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2304151: ESSENTIAL PHYSICS

Update: March 11, 2024

Kinetic theory of gas

- Molecular model of an ideal gas
- Molar specific heat of an ideal gas
- The equipartition of energy
- Distribution of molecular speeds
- Mean free path

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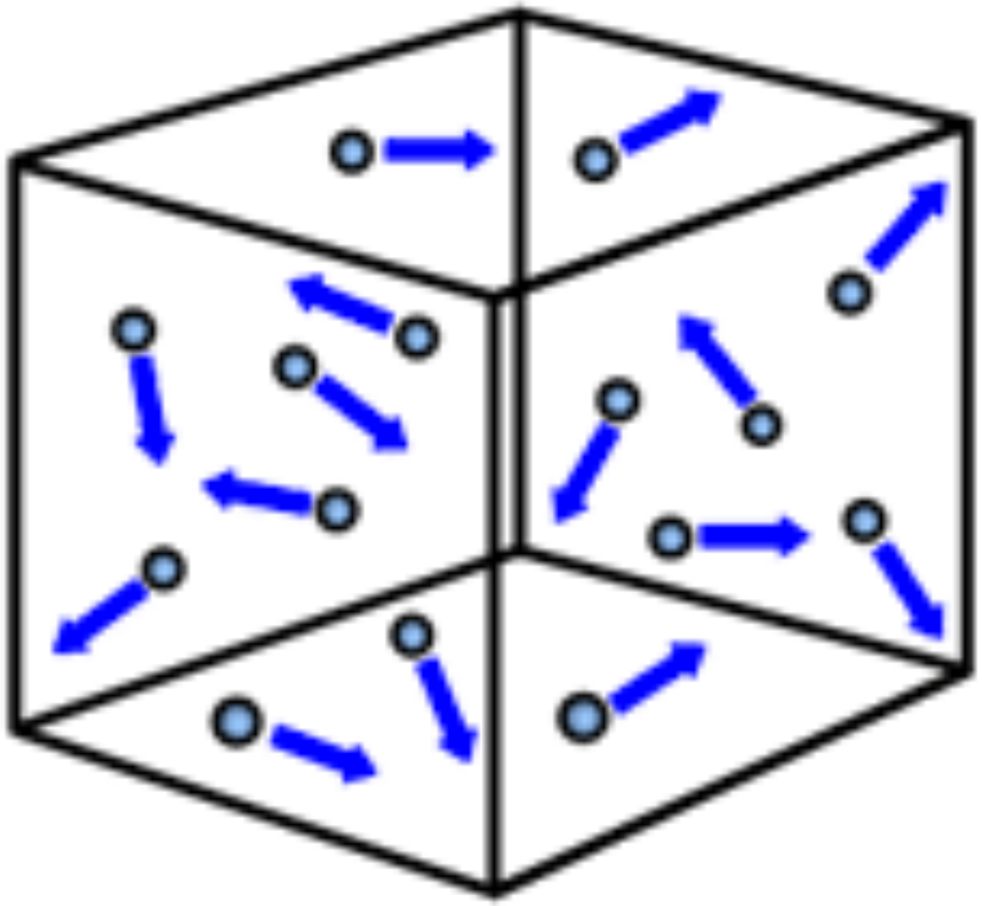
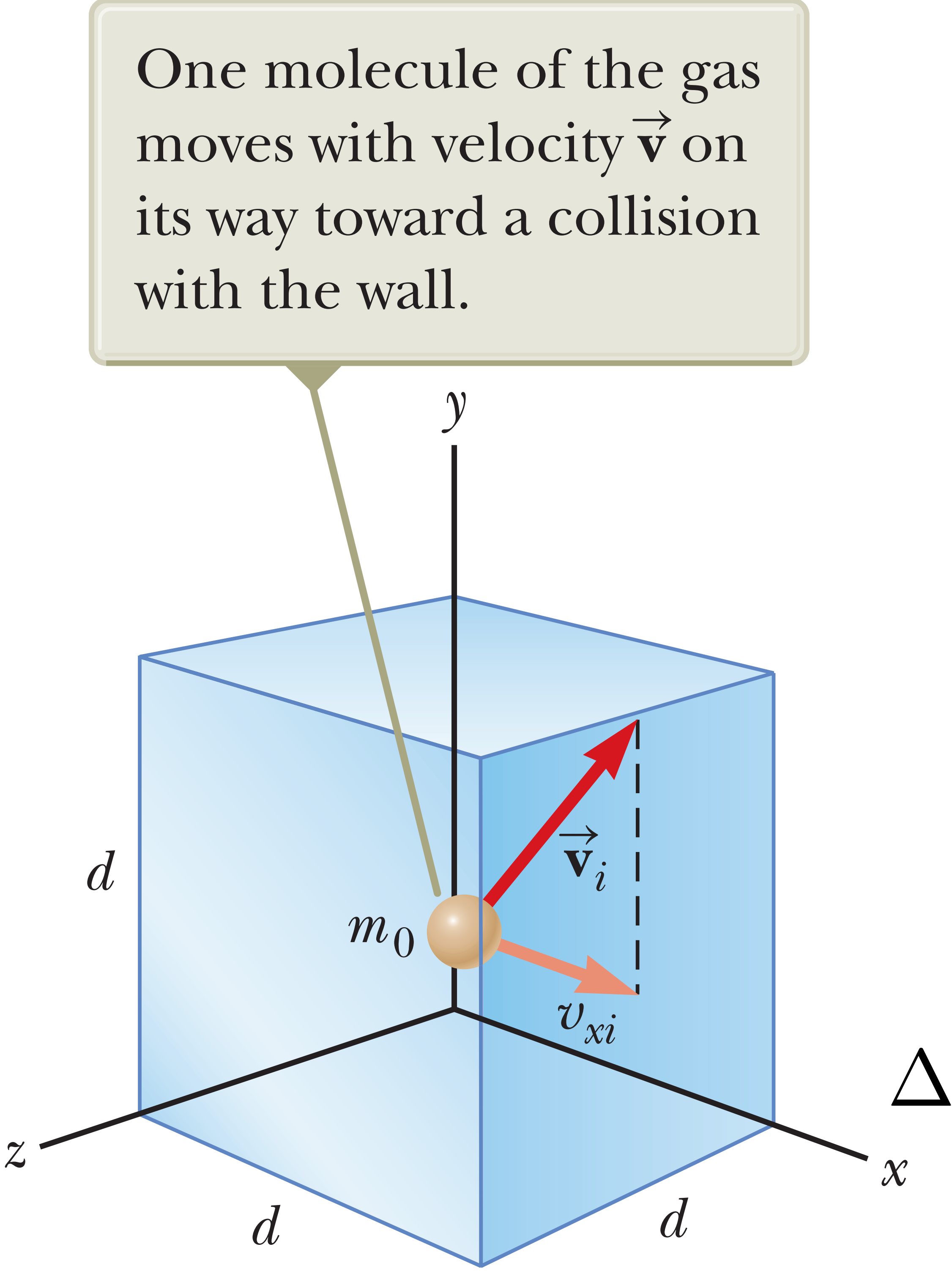
Molecular model of an ideal gas

