



Physics I Lecture 20-The Kinetic Theory of Gases-I

簡紋濱

國立交通大學 理學院 電子物理系

Outline

1. **Molecular Model of an Ideal Gas**
2. **Molar Specific Heat of an Ideal Gas**
3. Adiabatic Processes for an Ideal Gas
4. The Equipartition of Energy
5. Distribution of Molecular Speed

1. MOLECULAR MODEL OF AN IDEAL GAS

Ideal gas model:

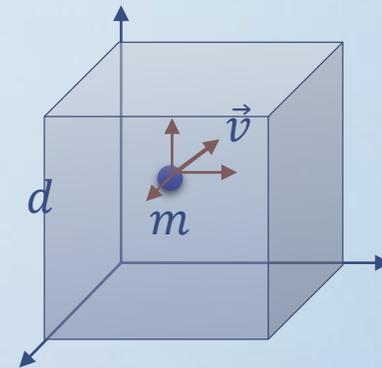
1. The number of molecules in the gas is large and the average separation among molecules is large compared with their size.
2. Newton's law of motion is strictly obeyed for each molecule, but molecules move randomly.
3. The molecules interact only by short-range force during elastic collisions.
4. The molecules make elastic collisions with the walls.
5. The gas under consideration is a pure substance; that is, all molecules are identical.

N molecules in the cube of length d

each molecule has a mass of m and

velocity $\vec{v} = v_x\hat{i} + v_y\hat{j} + v_z\hat{k}$

use impulse to estimate the force on the walls, assume an interval Δt between successive collisions on the wall



1. MOLECULAR MODEL OF AN IDEAL GAS

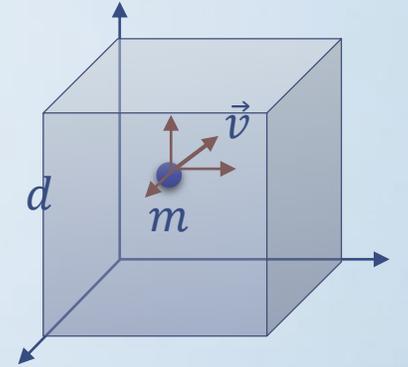
Ideal gas model:

$$\Delta t = \frac{2d}{v_{xi}}, \quad I = F\Delta t = 2mv_{xi} \quad F_i = \frac{2mv_{xi}}{\Delta t} = \frac{mv_{xi}^2}{d} \rightarrow F_{net} = \frac{m}{d} \sum_{i=1}^N v_{xi}^2$$

$$\sum_{i=1}^N v_{xi}^2 = N\langle v_x^2 \rangle, \langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle = \frac{1}{3}\langle v^2 \rangle \rightarrow \sum_{i=1}^N v_{xi}^2 = \frac{N}{3}\langle v^2 \rangle$$

$$F_{net} = \frac{Nm}{3d}\langle v^2 \rangle, P = \frac{F_{net}}{A} = \frac{F_{net}}{d^2} = \frac{Nm}{3d^3}\langle v^2 \rangle = \frac{Nm}{3V}\langle v^2 \rangle$$

$$P = \frac{2N}{3V} \left\langle \frac{mv^2}{2} \right\rangle \rightarrow PV = N \frac{2}{3} \left\langle \frac{mv^2}{2} \right\rangle$$



1. MOLECULAR MODEL OF AN IDEAL GAS

Ideal gas model:

$$PV = N \frac{2}{3} \left\langle \frac{mv^2}{2} \right\rangle \text{ compare with } PV = Nk_B T$$

$$\left\langle \frac{mv^2}{2} \right\rangle = \frac{3}{2} k_B T$$

We will learn the concept later from the equipartition theory.

