Chapter 10. Thermal physics

1. Temperature and Zeroth Law of Thermodynamics
2. Thermometer and Temperature Scale (reading)
3. Thermal Expansion of Solids and Liquids (reading)
4. Macroscopic Description of an Ideal Gas
5. The Kinetic Theory of Gases
6. Maxwell distribution
7. Boltzmann distribution

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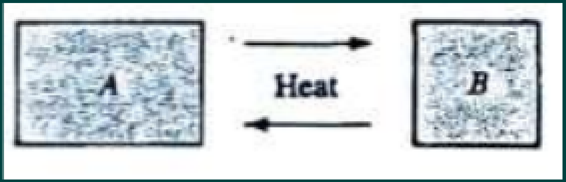
10.1. Temperature and Zeroth Law of Thermodynamics

- **Temperature (T):** is commonly associated with how hot or cold an object feels when we touch it.

Thermometer: used to measure temperature.

- **Heat:** a form of energy transferred from one object to another due to ΔT. (chaostic motion). **(≠ work)**

Thermal Equilibrium



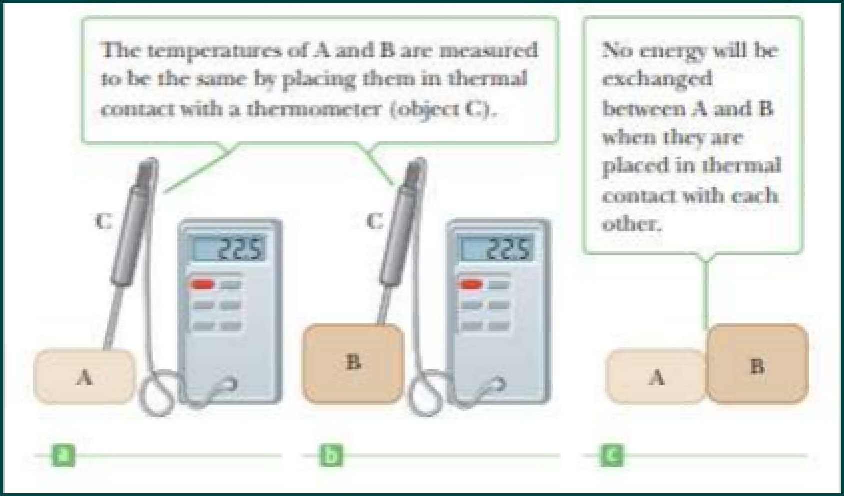
Two objects are in **thermal equilibrium** if they are in thermal contact and there is no net exchange of energy.

$$T_A = T_B$$

- If $T_A > T_B$: net heat flow from A to B
- If $T_A < T_B$: net heat flow from B to A

Zeroth Law of Thermodynamics

Zeroth Law of Thermodynamics: If objects A and B are separately in thermal equilibrium with a third object C, then A and B are in thermal equilibrium with each other.

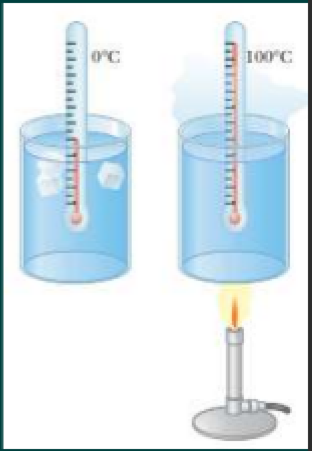


The temperatures of A and B are measured to be the same by placing them in thermal contact with a thermometer (object C).

No energy will be exchanged between A and B when they are placed in thermal contact with each other.