We will discuss the link between macroscopic and microscopic of an idea gas. In Kinetic theory (Newtonian mechanics), we consider that

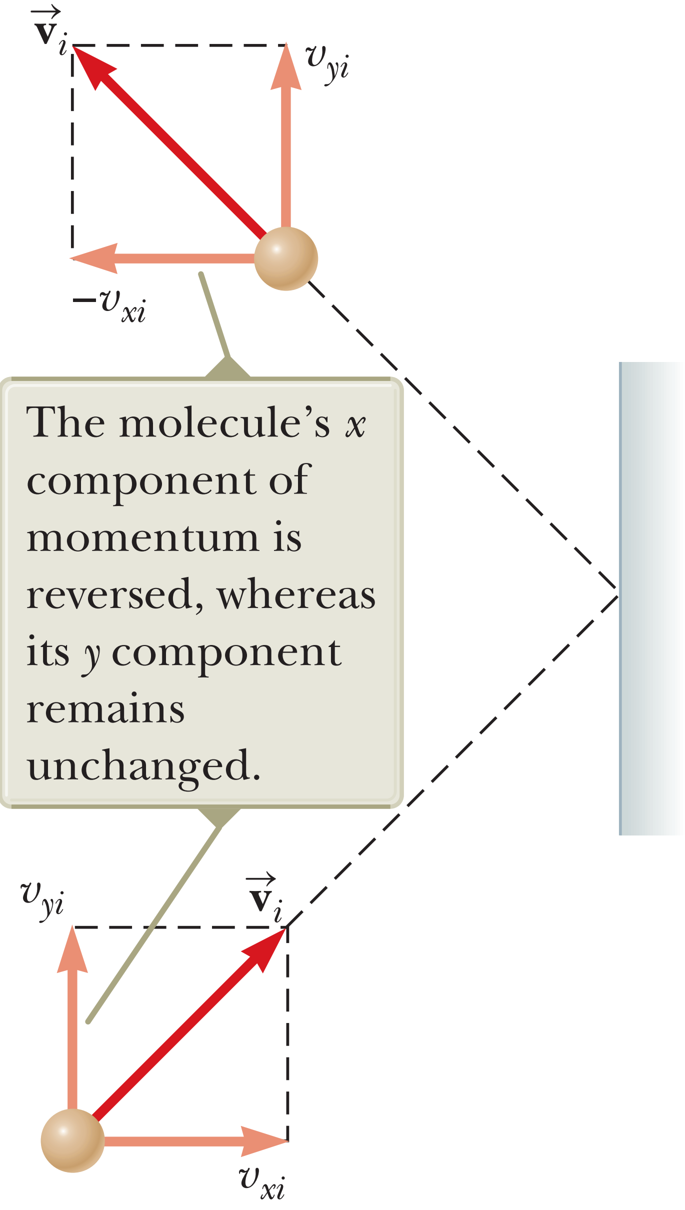
- Gas consists of identical “point” molecules of mass m.
- No interaction between molecules, except when they collide.
- Random motion.
- Collisions with wall are elastic.



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

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

Molecular model of an ideal gas

Consider the total pressure exerted on the wall:

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

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

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

What can you tell from this equation?

Theorem of equipartition of energy

Each degree of freedom contributes $\frac{1}{2}k_BT$ 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):

$$\begin{aligned} K_{tot,trans} &= N(\frac{1}{2}m_0\overline{v^2}) \\ &= \frac{3}{2}Nk_BT \\ &= \frac{3}{2}nRT \end{aligned}$$

root-mean-square (rms) speed:

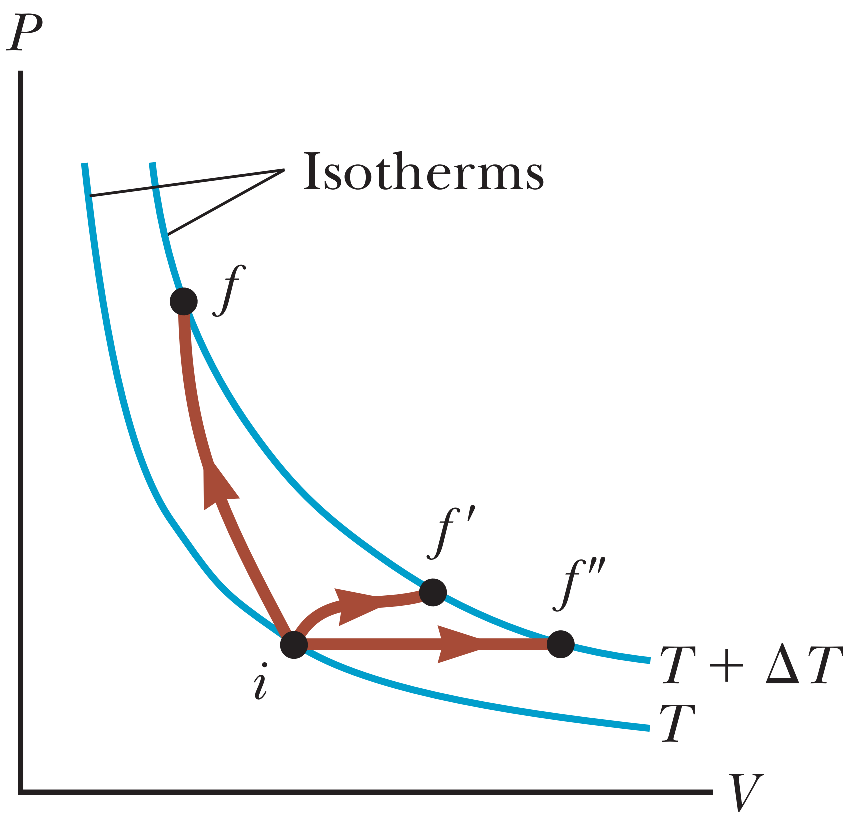
$$v_{rms} = \sqrt{\frac{3k_bT}{m_0}} = \sqrt{\frac{3RT}{M}}$$