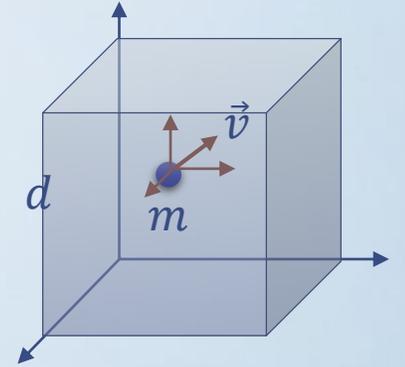
$$\text{one degree of freedom: } \left\langle \frac{mv_x^2}{2} \right\rangle = \frac{1}{2} k_B T$$

$$\text{three degree of freedom: } \left\langle \frac{mv^2}{2} \right\rangle = \frac{3}{2} k_B T$$

$$\text{The internal energy of an ideal gas: } E_{int} = N \left\langle \frac{mv^2}{2} \right\rangle = \frac{3}{2} Nk_B T$$

The root-mean-square speed of a molecule:

$$\langle v^2 \rangle = \frac{3k_B T}{m} \quad v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$$



1. MOLECULAR MODEL OF AN IDEAL GAS

Example: Please calculate the root-mean-square speed of a hydrogen molecule at room temperature.

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}, M = 0.002 \text{ kg}, R = 8.314 \frac{\text{J}}{\text{mol K}}, T = 300 \text{ K}$$

$$v_{rms} = 1930 \text{ m/s}$$

Example: A tank of volume 0.300 m^3 contains 2.00 mole of helium gas at 20.0°C . Assuming the helium behaves like an ideal gas,
(a) find the total internal energy of the gas.
(b) What is the root-mean-square speed of the helium atoms?

$$n = 2.0 \text{ mol}, T = 20^\circ\text{C} = 293.15 \text{ K}$$
$$\rightarrow E = \frac{3}{2} nRT = \frac{3}{2} (2.00)(8.314)(293.15) = 7310 \text{ J}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314)(293.15)}{0.004}} = 1350 \text{ m/s}$$

2. MOLAR SPECIFIC HEAT OF AN IDEAL GAS

Equations for an ideal gas:

$$PV = nRT \quad \Delta W = - \int PdV \quad \Delta E_{int} = \Delta Q + \Delta W \quad E_{int} = \frac{3}{2}nRT$$

Molar specific heat at constant volume:

$$C_V = \frac{(\Delta Q)}{n(\Delta T)}_{V=V_0} \quad \Delta V = 0 \rightarrow \Delta W = 0, \Delta E_{int} = \Delta Q \quad E_{int} = \frac{3}{2}nRT \rightarrow \Delta E_{int} = \frac{3}{2}nR(\Delta T)$$

$$C_V = \frac{(\Delta Q)}{n(\Delta T)} = \frac{(\Delta E)}{n(\Delta T)} = \frac{3nR(\Delta T)/2}{n(\Delta T)} = \frac{3R}{2}$$

Molar specific heat at constant pressure:

$$C_P = \frac{(\Delta Q)}{n(\Delta T)}_{P=P_0} \quad \Delta P = 0 \rightarrow \Delta W \neq 0 \quad PV = nRT \rightarrow P(\Delta V) = nR(\Delta T)$$

$$\Delta E_{int} = \frac{3}{2}nR(\Delta T), \Delta Q = \Delta E - \Delta W = \Delta E + P(\Delta V)$$

$$\Delta Q = \frac{3}{2}nR(\Delta T) + nR(\Delta T) \rightarrow C_P = \frac{\frac{3}{2}nR(\Delta T) + nR(\Delta T)}{n(\Delta T)} = C_V + R = \frac{5}{2}R$$

2. MOLAR SPECIFIC HEAT OF AN IDEAL GAS

The ratio of the two molar specific heats is defined: $\gamma = \frac{C_P}{C_V}$

The specific heats of monatomic, diatomic, and triatomic gas:

	C_P (J/mol K)	C_V (J/mol K)	$C_P - C_V$	$\gamma = C_P/C_V$
He	20.8	12.5	8.33	$1.67 \cong 5/3$
H ₂	28.8	20.4	8.33	$1.41 \cong 7/5$
CO ₂	37	28.5	8.5	$1.31 \cong 9/7$

Example: A cylinder contains 3.00 mol of helium gas at a temperature of 300 K. (a) If the gas is heated at constant volume, how much energy must be transferred by heat to the gas after it is heated to 500 K? (b) How much energy must be transferred by heat to the gas at constant pressure?

$$n = 3.00 \text{ mol}, \Delta T = 500 - 300 = 200 \text{ K}, C_V = 3R/2, C_P = 5R/2$$

$$R = 8.314 \frac{\text{J}}{\text{mol K}} \quad \Delta Q_V = nC_V(\Delta T) = (3.00)(3R/2)(200) = 7480 \text{ J}$$

$$\Delta Q_P = nC_P(\Delta T) = (3.00)(5R/2)(200) = 12500 \text{ J}$$

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3. ADIABATIC PROCESSES FOR AN IDEAL GAS

Adiabatic process: what is the P-V dependence?

$$\Delta Q = 0 \rightarrow \Delta E_{int} = \Delta W = -P\Delta V$$

$$E_{int} = nC_V T \rightarrow \Delta E_{int} = nC_V(\Delta T)$$

$$nC_V(\Delta T) = -P(\Delta V)$$

$$PV = nRT \rightarrow P(\Delta V) + V(\Delta P) = nR(\Delta T)$$

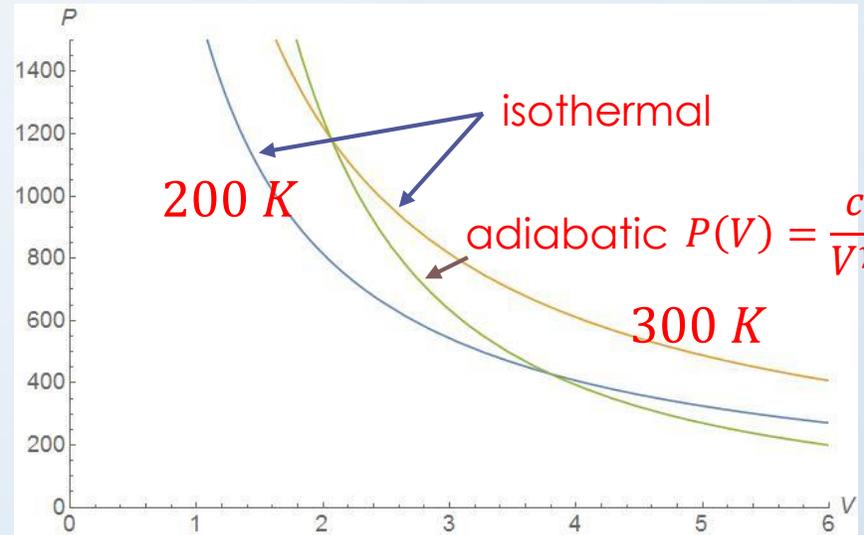
$$P(\Delta V) + V(\Delta P) = n(C_P - C_V)(\Delta T)$$

$$P(\Delta V) + V(\Delta P) = (C_P - C_V) \frac{-P(\Delta V)}{C_V}$$

$$P(\Delta V) + V(\Delta P) = (1 - \gamma)P(\Delta V) \rightarrow \gamma P(\Delta V) + V(\Delta P) = 0$$

$$\gamma \frac{dV}{V} + \frac{dP}{P} = 0 \rightarrow \gamma(\ln V - \ln V_0) = -\ln P + \ln P_0 \rightarrow \left(\frac{V}{V_0}\right)^\gamma = \left(\frac{P_0}{P}\right)$$

$$\rightarrow PV^\gamma = P_0 V_0^\gamma = \text{const}$$



3. ADIABATIC PROCESSES FOR AN IDEAL GAS

Example: The fuel-air mixture in the cylinder of a diesel engine at 20.0°C is compressed from an initial pressure of 1.00 atm and volume of 800 cm³ to a volume of 60.0 cm³. Assuming that the mixture behaves as an ideal gas with $\gamma = 1.4$ and that the compression is adiabatic, find the final pressure and temperature of the mixture.

