

Chapter 19

The Kinetic Theory of Gases

First Edition

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Contents

Preface	ii
Conventions and notation	iii
19 The Kinetic Theory of Gases	1
19.1 Moles, particles and the ideal-gas model	1
19.2 Pressure from momentum transfer	6
19.3 Temperature and translational energy	12
19.4 Molecular speed distributions	14
19.5 Mean free path and collisions	24
19.6 Heat capacities and equipartition	28
19.7 Adiabatic ideal-gas processes	32
19.8 Engineering, computation, and measurement connections	37
19.9 Chapter summary and working formula sheet	40
19.10 Advanced Topics for Technical and Engineering Students	42
19.11 Problems and complete solutions	46
19.12 Complete reasoned solutions	50
19.13 Bridge to Chapter 20	63

Preface

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Chapter 18 described temperature, heat transfer, internal energy, work, and the first law from a macroscopic viewpoint. This chapter asks what those macroscopic gas variables mean when matter is viewed as an enormous population of moving molecules. The central task is not to pretend that a gas is simple. It is to learn how a deliberately simple microscopic model can explain pressure, connect temperature with molecular motion, predict characteristic speed distributions, and expose exactly where additional physics is needed.

The chapter develops two descriptions in parallel. The molar language uses amount of substance n , the molar mass M_m , and the gas constant R . The particle language uses a count N , a single-particle mass m_{mol} , and the Boltzmann constant k_B . Their agreement is a recurring check, not a coincidence. Later, the same microscopic picture is extended to mean free paths, classical heat capacities, reversible adiabatic processes, and the stiffness that controls the speed of small sound disturbances in an ideal gas.

The Guideline

Treat kinetic theory as a model-building exercise. At every step identify the molecular assumptions, derive the macroscopic consequence, and then ask what would fail if the gas were dense, strongly interacting, out of equilibrium, anisotropic, or quantum mechanical.

Pedagogical boundary

This chapter introduces probability density only to the depth needed for molecular speeds. It does not develop a full statistical-mechanics formalism, partition functions, quantum statistics, or a complete transport theory. Entropy and the second law are reserved for Chapter 20, *Entropy and the Second Law of Thermodynamics*.

Conventions and notation

The thermal sign convention is the same as in Chapter 18: heat transferred *into* the selected system is positive, and work done *by* the system is positive. For a closed system with no change in bulk kinetic or external potential energy,

$$\Delta E_{\text{int}} = Q - W_{\text{by}}.$$

For reversible or quasi-static piston boundary work, $\delta W_{\text{by}} = p \, dV$ when the system pressure is the appropriate equilibrium pressure at the boundary. An arbitrary irreversible adiabatic process does not thereby acquire an equilibrium $p(V)$ curve.

Symbol	Meaning	SI unit
N	number of specified particles; a count	1
n	amount of substance	mol
$n_N = N/V$	particle number density	m^{-3}
N_A	Avogadro constant, exactly $6.022\,140\,76 \times 10^{23}$	mol^{-1}
k_B	Boltzmann constant, exactly $1.380\,649 \times 10^{-23}$	J K^{-1}
$R = N_A k_B$	molar gas constant	$\text{J mol}^{-1} \text{K}^{-1}$
m_{mol}	mass of one molecule or particle	kg
M_m	molar mass	kg mol^{-1}
p, V, T	absolute pressure, volume, absolute temperature	Pa, m^3 , K
$v_{\text{rms}}, v_{\text{mean}}, v_{\text{mp}}$	rms, mean, and most-probable molecular speeds	m s^{-1}
ℓ_{mfp}	mean free path in the stated collision model	m
$C_{V,m}, C_{p,m}$	molar heat capacities at constant V and p	$\text{J mol}^{-1} \text{K}^{-1}$
$\gamma = C_{p,m}/C_{V,m}$	heat-capacity ratio in the stated model	1
ρ	mass density	kg m^{-3}
c_w	propagation speed of a small sound disturbance	m s^{-1}

The exact numerical values of N_A and k_B above are SI defining values; the displayed value of $R = 8.314\,462\,618 \dots \text{J mol}^{-1} \text{K}^{-1}$ follows from their exact product. Numerical examples normally retain guard digits internally and round only the reported result.

Chapter 19

The Kinetic Theory of Gases

A sealed gas can look completely still. Its centre of mass can be at rest, its pressure gauge can give a steady reading, and its temperature can be constant. Microscopically, however, molecules move continually and collide on time scales far shorter than ordinary observation. Kinetic theory explains how this disordered motion produces orderly macroscopic variables.

An especially useful opening question is this: *If a sample is described once by 0.25 mol and once by a number of molecules, must the two descriptions predict the same pressure?* The answer must be yes if the bookkeeping and constants are consistent. We will use that simple demand for consistency to connect the particle and molar descriptions, and then push the microscopic model much further.

Learning goals

After studying the core and extension material, you should be able to:

- convert consistently between particle count, amount of substance, molecular mass, and molar mass;
- derive ideal-gas pressure from molecular momentum transfer and isotropy;
- relate absolute temperature to mean translational kinetic energy and rms speed;
- interpret a normalised speed probability density and distinguish its mode, mean, and rms value;
- estimate a mean free path in a stated dilute hard-sphere model;
- use classical equipartition conditionally, including the distinction between active and frozen modes;
- derive $C_{p,m} - C_{V,m} = R$ and the reversible, quasi-static adiabatic ideal-gas laws;
- compare isothermal, reversible adiabatic, and free-expansion limits without assigning a fictitious path to the last case;
- connect adiabatic gas stiffness to the speed of sound and validate a statistical model with synthetic molecular samples.

19.1 Moles, particles and the ideal-gas model

19.1.1 Amount of substance and particle bookkeeping

A particle count and an amount of substance are different physical quantities. The count N is dimensionless. The amount n is measured in moles. The connection is

$$N = nN_A. \quad (19.1)$$

In the present SI, one mole contains exactly $6.022\,140\,76 \times 10^{23}$ specified elementary entities. The word *specified* matters: the entities might be atoms, molecules, ions, or some other explicitly identified objects.

If the molar mass is M_m in kg mol^{-1} , the mass of one molecule is

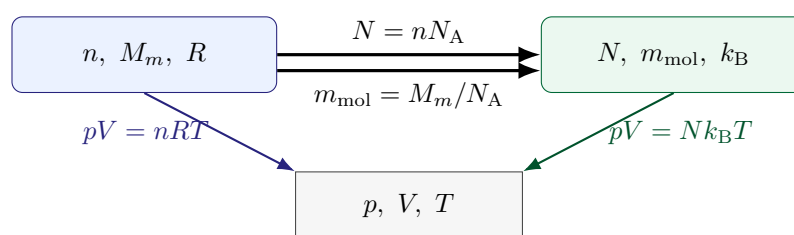
$$m_{\text{mol}} = \frac{M_m}{N_A}. \quad (19.2)$$

Using a molar mass in a formula that requires a single-particle mass is one of the most common unit errors in kinetic theory.

The ideal-gas equation of state can be written in either form,

$$pV = nRT = Nk_B T, \quad R = N_A k_B. \quad (19.3)$$

This equation is an equilibrium equation of state. It relates state variables; by itself it does not say how the gas reached the state, how quickly it changes, or whether every real gas behaves ideally.



The two languages must predict the same macroscopic state when the same physical sample is described consistently.

Figure 19.1: Particle–mole bookkeeping. N_A converts amount to count, while the same constant connects molar and per-particle masses and R to k_B . The diagram represents identities, not a dynamical process.

19.1.2 What “ideal” means in this chapter

The molecular model used for the basic derivation assumes a large number of particles in a dilute gas, negligible molecular volume compared with the container volume, negligible long-range interaction energy between collisions, short elastic collisions, and classical Newtonian motion. For the pressure derivation we also assume an equilibrium state with no bulk flow and an isotropic velocity distribution. These assumptions are physically useful, not universal truths about matter.

Caution

“Ideal gas” does not mean “every molecule has the same speed,” and it does not mean that molecules never collide. The simplest ideal-gas kinetic model ignores long-range intermolecular forces and the volume occupied by molecules while retaining elastic collisions that exchange momentum and redistribute molecular velocities.

Example 19.1: One gas state in two languages

A stipulated gas state has $n = 0.250$ mol, $V = 6.20$ L, $T = 300$ K, and molar mass $M_m = 28.0 \times 10^{-3} \text{ kg mol}^{-1}$. Convert to particle count and single-particle mass, then compute the pressure in both representations.

Particle conversion.

$$N = nN_A = (0.250)(6.02214076 \times 10^{23}) = 1.5055 \times 10^{23}.$$

$$m_{\text{mol}} = \frac{28.0 \times 10^{-3}}{6.02214076 \times 10^{23}} = 4.65 \times 10^{-26} \text{ kg}.$$

Molar equation of state. With $V = 6.20 \times 10^{-3} \text{ m}^3$,

$$p = \frac{nRT}{V} = 1.006 \times 10^5 \text{ Pa}.$$

Particle equation of state.

$$p = \frac{Nk_B T}{V} = 1.006 \times 10^5 \text{ Pa},$$

up to displayed rounding. The agreement checks the conversion $R = N_A k_B$ and the fact that both descriptions refer to the same state. The molar mass was needed to find m_{mol} ; it is not needed to evaluate p once n, V, T are known.

Guided checks

Check 1. If n doubles at fixed V and T , what happens to p ? It doubles because $p = nRT/V$ is proportional to n at fixed T, V .

Check 2. Does doubling molar mass at fixed n, V, T double the ideal-gas pressure? No. Molar mass changes molecular speeds at a given T , but $pV = nRT$ is unchanged.

Check 3. Why must pressure be absolute in the ideal-gas law? Because the equation of state is tied to thermodynamic state, not to an arbitrary atmospheric zero.

19.1.3 Absolute pressure, gauge pressure, and an inverse density measurement

A pressure sensor need not display the pressure required by an equation of state. A gauge referenced to the surrounding atmosphere displays the difference between the sample pressure and its reference pressure. Write

$$p_g = p - p_{\text{ref}}, \quad p = p_g + p_{\text{ref}}. \quad (19.4)$$

Here p is absolute pressure. A negative gauge reading can describe an ordinary positive absolute pressure below the reference; it does not imply a negative particle density. The reference must be measured or specified. It is not universally 100 kPa, and a sensor using a sealed reference need not be referenced to the current atmosphere. Before using a displayed pressure, identify the instrument's zero.