10.2. Thermometer and Temperature Scales

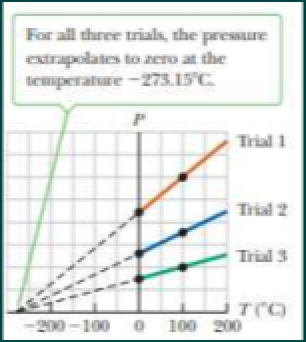
Celsius temperature scale:

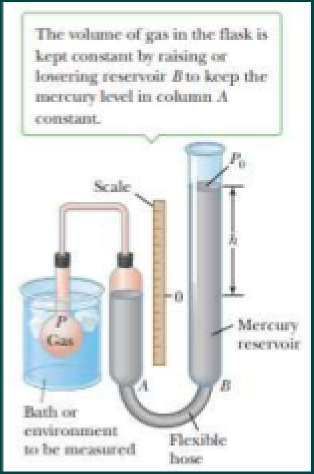


Mercury thermometer: *Because of thermal expansion, the level of the mercury rises as the temperature of the mercury changes from* ***0°C (the ice point of water)*** *to* ***100°C (the steam point of water)***.

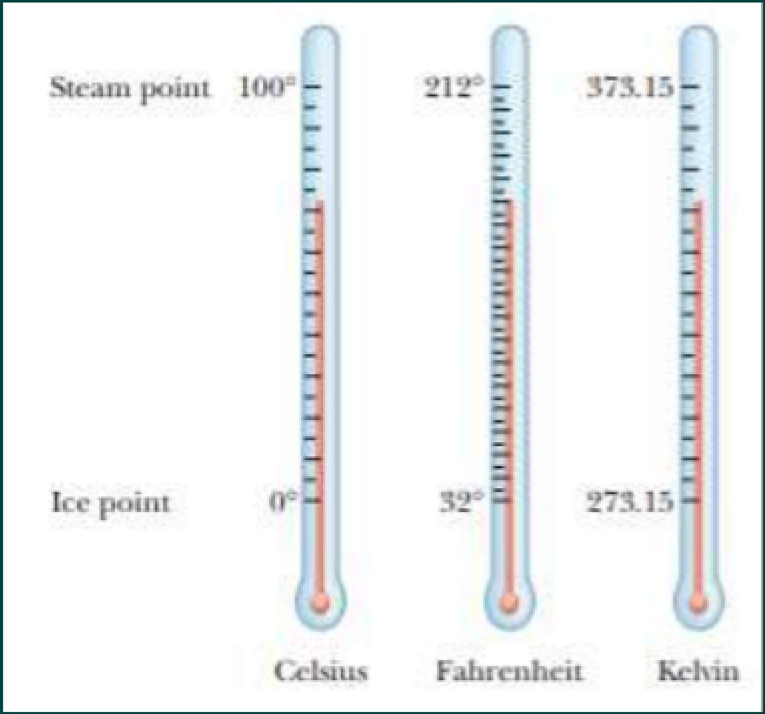
Kelvin scale:

$$T_C = T - 273.15$$


For all three trials, the pressure extrapolates to zero at the temperature −273.15°C.


The volume of gas in the flask is kept constant by raising or lowering reservoir *B* to keep the mercury level in column *A* constant.

The Celsius, Kelvin, and Fahrenheit Temperature Scales



The relationship between the Celsius and Fahrenheit temperature scales is

$$T_F = \tfrac{9}{5}T_C + 32$$

$$T_C = \tfrac{5}{9}(T_F - 32)$$

$$\Delta T_F = \tfrac{9}{5}\Delta T_C$$

$$T_C = T - 273.15$$

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10.4. Macroscopic Description of an Ideal Gas

♣ **States of matter**

- All matter consists of a very large number of molecules (or atoms). Gas: density ~ 10^{19} cm^{-3}.
- The spacing of these molecules and the forces between them determine whether the matter is a solid, a liquid or a gas.

♣ ***Gases*** have no fixed volume and no fixed shape.

- In gases, the separation of the molecules is large and the interaction between the molecules is small.
- The parameters of a gaseous state are **volume**, ***temperature*** and **pressure**.

10.4. Macroscopic Description of an Ideal Gas

- **An ideal gas** is a collection of atoms or molecules that move randomly and exert no long-range forces on each other. Each particle of the ideal gas is individually pointlike, occupying a negligible volume
- Most gases at room temperature and atmospheric pressure behave approximately as ideal gases.
- A gas usually consists of a very large number of particles, so it's convenient to express the amount of gas in a given volume in terms of the number of moles, n.