$$P_i = 1 \text{ atm}, V_i = 800 \text{ cm}^3, T_i = 293.15 \text{ K}, V_f = 60 \text{ cm}^3$$

In an adiabatic process, the P-V follows $P_i V_i^\gamma = P_f V_f^\gamma$.

$$P_f = \frac{P_i V_i^\gamma}{V_f^\gamma} = \frac{1.00 \times 800^{1.4}}{60.0^{1.4}} = 37.6 \text{ atm}$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \rightarrow T_f = \frac{T_i V_i^{\gamma-1}}{V_f^{\gamma-1}} = \frac{293.15 \times 800^{0.4}}{60.0^{0.4}} = 826 \text{ K}$$

4. THE EQUIPARTITION OF ENERGY

The theory of the equipartition of energy: In the equilibrium condition, each degree of freedom contributes an average energy of $k_B T/2$ per molecule.

Monatomic gas molecule: three degrees of freedom of translational motion

Diatomic gas molecule:

three degrees of freedom for translation motion

two degrees of freedom for rotational motion

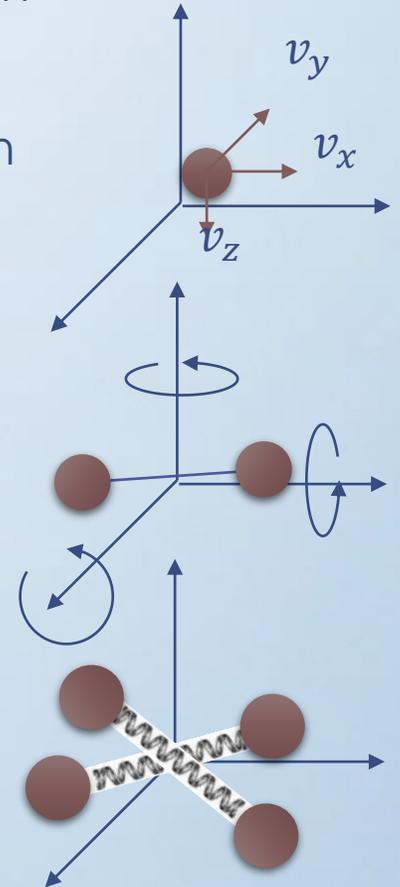
two degrees of freedom for vibrational motion

Molar specific heat of the diatomic gas system:

$C_V = \frac{3}{2}R, C_P = \frac{5}{2}R$ for molecules only in translational motion

$C_V = \frac{5}{2}R, C_P = \frac{7}{2}R$ for molecules in translational and rotational motion

$C_V = \frac{7}{2}R, C_P = \frac{9}{2}R$ for molecules in translational, rotational, and vibrational motion



