

Kinetic Theory of Gases

Kinetic theory explains the everyday gas laws (Boyle's, Charles', the ideal gas equation) as a direct consequence of molecules in random, ceaseless motion — pressure becomes the result of countless tiny collisions, and temperature becomes nothing more than a measure of average molecular kinetic energy. This chapter also picks up the degrees-of-freedom and specific-heat ideas from Thermodynamics and shows exactly where they come from: the law of equipartition of energy.

1. Assumptions of the Kinetic Theory of Gases

Kinetic theory models a gas as an enormous number of identical molecules in constant, random motion, and derives all of a gas's bulk behaviour purely from the mechanics of these molecules colliding with each other and with the container walls.

- A gas consists of a very large number of identical molecules in continuous, random motion, obeying Newton's laws of motion at every instant.
- The actual volume occupied by the molecules themselves is negligible compared to the volume of the container — this is exactly why an ideal gas is treated as a collection of point masses.
- Molecules exert no force on each other except during a collision — there are no long-range intermolecular attractions or repulsions assumed in the ideal gas model.
- All collisions (molecule–molecule and molecule–wall) are perfectly elastic, and the time spent in a collision is negligible compared to the time between successive collisions.
- Between collisions, molecules move in straight lines at constant velocity — this is what makes the statistical, average-based treatment of a huge number of molecules tractable in the first place.

2. The Gas Laws and the Ideal Gas Equation

Long before kinetic theory existed, three separate experimental laws described how pressure, volume, and temperature of a fixed amount of gas relate to each other — kinetic theory's real achievement is explaining why these laws hold, not just stating them.

Boyle's law (T, n constant)	$PV = \text{constant}$
Charles' law (P, n constant)	$V/T = \text{constant}$
Gay-Lussac's (pressure) law (V, n constant)	$P/T = \text{constant}$
Ideal gas equation	$PV = nRT = NkT$ ($k = R/N_A$, the Boltzmann constant)

- Avogadro's law: equal volumes of any ideal gas, at the same temperature and pressure, contain exactly the same number of molecules — independent of which gas it is.
- The Boltzmann constant $k = R/N_A \approx 1.38 \times 10^{-23} \text{ J/K}$ is simply the gas constant rescaled to a per-molecule basis, exactly as R is the gas constant on a per-mole basis.
- No real gas obeys $PV = nRT$ exactly at all conditions — it's an idealisation that real gases approach closely at low pressure and high temperature, where molecules are far apart and rarely interact.

3. Kinetic Theory's Derivation of Gas Pressure

Pressure on a container's wall is nothing mysterious — it's simply the cumulative effect of an enormous number of molecules continuously bouncing off that wall and transferring momentum to it on every collision.

Pressure of an ideal gas

$$P = (1/3)\rho\langle v^2 \rangle = (1/3)(N/V)m\langle v^2 \rangle$$

Pressure in terms of total kinetic energy

$$PV = (2/3)E, \text{ where } E = \text{total translational KE of the gas}$$

- ρ is the mass density of the gas ($= Nm/V$, where m is the mass of one molecule and N is the total number of molecules), and $\langle v^2 \rangle$ is the mean of the squared speed, averaged over all molecules.
- The factor of $1/3$ comes from molecular velocities being equally likely along all three spatial directions (x, y, z) — on average, exactly one-third of a molecule's mean square speed acts along any single direction, including the one perpendicular to a given wall.
- This single result — pressure arising purely from molecular momentum transfer — is the entire microscopic justification for every gas law in the previous section.

4. Kinetic Interpretation of Temperature and RMS Speed

Kinetic theory gives temperature a concrete physical meaning for the very first time: it is a direct measure of how much kinetic energy, on average, each molecule of the gas carries.

Average translational KE per molecule

$$\langle KE \rangle = (3/2)kT$$

RMS speed

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{(3kT/m)} = \sqrt{(3RT/M)}$$

- Average translational kinetic energy of a molecule depends ONLY on absolute temperature — not on the molecule's mass, identity, or the gas's pressure or volume. At a given T , light and heavy molecules carry exactly the same average translational KE.
- Since lighter molecules need higher speed to carry the same KE as heavier ones, v_{rms} is higher for gases of lower molar mass M at the same temperature — this is why hydrogen molecules move far faster on average than oxygen molecules at the same T .
- $T = 0 \text{ K}$ is the (unreachable) state at which average molecular kinetic energy — and hence all molecular motion — would fall to zero.

5. Molecular Speed Distribution

Not every molecule in a gas moves at the same speed — collisions constantly redistribute kinetic energy among molecules, producing a whole spread of speeds described by the Maxwell-Boltzmann speed distribution.

RMS speed

$$v_{\text{rms}} = \sqrt{(3RT/M)}$$

Average (mean) speed

$$v_{\text{avg}} = \sqrt{(8RT/\pi M)}$$

Most probable speed

$$v_{\text{p}} = \sqrt{(2RT/M)}$$

- For any gas at any temperature, these three characteristic speeds always follow the same fixed order: $v_{\text{rms}} > v_{\text{avg}} > v_{\text{p}}$ — rms speed is always the largest of the three, most probable speed the smallest.
- The Maxwell speed distribution curve rises from zero, peaks at v_{p} (the most common individual molecular speed), then falls off with a long tail toward higher speeds — it is not symmetric about its peak.
- As temperature rises, the entire distribution curve shifts toward higher speeds and flattens out (more molecules spread across a wider range of speeds), while the total area under the curve (representing the total number of molecules) stays the same.