Mass density provides a useful bridge between engineering measurements and molecular book-keeping. Let m_{gas} be the total mass of a single-species sample, so that $m_{\text{gas}} = nM_m = Nm_{\text{mol}}$. Dividing by volume gives

$$\rho = \frac{m_{\text{gas}}}{V} = \frac{nM_m}{V} = n_N m_{\text{mol}} = \frac{pM_m}{RT}. \quad (19.5)$$

Consequently a known composition predicts density, whereas a measured density at known p, T can infer a model molar mass:

$$M_m = \frac{\rho RT}{p}. \quad (19.6)$$

The units are $(\text{kg m}^{-3})(\text{J mol}^{-1})/(\text{Pa}) = \text{kg mol}^{-1}$, because $1 \text{ J} = 1 \text{ Pa m}^3$. This inference assumes the gas is sufficiently ideal and homogeneous, with no unaccounted condensed material in the mass measurement. It gives an effective molar mass for a mixture; it cannot identify the chemical species uniquely.

Statements about the effect of molecular mass require a clear choice of what is held fixed. At fixed particle count, volume, and temperature, changing the molecular mass does not change ideal pressure. At fixed *mass density* and temperature, increasing molar mass reduces the number density and therefore reduces pressure. These are consistent conclusions: the first comparison preserves

the number of particles, whereas the second preserves their total mass per volume. In an inverse problem, writing the quantities actually measured before selecting an equation prevents this hidden change of comparison. A dimensional check alone would not expose it, because both calculations can have correct units.

Figure 19.2 makes the pressure offset visible. The correct density line reaches zero at zero *absolute* pressure, which corresponds to $p_g = -p_{\text{ref}}$. A density calculated by treating a positive gauge reading as absolute pressure is too small for a known molar mass. Conversely, a molar mass inferred from that same wrong denominator is too large. These are two different uses of the same equation, so the direction of the error depends on which quantity is being inferred.

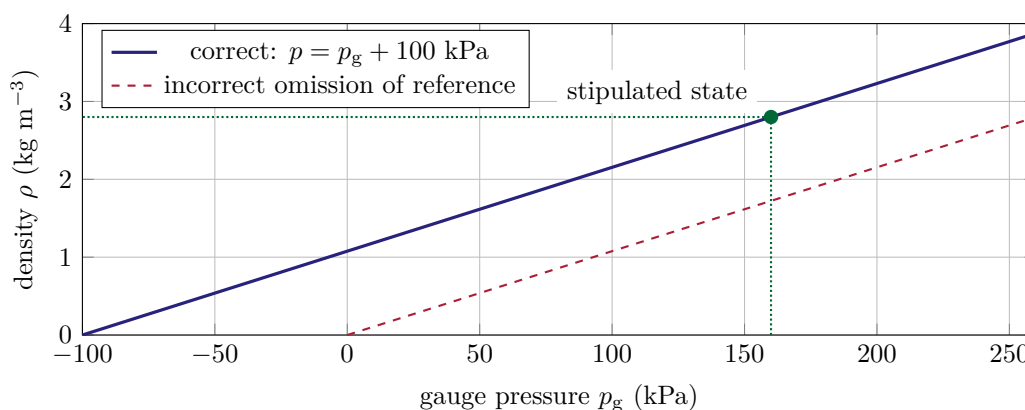


Figure 19.2: Absolute-pressure correction in an ideal density model at $T = 310$ K, $p_{\text{ref}} = 100$ kPa, and inferred $M_m = 27.7575$ g mol $^{-1}$. The correct line is $\rho = 2.80(p_g + 100)/260$, with pressures inserted numerically in kPa. The dashed line deliberately shows the erroneous formula using gauge pressure alone; it represents a calculation error. Both curves are analytic teaching models.

Example 19.2: Infer composition scale from mass density

Statement. A uniform gas at $T = 310$ K has stipulated density $\rho = 2.80$ kg m $^{-3}$. Its gauge reads 160 kPa relative to a stipulated 100 kPa reference. The sample volume is 12.0 L. Under the ideal-gas assumption, find its effective molar mass, sample mass, amount, and particle count. Quantify the error if the gauge reading is treated as absolute pressure. These inputs are stipulated teaching values, not laboratory observations.

Strategy and model. First restore the pressure zero, then infer the molar mass from Eq. (19.6). Use the independently specified volume only for the sample totals. We assume equilibrium, no leakage, and a density referring solely to gas.

$$p = (160 + 100) \text{ kPa} = 2.60 \times 10^5 \text{ Pa.}$$

$$M_m = \frac{(2.80)(8.314462618)(310)}{2.60 \times 10^5} = 2.78 \times 10^{-2} \text{ kg mol}^{-1}.$$

The mass and amount are

$$m_{\text{gas}} = \rho V = (2.80)(0.0120) = 0.0336 \text{ kg,} \quad n = \frac{pV}{RT} = 1.21 \text{ mol.}$$

Thus $N = nN_A = 7.29 \times 10^{23}$ specified particles. The independent bookkeeping check is $nM_m = 0.0336$ kg, agreeing with ρV before rounding.

Diagnose the wrong zero. Using 160 kPa instead would infer $M_{m,\text{wrong}} = 45.1$ g mol $^{-1}$. The error factor is $260/160 = 1.625$: the inferred mass scale is 62.5% too high. This calculation does not identify the gas as a particular species. Multiple mixtures can have the same effective molar mass and the same p, ρ, T .

19.1.4 Ideal mixtures: partial pressure is a particle-count contribution

Different species in a dilute equilibrium mixture share one volume and one temperature. They do not each occupy a separate fraction of the container. For species i with amount n_i , define its ideal partial pressure by

$$p_i = \frac{n_i RT}{V}, \quad p = \sum_i p_i = \frac{(\sum_i n_i) RT}{V}, \quad \frac{p_i}{p} = \frac{n_i}{\sum_j n_j} = x_i. \quad (19.7)$$

The mole fraction x_i is also the particle-count fraction when the specified entities are molecules or atoms of each species. Partial pressure is the pressure contribution attributed to that species in this ideal model. A mechanical gauge responds to the total momentum transfer from all species together.

For a mixture the mass-weighted bookkeeping becomes

$$m_{\text{gas}} = \sum_i n_i M_{m,i}, \quad M_{m,\text{mix}} = \sum_i x_i M_{m,i}, \quad \rho = \frac{p M_{m,\text{mix}}}{RT}. \quad (19.8)$$

Do not replace the mole fractions by mass fractions in the middle expression. A large particle can contribute strongly to the mixture mass while contributing no more pressure per particle than a small one at the same T . Its larger mass is compensated by a smaller thermal velocity second moment. The momentum-transfer derivation below explains this compensation microscopically.

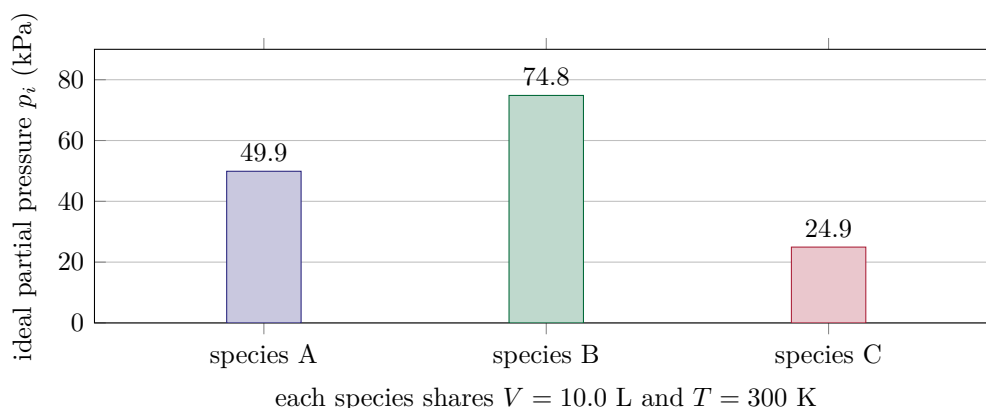


Figure 19.3: Calculated ideal partial pressures for the stipulated three-species mixture in Example 19.3. The heights are proportional to amounts 0.200, 0.300, and 0.100 mol, respectively. The bars do not represent subvolumes. Their sum is the total absolute pressure, 149.660 kPa; the molar masses affect mixture density but do not enter these pressure contributions.

Example 19.3: Pressure fractions and mass fractions differ

Statement. A model mixture in $V = 10.0$ L at $T = 300$ K contains $n_A = 0.200$, $n_B = 0.300$, and $n_C = 0.100$ mol. Their stipulated molar masses are 4.00, 28.0, and 40.0 g mol⁻¹. Find the partial pressures, total pressure, effective molar mass, and density. Then replace species A by the same amount of species B at unchanged V, T . Predict the changes.

Model and method. Assume a dilute, nonreacting mixture at common equilibrium temperature. Its total amount is $n = 0.600$ mol. Each pressure contribution is $n_i RT/V$, so

$$p_A = 49.9 \text{ kPa}, \quad p_B = 74.8 \text{ kPa}, \quad p_C = 24.9 \text{ kPa}, \quad p = 1.50 \times 10^2 \text{ kPa}.$$

The unrounded total is 149.660 kPa. The pressure fractions are 1/3, 1/2, and 1/6, matching Fig. 19.3. The masses are

$$m_A = 0.800 \text{ g}, \quad m_B = 8.40 \text{ g}, \quad m_C = 4.00 \text{ g}, \quad m_{\text{gas}} = 13.2 \text{ g}.$$

Hence $M_{m,\text{mix}} = 13.2/0.600 = 22.0 \text{ g mol}^{-1}$ and $\rho = 0.0132/0.0100 = 1.32 \text{ kg m}^{-3}$. Species A supplies one third of the pressure but only $0.800/13.2 = 6.06\%$ of the mass. Equal pressure fractions do not imply equal mass fractions.

Replacement and check. Replacing the 0.200 mol of A by B preserves the total number of particles, so the total pressure remains 149.660 kPa. The mass rises by $0.200(28.0 - 4.00) = 4.80 \text{ g}$. Thus $m_{\text{gas}} = 18.0 \text{ g}$, $M_{m,\text{mix}} = 30.0 \text{ g mol}^{-1}$, and $\rho = 1.80 \text{ kg m}^{-3}$. Substitution of these values into $p = \rho RT/M_{m,\text{mix}}$ reproduces the unchanged pressure. Both density and molar mass increase by the same factor.

19.2 Pressure from momentum transfer

Pressure is force per area. Kinetic theory asks how many molecular impacts, each far too small to see individually, produce a steady average force on a wall.