4. THE EQUIPARTITION OF ENERGY

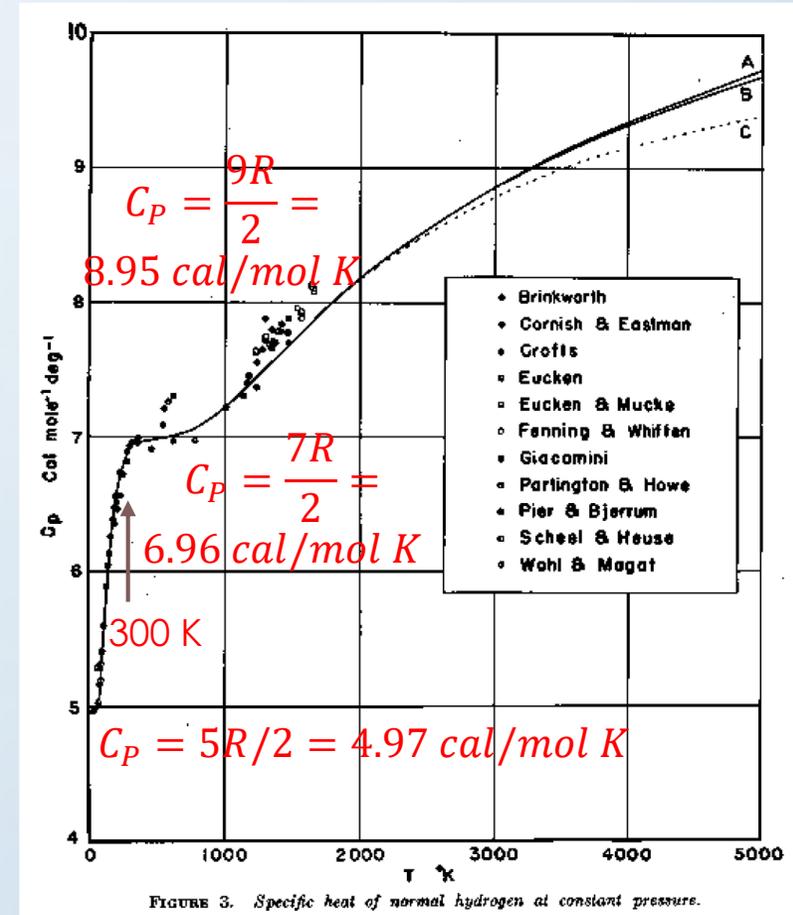
C_p molar specific heat at constant pressure of normal hydrogen molecules

U.S. Department of Commerce National Bureau of Standards, V41, P379 (1948).

The temperature dependence implies the energy quantization for rotational and vibrational motions.

It points out the difference between classical and quantum statistics.

$$\Delta E_{trans} < \Delta E_{rot} < \Delta E_{vib}$$



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5. DISTRIBUTION OF MOLECULAR SPEED

Probability and statistics: distribution functions (the probability of the occurrence times)

occurrence times of the i^{th} event: $n_i, \sum n_i = N$

distribution function: $f_i = n_i/N, \sum_{i=1}^m f_i = 1$

If the value of the i^{th} event is s_i

the average value is $s_{avg} = \langle s \rangle = \frac{\sum n_i s_i}{\sum n_i} = \sum \frac{n_i}{N} s_i = \sum f_i s_i$

the average of the square of the value is $(s^2)_{avg} = \langle s^2 \rangle = \sum f_i s_i^2$

the root-mean-square of the value is $s_{rms} = \sqrt{\langle s^2 \rangle}$

the standard deviation is $\sigma = \sqrt{\langle (s_i - \langle s \rangle)^2 \rangle} = \sqrt{\langle s^2 \rangle - \langle s \rangle^2}$

Continuous distribution: $f_i \rightarrow f(x), \sum f_i = 1 \rightarrow \int f(x) dx = 1$

the value is also a function of $x, s(x)$

the average of the value is $\langle s \rangle = \int s(x) f(x) dx$

$$\langle s^2 \rangle = \int [s(x)]^2 f(x) dx, s_{rms} = \sqrt{\langle s^2 \rangle}, \sigma = \sqrt{\langle s^2 \rangle - \langle s \rangle^2}$$

