Kinetic theory of gas

- Molecular model of an ideal gas
- Molar specific heat of an ideal gas
- The equipartition of energy
- Van der Waals forces (Optional)
- Distribution of molecular speeds
- Mean free path

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https://twiki.cern.ch/twiki/bin/view/Main/PhatSrimanobhasTeaching
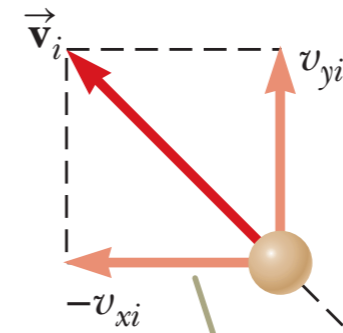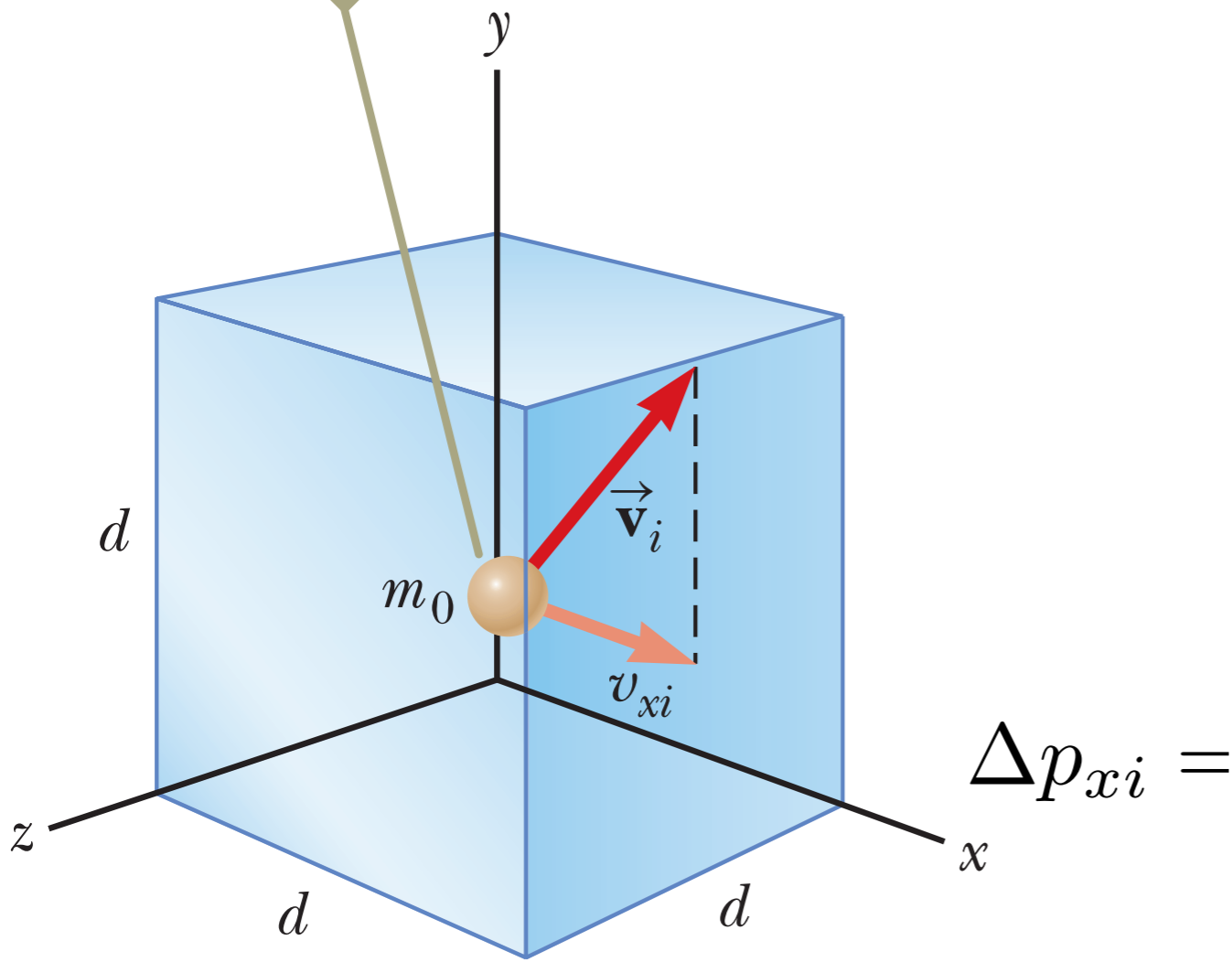
Molecular model of an ideal gas

We will discuss the link between macroscopic and microscopic of an idea gas. In Kinetic theory (Newtonian mechanics), we consider that
- Gas consists of identical "point" molecules of mass m.
- No interaction between molecules, except when they collide.
- Random motion.
- Collisions with wall are elastic.
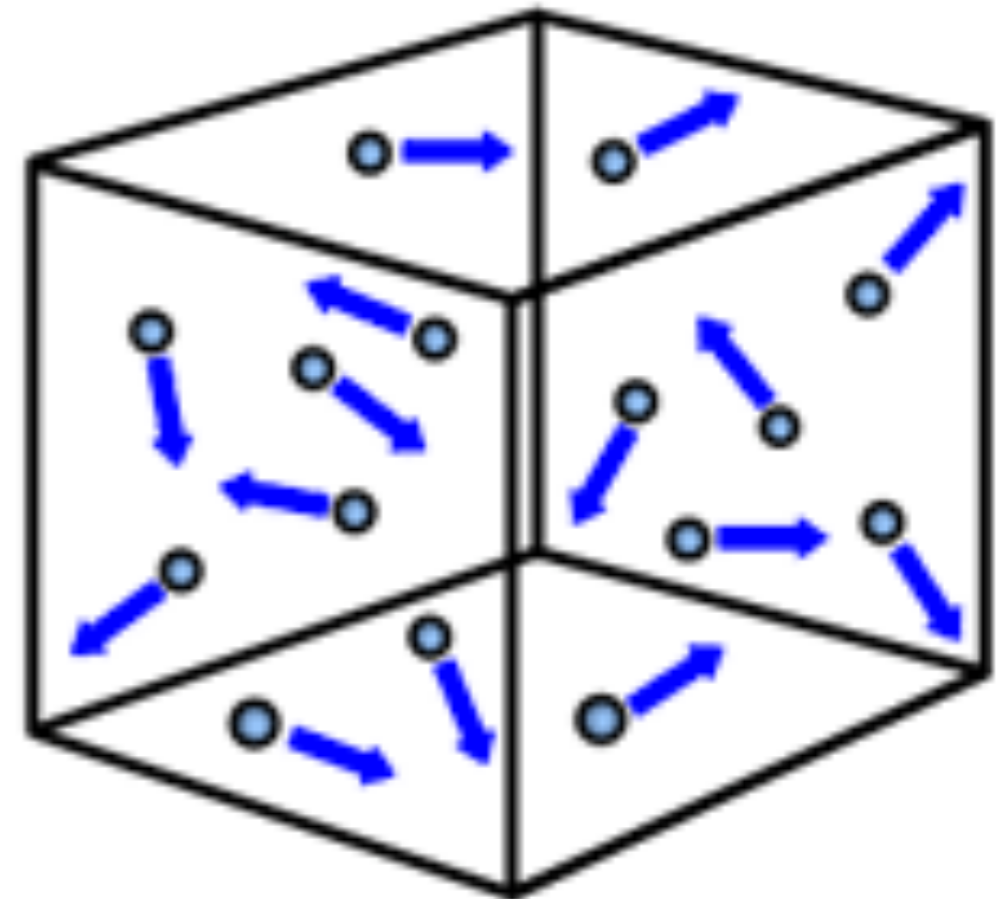
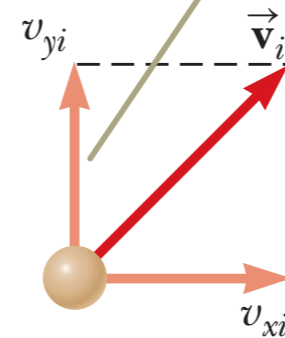# Molecular model of an ideal gas

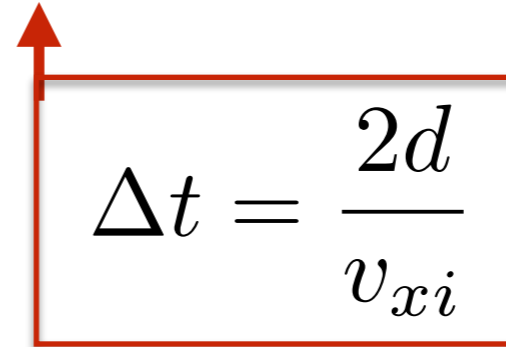One molecule of the gas moves with velocity $\vec{\mathbf{v}}$ on its way toward a collision with the wall.

The molecule's x component of momentum is reversed, whereas its y component remains unchanged.

$$\Delta p_{xi} =$$

Molecular model of an ideal gas

Apply the impulse-momentum theorem:

$$\bar{F}_{i,\text{on molecule}} = -\frac{2m_0 v_{xi}}{\Delta t} = -\frac{m_0 v_{xi}^2}{d}$$

$$\boxed{\Delta t = \frac{2d}{v_{xi}}}$$

Interval between 2 collisions with the same wall

By Newton's third law, the component of the long term average force exerted by the molecule on the wall:

$$\bar{F}_{i,\text{on wall}} = \frac{m_0 v_{xi}^2}{d}$$

Consider a very large number of molecules:

$$F = \frac{m_0}{d} \sum_{i=1}^{N} v_{xi}^2$$

Average force is the same over any time interval

Molecular model of an ideal gas

Consider the average value of the square of the x component of the velocity for N molecules:

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

Substitute it back to the force we get before

$$F = \frac{m_0}{d} N\overline{v_x^2}$$

Consider now the three components of velocity (for each molecule)

$$v_i^2 = v_{xi}^2 + v_{yi}^2 + v_{zi}^2$$

Average $\longrightarrow$ $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$

$$\overline{v^2} = 3\overline{v_x^2} \longleftarrow$$ Assumption that gas motion is an isotropic

Molecular model of an ideal gas

Consider the total pressure exerted on the wall:

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3}\left(\frac{N}{V}\right)m_0\overline{v^2}$$

$$= \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m_0\overline{v^2}\right)$$

Average K.E.

