume (**P = const**).

Fick's Law:

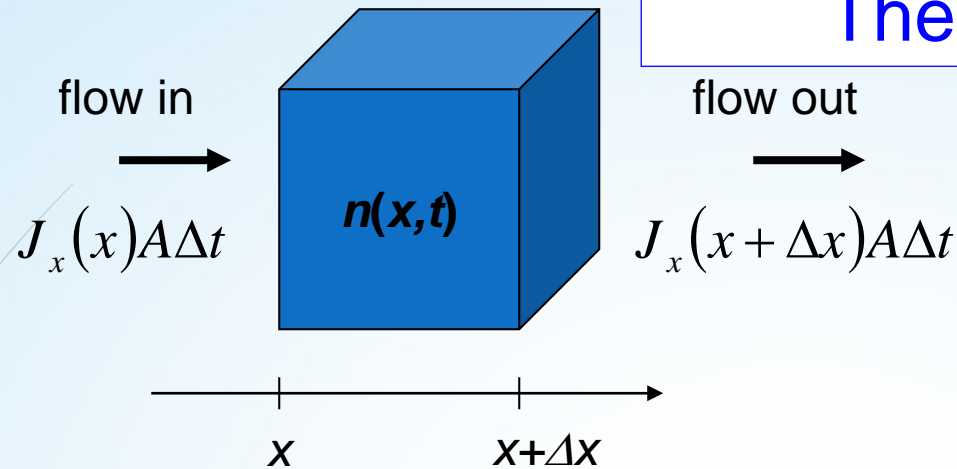$$J_x = -\frac{1}{3} l \, \bar{v} \, \frac{\partial n}{\partial x} = -D \frac{\partial n}{\partial x}$$

$$D = \frac{1}{3} l \, \bar{v}$$ - *the diffusion coefficient*

(numerical pre-factor depends on the dimensionality: 3D – 1/3; 2D – 1/2)

$$D = \frac{1}{3} l \, \bar{v}$$ its dimensions $[L]^2 [t]^{-1}$, its units $m^2 \, s^{-1}$

Typically, at normal conditions, **l** ~10^{-7} m, **v** ~300 m/s $\Rightarrow$ **D** ~ 10^{-5} $m^2 \, s^{-1}$
(in liquids, **D** is much smaller, ~10^{-10} $m^2 \, s^{-1}$)

The Diffusion Equation

flow in

flow out

$n(x,t)$

change of n inside:

$J_x(x)A\Delta t$

$J_x(x+\Delta x)A\Delta t$

$$\frac{\partial n}{\partial t} = -\frac{\partial J_x}{\partial x}$$

x $x+\Delta x$

combining with $J_x = -D\dfrac{\partial n}{\partial x}$

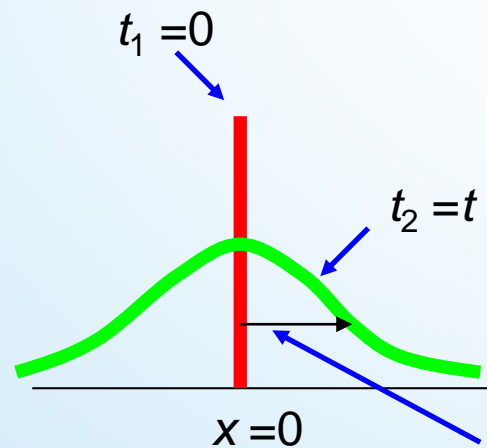we'll get the equation that describes one-dimensional diffusion:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2}$$

the diffusion equation

$t_1 = 0$

$t_2 = t$

the solution which corresponds to an initial condition that all particles are at $x=0$ at $t=0$:

$$n(x,t) = \frac{C}{\sqrt{Dt}}\exp\left(-\frac{x^2}{4Dt}\right)$$
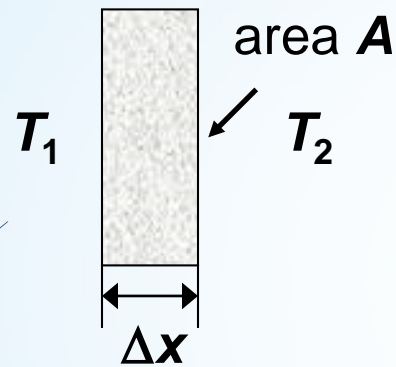
C is a normalization factor