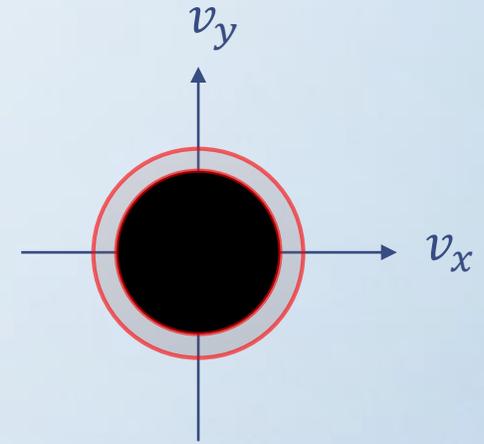
5. DISTRIBUTION OF MOLECULAR SPEED

The occurrence probability of a molecule with kinetic energy E follows the Maxwell-Boltzmann distribution:

$$P(E) = c \exp\left(-\frac{E}{k_B T}\right)$$

In a two dimensional system, the number of molecules is proportional to the ring area and the energy distribution function:

$$P(E)2\pi v dv, E = mv^2/2$$

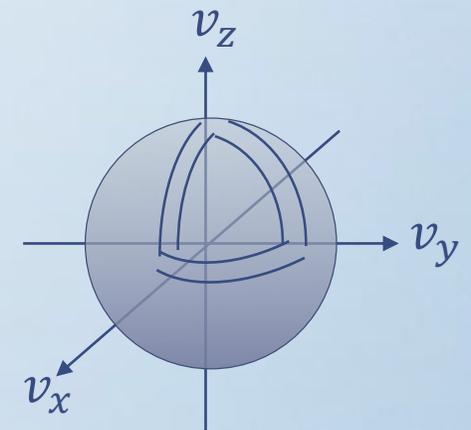


In a three dimensional system, the number of molecules is $N(v)dv \propto 4\pi v^2 dv \times \exp(-E/k_B T)$

$$N(v) = kv^2 \exp(-mv^2/2k_B T)$$

Normalize it by:

$$\int_0^\infty N(v)dv = N \rightarrow k = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$



5. DISTRIBUTION OF MOLECULAR SPEED

Mathematical methods: $N(v) = kv^2 \exp(-mv^2/2k_B T)$ & $\int_0^\infty N(v)dv = N \rightarrow k = ?$

$$f(v) = \exp\left(-\frac{mv^2}{2k_B T}\right), \text{ let } A = \frac{m}{2k_B T} \rightarrow f(A, v) = \exp(-Av^2)$$
$$I(A) = \int_0^\infty \exp(-Av^2)dv \rightarrow -\frac{dI}{dA} = \int_0^\infty v^2 \exp(-Av^2) dv$$

Let's calculate $I(A)$, put the one-dimensional integration into a two-dimensional space, and use the polar coordinate

$$I(A) = \frac{1}{2} \int_{-\infty}^\infty \exp(-Av^2)dv \rightarrow I^2(A) = \frac{1}{4} \int_{-\infty}^\infty \exp(-Av^2)dv \int_{-\infty}^\infty \exp(-Av^2)dv$$

$$I^2(A) = \frac{1}{4} \int_{-\infty}^\infty \int_{-\infty}^\infty \exp(-Ax^2) \exp(-Ay^2) dx dy$$

$$I^2(A) = \frac{1}{4} \int_0^\infty \int_0^{2\pi} \exp(-Ar^2) r d\theta dr = -\frac{\pi}{4A} \int_{r=0}^{r=\infty} \exp(-Ar^2) d(-Ar^2)$$

$$I^2(A) = \frac{\pi}{4A} \rightarrow I(A) = \frac{1}{2} \left(\frac{\pi}{A}\right)^{\frac{1}{2}}$$

5. DISTRIBUTION OF MOLECULAR SPEED

Number of molecules as a function of speed: $N(v)$

$$N(v) = kv^2 \exp(-mv^2/2k_B T) \text{ \& } \int_0^\infty N(v) dv = N \rightarrow k = ?$$

$$I(A) = \int_0^\infty \exp(-Av^2) dv = \frac{1}{2} \left(\frac{\pi}{A}\right)^{\frac{1}{2}} \rightarrow \int_0^\infty v^2 \exp(-Av^2) dv = -\frac{dI}{dA} = \frac{1}{4} \sqrt{\frac{\pi}{A^3}}$$

$$\rightarrow \int_0^\infty N(v) dv = k \int_0^\infty v^2 \exp(-mv^2/2k_B T) dv$$

$$= k \frac{1}{4\pi} \sqrt{\frac{8k_B^3 \pi^3 T^3}{m^3}} = N \rightarrow k = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2}$$