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

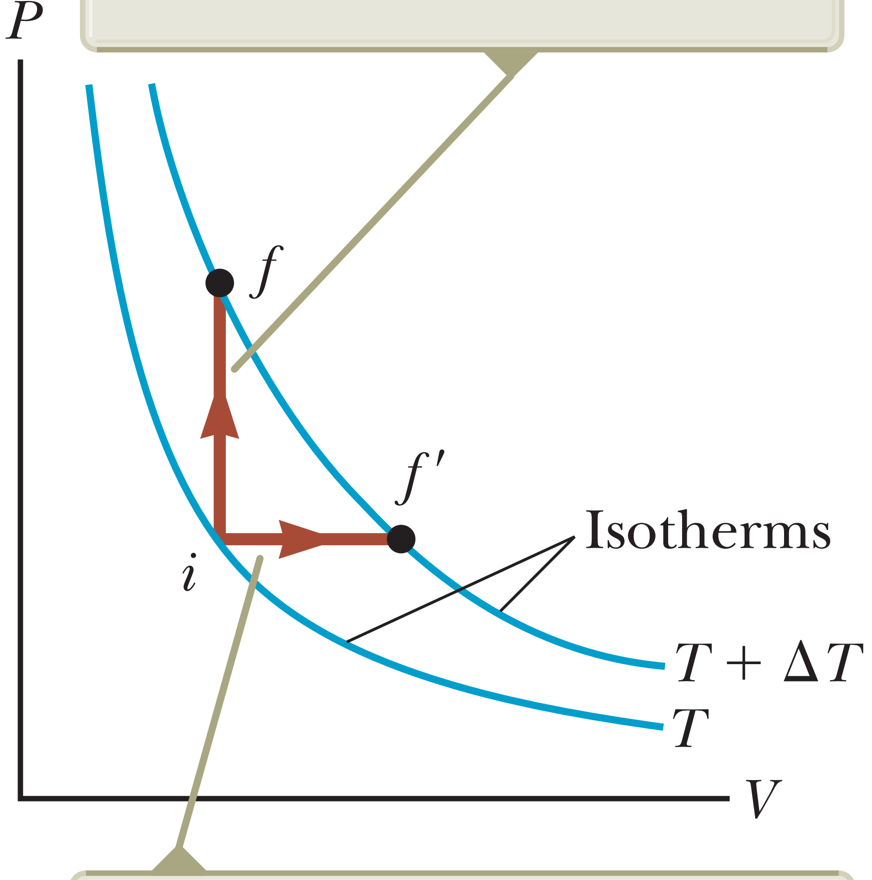
Start with simplest case when energy is added to the ideal monatomic gas:

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

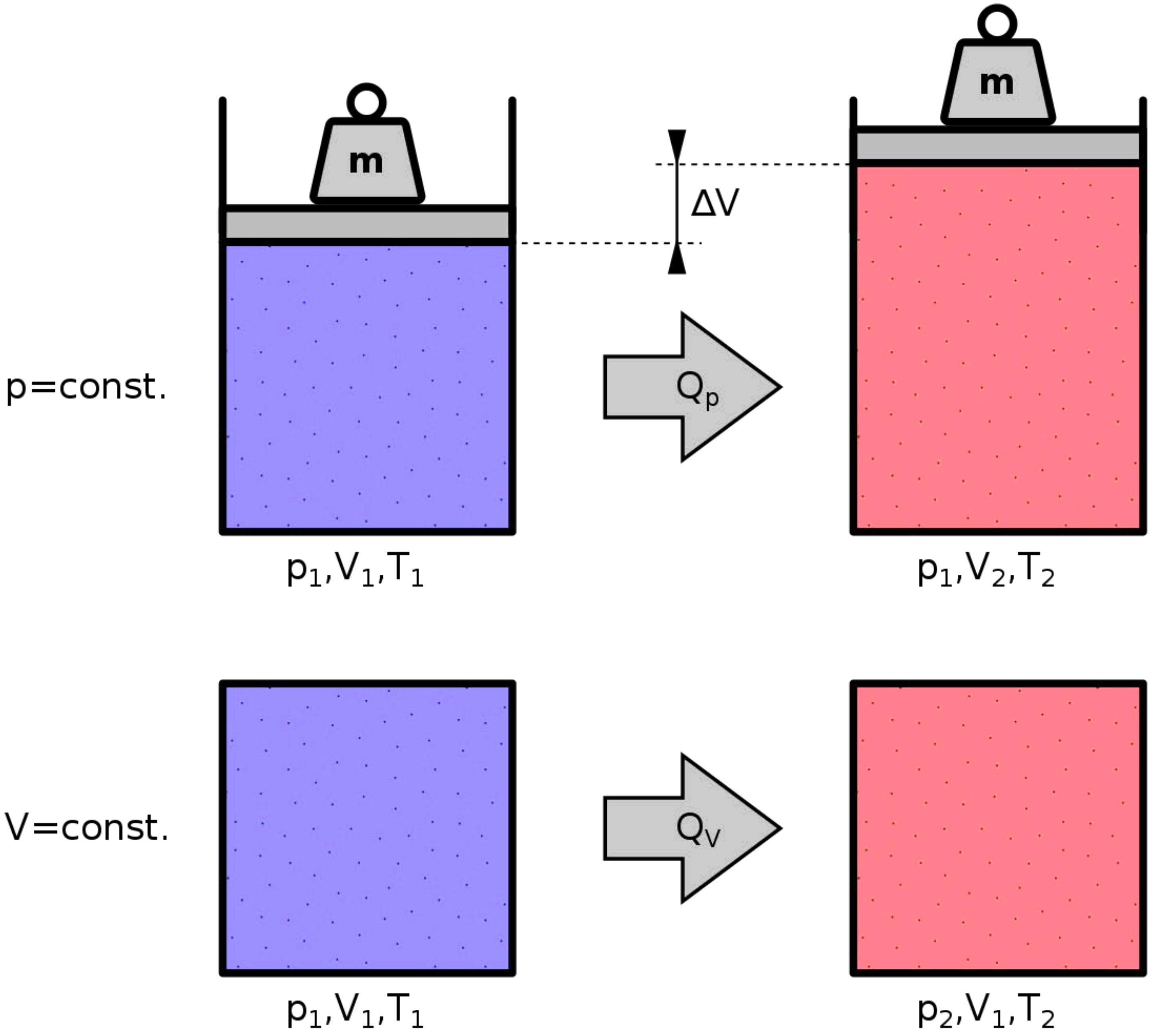
What will happen to the system?