Definition: One mole (mol) of any substance is that amount of the substance that contains as many particles (atoms, molecules, or other particles) as there are atoms in 12 g of the isotope carbon-12.

- This number is known as Avogadro's number and is given by $N_A = 6.02 \times 10^{23}$ particles/mole.
- **Relation of mass M and mole number n**

$$n = \frac{M}{molar\ mass, \mu}$$

$$m_{\text{atom}} = \frac{\text{molar mass}}{N_A}$$

The ideal gas laws

- First, when the gas is kept at a constant temperature, its pressure is inversely proportional to its volume (**Boyle's law**): If $T = const \; => \; P \sim \frac{1}{V}$
- Second, when the pressure of the gas is kept constant, the volume of the gas is directly proportional to the temperature (**Charles's law**): If $P = const \; => V \sim T$
- Third, when the volume of the gas is held constant, the pressure is directly proportional to the temperature (**Gay-Lussac's law**): If $V = const \; => P \sim T$

=> The ideal gas law (Equation of State): $\boxed{PV = nRT}$

- R is called the universal gas constant. In SI units, where pressure is expressed in pascals and volume in cubic meters,
  $\boldsymbol{R = 8.31\, J/mol.K}$
- If the pressure is expressed in atmospheres and the volume is given in liters (recall that 1 L = 10^3 cm^3=10^{-3} m^3), then $R = 0.082\,1\; L.atm/mol\;K$
- Using this value of R and the ideal equation, the volume occupied by 1 mol of any ideal gas at atmospheric pressure and at 0°C (273 K) is 22.4 L.

The ideal gas law (cont.)

From the ideal gas law: $PV = nRT$

$$R = 8.31\frac{J}{mol.K} = k_B N_A$$

- $k_B = 1.38 \times 10^{-23}\ J/K$: Bolztmann constant
- We can obtaine other form of the ideal gas law:

$$PV = nk_B N_A T = Nk_B T$$

- Because: $N = nN_A$ is the number of molecules in the gas system.

A gas which obeys the equation of state, pV = nRT , for all pressures, volumes and temperatures is called an ideal gas.

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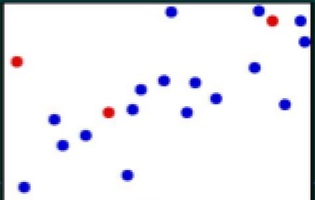
10.5. The Kinetic Theory of ideal Gases

10.5.1. The kinetic theory of ideal gases: a model makes the following assumptions:

1. An ideal gas always consists of a large number of molecules (10^{19} cm^{-3}).
2. The gas molecules are constantly in rapid, **free random** motion. Newtonian mechanics may be applied to the motion of the gas molecules. $T \sim \langle KE \rangle$
3. The gas molecules collide elastically with one another and the walls of the container.
4. There is no intermolecular forces except during collision
5. The volume of gas molecules is negligible compared to the volume of the container (which is also the volume of the gas).

(6. The duration of collision is negligible compared to the time interval between collisions)



10.5.2. Molecular Model for the Pressure of an Ideal Gas

- Consider an ideal gas consisting of N molecules in a container of volume V. m: mass of one molecule/atom.
- The container is a cube with edges of length d.

- Consider the collision of one molecule moving with a velocity v_x toward the right-hand face of the box
- After colliding elastically with the wall, the molecule moves in oposite x-direction with a velocity $-v_x$. The change in its momentum is

$$\Delta p_x = -mv_x - (mv_x) = -2mv_x$$

- Force that the molecule acts on the wall = - force of the wall on the molecule.

$$f_{nx/wall} = f_x = -\frac{\Delta p_x}{\Delta t} = \frac{2mv_x}{\Delta t} = \frac{2mv_x}{2d/v_x}$$

$$\boldsymbol{f_x = \frac{mv_x^2}{d}}$$

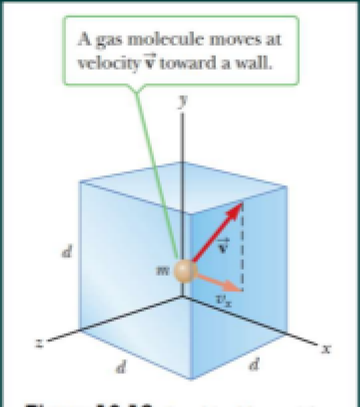

A gas molecule moves at velocity $\vec{v}$ toward a wall.