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp(-mv^2/2k_B T)$$

5. DISTRIBUTION OF MOLECULAR SPEED

The average speed of the gas molecules:

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp(-mv^2/2k_B T)$$

$$v_{avg} = \bar{v} = \langle v \rangle = \frac{1}{N} \int_0^{\infty} v N(v) dv = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} v^3 \exp(-mv^2/2k_B T) dv$$

$$I(A) = \int_0^{\infty} \exp(-Av^2) dv$$

$$\int_0^{\infty} v^3 \exp(-Av^2) dv = -\frac{1}{2A} \int_0^{\infty} v^2 d[\exp(-Av^2)]$$

$$= \left[-\frac{v^2}{2A} \exp(-Av^2) \right]_{v=0}^{v=\infty} + \frac{1}{A} \int_0^{\infty} v \exp(-Av^2) dv = -\frac{1}{2A^2} \int_{v=0}^{v=\infty} d[\exp(-Av^2)] = \frac{1}{2A^2}$$

$$\langle v \rangle = k \frac{1}{2A^2} = 4\pi \frac{m^{3/2}}{\pi^{3/2} (2k_B T)^{3/2}} \frac{1}{2(m/2k_B T)^2} = 2 \frac{(2k_B T)^{1/2}}{\pi^{1/2} m^{1/2}} = \sqrt{\frac{8k_B T}{\pi m}}$$

5. DISTRIBUTION OF MOLECULAR SPEED

The average kinetic energy of the gas molecules:

$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp(-mv^2/2k_B T)$$

$$\left\langle \frac{1}{2} mv^2 \right\rangle = 2\pi m \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^\infty v^4 \exp(-mv^2/2k_B T) dv$$

$$I(A) = \int_0^\infty \exp(-Av^2) dv = \frac{1}{2} \sqrt{\frac{\pi}{A}}, \quad \int_0^\infty v^2 \exp(-Av^2) dv = \frac{1}{4} \sqrt{\frac{\pi}{A^3}} = \frac{\pi^{1/2}}{4} A^{-3/2}$$

$$\int_0^\infty v^4 \exp(-Av^2) dv = \left(-\frac{d}{dA} \right) \int_0^\infty v^2 \exp(-Av^2) dv$$

$$= - \left(-\frac{3}{2} \right) \frac{\pi^{1/2}}{4} A^{-5/2} = \frac{3\pi^{1/2}}{8A^{5/2}}$$

$$\left\langle \frac{1}{2} mv^2 \right\rangle = 2\pi m \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{3\pi^{1/2}}{8} \left(\frac{2k_B T}{m} \right)^{5/2} = \frac{3}{2} k_B T \text{ equipartition theory}$$

5. DISTRIBUTION OF MOLECULAR SPEED

The distribution function:

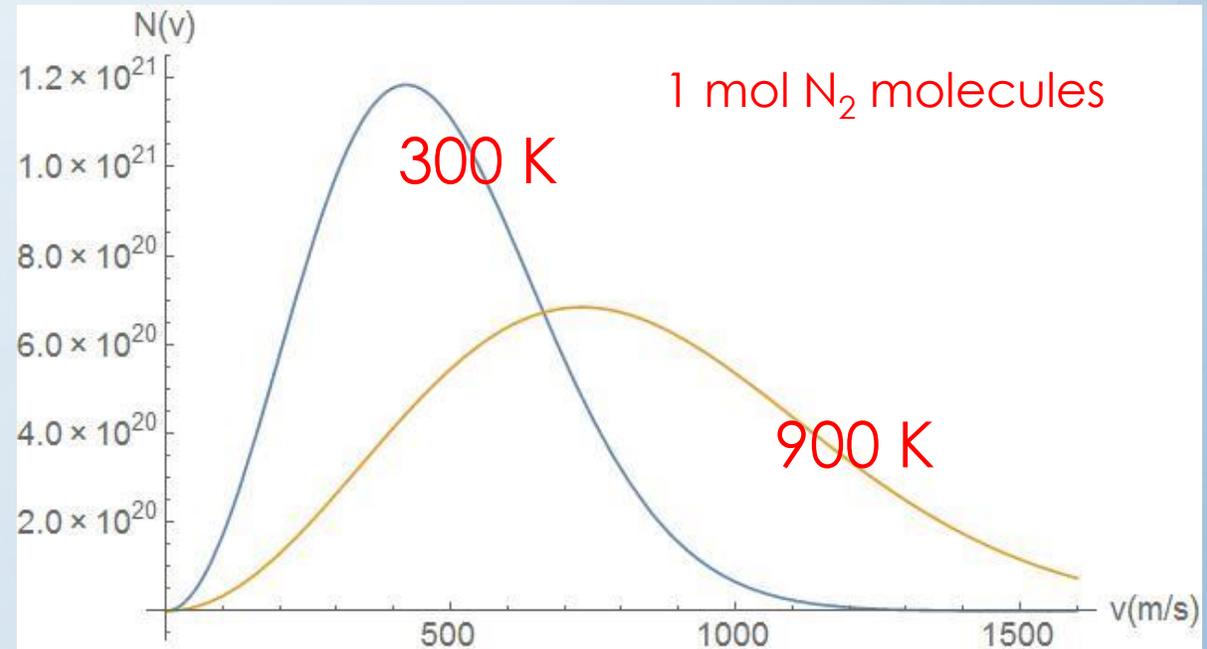
$$N(v) = 4\pi N \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 \exp(-mv^2/2k_B T)$$

$$\left[\frac{dN(v)}{dv} \right]_{v=v_{mp}} = 0 \rightarrow 2v_{mp} e^{-mv_{mp}^2/2k_B T} + v_{mp}^2 e^{-mv_{mp}^2/2k_B T} \left(-\frac{mv_{mp}}{k_B T} \right) = 0$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m}}$$



5. DISTRIBUTION OF MOLECULAR SPEED

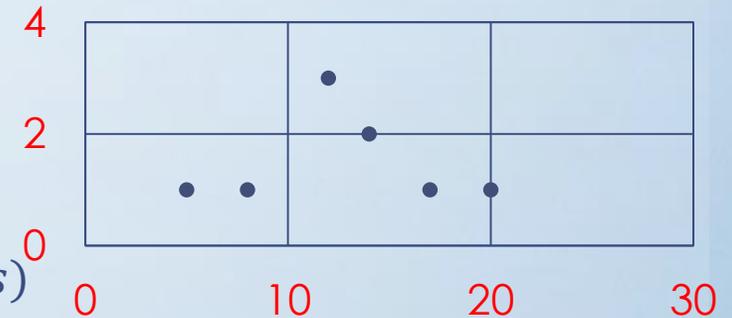
Example: Nine particles have speeds of 5.0, 8.0, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s. (a) Find the average speed. (b) What is the rms speed? (c) What is the most probable speed of the particles?

$$\langle v \rangle = \frac{5.0 + 8.0 + 12.0 \times 3 + 14.0 \times 2 + 17.0 + 20.0}{9} = 12.7 \text{ (m/s)}$$

$$v_{rms} = \sqrt{\frac{5.0^2 + 8.0^2 + 12.0^2 \times 3 + 14.0^2 \times 2 + 17.0^2 + 20.0^2}{9}} = 13.3 \text{ (m/s)}$$

$$v_{mp} = 12 \text{ (m/s)}$$

Distribution function



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