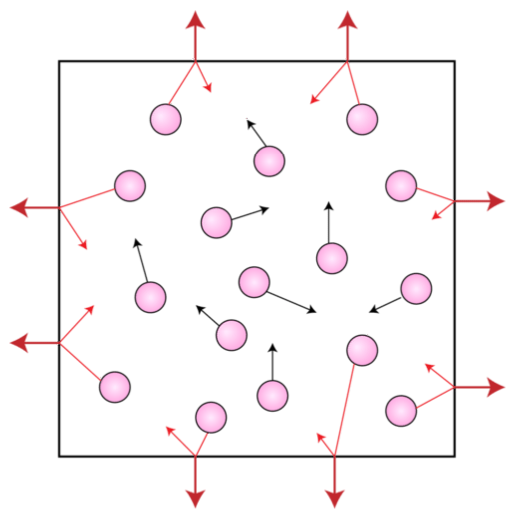
Kinetic theory of gases

C_P , C_V , γ and Specific heat



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Law of equipartition of energy

Energy supplied to a system is equally distributed amongst all the available degrees of freedom associated with each atom/molecule of the system.

Average kinetic energy of each atom of a mono-atomic gas is

$$\langle KE \rangle = \frac{3}{2} k\, T$$

Root mean square velocity of each atom/molecule is related to components as

$$v^2 = {v_x}^2 + {v_y}^2 + {v_z}^2$$

Total kinetic energy associated with motion of each atom/molecule may be understood as

$$\frac{1}{2} m {v_x}^2 + \frac{1}{2} m {v_x}^2 + \frac{1}{2} m {v_x}^2 = \frac{3}{2} k\, T$$

Contribution of each mode of motion (or degree of freedom) to the total energy of the atom/molecule is given by

$$\boxed{Energy_{\text{per entity and degree of freedom}} = \frac{1}{2} k\, T}$$

C_V, C_P and γ for a monoatomic gas

Atom of an ideal mono-atomic gas has 3 degrees of freedom. (i.e. it is free to move such that its motion can be uniquely described by specifying three coordinates x, y and z).

Internal energy is the sum of kinetic energy of its atoms (contribution from potential energies is neglected).

$$\boxed{Energy_{\text{per entity and degree of freedom}} = \frac{1}{2}k_B T}$$

$$\langle KE \rangle_{\text{per atom}} = \frac{3}{2}k_B T$$

$$KE_{\text{total}} = N\frac{3}{2}k_B T \quad \text{(i)}$$

$$U = nC_V T \quad \text{(ii)}$$

$$nC_V T = N\frac{3}{2}k_B T$$

$$C_V = \frac{3}{2}R \quad \text{(iii)}$$

Using $C_P - C_V = R$ we get

$$C_P = \frac{5}{2}R \quad \text{(iv)}$$

Using equation (iii) and (iv)

$$\gamma = \frac{5}{3} \quad \text{(v)}$$

C_V, C_P and γ for a diatomic gas (rigid)

Molecule of an ideal di-atomic gas has 5 degrees of freedom. (three coordinates x, y and z and rotations about two possible mutually perpendicular axes).

Internal energy is the sum of kinetic energy of its atoms (contribution from potential energies is neglected).

$$\boxed{Energy_{\text{per entity and degree of freedom}} = \frac{1}{2}k_B T}$$

$$\langle KE \rangle_{\text{per atom}} = \frac{5}{2}k_B T$$

$$KE_{\text{total}} = N\frac{5}{2}k_B T \quad \text{i}$$

$$U = nC_V T \quad \text{ii}$$

$$nC_V T = N\frac{5}{2}k_B T$$

$$C_V = \frac{5}{2}R \quad \text{iii}$$

Using $C_P - C_V = R$ we get

$$C_P = \frac{7}{2}R \quad \text{iv}$$

Using equation (iii) and (iv)

$$\gamma = \frac{7}{5} \quad \text{v}$$

C_V, C_P and γ for a diatomic gas (non-rigid)

Molecule of a diatomic non-rigid gas has 7 degrees of freedom. (three coordinates x, y and z , rotations about 2 mutually perpendicular axes and 2 modes of vibration).

Internal energy is the sum of kinetic energy of its atoms (contribution from potential energies is neglected).

$$\boxed{Energy_{\text{per entity and degree of freedom}} = \frac{1}{2}k_B T}$$

$$\langle KE \rangle_{\text{per atom}} = \frac{7}{2}k_B T$$

$$KE_{\text{total}} = N\frac{7}{2}k_B T \quad \text{i}$$

$$U = nC_V T \quad \text{ii}$$

$$nC_V T = N\frac{7}{2}k_B T$$

$$C_V = \frac{7}{2}R \quad \text{iii}$$

Using $C_P - C_V = R$ we get

$$C_P = \frac{9}{2}R \quad \text{iv}$$

Using equation (iii) and (iv)

$$\gamma = \frac{9}{7} \quad \text{v}$$

C_V, C_P and γ for a polyatomic gas

A polyatomic molecule , in general has 3 translational degrees of freedom, 3 rotational degrees of freedom and a certain number (f) of vibrational modes.