19.2.1 Impulse from one molecule

Consider a cube of side L and volume $V = L^3$. A molecule of mass m_{mol} has velocity component v_x normal to the right wall. For a perfectly elastic collision with that stationary wall, the molecular momentum component changes from $+m_{\text{mol}}v_x$ to $-m_{\text{mol}}v_x$,

$$\Delta p_{x,\text{molecule}} = -2m_{\text{mol}}v_x. \quad (19.9)$$

The impulse delivered to the wall is opposite,

$$J_{x,\text{wall}} = +2m_{\text{mol}}v_x. \quad (19.10)$$

In a collision-free pedagogical trajectory between specular walls, the same molecule returns to that wall after travelling a round-trip distance $2L$, so for $v_x > 0$ the time between successive impacts on the same wall is $\Delta t = 2L/v_x$. Its time-averaged force contribution is therefore

$$\overline{F}_x = \frac{2m_{\text{mol}}v_x}{2L/v_x} = \frac{m_{\text{mol}}v_x^2}{L}. \quad (19.11)$$

The sign of the original v_x disappears because the pressure depends on v_x^2 . Molecules travelling toward either wall contribute a positive normal stress to the wall they hit.

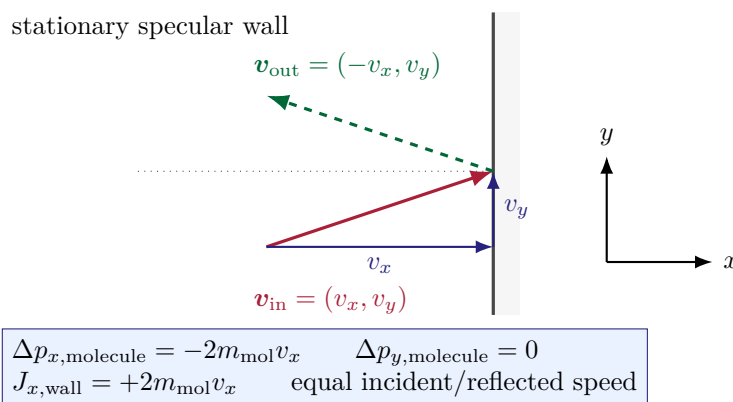


Figure 19.4: Specular elastic reflection at a stationary wall. Incident and outgoing vectors meet the same contact point and have equal lengths; the normal component changes sign, while the tangential component is unchanged. Geometry uses a common display scale and does not represent a wall of molecular thickness.

19.2.2 Sum over molecules and use isotropy

For N molecules, add Eq. (19.11) and divide by the wall area L^2 :

$$p = \frac{m_{\text{mol}}}{L^3} \sum_{i=1}^N v_{x,i}^2 = \frac{N}{V} m_{\text{mol}} \langle v_x^2 \rangle. \quad (19.12)$$

In an equilibrium gas with no preferred direction,

$$\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle, \quad (19.13)$$

and because $v^2 = v_x^2 + v_y^2 + v_z^2$,

$$\langle v_x^2 \rangle = \frac{1}{3} \langle v^2 \rangle. \quad (19.14)$$

Thus

$$p = \frac{1}{3} \frac{N}{V} m_{\text{mol}} \langle v^2 \rangle. \quad (19.15)$$

The factor $1/3$ is a statement about isotropy in three dimensions; it is not a geometric property of the cubic box itself.

Key message

The mean molecular velocity can be zero while the pressure is nonzero. Equilibrium with no bulk flow gives $\langle \mathbf{v} \rangle = \mathbf{0}$, but $\langle v^2 \rangle > 0$ at any nonzero temperature.

Example 19.4: From a component-velocity moment to pressure

A stipulated isotropic molecular state has $N = 2.50 \times 10^{23}$ particles in $V = 8.00 \times 10^{-3} \text{ m}^3$. Each particle has mass $m_{\text{mol}} = 4.65 \times 10^{-26} \text{ kg}$, and the component moment is $\langle v_x^2 \rangle = 8.90 \times 10^4 \text{ m}^2 \text{ s}^{-2}$. Find the wall pressure.

Using Eq. (19.12),

$$p = \frac{2.50 \times 10^{23}}{8.00 \times 10^{-3}} (4.65 \times 10^{-26}) (8.90 \times 10^4) \simeq 1.29 \times 10^5 \text{ Pa}.$$

The units reduce as $(\text{m}^{-3})(\text{kg})(\text{m}^2 \text{ s}^{-2}) = \text{kg m}^{-1} \text{ s}^{-2} = \text{Pa}$. If the velocity distribution were anisotropic, the three normal stresses could differ and the single scalar pressure used here would not capture the full mechanical state.

19.2.3 A local collision-flux derivation that permits intermolecular collisions

The one-molecule round-trip argument is a helpful introduction to momentum transfer. Its specific return time $2L/|v_x|$ assumes the molecule keeps its normal speed between wall impacts. An intermolecular collision can change that speed and redirect the particle, so a tagged molecule in a collisional gas need not return on that schedule. Pressure nevertheless has the same dilute equilibrium result. To establish it, count particles reaching a small wall patch during a short time interval, rather than tracking one particle throughout its history.

Take the right wall to have outward normal $+x$ and patch area A . Let $G(\mathbf{v})$ be the local velocity probability density immediately adjacent to it, normalized by $\int G(\mathbf{v}) d^3v = 1$. Here $d^3v = dv_x dv_y dv_z$, and $n_N G d^3v$ is the local number density in a small velocity range. For a particle with $v_x > 0$, the initial positions that can reach the patch within dt occupy a thin prism of volume $Av_x dt$; Fig. 19.5 shows this geometry. The expected incident count in that velocity range is therefore

$$dN_{\text{hit}} = n_N A v_x dt G(\mathbf{v}) d^3v, \quad v_x > 0. \quad (19.16)$$

The tangential velocity shifts the prism sideways but does not change its volume. For a homogeneous wall region and a patch large compared with molecular scales, edge effects cancel in the flux per unit area. We choose dt short compared with the collision time for this local count. The probability of an additional intermolecular collision during the infinitesimal flight then vanishes in the flux limit. Collisions earlier in a particle's history are fully allowed and determine the local distribution G .

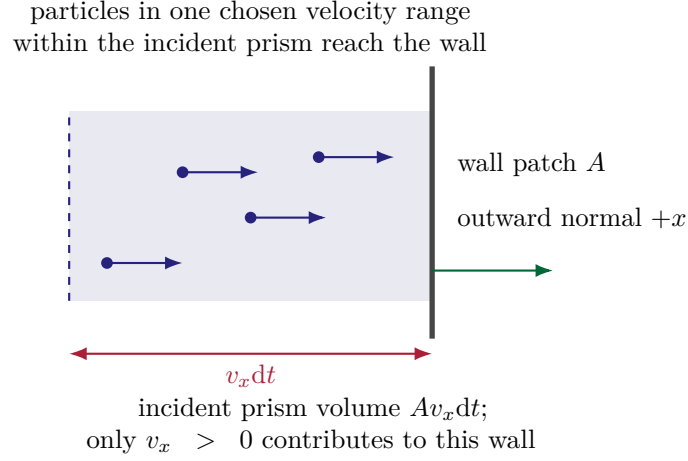


Figure 19.5: Local collision-flux construction, drawn for $v_y = v_z = 0$. Positions, speeds, and prism width are schematic. Tangential components shear the incident prism without changing its volume $Av_x dt$. The shaded depth belongs to a chosen velocity range: a different v_x gives a different incident prism. Counting this instantaneous flux avoids assuming a collision-free round trip through the whole container.

Each incident particle delivers normal impulse $2m_{\text{mol}}v_x$ at a stationary specular wall. Multiplying impulse by incident count and dividing by Adt gives the normal momentum flux

$$p_x = 2n_N m_{\text{mol}} \int_{v_x > 0} v_x^2 G(\mathbf{v}) d^3v. \quad (19.17)$$

At equilibrium without flow, the distribution is unchanged under $v_x \mapsto -v_x$. The two half-space integrals of $v_x^2 G$ are then equal, so

$$p_x = n_N m_{\text{mol}} \langle v_x^2 \rangle. \quad (19.18)$$

Isotropy subsequently gives $p_x = p_y = p_z = \rho \langle v^2 \rangle / 3$. Notice that reflection symmetry in one component and full isotropy are distinct assumptions. The first removes the factor of two from the half-space integral; the second permits replacing one component second moment by one third of the speed second moment. Neither requires every molecule to have the same speed.

This derivation also explains why selecting molecules by wall impacts biases a sample toward large positive normal velocity. A particle with twice v_x crosses twice as much incident volume in the same time and transfers twice as much normal momentum per impact. Both factors are required; together they produce v_x^2 . Counting only impulses while assigning an equal impact frequency to all particles would lose one factor of velocity.

The force averaged over an observation interval Δt_{obs} can be written directly in terms of individual collision impulses:

$$\bar{F}_x = \frac{\sum_{a \text{ in interval}} J_{x,a}}{\Delta t_{\text{obs}}}, \quad \bar{p}_x = \frac{\bar{F}_x}{A}. \quad (19.19)$$

The label a counts impacts rather than distinct molecules; one molecule may appear several times. No collision duration enters this average. Dividing an impulse by the microscopic contact duration instead gives the average force *during that impact*, a different quantity. A stationary elastic collision can exert a large instantaneous force and still do zero work, because the wall does not move.

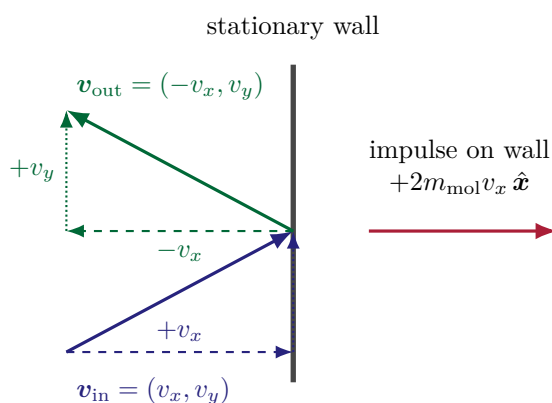
For a macroscopic patch, an ordinary sensor averages enormous numbers of arrivals and displays a nearly steady pressure. A sufficiently small patch observed sufficiently briefly experiences fluctuations. The infinitesimal-time counting derivation concerns the expected flux from the distribution; it does not assert that a finite microscopic patch receives a deterministic fractional molecule in every interval. In a homogeneous stationary gas, suitable long-time averages approach the corresponding statistical expectations. This is why a mechanical measurement can be stable although the microscopic momentum transfers remain discrete. The equilibrium result also does not depend on a cubic container: the cube simplified the first trajectory argument, whereas the local patch calculation applies to a planar element of a general boundary under the same dilute, homogeneous, specular conditions.

19.2.4 Specular reflection reverses only the normal component

A vector arrow leaving a vertical wall need not point horizontally to the left. For a stationary smooth wall, the incoming and outgoing velocities obey

$$\mathbf{v}_{\text{out}} = (-v_x, v_y, v_z), \quad \Delta \mathbf{p}_{\text{molecule}} = (-2m_{\text{mol}}v_x, 0, 0). \quad (19.20)$$

The wall receives the opposite impulse. The tangential components retain both their magnitude and their sign in this ideal specular model. Figure 19.6 distinguishes the trajectory from the impulse. The incoming and outgoing velocity vectors have equal lengths, so the molecular kinetic energy is unchanged, although its momentum is changed.