You now have the link between macroscopic world (pressure) with microscopic world (K.E.) of the gas molecules. What can you tell from this equation? Does the pressure depend on the type of gas?

Molecular model of an ideal gas

Molecular interpretation of temperature

$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

What can you tell from this equation?

Theorem of equipartition of energy

Each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of a system, where possible degrees of freedom are those associated with translation, rotation, and vibration of molecules.

Molecular model of an ideal gas

The total kinetic energy (N molecules):

$$K_{tot,trans} = N(\frac{1}{2}m_0\overline{v^2})$$

$$= \frac{3}{2}Nk_BT$$
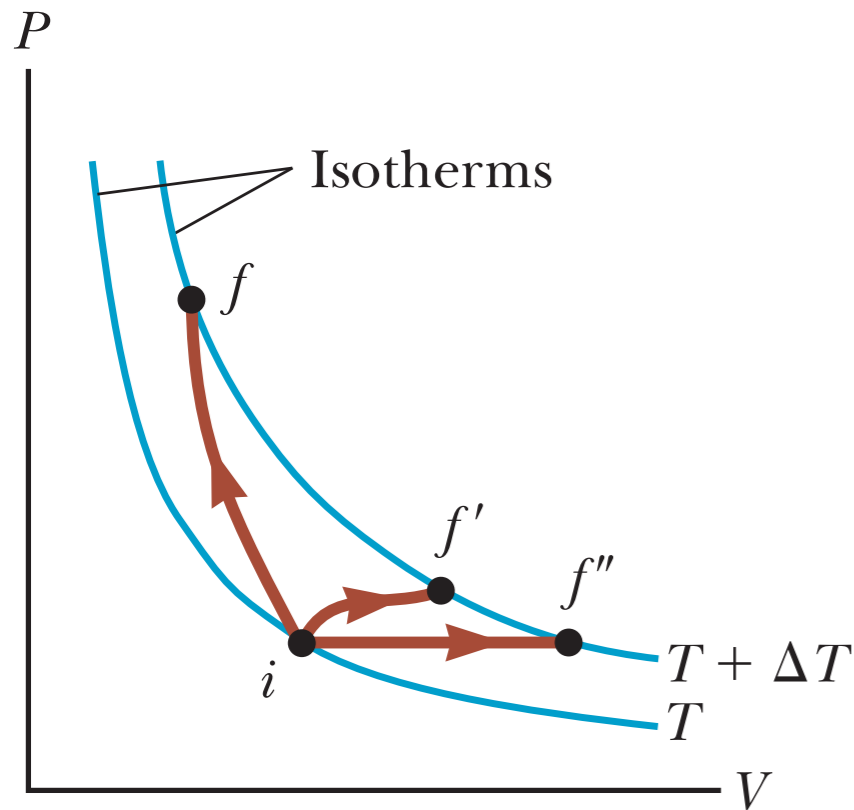
$$= \frac{3}{2}nRT$$

root-mean-square (rms) speed:

$$v_{rms} = \sqrt{\frac{3k_bT}{m_0}} = \sqrt{\frac{3RT}{M}}$$

This expression shows that, at a given temperature, lighter molecules move faster, on the average, than do heavier molecules.

Example

What is the total translational kinetic energy of Neon gas with mass 1 gram at 30°C (Atomic mass of Neon is 20.18u)

Molar specific heat of an ideal gas

We will review this topic again when we talk about the first law of Thermodynamics.

Consider an ideal gas undergoing several processes such that the change in temperature is $\Delta T = T_f - T_i$. We normally consider 2 cases:

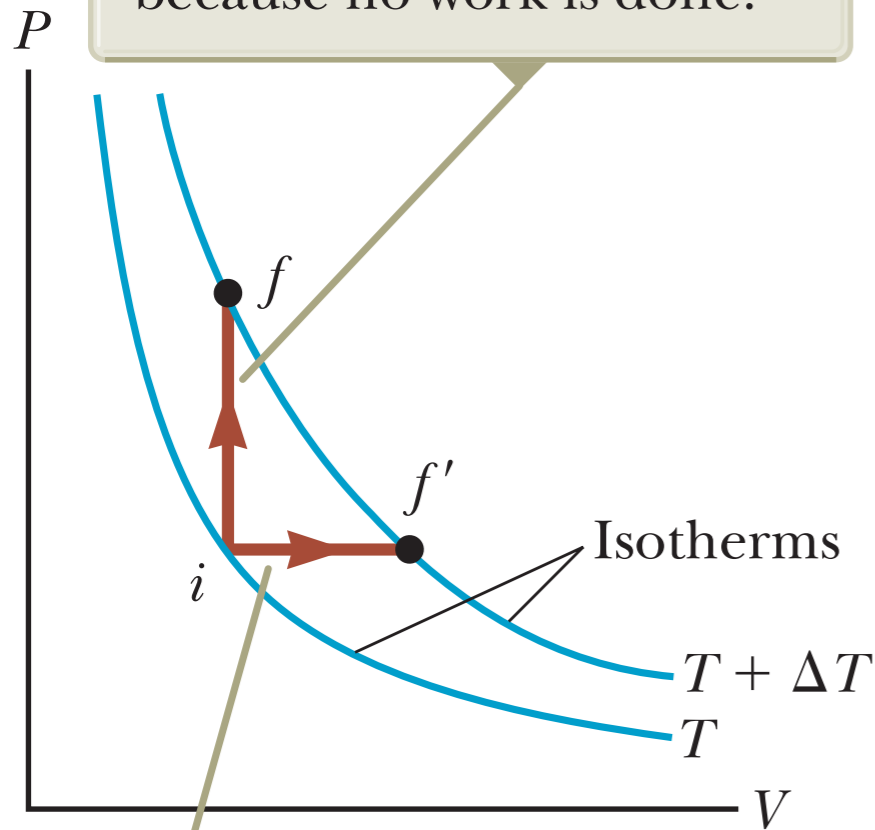- Constant volume
- Constant pressure

Start with simplest case when energy is added to the ideal monatomic gas:

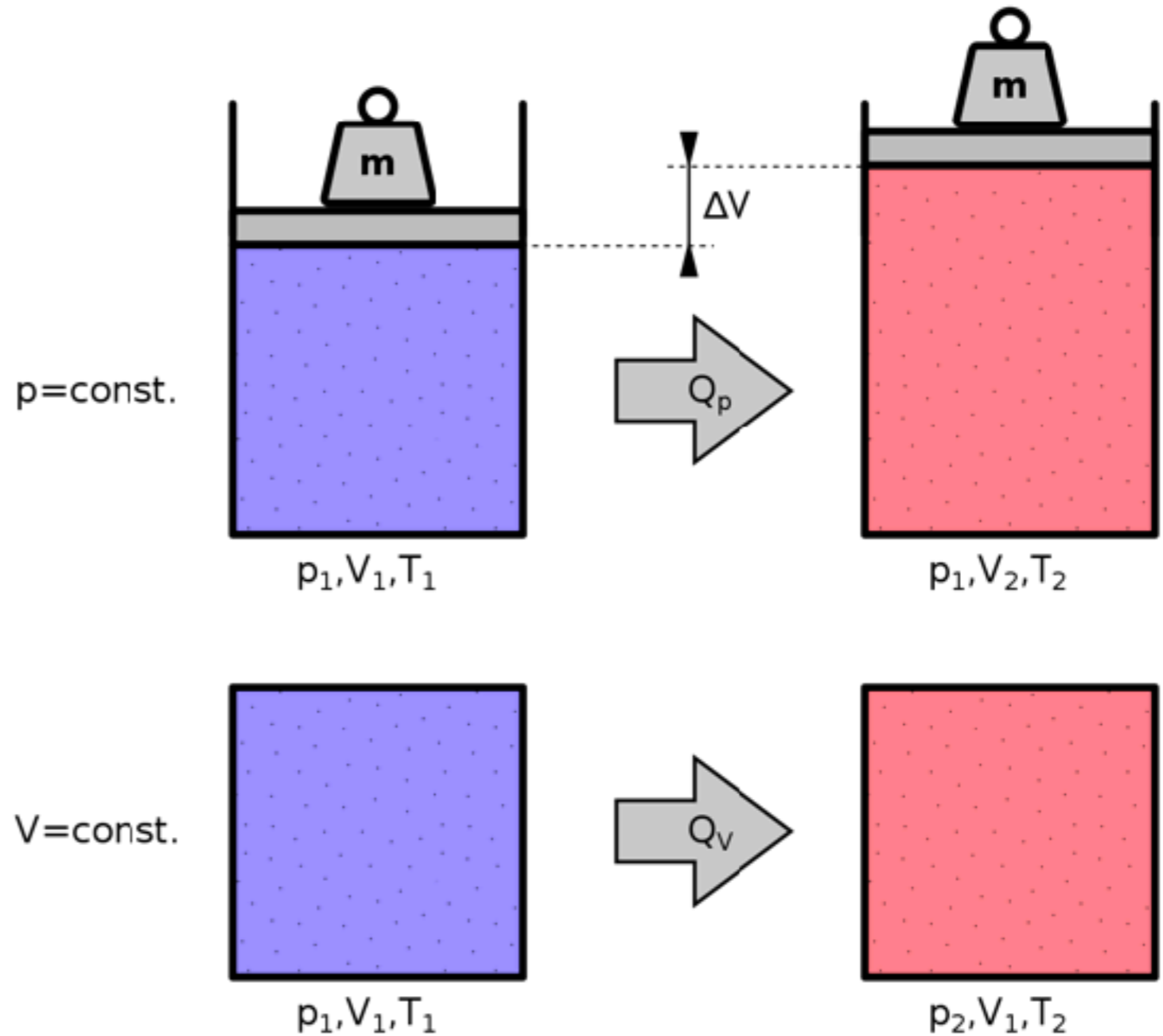$$E_{\text{int}} = K_{\text{tot,trans}} = \frac{3}{2}nRT = \frac{3}{2}Nk_BT$$

What will happen to the system?