Using the law of equipartition of energy we get

$$U = \left(\frac{3}{2}k_B T + \frac{3}{2}k_B T + f \times k_B T \right) N_A \quad \text{i}$$

$$U = (3 + f) N_A k_B T$$

Using $U = nC_V T$ we get

$$C_V = (3 + f) R \quad \text{ii}$$

$$C_P = (4 + f) R \quad \text{iii}$$

$$\gamma = \frac{C_P}{C_V} = \frac{(4 + f)}{(3 + f)} \quad \text{iv}$$

Note (based on question in JEE / NEET)

- For a n number of modes of vibrations the degrees of freedom is $2n$.
- Any diatomic molecule is treated as a rigid rotor (unless mentioned otherwise)

Specific heat capacity of solids

Consider a solid of N atoms. Each atom of the sample of solid vibrates about its mean position.

Average energy, per atom, associated with oscillation in one dimension is

$$\langle KE \rangle_{\text{per atom}} = 2 \times \frac{1}{2} k_{\text{B}} T$$

$$\langle KE \rangle_{\text{per atom}} = k_{\text{B}} T$$

Considering all the three dimensions we get

$$\langle KE \rangle_{\text{per atom}} = 3 k_{\text{B}} T$$

Total energy of the atoms in a sample of one mole of solid is

$$U = 3 k_{\text{B}} N_{\text{A}} T$$

$$\boxed{C = 3 R}$$

The prediction generally agrees with experimental values at ordinary temperature

Specific heat capacity of water

Assume water to be a solid.
Average energy associated with each atom of water is $3k_B T$.
Water molecule has three atoms, two hydrogen and one oxygen therefore

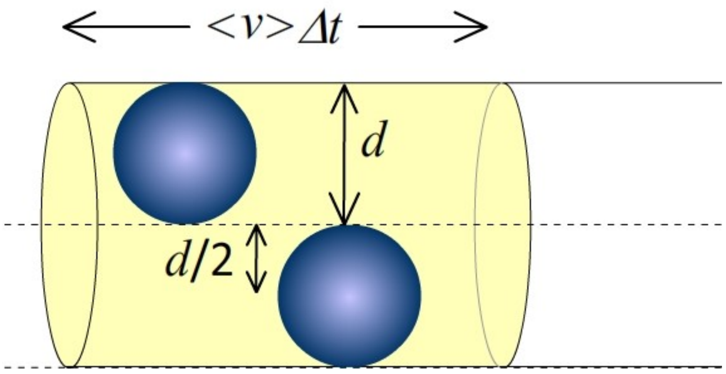
$$U = 3 \times 3\, k_B T \times N_A$$

$$U = 9\, RT$$

$$C = 9R$$

The prediction generally agrees with experimental values at ordinary temperature

Mean free path



Assume molecules of gas to be spherical with a diameter d. Let v be their average speed at a particular temperature.

Volume swept by the radius vector joining their centers is

$$\text{volume} = \pi d^2 < v > \Delta t$$

If n_o is the number of molecules per unit volume then the number of collisions that the molecule undergoes in this interval of time is

$$\text{no. of collisions} = n \times \pi d^2 < v > \Delta t$$

$$\text{no. of collisions per unit time} = n \times \pi d^2 < v >$$

Time between successive collisions is therefore

$$\tau = \frac{1}{n \times \pi d^2 < v >}$$

Mean free path (λ) is given by $< v > \tau$ therefore

$$\lambda = \frac{1}{n \times \pi d^2}$$

A more accurate treatment considering v_{rel} gives

$$\boxed{\lambda = \frac{1}{\sqrt{2}\, n \times \pi d^2}}$$

Mean free path

Consider a gas at pressure P and absolute temperature T. Using ideal gas equation

$$PV = \mu RT$$

$$PV = \frac{N}{N_A} RT$$

$$P = \frac{N}{V}\frac{R}{N_A} T$$

$$P = n k_B T$$

$$n = \frac{P}{k_B T}$$

Mean free path was given by the relation

$$\lambda = \frac{1}{\sqrt{2}\, n \times \pi d^2}$$

Substituting the value of n we get

$$\boxed{\lambda_{mean} = \frac{k_B\ T}{\sqrt{2}\pi d^2 P}}$$

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