Molar specific heat of an ideal gas

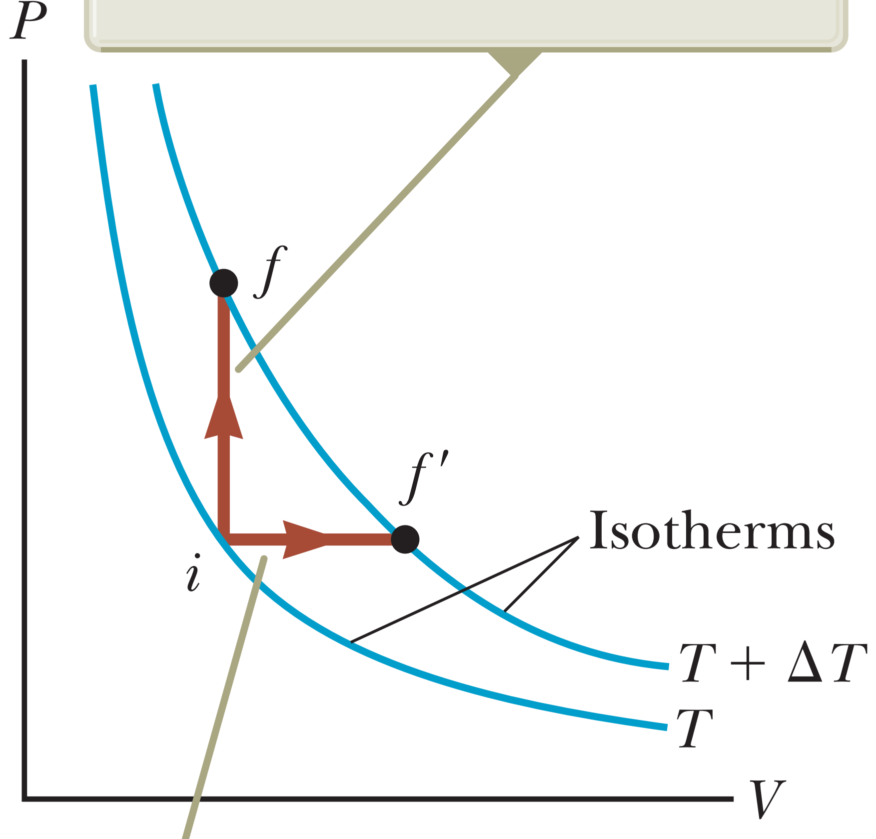
For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.



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



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.