Normal momentum reverses; tangential momentum is conserved.
Arrows depict velocity components, not force components.

Figure 19.6: Verified specular-reflection geometry in the xy plane, with $v_x > 0$ and $v_y > 0$. Equal horizontal magnitudes and equal positive vertical components give equal incoming and outgoing speeds. The wall impulse points along the outward normal; it is distinct from the reflected velocity. The unshown v_z component is also unchanged.

Real walls may exchange energy with molecules and scatter them diffusely; surface accommodation then needs a more detailed model. The elastic specular construction is sufficient for the present elementary derivation. It should not be confused with a statement that every real molecule reflects like a geometrical-optics ray.

Example 19.5: Check a reflection and its momentum flux

Statement. A particle with $m_{\text{mol}} = 4.65 \times 10^{-26}$ kg approaches a stationary $+x$ wall with $\mathbf{v}_{\text{in}} = (300, 200, -100) \text{ m s}^{-1}$. Find its reflected velocity, wall impulse, and energy change. In a separate short-time toy population with number density $2.00 \times 10^{25} \text{ m}^{-3}$, half the particles have $v_x = +300 \text{ m s}^{-1}$ and half have $v_x = -300 \text{ m s}^{-1}$. Find the incident number flux and

normal stress on the $+x$ wall. This toy population is not claimed to be a Maxwell equilibrium gas.

Reflection. The model reverses the normal component, giving $\mathbf{v}_{\text{out}} = (-300, 200, -100) \text{ m s}^{-1}$. The wall impulse is

$$\mathbf{J}_{\text{wall}} = (2m_{\text{mol}} 300, 0, 0) = (2.79 \times 10^{-23}, 0, 0) \text{ kg m s}^{-1}.$$

Both squared speeds equal $300^2 + 200^2 + (-100)^2 = 1.40 \times 10^5 \text{ m}^2 \text{ s}^{-2}$, so $K_{\text{in}} = K_{\text{out}} = 3.255 \times 10^{-21} \text{ J}$ and $\Delta K = 0$.

Flux. Only the positive half of the population arrives at this wall. Its incident number flux is $(n_N/2)(300) = 3.00 \times 10^{27} \text{ m}^{-2} \text{ s}^{-1}$. Multiplying by impulse per arrival gives

$$p_x = (3.00 \times 10^{27})(2.79 \times 10^{-23}) = 8.37 \times 10^4 \text{ Pa}.$$

The moment check gives the same result: $p_x = n_N m_{\text{mol}} (300)^2$. A $1.00 \text{ cm}^2 = 1.00 \times 10^{-4} \text{ m}^2$ patch therefore experiences mean normal force 8.37 N . No $1/3$ factor was used, because the statement provides a normal-component moment and does not establish isotropy.

19.2.5 Random motion, bulk flow, and anisotropic normal stresses

In a flowing gas, define the bulk velocity by $\mathbf{u} = \langle \mathbf{v} \rangle$ and the random or *peculiar* velocity by $\mathbf{c} = \mathbf{v} - \mathbf{u}$. Then $\langle \mathbf{c} \rangle = \mathbf{0}$ by definition. Expanding the squared speed gives

$$\langle v^2 \rangle = u^2 + \langle c^2 \rangle, \quad \frac{1}{2} \rho \langle v^2 \rangle = \frac{1}{2} \rho u^2 + \frac{1}{2} \rho \langle c^2 \rangle. \quad (19.21)$$

The cross term vanishes because $\mathbf{u} \cdot \langle \mathbf{c} \rangle = 0$. The first energy density is organized bulk kinetic energy; the second is random translational energy density. Temperature is linked to the second, in the local equilibrium model. Merely changing the observer's inertial frame changes $\mathbf{u}$, and must not change the gas temperature.

The dilute kinetic stress components are

$$\Pi_{ij} = \rho \langle c_i c_j \rangle, \quad p_x = \Pi_{xx}, \quad p_y = \Pi_{yy}, \quad p_z = \Pi_{zz}. \quad (19.22)$$

The subscripts i, j denote Cartesian directions. For the reflection-symmetric distributions used here, the normal components describe wall momentum transfer in the local rest frame. An isotropic distribution has equal diagonal components and vanishing off-diagonal components, leaving one scalar thermal pressure p . Outside that model, unequal directional spreads can produce different normal stresses. Zero bulk velocity by itself does not imply isotropy. Conversely, a locally equilibrated gas may have a nonzero bulk velocity and an isotropic random distribution in its own rest frame.

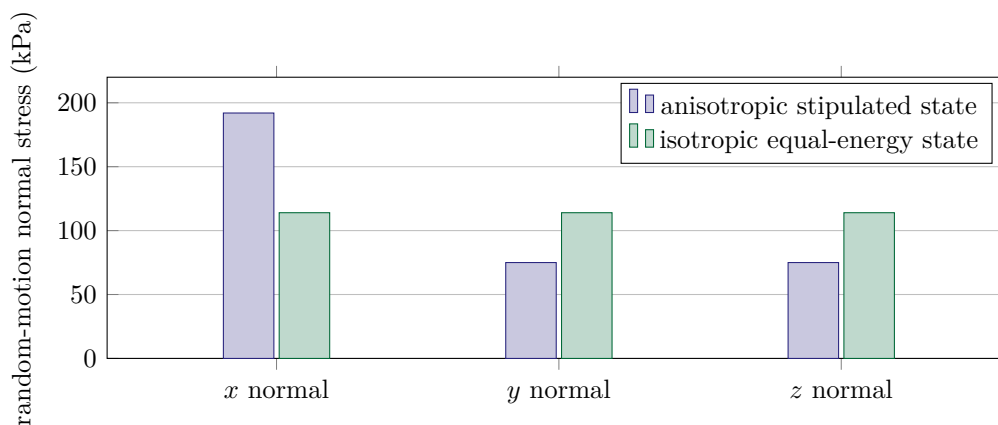


Figure 19.7: Directional normal stresses for Example 19.6 and an isotropic comparison at the same density and random translational energy. The sums of the three stress components are identical, 342 kPa, but a scalar 114 kPa describes only the isotropic comparison. The bars are calculated model quantities; no measured anisotropic gas is claimed.

The total flux of x momentum across an imaginary plane normal to x includes a convective term ρu_x^2 as well as Π_{xx} . This distinction matters when a stream transports momentum through a device. It does not authorize adding ρu_x^2 to the pressure of a sealed equilibrium vessel, or assigning a stagnation pressure without analyzing how the flow is stopped. The mechanical boundary conditions and the chosen frame still have to be specified.

Example 19.6: Diagnose a scalar-pressure shortcut

Statement. A model local population has density $\rho = 1.20 \text{ kg m}^{-3}$ and independent, reflection-symmetric random components with rms values 400, 250, and 250 m s^{-1} along x, y, z . Compute the three normal stresses and random translational energy density. Compare with an isotropic population having the same density and random energy. If an observer measures bulk velocity $\mathbf{u} = (300, 0, 0) \text{ m s}^{-1}$, determine the additional bulk kinetic energy density and explain why it is excluded from temperature.

Directional calculation. Square each stated component rms value before multiplying by density:

$$p_x = (1.20)(400)^2 = 192 \text{ kPa}, \quad p_y = p_z = (1.20)(250)^2 = 75.0 \text{ kPa}.$$

The random energy density is

$$e_{\text{trans}} = \frac{1}{2}\rho\langle c^2 \rangle = \frac{1}{2}(192 + 75.0 + 75.0) \text{ kPa} = 171 \text{ kJ m}^{-3}.$$

An isotropic equal-energy population has $p = (192 + 75.0 + 75.0)/3 = 114 \text{ kPa}$. It has the same total random energy, but different x -normal stress. Thus the isotropic replacement would underestimate this state's x stress by 78.0 kPa; averaging is not a repair for missing isotropy.

Bulk motion. The extra energy density is $e_{\text{bulk}} = \frac{1}{2}(1.20)(300)^2 = 54.0 \text{ kJ m}^{-3}$, and the total laboratory translational energy density is 225 kJ m^{-3} . The random component statistics are unchanged by this frame shift. Assigning temperature from the laboratory $\langle v^2 \rangle$ would count an observer-dependent energy. Furthermore, the anisotropic state need not possess one equilibrium thermodynamic temperature at all: a kinetic energy scale alone does not establish equilibrium.

19.3 Temperature and translational energy

Equating the macroscopic ideal-gas law $pV = Nk_B T$ with the kinetic result in Eq. (19.15) gives

$$Nk_B T = \frac{1}{3} N m_{\text{mol}} \langle v^2 \rangle. \quad (19.23)$$

Therefore

$$\langle K_{\text{trans}} \rangle = \frac{1}{2} m_{\text{mol}} \langle v^2 \rangle = \frac{3}{2} k_B T. \quad (19.24)$$

This relation is about a mean translational kinetic energy per molecule. It does not say every molecule has the same energy, and it does not by itself give the full internal energy of a polyatomic gas.

Define the root-mean-square speed by

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3k_B T}{m_{\text{mol}}}} = \sqrt{\frac{3RT}{M_m}}. \quad (19.25)$$

At the same temperature, lighter molecules have a larger rms speed. The mean translational energy per molecule nevertheless remains $3k_B T/2$ for every classical ideal gas in equilibrium.

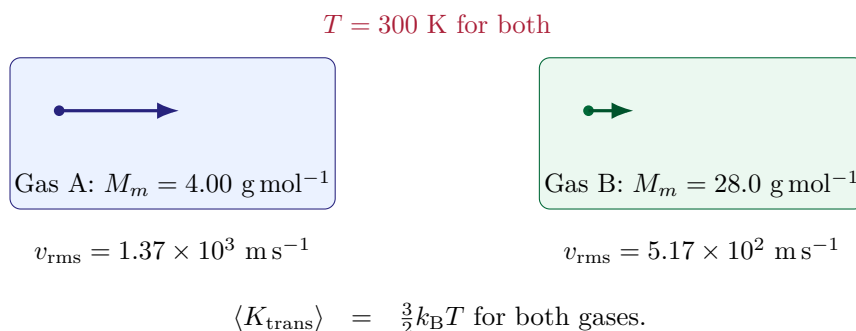


Figure 19.8: Equal temperature does not mean equal molecular speed. The lighter stipulated gas has the larger rms speed, but both gases have the same mean translational kinetic energy per molecule.