6. Degrees of Freedom and the Law of Equipartition of Energy

The law of equipartition of energy is the deeper principle that the degrees-of-freedom results from Thermodynamics actually come from: in thermal equilibrium, energy distributes itself equally across every independent way a molecule can move or store energy.

Law of equipartition of energy

Average energy per degree of freedom = $(1/2)kT$

Total average energy per molecule

$\langle E \rangle = (f/2)kT$, f = number of degrees of freedom

- A degree of freedom is any independent coordinate needed to fully specify a molecule's energy — translational motion contributes 3 (one for each spatial direction), and a molecule can additionally have rotational and vibrational degrees of freedom depending on its structure.
- Monoatomic molecules (like helium, argon): only translational motion is possible, so $f = 3$.
- Diatomic molecules (like O_2 , N_2) at ordinary temperatures: 3 translational + 2 rotational (about the two axes perpendicular to the bond) = $f = 5$. At very high temperatures, vibration along the bond axis becomes significant too, adding up to 2 more ($f = 7$).
- Non-linear (e.g., triangular) polyatomic molecules: 3 translational + 3 rotational = $f = 6$, before counting any vibrational contributions.
- Each vibrational mode contributes 2 degrees of freedom (not 1) because it stores energy both kinetically and as potential energy in the 'spring' of the bond — this is why a vibrating diatomic molecule's f jumps by 2, not 1.

7. Specific Heats of Gases via Equipartition

Once the equipartition law fixes how much energy a molecule carries per degree of freedom, the specific heats of a gas follow immediately — this is exactly where the C_v , C_p , and γ formulas used throughout Thermodynamics actually come from.

Molar specific heat at constant volume

$C_v = (f/2)R$

Molar specific heat at constant pressure

$C_p = C_v + R = [(f+2)/2]R$

Ratio of specific heats

$\gamma = C_p/C_v = 1 + 2/f$

- Monoatomic ($f=3$): $C_v = (3/2)R$, $\gamma = 5/3 \approx 1.67$. Diatomic without vibration ($f=5$): $C_v = (5/2)R$, $\gamma = 7/5 = 1.4$. Diatomic with vibration active ($f=7$): $\gamma = 9/7 \approx 1.29$.
- As more degrees of freedom become available to a molecule (rotation, then vibration), its γ moves progressively closer to 1 — more ways to store energy means a smaller fractional difference between heating at constant pressure and constant volume.
- This is the microscopic reason gases with more complex molecular structure have a lower γ than simple monoatomic gases — there's simply more places for absorbed energy to go besides straightforward translational speed.

8. Mean Free Path

Molecules don't travel forever in a straight line — they constantly collide with neighbouring molecules, and the mean free path is the average distance a molecule manages to travel between one collision and the next.

Mean free path

$\lambda = 1/(\sqrt{2} \pi d^2 n)$

- d is the effective diameter of a molecule and n is the number density of molecules (number per unit volume) — λ depends only on how crowded the gas is and how 'big' its molecules effectively are, not on their speed.
- λ is inversely proportional to number density n — compressing a gas (increasing n at fixed temperature) shortens the mean free path; a gas at very low pressure has a correspondingly long mean free path.
- The factor $\sqrt{2}$ (rather than 1) appears because both the molecule being tracked and the molecules it might collide with are moving — using the relative speed between colliding molecules, rather than treating other molecules as stationary targets, brings in this extra $\sqrt{2}$.

9. Real Gases and Deviation from Ideal Behaviour

Two of kinetic theory's core assumptions — negligible molecular size and no intermolecular forces — are only approximations, and real gases visibly deviate from $PV = nRT$ whenever pressure gets high or temperature gets low enough for these approximations to break down.

Van der Waals equation (1 mole)

$$(P + a/V^2)(V - b) = RT$$

- The constant 'a' corrects for intermolecular attraction — real molecules pull on each other slightly, which reduces the pressure they actually exert on the container walls compared to a perfectly non-interacting ideal gas.
- The constant 'b' corrects for the finite size of molecules — it represents the 'excluded volume' that real molecules physically occupy and so cannot be compressed into, meaning the gas can never truly be squeezed into zero volume.
- Real gas behaviour approaches ideal gas behaviour most closely at low pressure (molecules far apart, attraction negligible) and high temperature (molecules moving fast enough that the brief attractive pull during near-misses barely matters).
- Every real gas has a critical temperature above which it cannot be liquefied no matter how much pressure is applied — beyond this point, the distinction between the liquid and gaseous phases of that substance disappears entirely.

10. Brownian Motion and Experimental Evidence for Molecular Motion

Before kinetic theory could be directly confirmed, the strongest visible evidence for molecules being in constant random motion came from watching much larger particles being jostled around by the invisible molecules surrounding them.

- Brownian motion is the continuous, random, zig-zag movement of small particles (like pollen grains or smoke particles) suspended in a fluid, caused by countless lopsided collisions with the fluid's own rapidly moving molecules.
- Brownian motion is more vigorous at higher temperatures (faster-moving fluid molecules deliver more energetic impacts) and for smaller suspended particles (which are more easily knocked off course by an uneven number of collisions on each side).
- Einstein's theoretical analysis of Brownian motion, later confirmed experimentally, provided some of the first solid quantitative evidence for the real, physical existence of molecules — at a time when their existence was still debated.
- Avogadro's number, $N_A \approx 6.022 \times 10^{23}$ per mole, is the bridge between the molecular (per-molecule) and macroscopic (per-mole) descriptions of a gas — it is what connects k (Boltzmann constant) to R (universal gas constant) via $k = R/N_A$.