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

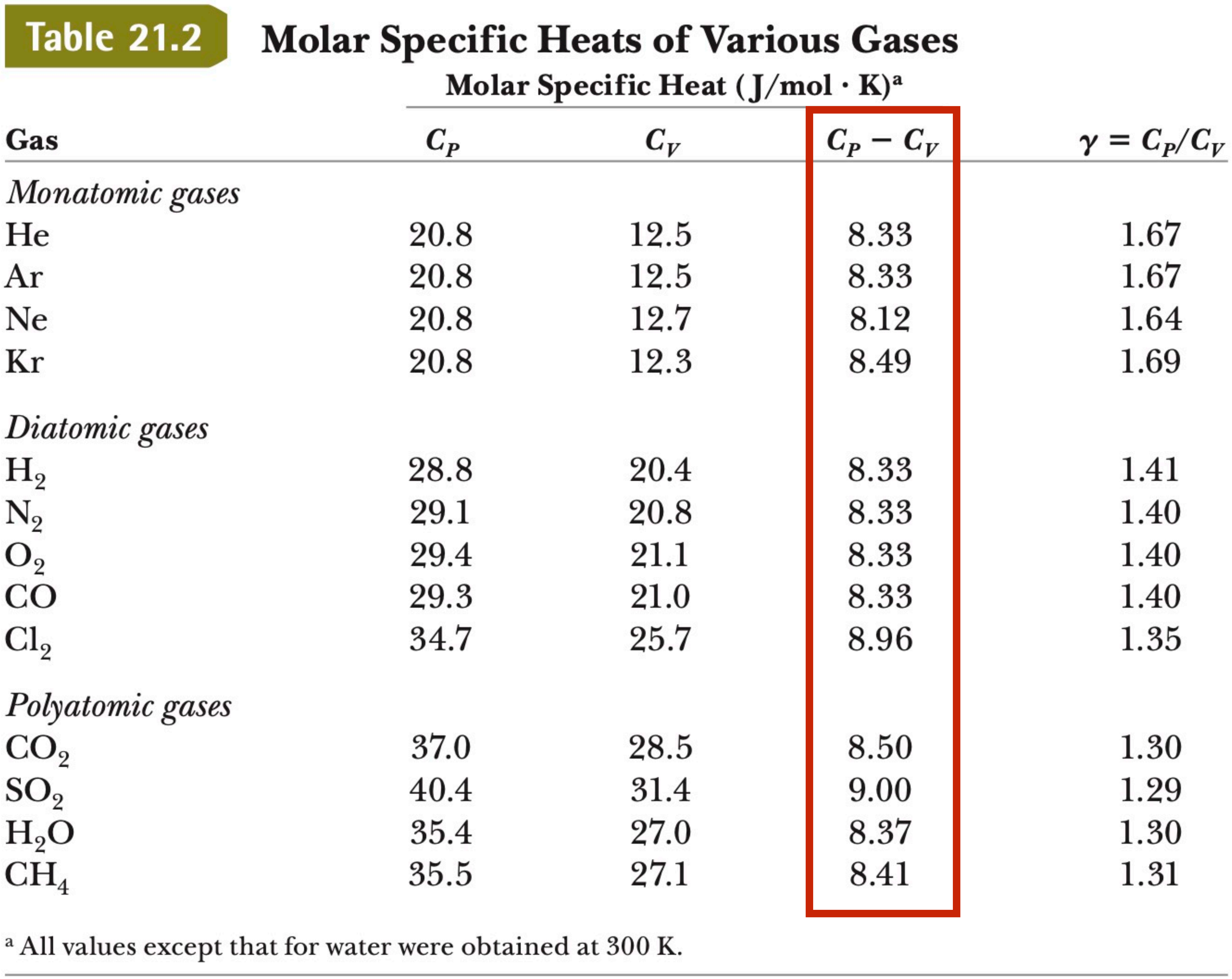


Table 21.2 **Molar Specific Heats of Various Gases**

Gas	C_P	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
	Molar Specific Heat (J/mol · K)[a]			
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

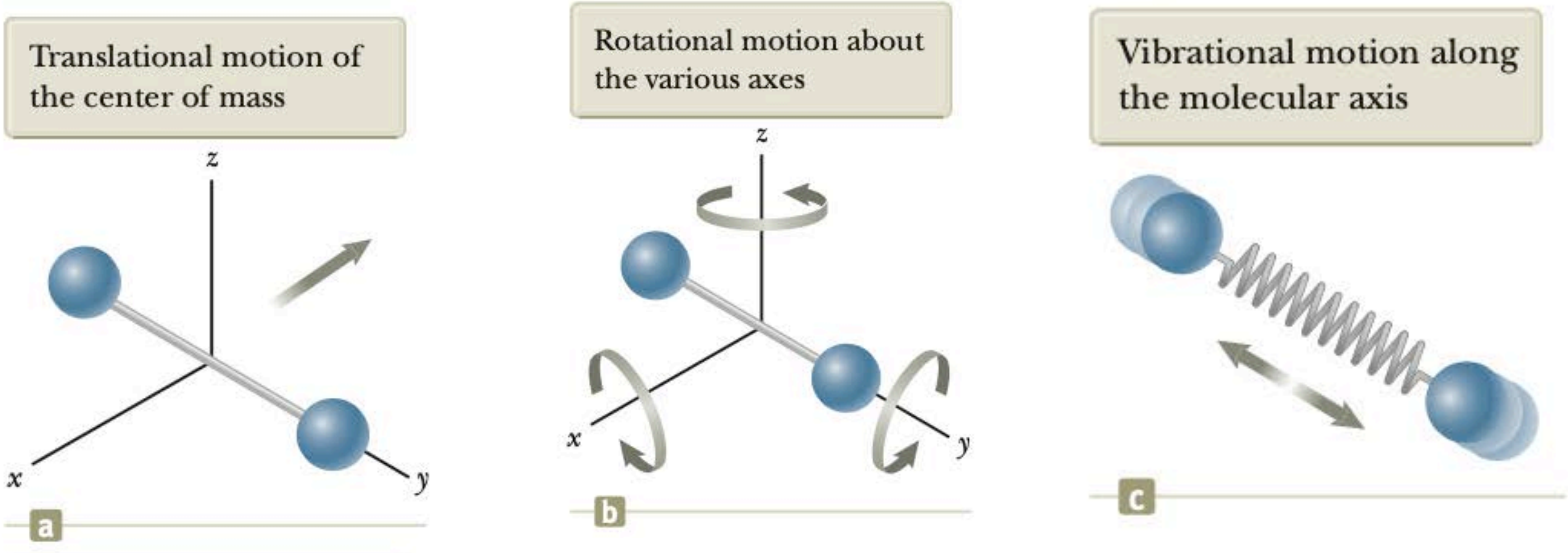
$$\frac{1}{2}m_0\overline{v^2} = \frac{3}{2}k_BT$$

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,

$$\frac{1}{2}k_BT$$

Classical equipartition of energy

The equipartition of energy (diatomic molecule)