Example 19.7: Compare two gases at equal temperature

Take two stipulated molar masses, $M_{m,A} = 4.00 \times 10^{-3} \text{ kg mol}^{-1}$ and $M_{m,B} = 28.0 \times 10^{-3} \text{ kg mol}^{-1}$, at $T = 300 \text{ K}$.

$$v_{\text{rms},A} = \sqrt{\frac{3RT}{M_{m,A}}} = 1.37 \times 10^3 \text{ m s}^{-1}, \quad v_{\text{rms},B} = 5.17 \times 10^2 \text{ m s}^{-1}.$$

Their ratio is

$$\frac{v_{\text{rms},A}}{v_{\text{rms},B}} = \sqrt{\frac{M_{m,B}}{M_{m,A}}} = \sqrt{7} \simeq 2.65.$$

But each molecule has the same mean translational energy,

$$\langle K_{\text{trans}} \rangle = \frac{3}{2} k_B T = 6.21 \times 10^{-21} \text{ J}.$$

In an equilibrium sample with no bulk flow, $\langle \mathbf{v} \rangle = \mathbf{0}$ for both gases. Large molecular speeds do not imply that the gas as a whole is moving through the laboratory.

19.3.1 Moving pistons connect collision mechanics to work and heating

Stationary elastic walls change molecular momentum without changing kinetic energy. A moving wall behaves differently. Let a massive piston normal to x move at speed U along $+x$ while a molecule approaches with $v_x > U$. The piston mass is treated as sufficiently large that one molecular collision does not appreciably change U . Transform to the piston frame: the incoming normal speed is $v_x - U$. Elastic reflection reverses this relative speed, and transforming back gives

$$v'_x - U = -(v_x - U), \quad v'_x = 2U - v_x. \quad (19.26)$$

Tangential components remain unchanged. The impulse on the piston and the molecular kinetic-energy change are

$$J_{x,\text{piston}} = m_{\text{mol}}(v_x - v'_x) = 2m_{\text{mol}}(v_x - U), \quad (19.27)$$

$$\Delta K_{\text{molecule}} = \frac{1}{2}m_{\text{mol}}[(2U - v_x)^2 - v_x^2] = -2m_{\text{mol}}U(v_x - U) = -UJ_{x,\text{piston}}. \quad (19.28)$$

The product UJ is the energy transferred by the molecule to the piston under the constant-speed, massive-piston approximation. It has units $(\text{m s}^{-1})(\text{kg m s}^{-1}) = \text{J}$. A receding piston, $U > 0$, takes energy from the molecule. An approaching piston, $U < 0$, gives energy to it. The impulse on the piston remains positive for the incident collision, while the direction of piston motion decides the work sign.

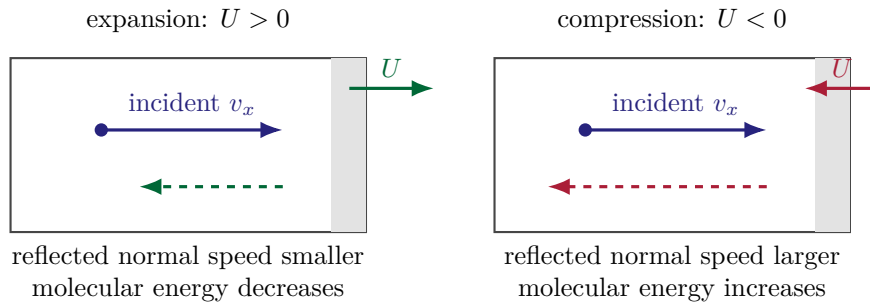


Figure 19.9: Microscopic work transfer at an expanding or compressing massive piston. The arrows are schematic and show the regime $|U| \ll v_x$ for the depicted leftward reflections. Dashed arrows depict reflected velocity, while solid arrows depict incidence and piston motion. Relative-frame reflection yields $v'_x = 2U - v_x$ and $\Delta K_{\text{molecule}} = -UJ_{x,\text{piston}}$.

Example 19.8: Molecular work in expansion and compression

Statement. A molecule of mass 4.65×10^{-26} kg approaches a massive piston with $(v_x, v_y, v_z) = (400, 120, 0) \text{ m s}^{-1}$. The piston first recedes at $U = +10.0 \text{ m s}^{-1}$. Find the reflected velocity, impulse on the piston, and molecular energy change. Repeat for a piston approaching at $U = -10.0 \text{ m s}^{-1}$, using the same stipulated incident velocity.

Expansion collision. Reflecting in the piston frame gives $\mathbf{v}' = (-380, 120, 0) \text{ m s}^{-1}$. The normal impulse is $J = 2(4.65 \times 10^{-26})(400 - 10.0) = 3.627 \times 10^{-23} \text{ kg m s}^{-1}$. Therefore

$$\Delta K = -UJ = -3.627 \times 10^{-22} \text{ J}.$$

The direct energy check is $K_i = \frac{1}{2}m_{\text{mol}}(400^2 + 120^2) = 4.0548 \times 10^{-21} \text{ J}$ and $K_f = \frac{1}{2}m_{\text{mol}}(380^2 + 120^2) = 3.6921 \times 10^{-21} \text{ J}$. Their difference matches $-UJ$.

Compression collision. Now $\mathbf{v}' = (-420, 120, 0) \text{ m s}^{-1}$, $J = 3.813 \times 10^{-23} \text{ kg m s}^{-1}$, and $\Delta K = -(-10.0)J = +3.813 \times 10^{-22} \text{ J}$. The outgoing energy is $4.4361 \times 10^{-21} \text{ J}$, again agreeing with the direct difference. The two changes have slightly different magnitudes because the incident relative speeds are 390 and 410 m s^{-1} .

Interpretation and limit. Compression transfers energy into molecular motion; expansion transfers energy out. For $U = 0$, both the energy change and piston work vanish while a normal impulse remains. This exact limit separates force from work. The calculation is for individual elastic collisions and does not alone determine a gas temperature or a reversible process law.

In a slowly moving piston model, many such collisions occur while the gas remains close to equilibrium. Their summed normal force approaches pA , and the piston displacement gives $dV = AUdt$. Hence the work rate delivered by the gas is $\dot{W}_{by} = pAU$, and the incremental work is $\delta W_{by} = pdV$. If the closed gas is thermally insulated, its internal-energy change is $dE_{int} = -pdV$: expansion cools the gas and compression heats it in the ideal model. Intermolecular collisions redistribute the directional energy change among particles and directions; they do not create the energy transferred by the piston.

The qualification “slowly” concerns internal equilibration, whereas thermal insulation concerns heat transfer through the boundary. They are different conditions. A rapid moving piston can produce nonuniform flow and anisotropic distributions, for which an equilibrium gas pressure and temperature along the entire path are not established. A slowly compressed gas can remain isothermal if heat leaves sufficiently effectively. These distinctions explain why the same molecular collision mechanism is consistent with several macroscopic process constraints, whose detailed energy balances are developed in the adiabatic-process section.

19.4 Molecular speed distributions

An rms speed compresses an entire population into one number. Real equilibrium molecules occupy a broad range of speeds. A probability density is the correct language for describing that range.

19.4.1 Probability density and normalisation

For a classical ideal gas at equilibrium, the Maxwell speed probability density is

$$f(v) = 4\pi \left(\frac{m_{mol}}{2\pi k_B T} \right)^{3/2} v^2 \exp\left(-\frac{m_{mol} v^2}{2k_B T} \right), \quad v \geq 0. \quad (19.29)$$

It is normalised so that

$$\int_0^\infty f(v) dv = 1. \quad (19.30)$$

Because $f(v) dv$ is a probability, $f(v)$ has units of inverse speed. The value of the density at one exact speed is not itself a probability; an interval or an integral is required.

A useful dimensionless speed is

$$u = \frac{v}{\sqrt{2k_B T / m_{mol}}}, \quad (19.31)$$

for which

$$f_u(u) = \frac{4}{\sqrt{\pi}} u^2 e^{-u^2}, \quad u \geq 0. \quad (19.32)$$

The dimensionless form separates the universal curve shape from the thermal speed scale.

19.4.2 Mode, mean, and rms speed

The most probable speed is the mode of $f(v)$. Differentiating the density and setting the derivative to zero gives

$$v_{mp} = \sqrt{\frac{2k_B T}{m_{mol}}} = \sqrt{\frac{2RT}{M_m}}. \quad (19.33)$$

The mean speed is the first moment,

$$v_{\text{mean}} = \int_0^\infty v f(v) dv = \sqrt{\frac{8k_B T}{\pi m_{\text{mol}}}}, \quad (19.34)$$

and the rms speed is the square root of the second moment,

$$v_{\text{rms}} = \left(\int_0^\infty v^2 f(v) dv \right)^{1/2} = \sqrt{\frac{3k_B T}{m_{\text{mol}}}}. \quad (19.35)$$

Thus

$$v_{\text{mp}} < v_{\text{mean}} < v_{\text{rms}}. \quad (19.36)$$

A symmetric distribution could make mean, median, and mode coincide, but the Maxwell speed density is skewed toward high speeds.

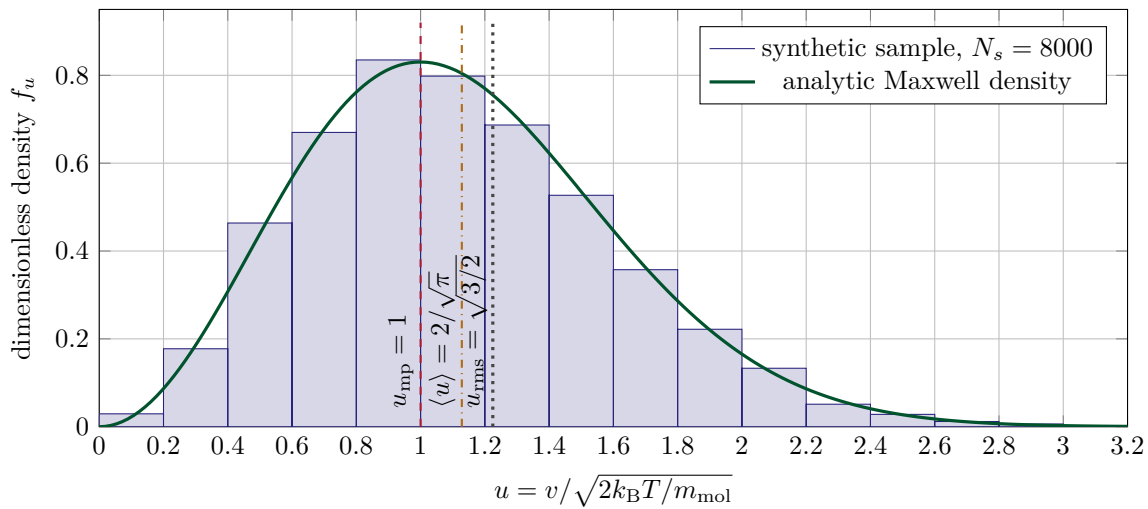


Figure 19.10: Analytic Maxwell speed density and a synthetic histogram generated from 8000 independent three-component Gaussian velocity samples with declared seed 1904. The histogram is calculated model data, not a measurement. The plotted markers are analytic mode, mean, and rms values. The bars are normalised by the full sample count; three synthetic points lie above the plotted cutoff, so the displayed histogram area is 0.999625. The analytic probability above $u = 3.2$ is about 1.35×10^{-4} .