Molar specific heat of an ideal gas

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

P

f

f'

Isotherms

i

$T + \Delta T$

T

V

ΔV

m

$p = const.$

Q_p

p_1, V_1, T_1

p_1, V_2, T_2

m

$V = const.$

Q_v

p_1, V_1, T_1

p_2, V_1, T_2

Molar specific heat of an ideal gas

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.
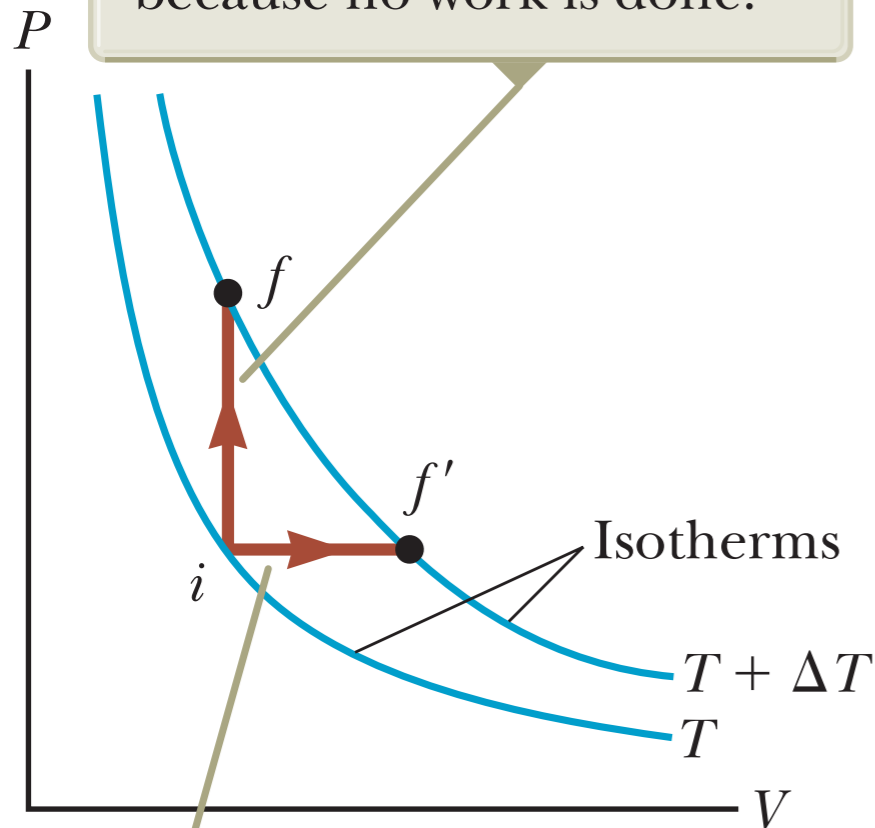
P

f

f'

i

Isotherms

$T + \Delta T$

T

V

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

In case of constant volume:

$$C_v = \frac{1}{n} \frac{dE_{int}}{dT}$$

and $Q = \Delta E_{int} = nC_v\Delta T$

So we will have

In case of constant pressure:

Molar specific heat of an ideal gas

Table 21.2   **Molar Specific Heats of Various Gases**

Molar Specific Heat (J/mol · K)[a]

Gas	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic gases				
H_2	28.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Polyatomic gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30
CH_4	35.5	27.1	8.41	1.31

[a] All values except that for water were obtained at 300 K.

Predictions based on the model for molar specific heat agree quite well with the behavior of monatomic gases, but not with the behavior of complex gases.

The equipartition of energy

Our assumption:

Translational in 3 dimensions

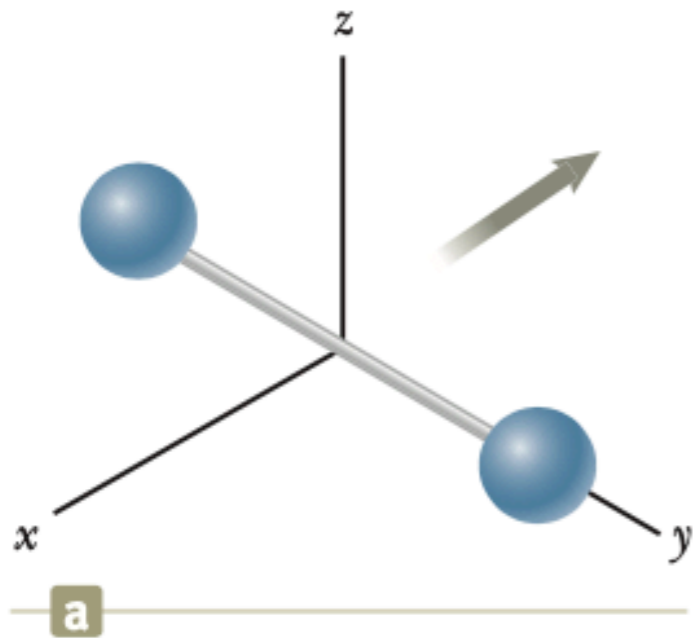$$\frac{1}{2} m_0 \overline{v^2} = \frac{3}{2} k_B T$$

The internal energy of a gas, however, includes contributions from the *translational, vibrational, and rotational motion* of the molecules. Each degree of freedom contributes, on average,
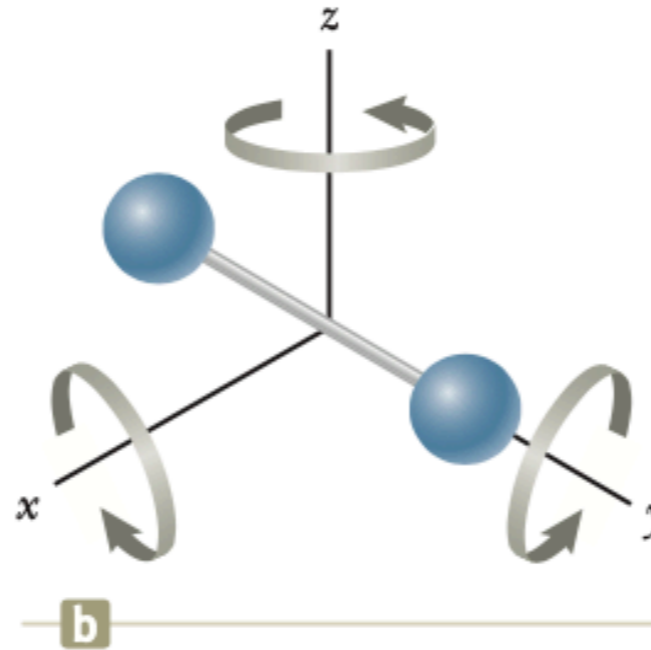
$$\frac{1}{2} k_B T$$

Classical equipartition of energy

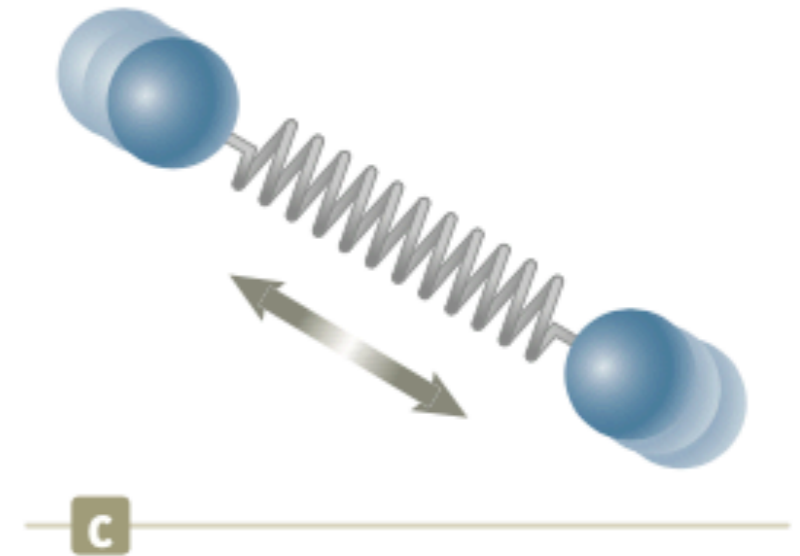# The equipartition of energy (diatomic molecule)