$x=0$

the **rms** displacement of particles: $\sqrt{\langle x^2 \rangle} \approx \sqrt{Dt}$
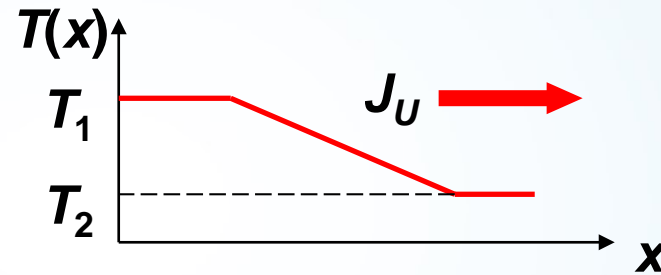
Static Energy Flow by "Heat" Conduction

In general, the energy transport due to molecular motion is described by the equation of heat conduction:

$$\frac{\partial T}{\partial t} = -\frac{1}{C}\frac{\partial J_U}{\partial x} = \frac{K_{th}}{C}\frac{\partial^2 T}{\partial x^2} \qquad J_U = -K_{th}\frac{\partial T}{\partial x}$$

area **A**

T_1 T_2

Δx

Heat conduction   (static heat flow, ΔT = const)

$T(x)$

T_1 J_U

T_2

x

Fourier Heat Conduction Law

$$\delta Q \propto \frac{\Delta T \Delta t}{\Delta x} A \quad \Rightarrow \quad \boxed{J_U \equiv \frac{\delta Q}{\Delta t} = -K_{th} A \frac{\Delta T}{\Delta x}}$$

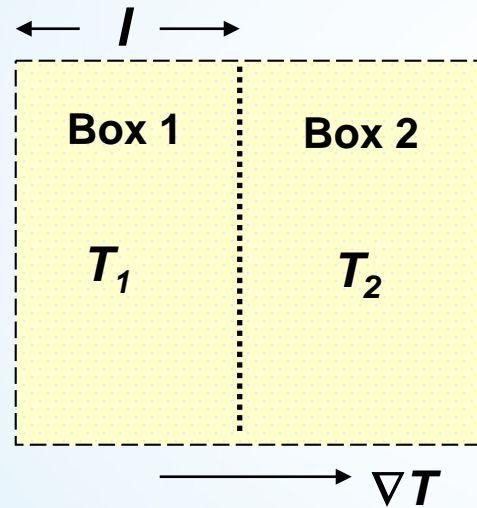**"-"** - if **T** increases from left to right, energy flows from right to left

K_{th} [$W/K \cdot m$] – the thermal conductivity (material-specific)

Thermal Conductivity of an Ideal Gas

Energy "flow", $\Delta t \sim \tau$:

the time between two consecutive collisions $\tau = \dfrac{l}{v}$

$$\frac{\delta Q}{\tau} = \frac{1}{2}\frac{(U_1 - U_2)}{\tau} = \frac{1}{2}\frac{C_V(T_1 - T_2)}{\tau} = \frac{1}{2}\frac{C_V}{\tau}\frac{l}{dx}\frac{dT}{dx} = \frac{1}{2}C_V\bar{v}\frac{dT}{dx}$$

$\Updownarrow$

$$\frac{\delta Q}{\tau} = -K_{th}A\frac{\Delta T}{\Delta x} \implies K_{th} = \frac{1}{2}\frac{C_V\bar{v}}{A} = \frac{1}{2}\frac{C_V l\bar{v}}{Al} = \frac{1}{2}\frac{C_V}{V}l\,\bar{v}$$

Box 1   Box 2

T_1 T_2

∇T

the specific heat capacity
$$c_V \equiv \frac{C_V}{V} = \frac{\frac{f}{2}Nk_B}{V} = \frac{f}{2}nk_B$$

$$\boxed{K_{th} = \frac{f}{4}nk_B\,l\,\bar{v}}$$

The thermal conductivity of air at norm. conditions:

$$K_{th} = \frac{f}{4}nk_B\,l\,\bar{v} = \frac{5}{4}\times 2.4\cdot 10^{25}\,\text{m}^{-3}\times 1.38\cdot 10^{-23}\,\text{J/K}\times 10^{-7}\,\text{m}\times 500\,\text{m/s} \approx 0.02\,\frac{\text{W}}{\text{m}\cdot\text{K}}$$