Figure 10.13 A cubical box with sides of length *d* containing an ideal gas.

The time interval between two collisions with the same wall

$$\Delta t = \frac{distance}{speed} = \frac{2d}{v_x}$$

10.5.2. Molecular Model for the Pressure of an Ideal Gas (cont.)

- Force that all molecule act on the wall:

$$F_x = \sum_{i=1}^{N} \frac{m v_{ix}^2}{d}$$

$$F_x = \frac{Nm}{d} \cdot \frac{\sum_{i=1}^{N} v_{ix}^2}{N} = \frac{Nm}{d} \overline{v_x^2}$$

Where $\overline{v_x^2}$ is the average value of the square of the velocity in the x-direction for N molecules

$$\overline{v_x^2} = \frac{\sum_{i=1}^{N} v_{ix}^2}{N}$$

We have: $\overline{\mathrm{v}_\mathrm{x}^2} + \overline{\mathrm{v}_\mathrm{y}^2} + \overline{\mathrm{v}_\mathrm{z}^2} = \overline{\mathrm{v}^2}$, + randomly motion so $\overline{\mathrm{v}_\mathrm{x}^2} = \overline{\mathrm{v}_\mathrm{y}^2} = \overline{\mathrm{v}_\mathrm{z}^2} = \frac{1}{3}\overline{\mathrm{v}^2}$

- Pressure on the wall:

$$P = \frac{F_x}{A} = \frac{Nm}{d.A} \overline{v_x^2} = \frac{1}{3} \frac{N}{V} m \overline{v^2}$$

$d.A = V$

volume of the gas.

$$\boxed{P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2} m \overline{v^2}\right)}$$

10.5.2. Molecular Model for the Pressure of an Ideal Gas (cont.)

$$\boxed{P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right)}$$

- => the pressure is proportional to the number of molecules per unit volume $\mathrm{n}_0 = \frac{N}{V}$ and to the average translational kinetic energy of a molecule, $\frac{1}{2}m\overline{v^2}$

$$\boxed{P = \frac{2}{3}n_0 < KE_{trans} >}$$

10.5.3. Degree of freedom

- **Definition**: The number of degrees of freedom, i, of a gas is the number of **independent** parameters used to determine the position of each molecule in the gas.

For monoatomic gas: i = 3.

For diatomic gas: i = 5.

For polyatomic gas (three or more atoms): i = 6.

♣ Equipartition theorem

In thermal equilibrium, the average energy is shared equally to every degree of freedom,

$$< KE >_{1degree} = \frac{1}{2} k_B T$$

♣ Average kinetic energy:

- For monoatomic gas: $< KE > = \frac{3}{2} k_B T$ and i = 3.
- For any gas with the number **i** of degrees of freedom:

$$< KE > = \frac{i}{2} k_B T$$

10.5.4 Molecular Interpretation of Temperature

- Starting with: $P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right)$
- Using the equation of state for an ideal gas:

$$PV = Nk_BT,$$

=> $$T = \frac{2}{3k_B}\left(\frac{1}{2}m\overline{v^2}\right) \qquad (*)$$

The temperature of a gas is a direct measure of the average molecular kinetic energy of the gas.

- As the temperature of a gas increases, the molecules move with higher average kinetic energy. Rearranging equation (*), we can relate the translational molecular kinetic energy to the temperature:

$$KE_{translational(1molecule)} = \frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

- **Total translational kinetic energy of a gas:**

$$KE_{trans} = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}Nk_BT$$

10.5.5. The internal energy U of an ideal gas

$$U = KE_{(randomly)} + PE_{interaction}$$

For ideal gas, no interaction between molecules: $PE_{interaction} = 0$

$$U = KE_{(randomly)} = KE_{trans} + KE_{rotation}$$

The internal energy U = The total kinetic energy.