Translational motion of the center of mass

Rotational motion about the various axes

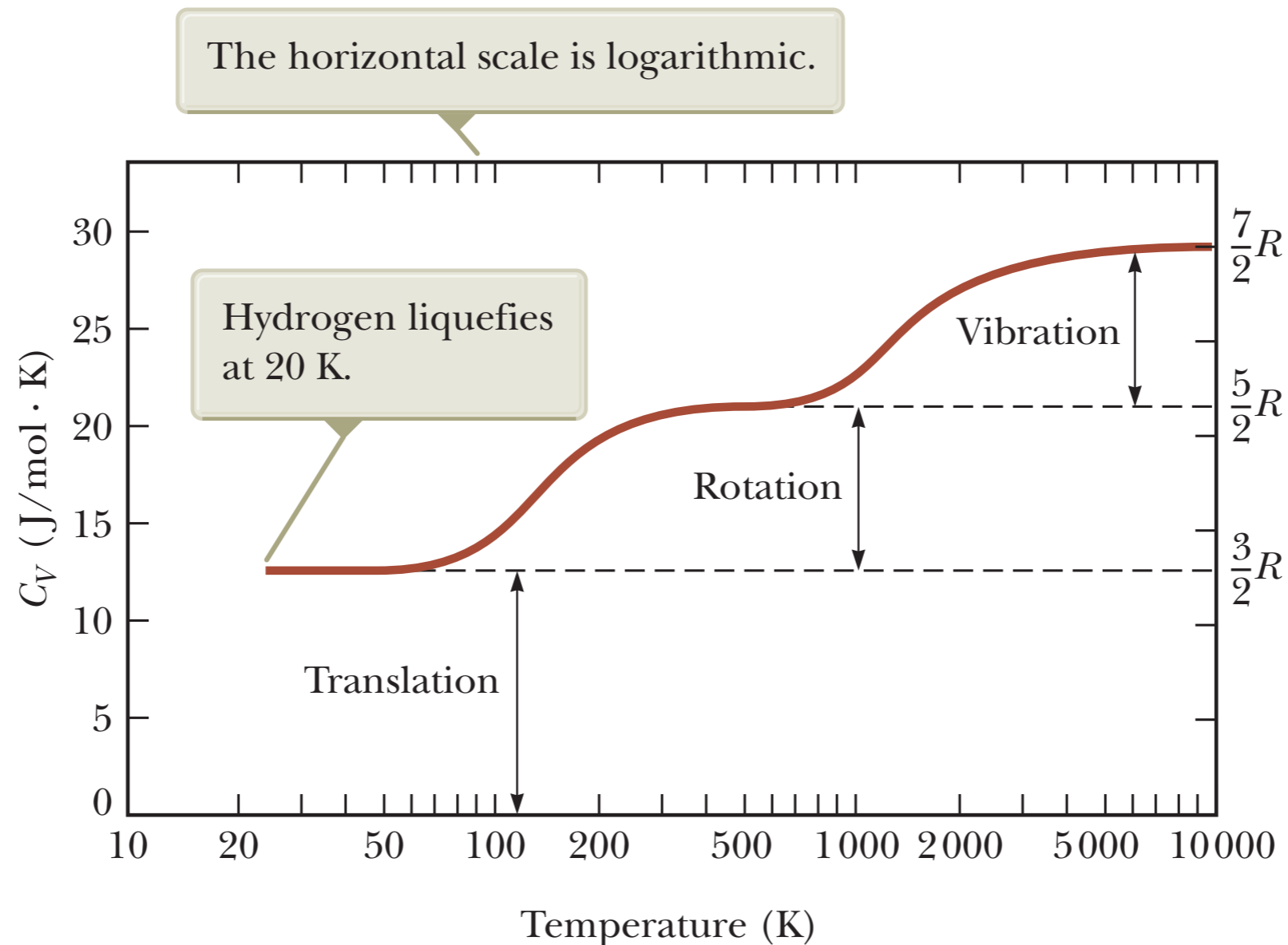Vibrational motion along the molecular axis

The equipartition of energy

	Monatomic	Linear molecules	Non-linear molecules	Energy multiplication
การเลื่อนตำแหน่ง	3	3	3	$\frac{1}{2}k_B T$
การหมุน	0	2	3	$\frac{1}{2}k_B T$
การสั่น	0	3N-5	3N-6	$k_B T$

Try H_2O:

The equipartition of energy

For low temperatures, the diatomic hydrogen gas behaves like a monatomic gas. As the temperature rises to room temperature, its molar specific heat rises to a value for a diatomic gas, consistent with the inclusion of rotation but not vibration. For high temperatures, the molar specific heat is consistent with a model including all types of motion.
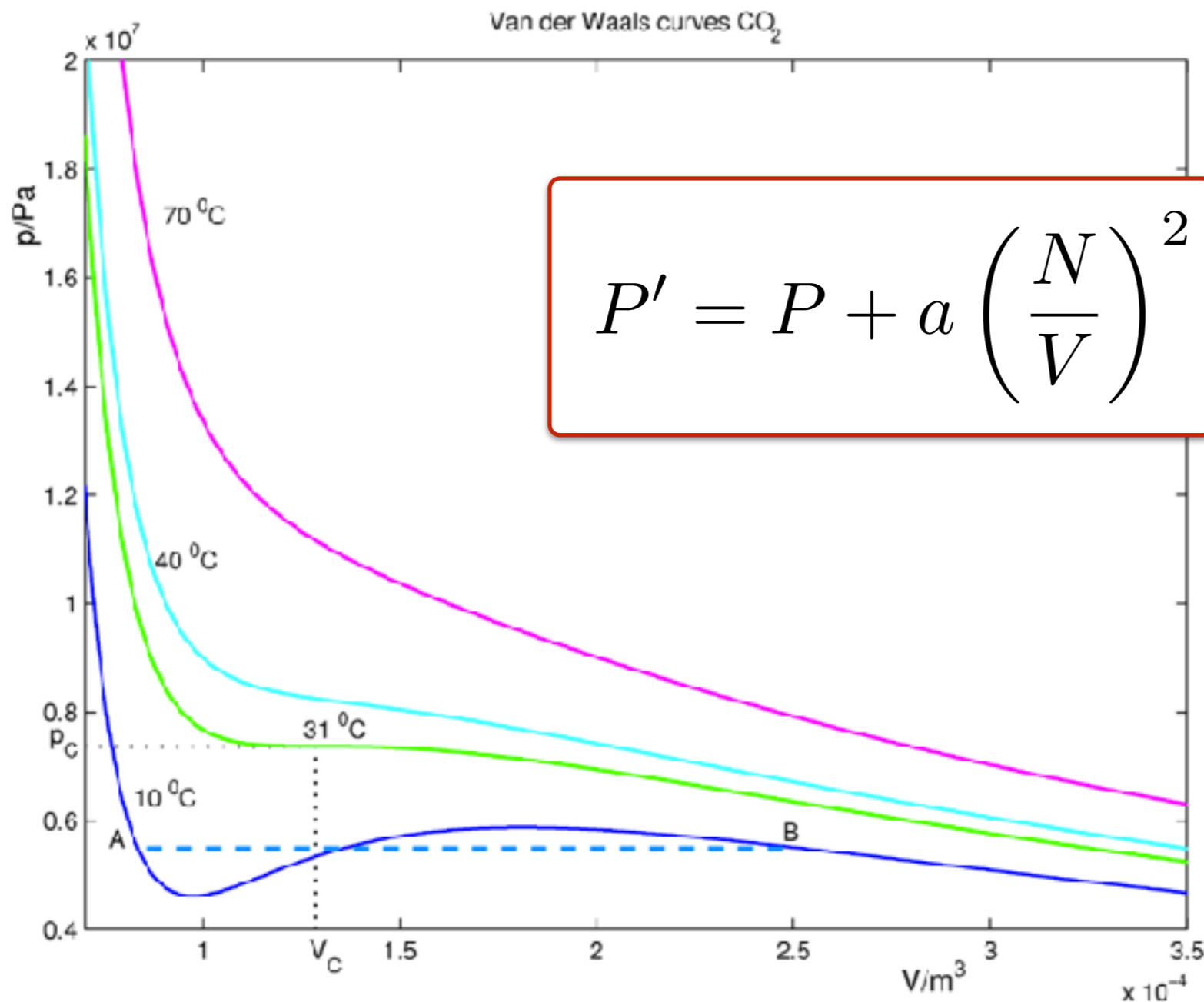
Ideal gas - real gas

The Van der Waals equation is an equation of state that generalizes the ideal gas law based on plausible reasons that real gases do not act ideally. It is a modified version of an ideal gas law by considering:

(1) Interaction between gas molecules
(2) Gas is not a point-like particle, volume is

Van der Waals equation

Consider n mole of gas at the pressure P, Volume V and temperature T (Kelvin).