Example 19.9: Analytic moments versus a synthetic molecular sample

Use the dimensionless distribution in Eq. (19.32). Its analytic values are

$$u_{\text{mp}} = 1, \quad \langle u \rangle = \frac{2}{\sqrt{\pi}} = 1.12838, \quad u_{\text{rms}} = \sqrt{\frac{3}{2}} = 1.22474.$$

A deterministic synthetic experiment generated 8000 three-component Gaussian samples with component standard deviation $1/\sqrt{2}$ and random seed 1904, then formed $u = \sqrt{u_x^2 + u_y^2 + u_z^2}$. It produced

$$\bar{u} = 1.12465, \quad \sqrt{\overline{u^2}} = 1.22123.$$

The deviations from the analytic moments are finite-sample fluctuations. The analytic curve, not the histogram, defines the equilibrium model. A larger sample should generally reduce sampling noise, but no particular finite sample is required to match the exact moments digit by digit.

Caution

A histogram depends on sample size and bin choices. Matching the shape visually is not enough to validate a simulation. Check normalisation, at least one analytic moment, the expected ordering of characteristic speeds, and the parameter scaling.

19.4.3 Reading a density: heights, intervals, and unequal bins

The Maxwell curve answers a population question: what fraction of molecules have speeds within a specified interval? It does not assign a finite fraction to one exact speed. For an ideal continuous model,

$$P(v_1 \leq v < v_2) = \int_{v_1}^{v_2} f(v) dv, \quad P(v = v_1) = 0.$$

An instrument has finite resolution, so its recorded “speed of 500 m s^{-1} ” actually represents a bin around that value. The model probability refers to that bin. This distinction also explains why a density may be larger than one without violating probability: a density has inverse-coordinate units, whereas its area is dimensionless.

Write the thermal speed scale as

$$s = \sqrt{\frac{2k_B T}{m_{\text{mol}}}} = \sqrt{\frac{2RT}{M_m}}, \quad u = \frac{v}{s}. \quad (19.37)$$

Here s is a speed, rather than the standard deviation of the speed distribution. It equals v_{mp} . Under the change of coordinate,

$$f(v) dv = f_u(u) du, \quad f(v) = \frac{1}{s} f_u(v/s). \quad (19.38)$$

Thus both horizontal and vertical scales change. Converting a speed axis from metres per second to kilometres per second multiplies the numerical density by 1000; leaving the ordinate unchanged would divide every probability by 1000. An axis labelled only “number of molecules” does not represent the normalized probability density $f(v)$.

For a histogram, bin j has endpoints b_j, b_{j+1} , width $\Delta u_j = b_{j+1} - b_j$, and count n_j out of the complete sample of N_s molecules. The density height is

$$h_j = \frac{n_j}{N_s \Delta u_j}, \quad h_j \Delta u_j = \frac{n_j}{N_s}. \quad (19.39)$$

The right-hand side is the estimated bin probability. For unequal bins, their areas, rather than their heights, compare probabilities. A broad bin can contain more molecules while having a smaller density height. In the limit of small bins, an average density approaches the local value of f_u , but taking excessively narrow bins in a finite sample makes the statistical fluctuations prominent.

Figure 19.11 makes this distinction visible using exact integrated probabilities. The curve can pass above or below a rectangle within a bin; its net area across that entire bin equals the rectangle’s area. A midpoint approximation, $P_j \simeq f_u[(b_j + b_{j+1})/2] \Delta u_j$, is useful for sufficiently narrow bins but need not reproduce broad-bin probabilities accurately. If numerical quadrature is used instead, check refinement of the integration mesh separately from truncation of the upper integration limit. Finer spacing improves discretization error but cannot restore a tail lying outside the chosen interval. Treating the maximum plotted speed as an exact physical maximum confuses these two issues.

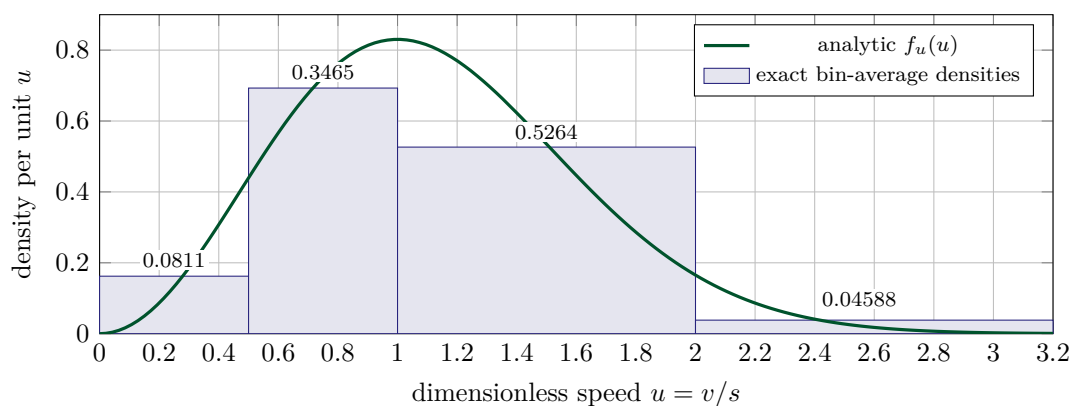


Figure 19.11: Unequal bins of the Maxwell density. Numbers above the rectangles are their dimensionless *areas*, not their heights. The bin from 1 to 2 has a larger probability than the taller rectangle from 0.5 to 1. These rectangles are analytic bin averages; they are not measured counts. Their total area is 0.999865 because the speed tail above $u = 3.2$ is outside the displayed interval.

Example 19.10: Unequal-bin probabilities

An analytic Maxwell population is grouped into bins with edges 0, 0.5, 1, 2, 3.2. Determine the bin probabilities and the corresponding density heights. Explain why the highest rectangle need not contain the largest fraction, and account for the missing area.

Solution. Integration of f_u , or evaluation of the cumulative formula developed below, gives the following results:

Interval	Width	Probability	Density height
$[0, 0.5)$	0.5	0.081109	0.162217
$[0.5, 1)$	0.5	0.346485	0.692969
$[1, 2)$	1.0	0.526395	0.526395
$[2, 3.2)$	1.2	0.045877	0.038231

Each height is its probability divided by the width. The bin from 1 to 2 contains about 52.64% of the molecules, exceeding the 34.65% in the taller bin from 0.5 to 1. A height comparison would miss the factor of two in their widths. Summing the probabilities gives 0.999865, leaving 1.34978×10^{-4} above 3.2. The full density is normalized; the graph shows a finite interval of it. Dividing the displayed bin probabilities by their sum instead would describe a *conditional* population restricted to $u < 3.2$, a different question.

19.4.4 Temperature and mass on physical speed axes

The dimensionless curve conceals neither a change of physics nor a new equilibrium law. It removes the single scale s . A physical plot restores that scale and makes clear how many metres per second the molecular speeds represent. If temperature changes by a factor a at fixed molecular mass,

$$s_{\text{new}} = \sqrt{a} s_{\text{old}}, \quad f_{\text{new}}(v) = \frac{1}{\sqrt{a}} f_{\text{old}}\left(\frac{v}{\sqrt{a}}\right). \quad (19.40)$$

The distribution moves towards larger speeds and broadens in absolute speed units. Its peak decreases because the area must remain one. Heating does not raise every ordinate of a normalized density, and no single molecule has to acquire precisely the change in mean kinetic energy. The comparison concerns equilibrated populations before and after the change; molecules exchange energy in collisions while the gas approaches the new equilibrium.

Figure 19.12 applies this transformation on the same physical axes for three temperatures. Comparing only their peak locations would miss the changes in spread and density height.

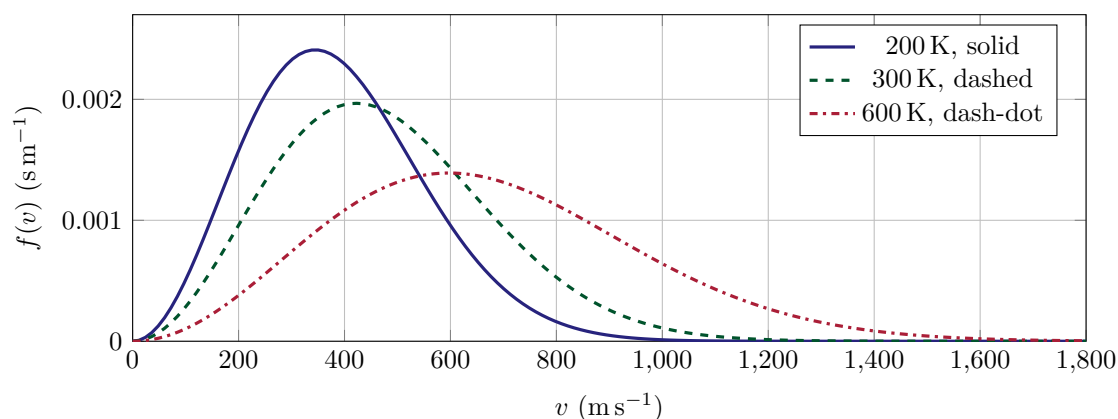


Figure 19.12: Analytic equilibrium speed densities for stipulated nitrogen with $M_m = 0.0280 \text{ kg mol}^{-1}$. Physical speed and inverse-speed axes display the temperature scaling. All full curves have unit area on $0 \leq v < \infty$; finite graph limits do not define a maximum molecular speed. Line patterns distinguish the temperatures in grayscale.

Example 19.11: Heating changes the whole speed distribution

A dilute nitrogen population with stipulated $M_m = 0.0280 \text{ kg mol}^{-1}$ reaches equilibrium at 600 K after starting at 300 K. Calculate its most probable, mean, and rms speeds at both temperatures and the change in density peak. Is the factor multiplying the mean translational energy also the factor multiplying the mean speed?

Solution. Using $R = 8.314462618 \text{ J mol}^{-1} \text{ K}^{-1}$ gives the thermal scale $s = 422.098 \text{ m s}^{-1}$ at 300 K and 596.937 m s^{-1} at 600 K. The three characteristic speeds are s , $2s/\sqrt{\pi}$, and $\sqrt{3/2}s$:

T (K)	v_{mp}	v_{mean}	v_{rms}
Speeds in m s^{-1}			
300	422.10	476.29	516.96
600	596.94	673.57	731.10

These guard digits expose the common factor $\sqrt{2}$; the stipulated molar mass warrants about three significant figures in practical answers. At $u = 1$, the density maximum is

$$f(s) = \frac{4}{\sqrt{\pi} e s}.$$

It decreases from 0.00196688 to 0.00139079 s m^{-1} , exactly the factor $1/\sqrt{2}$. The mean translational kinetic energy $3k_B T/2$ doubles. Squared speeds scale with T , whereas speeds scale with $\sqrt{T}$; doubling temperature cannot double the mean speed.