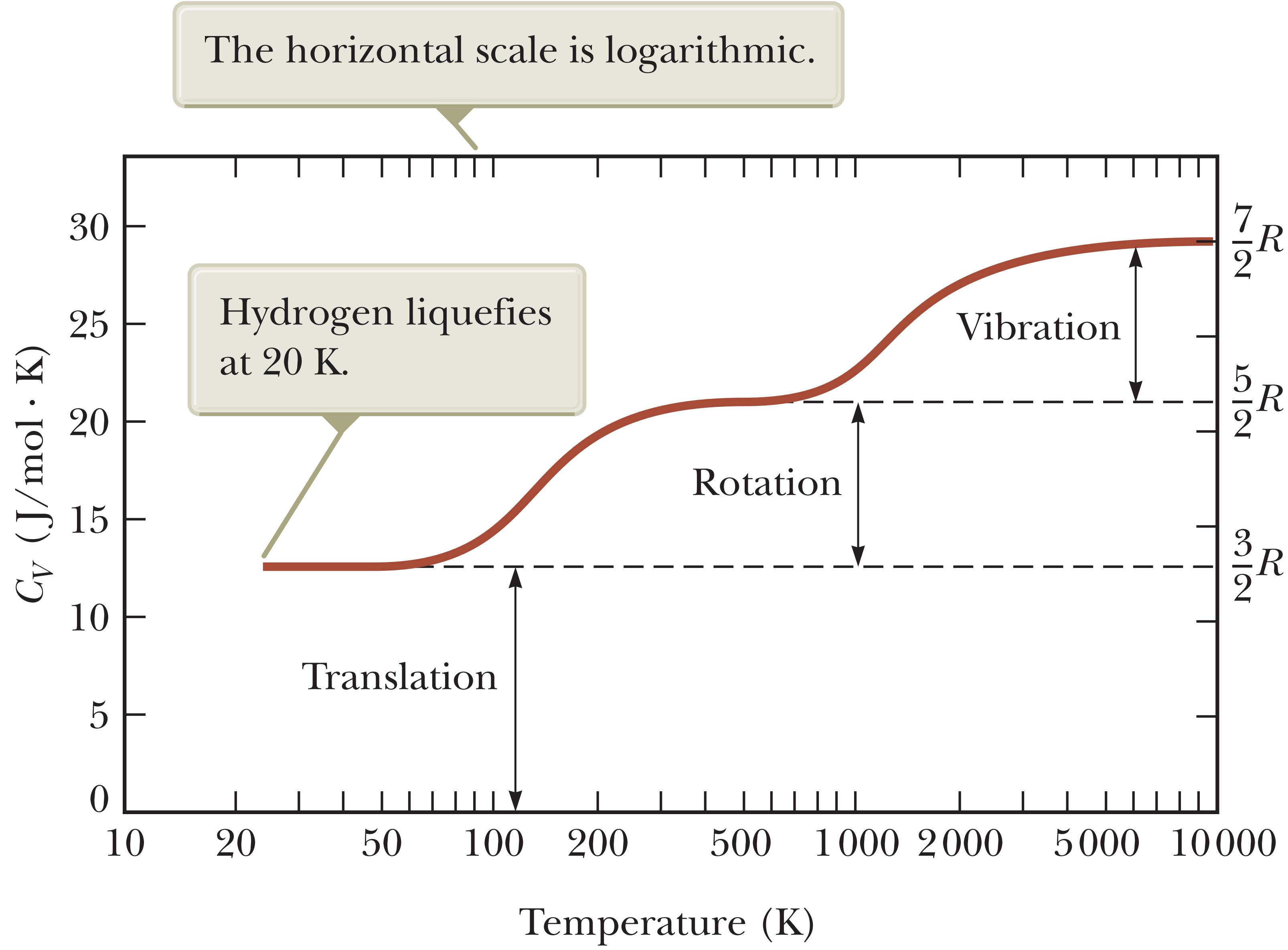


The equipartition of energy

	Monatomic	**Linear molecules**	**Non-linear molecules**	**Energy multiplication**
Translation	3	3	3	$\frac{1}{2}k_BT$
Rotation	0	2	3	$\frac{1}{2}k_BT$
Vibration	0	3N-5	3N-6	k_BT

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.

Distribution of molecular speeds

Back to what we discuss before:

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

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

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

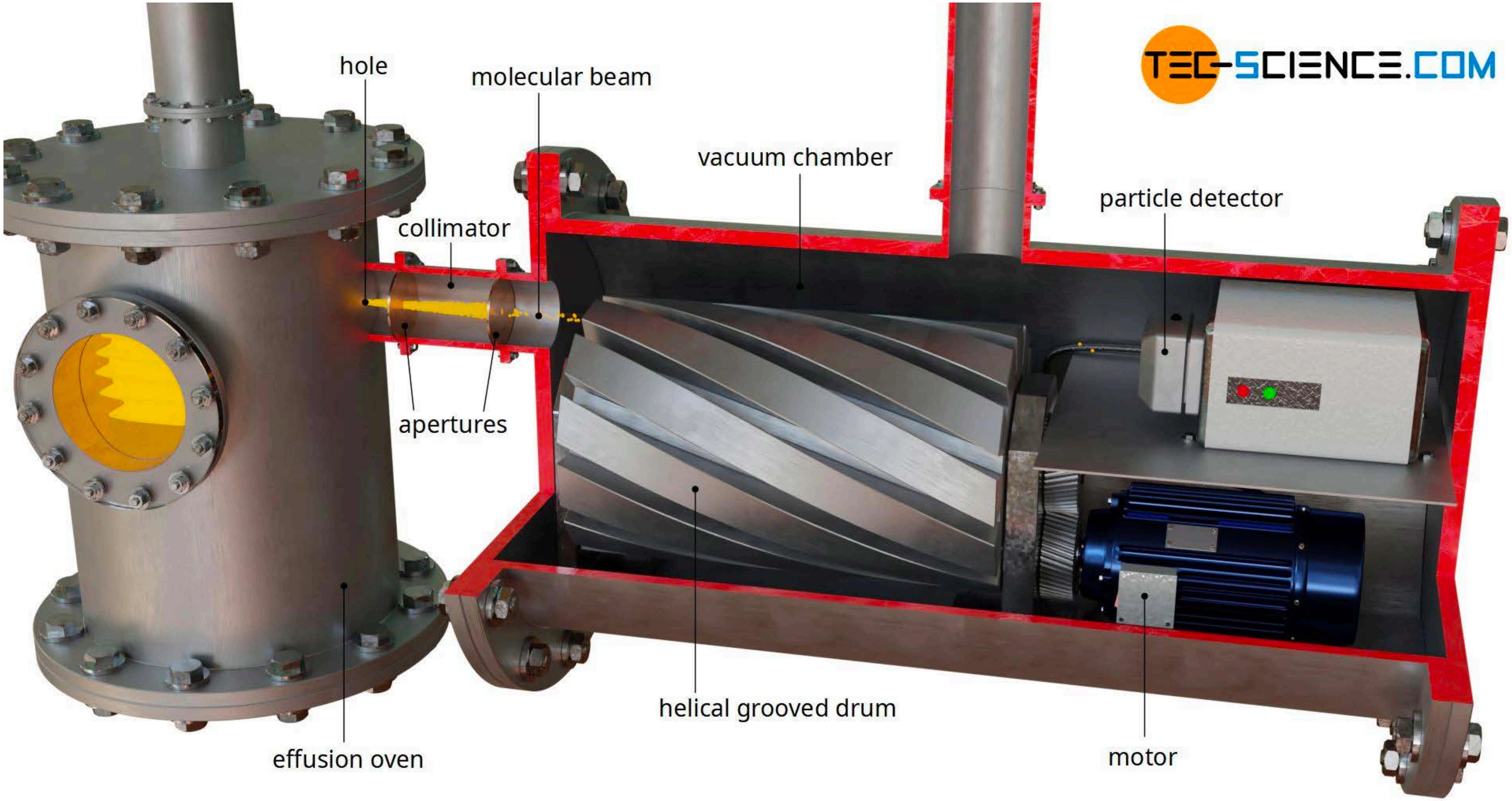
Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)	Gas	Molar Mass (g/mol)	v_{rms} at 20°C (m/s)
H_2	2.02	1902	NO	30.0	494
He	4.00	1352	O_2	32.0	478
H_2O	18.0	637	CO_2	44.0	408
Ne	20.2	602	SO_2	64.1	338
N_2 or CO	28.0	511			