$$P' = P + a \left(\frac{N}{V} \right)^2$$

$$V' = V - Nb$$

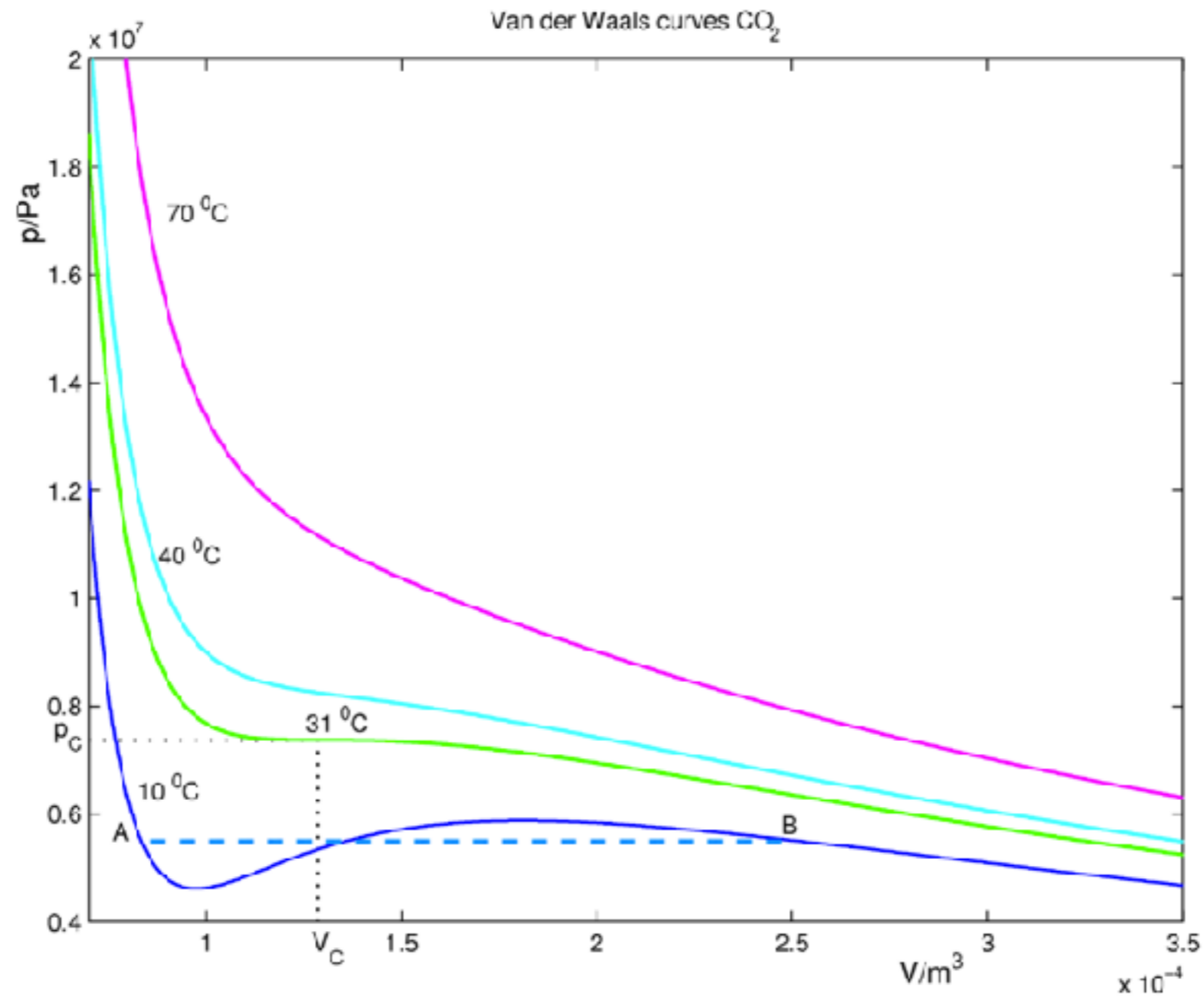$$P'V' = Nk_BT$$

$$N = N_A n$$

Van der Waals equation

If $N \ll V$ we will get ideal gas equation.

Van der Waals equation

Arrange the equation, we will get

$$PV^3 - N(k_B T + Pb)V^2 + N^2 aV - N^3 ab = 0$$

Van der Waals curves CO$_2$

Van der Waals equation

$$V' = V - Nb$$

$$P'V' = Nk_BT$$

$$P' = P + a\left(\frac{N}{V}\right)^2$$

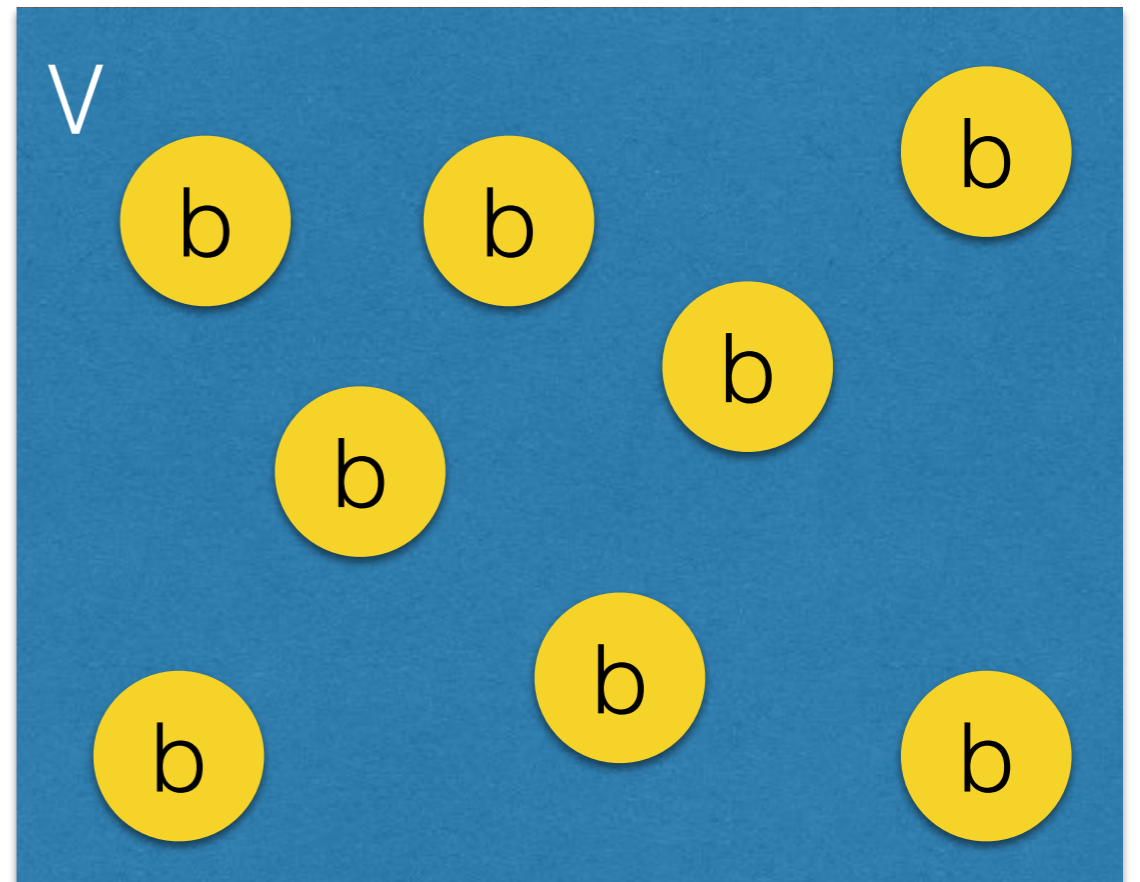a and b are Empirical constants (also depend on type of gas).

The constant a provides a correction for the intermolecular forces.

The constant b is a correction for finite molecular size and its value is the volume of one mole of the atoms or molecules.

V

b b b b b b b b b

Van der Waals equation

Van der Waals curves CO_2
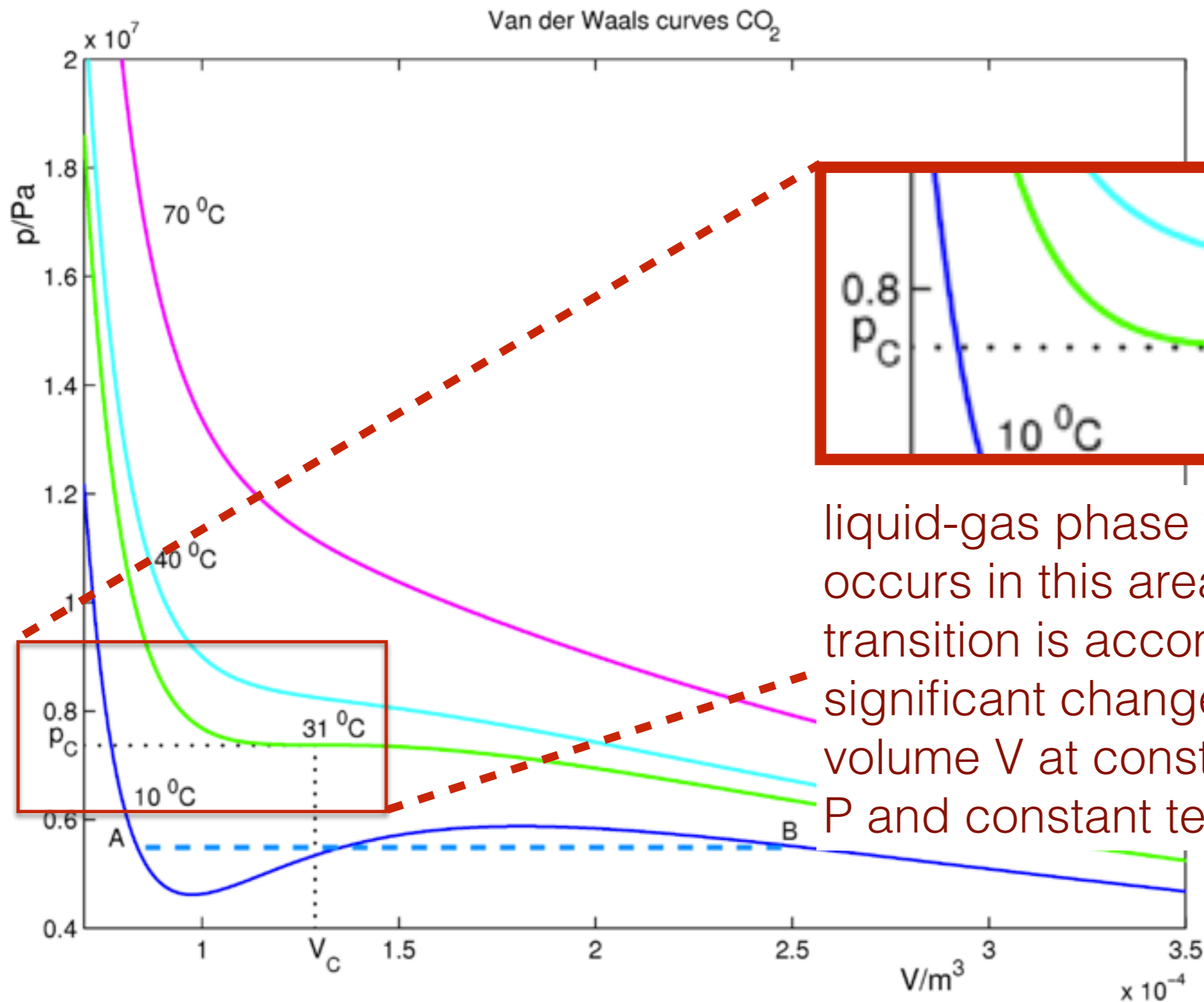
liquid-gas phase transition occurs in this area. This transition is accompanied by a significant change in the volume V at constant pressure P and constant temperature T.