At a common temperature, the characteristic speed scales instead as $M_m^{-1/2}$. The kinetic energy distribution has the same translational mean for each species, even though the speed distributions differ. This is a comparison of gases in thermal equilibrium, with no directed bulk flow. A drifting gas requires the velocity relative to its mean flow before an equilibrium component law can be applied.

Figure 19.13 holds the temperature fixed and changes only the molecular mass, making the complementary scaling explicit. The chemical labels specify the stipulated masses rather than introduce a new probability law for each species.

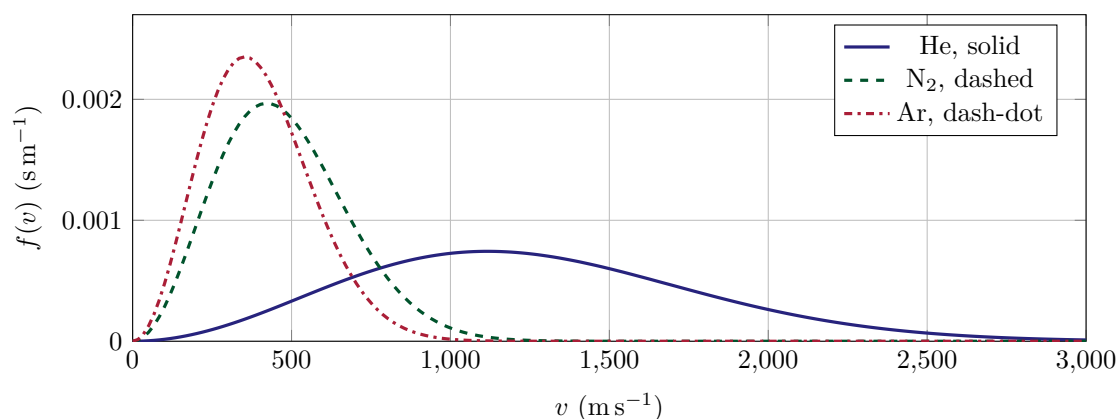


Figure 19.13: Analytic mass comparison at 300 K, using stipulated molar masses 0.00400 , 0.0280 , and $0.0400 \text{ kg mol}^{-1}$ for He, nitrogen, and Ar. The lighter species has a broader speed distribution and a lower density peak. The curves compare *probability densities*, each normalized over its full range, rather than molecule counts in samples of unequal size.

Example 19.12: Equal temperature, unequal molecular speeds

Use the masses stipulated in Fig. 19.13 to compare the rms speeds of He, nitrogen, and Ar at 300 K. Determine whether helium also has the greatest mean translational energy.

Solution. The rms formula $\sqrt{3RT/M_m}$ gives

$$v_{\text{rms}}(\text{He}) = 1368 \text{ m s}^{-1}, \quad v_{\text{rms}}(\text{N}_2) = 517.0 \text{ m s}^{-1}, \quad v_{\text{rms}}(\text{Ar}) = 432.5 \text{ m s}^{-1}.$$

The helium-to-nitrogen speed ratio is $\sqrt{0.0280/0.00400} = \sqrt{7} = 2.646$. To check the energy comparison, substitute the rms definition:

$$\langle K_{\text{tr}} \rangle = \frac{1}{2} m_{\text{mol}} \langle v^2 \rangle = \frac{1}{2} m_{\text{mol}} \frac{3k_{\text{B}}T}{m_{\text{mol}}} = \frac{3}{2} k_{\text{B}}T = 6.21292 \times 10^{-21} \text{ J}.$$

All three species share this mean energy per molecule. Helium's smaller mass compensates its larger mean squared speed. Computing $\frac{1}{2} m_{\text{mol}} v_{\text{mean}}^2$ would give a different answer because $\langle v^2 \rangle \neq \langle v \rangle^2$. The comparison concerns translation; the internal rotational and vibrational energies of nitrogen require the separate active-mode discussion later in the chapter.

19.4.5 From signed components to nonnegative speed

Before studying the full derivation in the advanced section, distinguish the objects being counted. A Cartesian velocity component can be positive or negative. At rest on average, its dimensionless value $w = v_x/s$ has the symmetric Gaussian density

$$g_w(w) = \frac{1}{\sqrt{\pi}} e^{-w^2}, \quad -\infty < w < \infty; \quad \langle w \rangle = 0, \quad \langle w^2 \rangle = \frac{1}{2}. \quad (19.41)$$

Its maximum occurs at zero. The speed $u = \sqrt{w_x^2 + w_y^2 + w_z^2}$ is nonnegative; it is not one of the components and does not obey the same density. Zero mean velocity therefore coexists with positive mean speed and finite pressure.

Figure 19.14 compares the two densities on their appropriate domains. The common vertical range helps compare their shapes, but their horizontal variables count different objects.

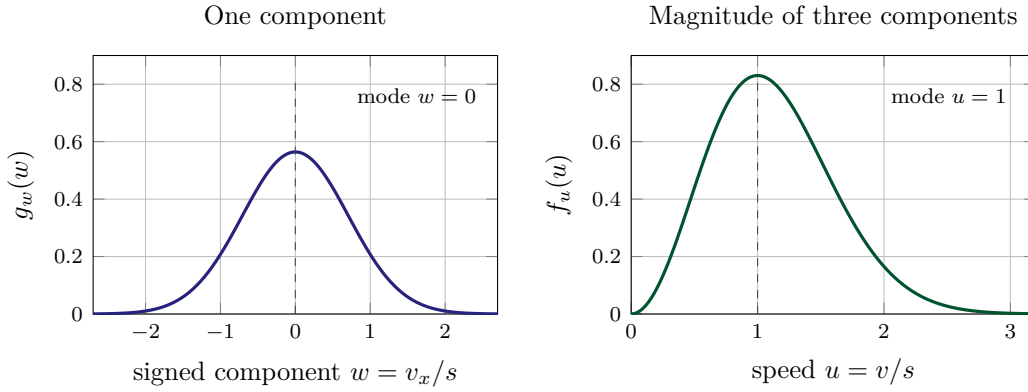


Figure 19.14: Component density and speed density are distinct even for the same equilibrium model. A signed component peaks at zero; the speed peaks away from zero. Both dimensionless densities have unit area over their own full domains. The speed curve includes the multiplicity of velocity vectors in a spherical shell; taking only the positive half of the component Gaussian would not reproduce it.

The geometric reason is that a small region around the origin in three-dimensional velocity space contains few velocity vectors, while a shell at nonzero radius includes vectors in all directions. Isotropy makes the joint density constant over a shell of fixed radius. The shell volume is $4\pi v^2 dv$, supplying the factor v^2 in the speed law. Although the Boltzmann factor decreases with increasing kinetic energy, this geometric multiplicity initially increases. Their product has an interior maximum. This explanation anticipates the detailed change of variables in the advanced section without treating the shell picture as an extra physical force on molecules.

19.4.6 Moments, spread, and the median

A distribution provides more information than a characteristic speed. Its moments weight all speeds, including the tail. A convenient integral family is

$$I_n = \int_0^\infty u^n e^{-u^2} du, \quad I_n = \frac{n-1}{2} I_{n-2} \quad (n > 1). \quad (19.42)$$

To establish the recurrence, integrate by parts with u^{n-1} as the differentiated factor and $ue^{-u^2} du = -\frac{1}{2}d(e^{-u^2})$ as the integrated factor. The boundary term vanishes at both endpoints for $n > 1$. The starting integrals are $I_0 = \sqrt{\pi}/2$ and $I_1 = 1/2$. Consequently $I_2 = \sqrt{\pi}/4$, $I_3 = 1/2$, $I_4 = 3\sqrt{\pi}/8$, and $I_6 = 15\sqrt{\pi}/16$. These values supply normalization and moments:

$$\langle u \rangle = \frac{4}{\sqrt{\pi}} I_3 = \frac{2}{\sqrt{\pi}}, \quad \langle u^2 \rangle = \frac{4}{\sqrt{\pi}} I_4 = \frac{3}{2}, \quad (19.43)$$

$$\langle u^4 \rangle = \frac{4}{\sqrt{\pi}} I_6 = \frac{15}{4}. \quad (19.44)$$

The second moment controls mean translational energy; the fourth will help assess sampling fluctuations of that energy estimate.

The speed variance measures the spread about the mean:

$$\text{Var}(u) = \langle u^2 \rangle - \langle u \rangle^2 = \frac{3}{2} - \frac{4}{\pi} = 0.2267604553, \quad \sigma_v = s \sqrt{\frac{3}{2} - \frac{4}{\pi}}. \quad (19.45)$$

The standard deviation σ_v is about $0.476194s$ and is not v_{rms} . The rms averages squares about zero; the standard deviation averages squared departures from the mean. For speeds, whose mean is positive, these operations give substantially different values. For a zero-mean component they coincide. Thus the same words “rms fluctuation” require an explicit statement of the reference mean.

The median $u_{1/2}$ divides the *area* in half:

$$\int_0^{u_{1/2}} f_u(u) du = \frac{1}{2}.$$

It is not located halfway across the horizontal extent of a drawing or halfway up the density maximum. The cumulative calculation below gives $u_{1/2} = 1.087652\dots$, so the ordering is

$$u_{\text{mp}} = 1 < u_{1/2} = 1.087652\dots < \langle u \rangle = 1.128379\dots < u_{\text{rms}} = 1.224745\dots \quad (19.46)$$

The right tail raises moment-based averages; the mode marks the local density maximum, and the median is set by an equal-area requirement. Each number answers a different question. None is the speed of every molecule, and the mode does not imply that a finite fraction have precisely $u = 1$.

19.4.7 Cumulative probabilities and high-speed tails

An antiderivative is useful when a detector counts molecules above a threshold. Define the error function locally by

$$\text{erf}(a) = \frac{2}{\sqrt{\pi}} \int_0^a e^{-t^2} dt, \quad \text{erfc}(a) = 1 - \text{erf}(a).$$

The identity $d(ue^{-u^2})/du = (1 - 2u^2)e^{-u^2}$ yields

$$F(a) = P(u \leq a) = \text{erf}(a) - \frac{2a}{\sqrt{\pi}} e^{-a^2}, \quad (19.47)$$

$$Q(a) = P(u > a) = \text{erfc}(a) + \frac{2a}{\sqrt{\pi}} e^{-a^2}. \quad (19.48)$$

Differentiation gives $F'(a) = f_u(a)$ and $Q'(a) = -f_u(a)$; $F(0) = 0$, $Q(0) = 1$, and their limiting values are 1 and 0. These checks verify the signs and normalization. A finite threshold v_c maps to $a = v_c/s$, so the probability above it is $Q(v_c/s)$.