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.



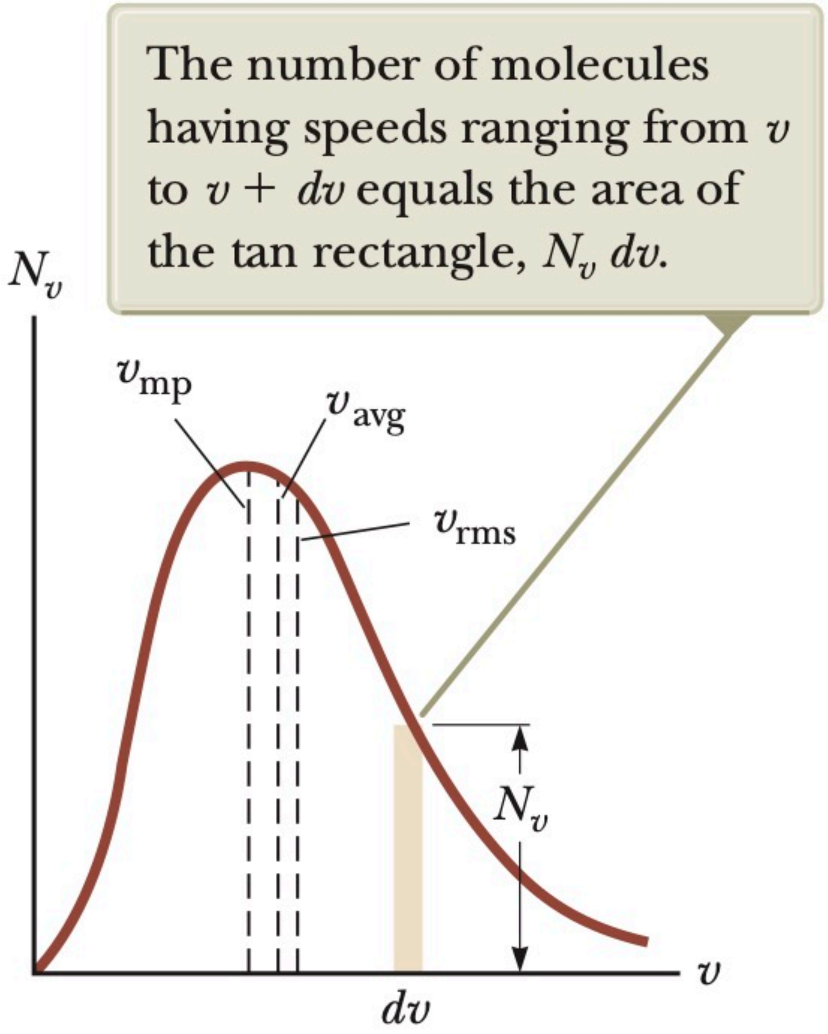
https://www.tec-science.com/thermodynamics/kinetic-theory-of-gases/determination-of-the-velocity-distribution-in-a-gas/

Distribution of molecular speeds

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

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

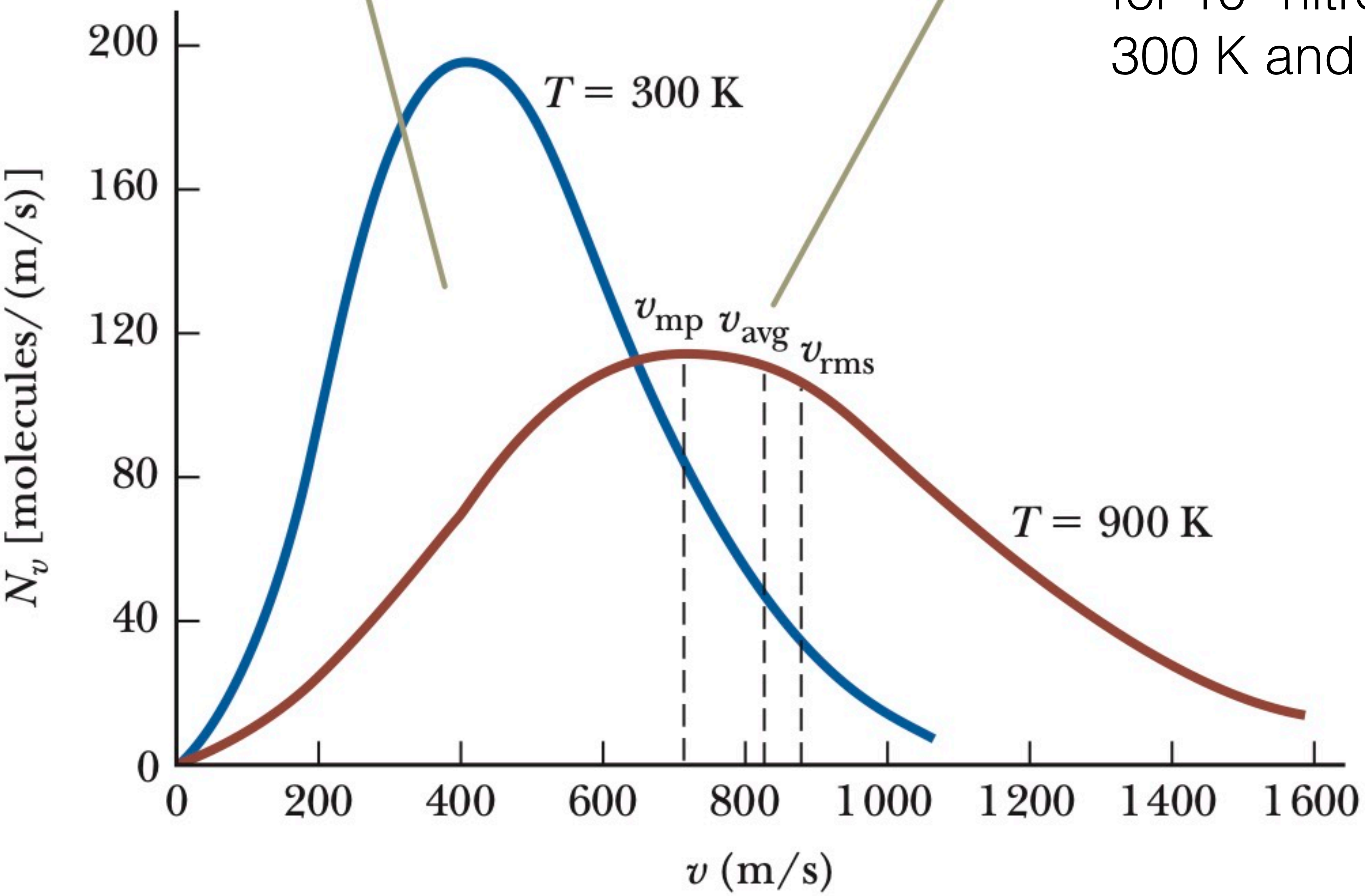
Maxwell–Boltzmann speed distribution function. If N is the total number of molecules, the number of molecules with speeds between v and $v + dv$ is $dN = N_v dv$.