Distribution of molecular speeds

Back to what we discuss before:

$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_BT$$

$$v_{rms} = \sqrt{\frac{3k_bT}{m_0}} = \sqrt{\frac{3RT}{M}}$$

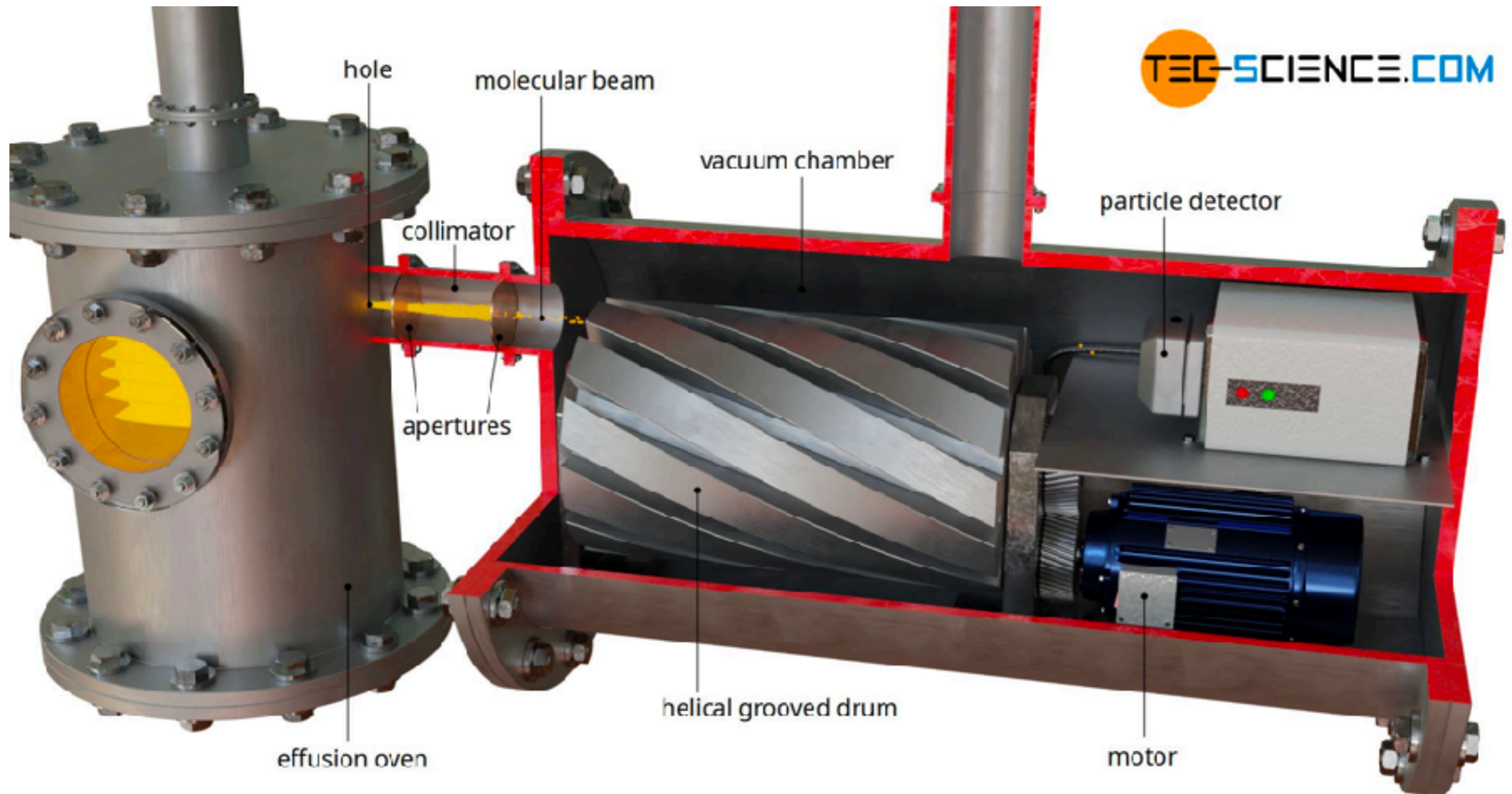**Table 21.1**   **Some Root-Mean-Square (rms) Speeds**

Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H_2	2.02	1902	NO	30.0	494
He	4.00	1352	O_2	32.0	478
H_2O	18.0	637	CO_2	44.0	408
Ne	20.2	602	SO_2	64.1	338
N_2 or CO	28.0	511			

Example

A 7.00-L vessel contains 3.50 moles of gas at a pressure of 1.60×10^6 Pa. Find (a) the temperature of the gas and (b) the average kinetic energy of the gas molecules in the vessel. (c) What additional information would you need if you were asked to find the average speed of the gas molecules?

Distribution of molecular speeds

Thus far, we have considered only average values of the energies of all the molecules in a gas and have not addressed the distribution of energies among individual molecules.
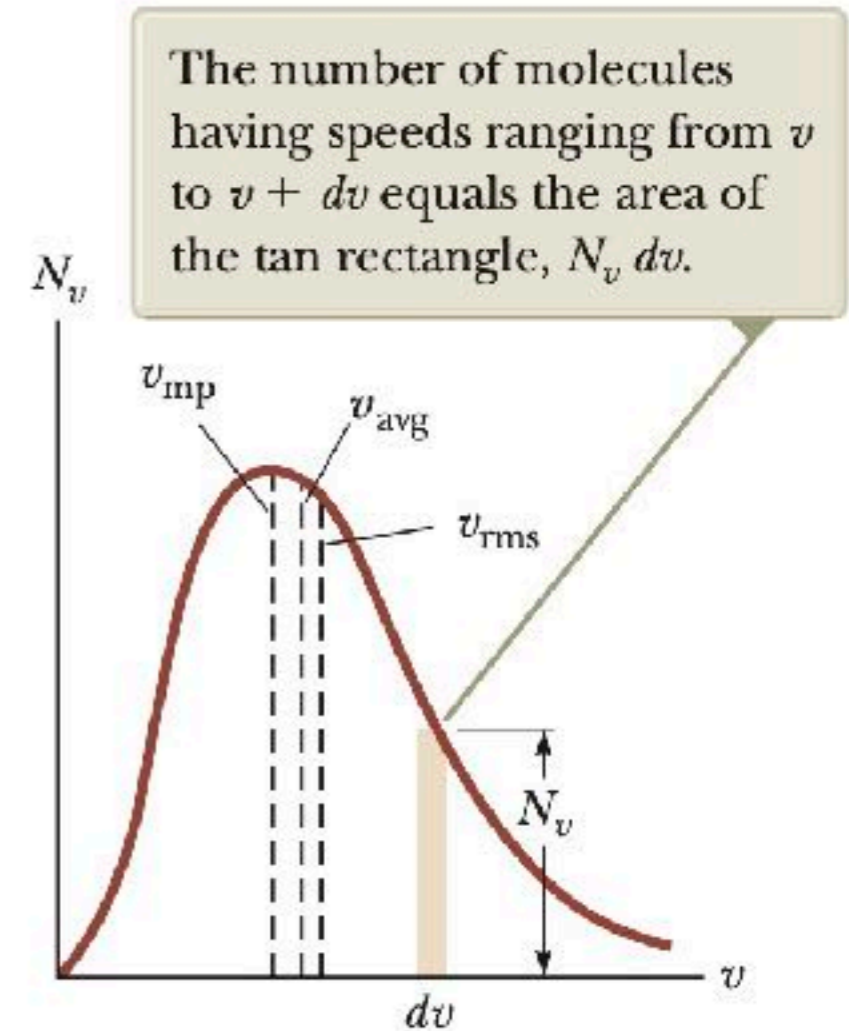

https://www.tec-science.com/thermodynamics/kinetic-theory-of-gases/determination-of-the-velocity-distribution-in-a-gas/

Distribution of molecular speeds

The fundamental expression that describes the distribution of speeds of N gas molecules is

$$N_v = 4\pi N \left(\frac{m_0}{2\pi k_B T}\right)^{3/2} v^2 e^{-m_0 v^2/2k_B T}$$

Maxwell–Boltzmann speed distribution function. If N is the total number of molecules, the number of molecules with speeds between v and $v + dv$ is $dN = N_v dv$.