- For **a monatomic** gas, translational kinetic energy is the only type of energy the molecules can have, so the internal energy U for a monatomic gas:

$$\boldsymbol{U = KE_{trans} = \frac{3}{2}Nk_BT}$$

example: He, Ne, Ar, ...

- For **a diatomic** gas $\boldsymbol{U = KE_{trans} + KE_{rotation} = \frac{3}{2}Nk_BT + \frac{2}{2}Nk_BT = \frac{5}{2}Nk_BT}$

example: O_2, N_2, CO, H_2, ...

- For triatomic atom gases: (H_2O, CO_2, ...) NH_4, ...

$$\boldsymbol{U = KE_{trans} + KE_{rotation} = \frac{3}{2}Nk_BT + \frac{3}{2}Nk_BT = \frac{6}{2}Nk_BT}$$

10.5.4. The internal energy U of an ideal gas

- In general”

$$U = \frac{i}{2} N k_B T = \frac{i}{2} . \frac{M}{\mu} N_A k_B T$$

$$U = \frac{i}{2} . \frac{M}{\mu} RT = \frac{i}{2} PV$$

$$PV = nRT$$

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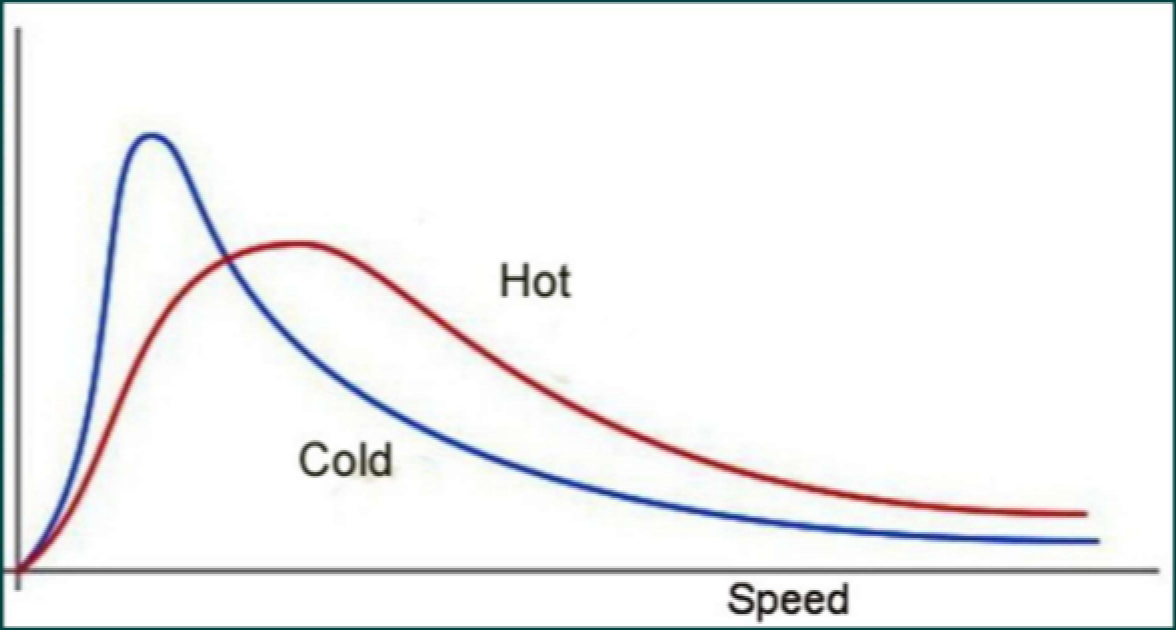
10.6. Maxwell distribution ⇒ on speed

♣ For a real gas system, the speed of the particles is continuously distributed (can have any value). The distribution depends on the temperature and properties of the system.