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

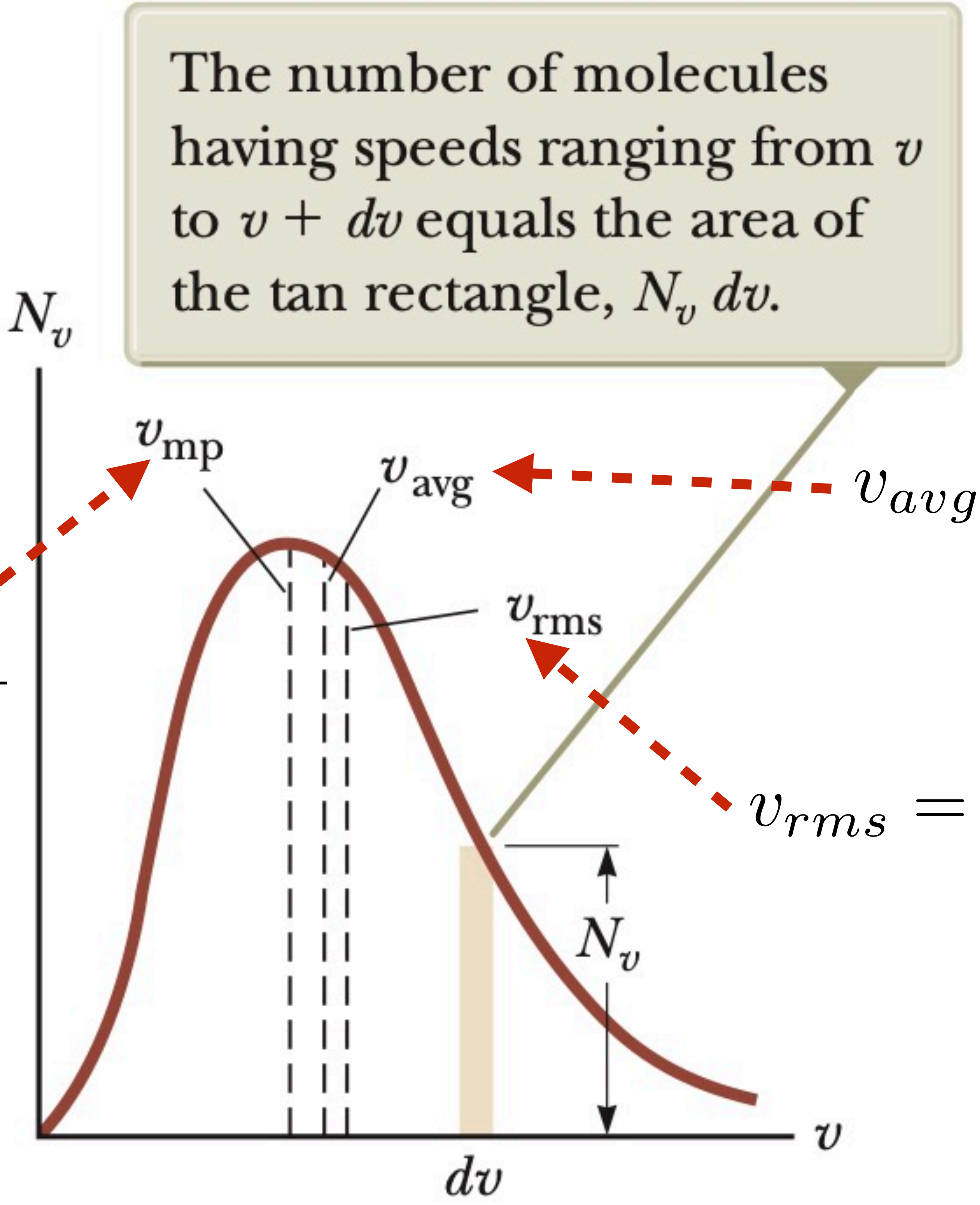
The total area under either curve is equal to N, the total number of molecules. In this case, $N = 10^5$.

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, $N_v\, dv$.

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

$$v_{mp} = \sqrt{\frac{2k_BT}{m_0}}$$

$$v_{rms} = \sqrt{\frac{3k_BT}{m_0}}$$

Example

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}