The number of molecules having speeds ranging from v to $v + dv$ equals the area of the tan rectangle, $N_v\, dv$.
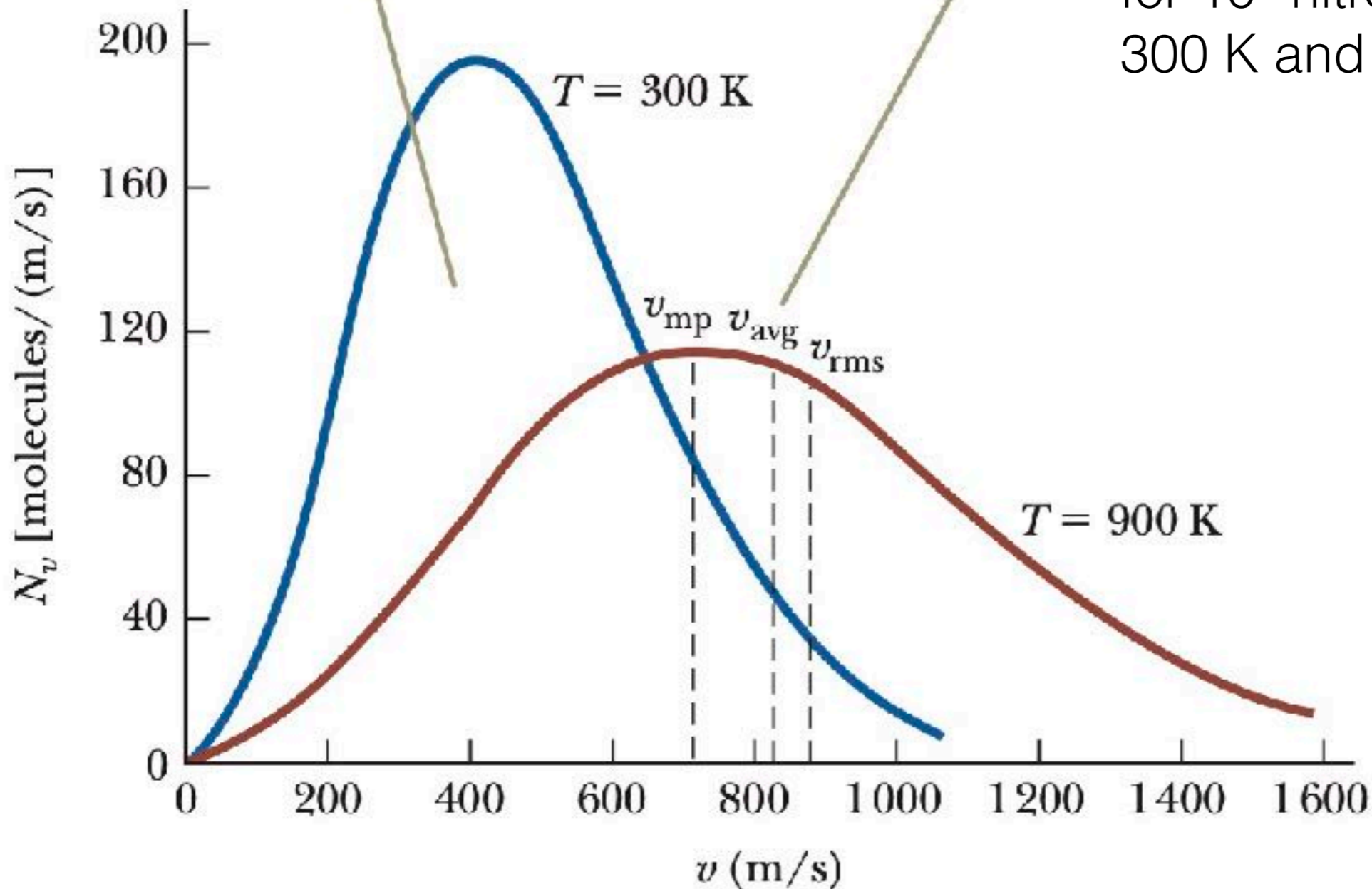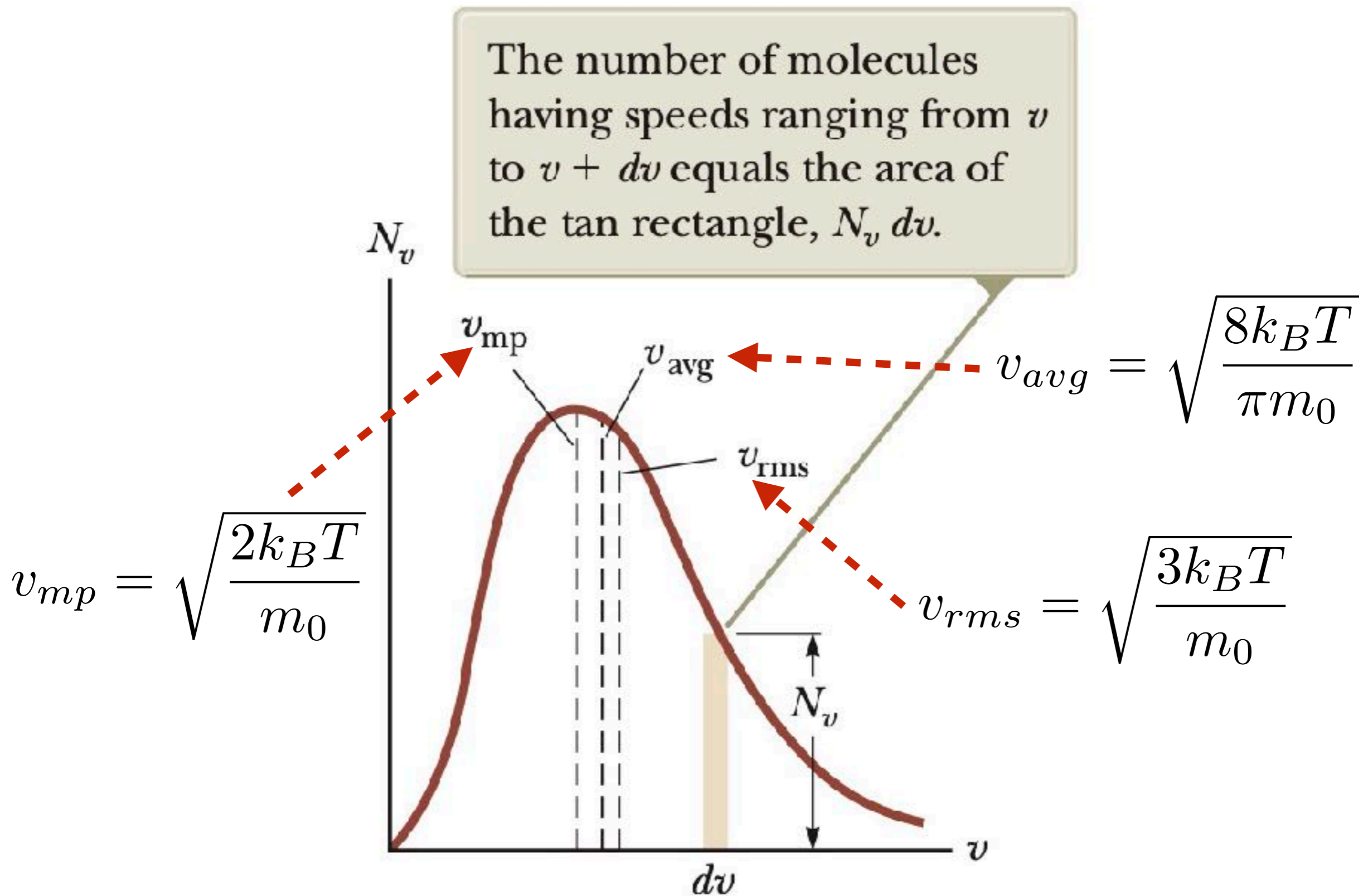
Distribution of molecular speeds

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

Note that $v_{rms} > v_{avg} > v_{mp}$.

The speed distribution function for 10^5 nitrogen molecules at 300 K and 900 K.

Distribution of molecular speeds

The number of molecules having speeds ranging from v to $v + dv$ equals the area of the tan rectangle, $N_v \, dv$.

$$v_{avg} = \sqrt{\frac{8k_B T}{\pi m_0}}$$

$$v_{mp} = \sqrt{\frac{2k_B T}{m_0}}$$

$$v_{rms} = \sqrt{\frac{3k_B T}{m_0}}$$

Distribution of molecular speeds

Table B.6   Gauss's Probability Integral and Other Definite Integrals

$$\int_0^\infty x^n \, e^{-ax} \, dx = \frac{n!}{a^{n+1}}$$

$$I_0 = \int_0^\infty e^{-ax^2} \, dx = \frac{1}{2}\sqrt{\frac{\pi}{a}} \quad \text{(Gauss's probability integral)}$$

$$I_1 = \int_0^\infty x e^{-ax^2} \, dx = \frac{1}{2a}$$

$$I_2 = \int_0^\infty x^2 \, e^{-ax^2} \, dx = -\frac{dI_0}{da} = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}$$

$$I_3 = \int_0^\infty x^3 \, e^{-ax^2} \, dx = -\frac{dI_1}{da} = \frac{1}{2a^2}$$

$$I_4 = \int_0^\infty x^4 \, e^{-ax^2} \, dx = \frac{d^2 I_0}{da^2} = \frac{3}{8}\sqrt{\frac{\pi}{a^5}}$$

$$I_5 = \int_0^\infty x^5 \, e^{-ax^2} \, dx = \frac{d^2 I_1}{da^2} = \frac{1}{a^3}$$