(exp. value – 0.026 W/m·K)

Viscosity

•Consider a plate moving parallel to another plate with a layer of gas between them. The gas in contact with either plate is at rest relative to the plate, so there is a velocity gradient in the gas. A force *F* is applied to each plate to maintain the motion, and the area of the upper plate is *A*.
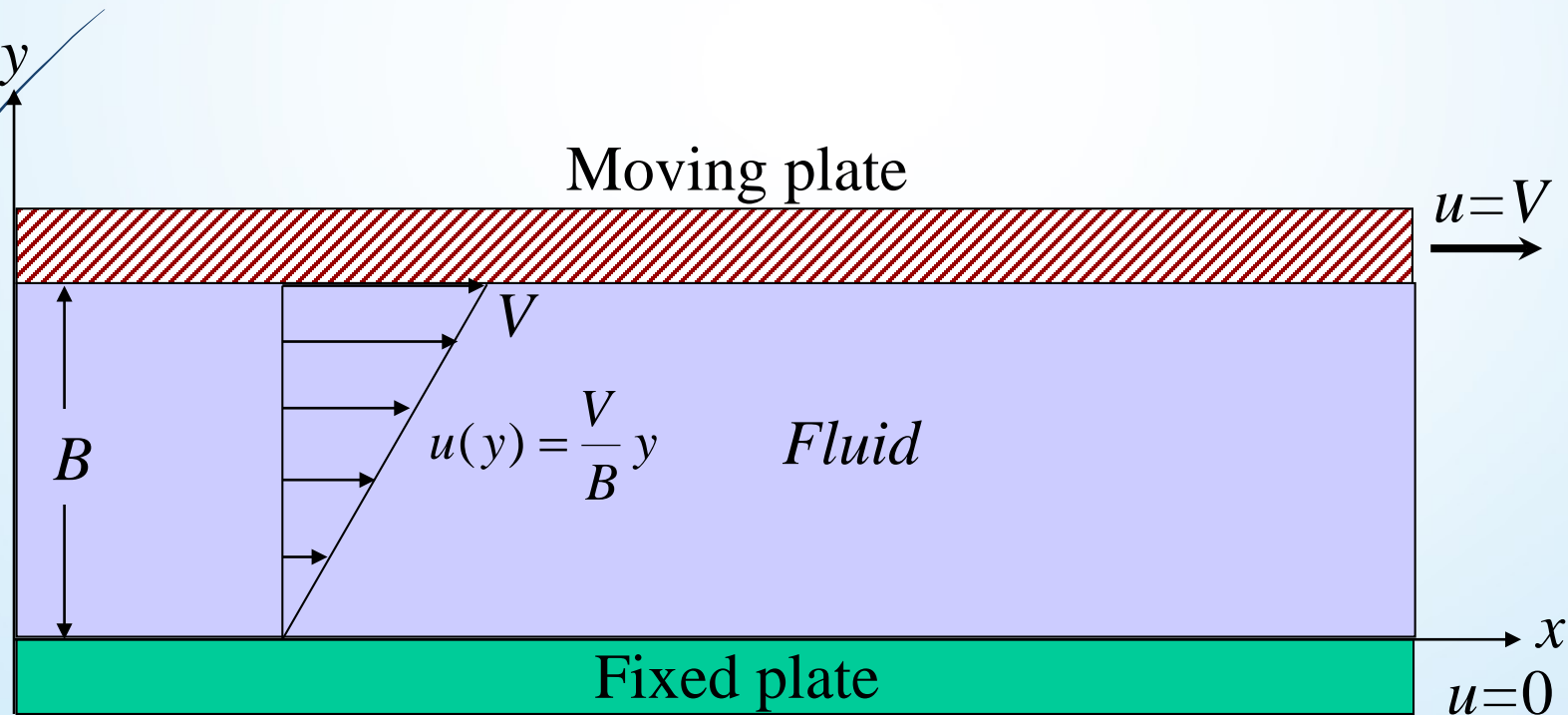
Viscosity