10.6. Maxwell distribution

- Consider a system of N particles which have discrete values of speed: dN particles have speed v to v+dv ,
- The value of dN depends on:
  - the total number N of particles: dN ∝ N,
  - the width of the range: dN ∝ dv,
  - and the value v of the speed at which the range is chosen.
- Therefore: dN = F(v)Ndv
- The value of F(v)dv = dN/N is the probability for any particle of the system to have speed in the range (v, v+dv).
- The function F(v) is called the distribution function of the molecules with speed.
- **For the whole system:**

$$\int \frac{dN}{N} = 1 \rightarrow \int_0^\infty F(v)dv = 1 \text{ (normalized condition)}$$

10.6. Maxwell distribution

Maxwell distribution function

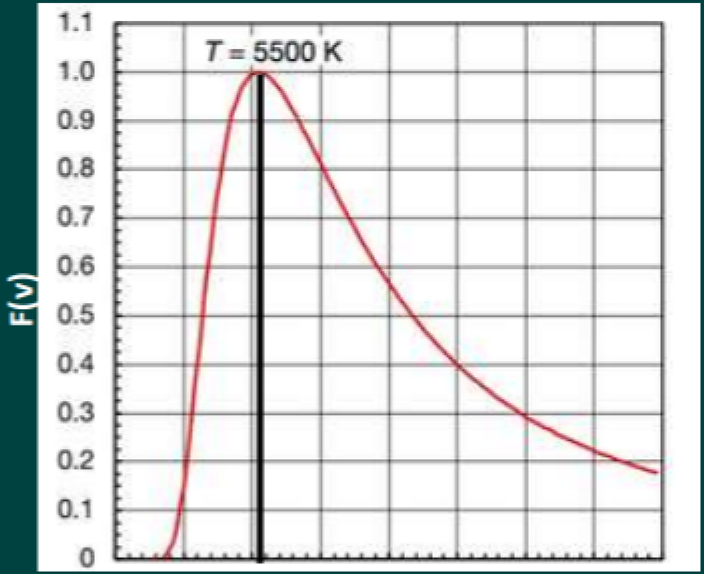
- The function depends on kinetic

$$F(v) = const.\,v^2.\,e^{-\frac{mv^2}{2kT}}$$

$$const = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2}$$

$$F(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2}.\,e^{-\frac{mv^2}{2kT}}.\,v^2$$

$$\Rightarrow \frac{dN}{N} = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2}.\,e^{-\frac{mv^2}{2kT}}.\,v^2.\,dv$$



$$\sqrt{\frac{2kT}{m}}$$

10.6. Maxwell distribution

Maxwell distribution function

- Mean values of a function A(v):

$$A_{avg} = \int_0^\infty F(v)A dv$$

For example: everage speed

$$v_{avg} = \int_0^\infty F(v)v dv$$

Average of “speed square”

$$< v^2 >_{avg} = \int_0^\infty F(v)v^2 dv$$

10.6. Maxwell distribution

$$\Rightarrow \frac{dF(v)}{dv} = 0$$

Typical speed

- "Most probable speed": at which, the F(v) is maximum

$$v_{mp} = \sqrt{\frac{2kT}{m}}$$

- Mean speed:

$$v_{avg} = \bar{v} = \int_0^\infty F(v)vdv = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi \mu}}$$

- Root-mean-square speed:

$$v_{r.m.s} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\mu}}$$

10.6 Maxwell speed distribution

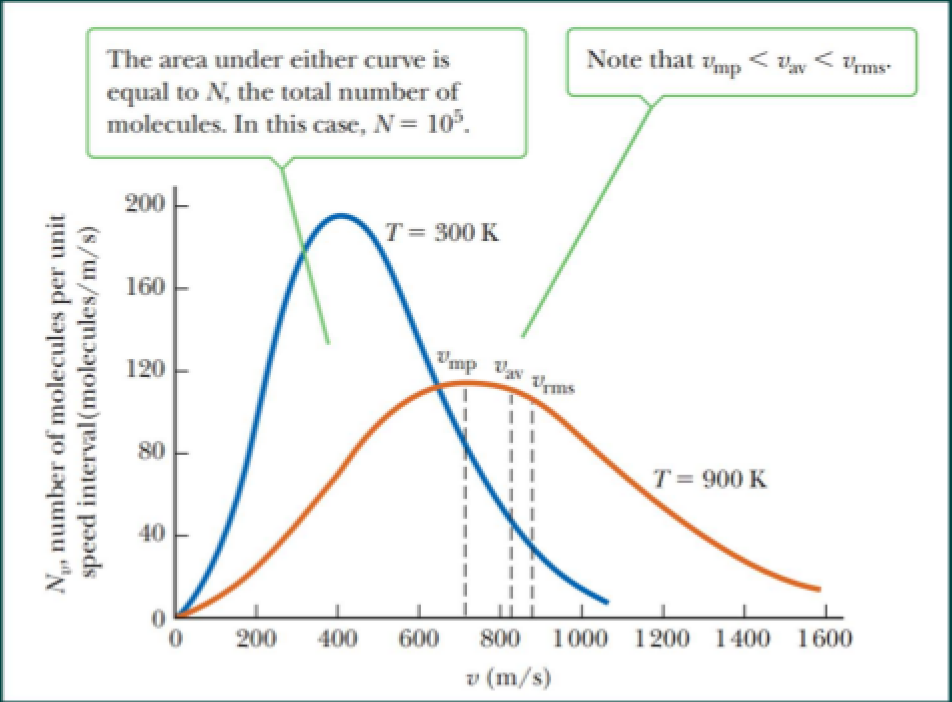
$$F(v) = \frac{4}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{3/2} . e^{-\frac{mv^2}{2kT}} \; . v^2$$

$$F(v) = \frac{4}{\sqrt{\pi}}\left(\frac{\mu}{2RT}\right)^{3/2} . e^{\left(-\frac{\mu v^2}{2RT}\right)} \; . v^2$$

$$v_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{\mu}}$$

$$v_{avg} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi\mu}}$$

$$v_{r.m.s} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\mu}}$$

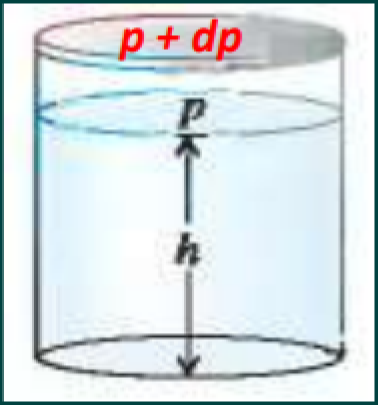


The area under either curve is equal to N, the total number of molecules. In this case, $N = 10^5$.

Note that $v_{mp} < v_{av} < v_{rms}$.

10.7. Boltzmann distribution

♣ Atmospheric pressure



- Suppose that the gas in the uniform gravitational field of the Earth is an ideal gas. Let p be the pressure at height z: $dp = -\rho g dz$
- For a small amount (mass dM and volume dV) of gas at z:

$$pdV = \frac{dM}{\mu} RT \rightarrow \rho = \frac{dM}{dV} = p\mu RT$$

$$\frac{dp}{p} = -\frac{\mu g}{RT} dz \Rightarrow \int_{P_0}^{P} \frac{dp}{p} = \int_0^z -\frac{\mu g}{RT} dz$$

$\varphi T = \text{const}$

$$\rightarrow p = p_0 \exp(-\mu \frac{gz}{RT})$$

Atmospheric pressure formula

Here, p_0 is the pressure at $z = 0$.

10.7. Boltzmann distribution

♣ Let n_0 be the molecular density (number of molecules per unit volume):

$$p \propto n_0 \rightarrow \boxed{n_0(z) = n_0(0)\exp\left(-\frac{\mu g z}{RT}\right) = n_0(0)\exp\left(-\frac{mgz}{k_B T}\right)}$$

Here, μ is the molar mass, m is the molecular mass, and mgz is the gravitational potential energy of the molecule. PE=mgz: the potential energy.

$$\rightarrow \boxed{\boldsymbol{n_0(z) = n_0(0)\,exp\left(-\frac{PE}{k_B T}\right)}}$$

This is called the Boltzmann distribution, the distribution of particles in term of potential energy.