$$\vdots$$

$$I_{2n} = (-1)^n \frac{d^n}{da^n} I_0$$

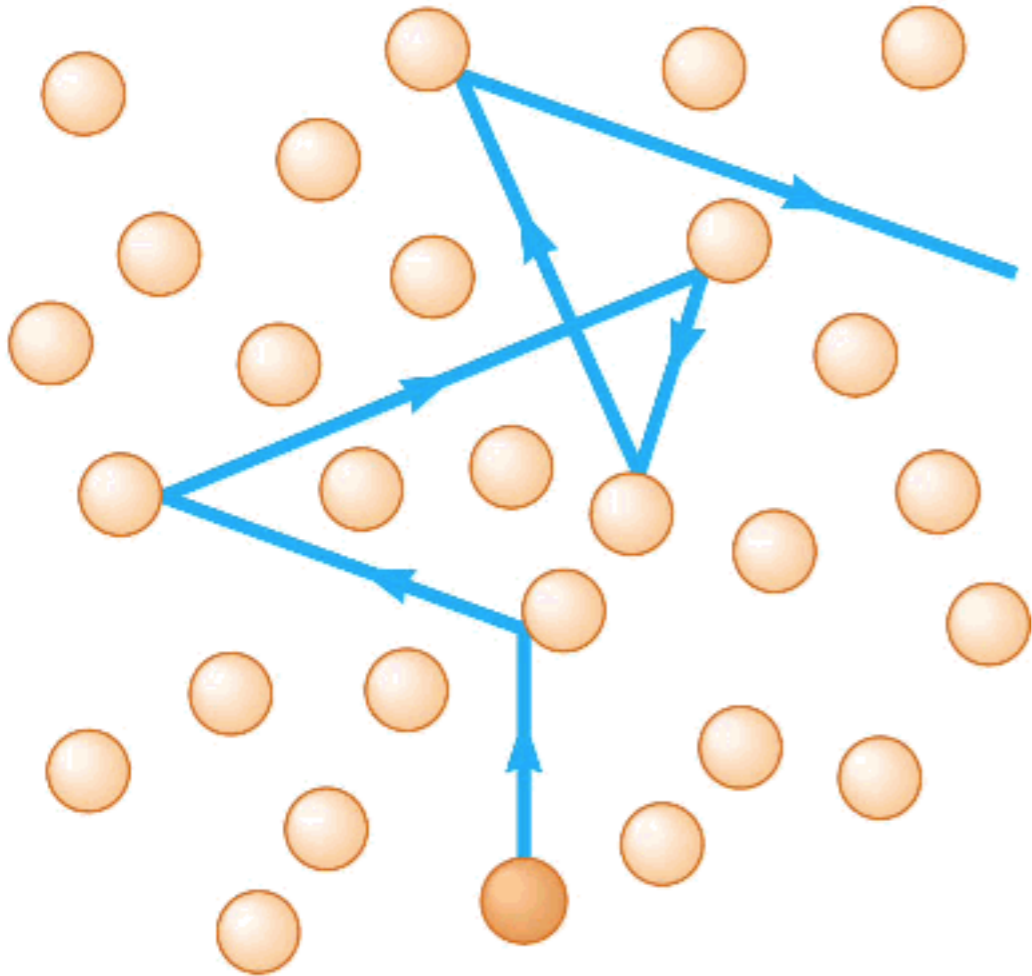$$I_{2n+1} = (-1)^n \frac{d^n}{da^n} I_1$$

ตัวอย่าง

Nine particles have speeds of 5.00, 8.00, 12.0, 12.0, 12.0, 14.0, 14.0, 17.0, and 20.0 m/s. Find v_{avg}, v_{rms}, v_{mp}

ตัวอย่าง

A 0.500-mol sample of hydrogen gas is at 300 K.

- Find the average speed, the rms speed, and the most probable speed of the hydrogen molecules.
- Find the number of molecules with speeds between 400 m/s and 401 m/s.
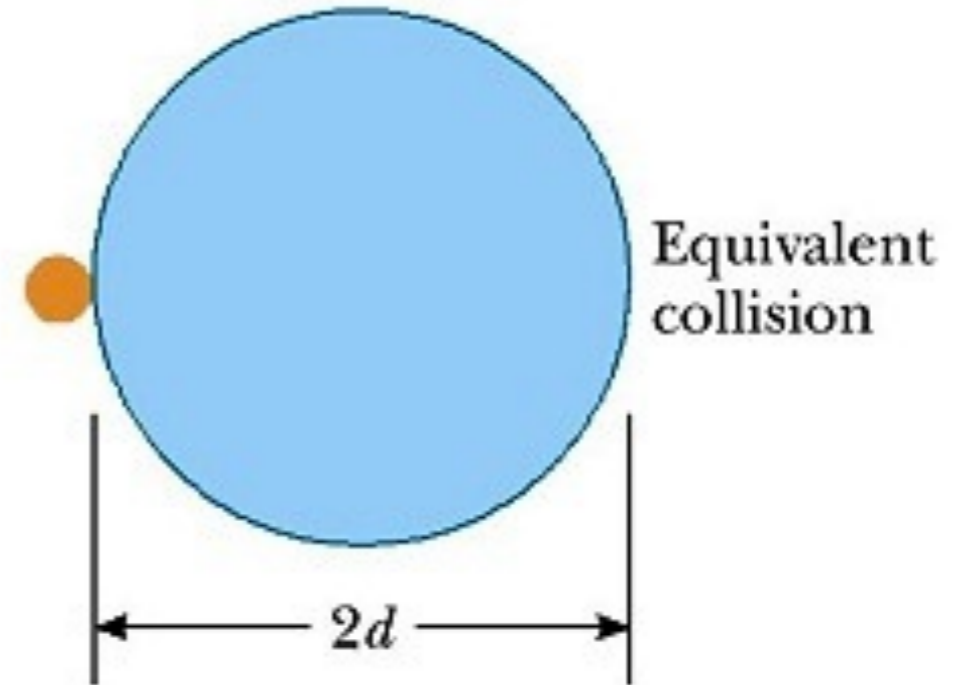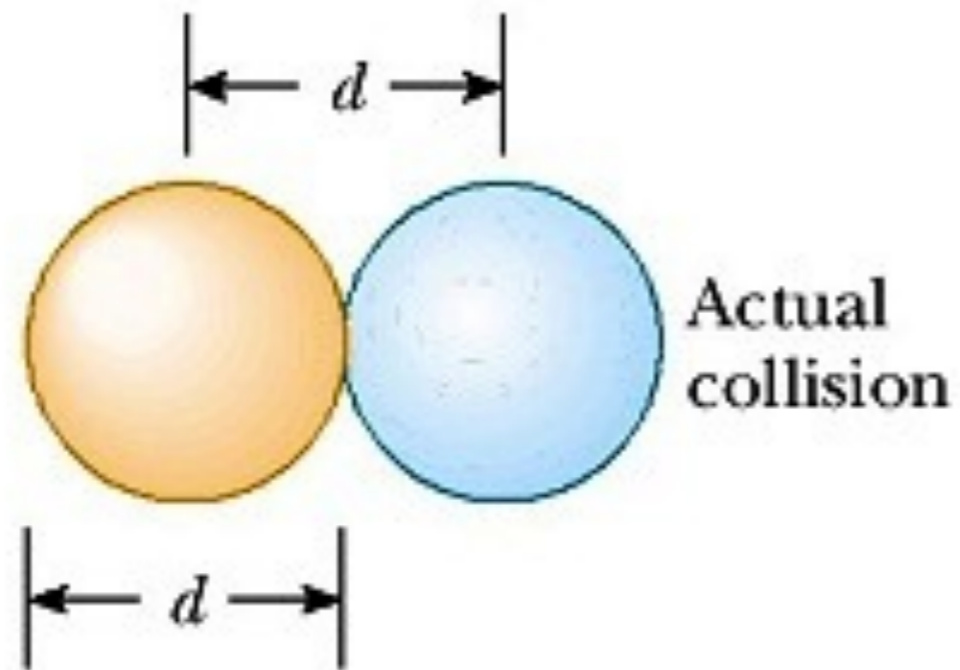
Mean free path

The mean free path, of a molecule is the average distance that a molecule travels before colliding with another molecule. It is given by
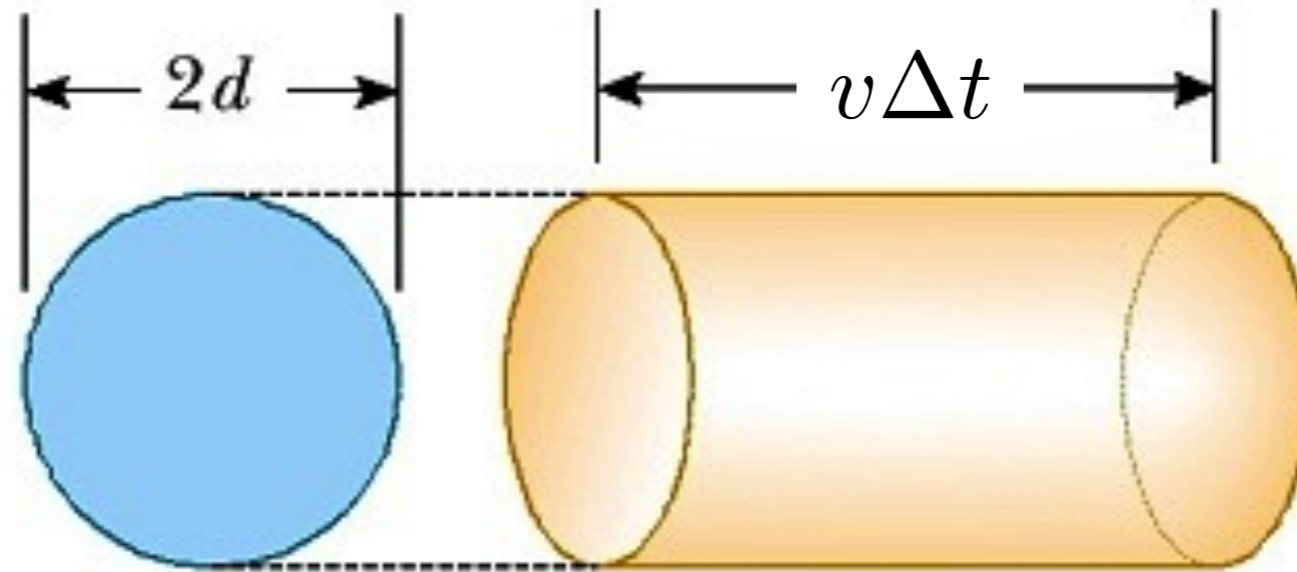
$$\lambda = \frac{1}{\sqrt{2}\pi d^2 (N/V)}$$

where d is the diameter of the molecule and N/V is the number of molecules per unit volume. The number of collisions that a molecule makes with other molecules per unit time, or collision frequency f, is given by $f = v_{avg}/\lambda$

Mean free path (How to prove?)

Actual collision — diameter d

Equivalent collision — diameter $2d$

Mean free path (How to prove?)

Mean free path (How to prove?)

Example

If the diameter of an oxygen molecule is 2.00×10^{-10} m, (a) find the mean free path of the molecules in a scuba tank that has a volume of 12.0 L and is filled with oxygen at a gauge pressure of 100 atm at a temperature of 25.0°C. What is the average time interval between molecular collisions for a molecule of this gas?