- Newton's Law of Viscosity $\tau = \mu \dfrac{dV}{dy}$

- Viscosity $\qquad \mu = \dfrac{\tau}{dV / dy}$

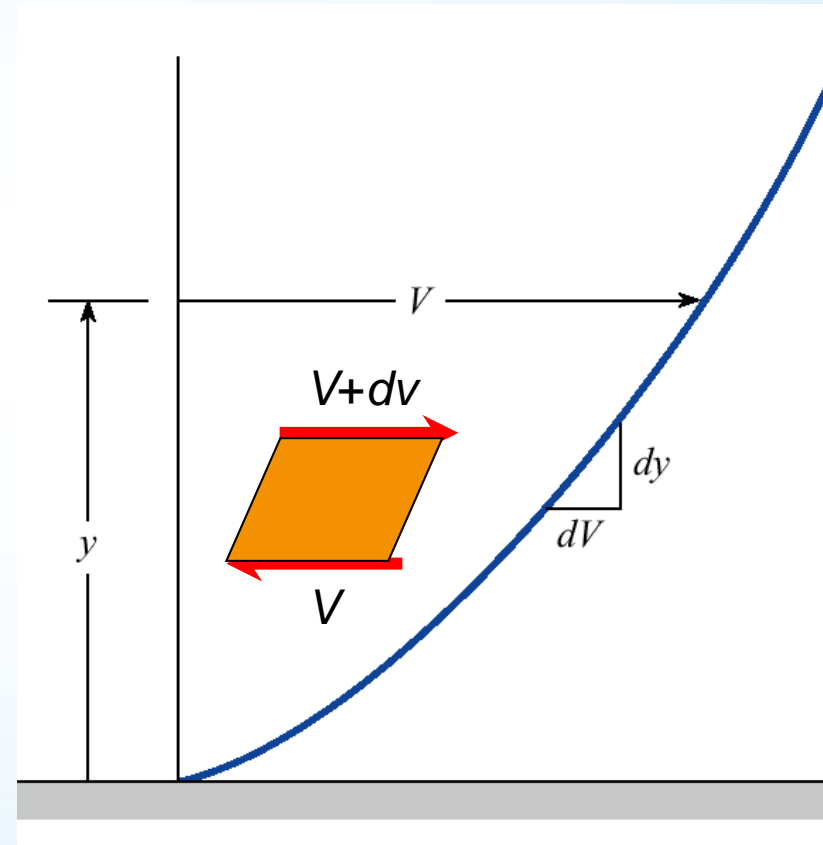- Units $\qquad \dfrac{N / m^2}{m / s / m} = \dfrac{N \cdot s}{m^2}$

- Water (@ 20°C)
  - m = $1x10^{-3}$ N-s/m²
- Air (@ 20°C)
  - m = $1.8x10^{-5}$ N-s/m² $\nu = \dfrac{\mu}{\rho}$
- Kinematic viscosity

Control Questions

1. Thermodynamical temperature.

2. Degrees of freedom. Internal energy.

3. Ideal vs. real gases.

4. Phase transformations.

5. Transport phenomena.

Recommended literature:

Basic:

1. Vladimir Timanyuk, Elena Zhivotova, Igor Storozhenko. Biophysics: Textbook for students of higher schools / Kh.: NUPh, Golden Pages, 2011.- 576p.

2. Vladimir Timaniuk, Marina Kaydash, Ella Romodanova. Physical methods of analysis / Manual for students of higher schools/– Kharkiv: NUPh: Golden Pages, 2012. – 192 p.

3. Philip Nelson. Biological Physics. – W. H. Freeman, 1st Edition, 2007. – 600 p.

4. Biophysics, physical methods of analysis. Workbook: Study guide for the students of higher pharmaceutical educational institutions / Pogorelov S. V., Krasovskyi I. V., Kaydash M. V., Sheykina N. V., Frolova N. O., Timaniuk V. O., Romodanova E.O., Kokodii M.H. – Kharkiv., – 2018. – 130 p.

5. Center for distance learning technologies of NPhaU. Access mode: http://nuph.edu.ua/centr-distancijjnih-tehnologijj-navcha/

Support:

1. Eduard Lychkovsky. Physical methods of analysis and metrology: tutorial / Eduard Lychkovsky, Zoryana Fedorovych. – Lviv, 2012. – 107 p.

2. Daniel Goldfarb. Biophysics DeMYSTiFied. – McGraw-Hill Professional, 1st Edition, 2010. – 400 p.

Thanks for your attention