For a very small tail, computing $1 - F(a)$ numerically can subtract two nearly equal numbers. The positive terms in the explicit $Q(a)$ formula avoid this cancellation when a numerical library evaluates erfc accurately. A logarithmic tail plot also makes small probabilities visible that appear almost indistinguishable from zero on the cumulative plot. It does not create a sharp speed cutoff: the classical Maxwell law has nonzero probability at every finite positive speed. At relativistic temperatures or energies this classical nonrelativistic law requires replacement rather than extrapolation.

Figure 19.15 uses both an ordinary cumulative plot and a logarithmic survival plot to answer the same interval question. The two ordinates add to one at a given threshold, despite their different visual scales.

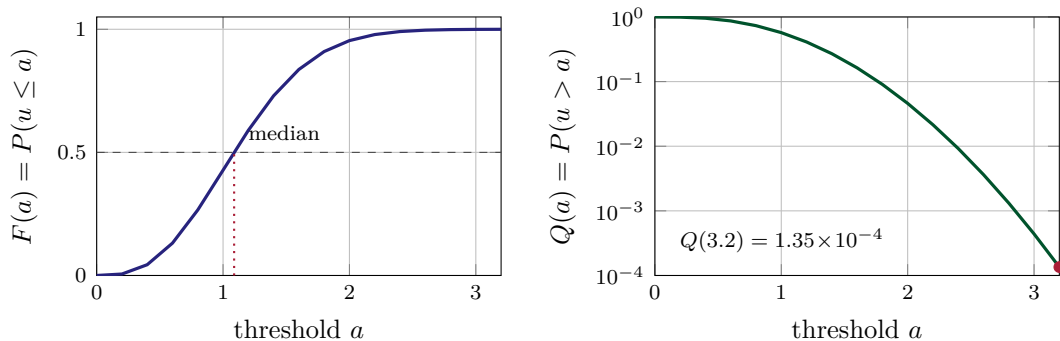


Figure 19.15: Analytic cumulative probability (left) and survival probability (right), evaluated at the inline tabulated thresholds. The right ordinate is logarithmic. The median is the threshold at cumulative area 1/2. The small tail above 3.2 is easily missed by looking only at the nearly unit-height cumulative curve. Lines connect computed model values and are not fits to measurements.

Example 19.13: Spread, median, and a detector threshold

For nitrogen at 300 K with the stipulated molar mass $0.0280 \text{ kg mol}^{-1}$, calculate the speed standard deviation and median. Find the equilibrium fraction above 1000 m s^{-1} and the expected count in an ideal independent sample of one million molecules. State how a plot ending at $u = 3.2$ affects normalization.

Solution. With $s = 422.098 \text{ m s}^{-1}$, the variance formula gives $\sigma_v = 0.476194s = 201.001 \text{ m s}^{-1}$. Numerical solution of $F(u_{1/2}) = 1/2$ gives $u_{1/2} = 1.087652$, hence $v_{1/2} = 459.096 \text{ m s}^{-1}$. These are below the rms speed 516.963 m s^{-1} and answer different questions about the distribution. The threshold is $a = 1000/422.098 = 2.369116$. Substitution in Eq. (19.48) gives $Q(a) = 0.01056735$, about 1.057%. The expected count is therefore $10^6 Q(a) = 10567.4$. An actual count fluctuates: the binomial standard deviation is $\sqrt{10^6 Q(a)[1 - Q(a)]} = 102.3$ molecules. The expectation is not a guarantee of that exact count. For comparison, at 600 K the same physical threshold has a smaller by $\sqrt{2}$, and the fraction increases to 0.132051, about 13.21%. At the finite plotting cutoff $u = 3.2$, the omitted analytic probability is $Q(3.2) = 0.0001349782$. Thus the plotted analytic area is 0.9998650218 rather than one. Neither truncating the graph nor changing its vertical range eliminates that tail physically. Renormalizing the visible curve would replace the full population law with a conditional law and must be stated explicitly.

19.4.8 A reproducible synthetic sample and its uncertainty

A simulation tests whether a stated numerical construction behaves like the analytic model. It is not independent experimental evidence for the Maxwell law. Here the construction uses three independent zero-mean Gaussian components, each with dimensionless standard deviation $1/\sqrt{2}$, and computes their vector magnitude. The random-generator seed selects a reproducible numerical realization. It does not remove the finite-sample uncertainty of the estimator.

The declared realization uses NumPy's `Generator(PCG64(1904))`, the `normal` method, and an 8000×3 array filled in row order. The numbers below were reproduced using NumPy 2.3.5. Stating the generator and the order of draws matters: a different random generator, or generating three separate arrays instead of one array, need not produce the same realization. The analytic targets remain unchanged. The essential construction is

```
import numpy as np
rng = np.random.Generator(np.random.PCG64(1904))
xyz = rng.normal(0.0, 1/np.sqrt(2), size=(8000, 3))
u = np.sqrt(np.sum(xyz*xyz, axis=1))
edges = np.arange(17)*0.2
counts, _ = np.histogram(u, bins=edges)
density = counts/(len(u)*np.diff(edges))
print(u.mean(), np.mean(u*u), np.sqrt(np.mean(u*u)))
print(counts, np.count_nonzero(u > 3.2))
```

This code is explanatory and optional; all data needed to typeset the plots are already inside this chapter. A histogram library's `density=True` setting may normalize only the observations inside the provided bin range. The explicit full-count denominator above keeps the three excluded observations visible in the normalization accounting. The final histogram bin includes its upper edge under NumPy's convention; the continuous model assigns zero probability to that edge alone.

Figure 19.10 displays the declared realization with areas that match the count normalization. Plotting bars with a fixed width in typographic points would break this connection when the graph is resized: the counted interval is a width in the speed coordinate, rather than a width on the printed page. Rectangles whose endpoints are the actual bin edges preserve that meaning under resizing. An independent sample produced with a different seed should fluctuate around the same

curve, while its detailed bars will differ. Agreement is judged by the declared distribution and uncertainties, not by a requirement to match this particular pattern of bar heights.

Why require moments as well as a graph? The mean of u tests one weighted integral, and the mean of u^2 tests the energy scale. A sample can look smooth while using the wrong component variance or a wrong normalization. Here the exact targets are $2/\sqrt{\pi}$ and $3/2$. For independent samples, the theoretical standard errors are

$$\text{SE}(\bar{u}) = \sqrt{\frac{3/2 - 4/\pi}{N_s}}, \quad \text{SE}(\overline{u^2}) = \sqrt{\frac{\langle u^4 \rangle - \langle u^2 \rangle^2}{N_s}} = \sqrt{\frac{3/2}{N_s}}. \quad (19.49)$$

Independence makes the variance of a sample mean equal to the individual variance divided by N_s . These expressions quantify expected fluctuations; they are not deterministic bounds on every realization. Correlated sampling would change this uncertainty estimate and must be examined rather than assumed away.

Example 19.14: Verifying the synthetic experiment

Check normalization, the mean speed, the mean squared speed, and the tail count for the declared 8000-molecule sample. Assess its agreement with the analytic targets using the standard errors.

Solution. The bin counts, in order from 0 to 3.2, are

$$47, 284, 742, 1072, 1336, 1277, 1099, 843, 572, 355, 213, 82, 45, 19, 10, 1.$$

Their sum is 7997. Dividing each by 8000×0.2 gives the inline histogram heights; multiplying each height by 0.2 and summing gives 0.999625. Adding the three excluded observations restores one. Using the full observations, including those three, gives

$$\bar{u} = 1.124651083, \quad \overline{u^2} = 1.491405409, \quad \sqrt{\overline{u^2}} = 1.221231104.$$

The mean has standard error 0.00532401; its departure from 1.128379167 is -0.7002 standard errors. The mean squared speed has standard error 0.0136931; its departure from 1.5 is -0.6277 standard errors. Both differences are ordinary finite-sample fluctuations for this stated independent model. The unbiased sample speed variance is 0.2265937, consistent in scale with the analytic 0.2267605.

The analytic expected number above 3.2 is $8000Q(3.2) = 1.07983$. An observed count of three is possible because an expected count is an average over repeated experiments. The binomial tail is approximately described here by a Poisson law of mean 1.07983; its probability of at least three is about 0.096. Thus three outlying speeds do not contradict the model. A reproducibility test compares the actual counts with the declared realization, while a statistical model test compares estimators with their appropriate uncertainty.

The first 100, 500, 2000, and 8000 rows of the same generated array provide one illustration of sample-size dependence:

N_s	$\bar{u}$	$\overline{u^2}$	SE of $\bar{u}$	SE of $\overline{u^2}$
100	1.066231	1.319430	0.047619	0.122474
500	1.087790	1.375617	0.021296	0.054772
2000	1.116754	1.464816	0.010648	0.027386
8000	1.124651	1.491405	0.005324	0.013693

All entries are synthetic, dimensionless, and drawn from nested prefixes, so the four rows are not independent repeated experiments. The standard errors decrease as $N_s^{-1/2}$. These particular

estimates move closer to their targets, but another sequence can overshoot or temporarily move away. Convergence of a sampling method does not imply monotonic improvement after every additional molecule. When comparing generators or physical models, use repeated independent realizations or a justified uncertainty calculation, alongside dimensional and normalization checks. The verified distribution now supplies the average speed needed to interpret collision estimates in the next section.

19.5 Mean free path and collisions

The ideal-gas equation of state can work well while molecules are colliding billions of times per second. The mean free path is a model-dependent average distance travelled between collisions.

19.5.1 Collision cross-section

Model identical molecules as hard spheres of collision diameter d . A collision occurs if the centre of another molecule passes within a transverse distance d of the chosen molecule's centre. If all other molecules were fixed, a moving molecule would sweep a collision cylinder with cross-sectional area

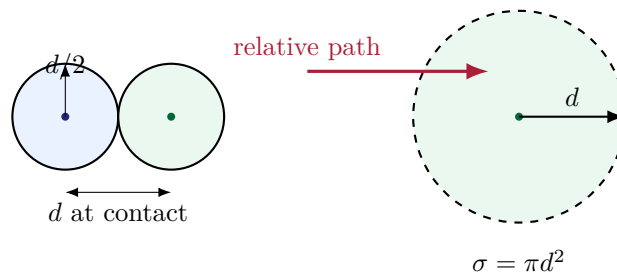
$$\sigma = \pi d^2. \quad (19.50)$$

For number density $n_N = N/V$, the stationary-background estimate would be $\ell_0 = 1/(n_N \sigma)$. In an equilibrium gas, the other molecules move too. The relative-motion correction for identical particles with a Maxwellian velocity distribution gives

$$\ell_{\text{mfp}} = \frac{1}{\sqrt{2} n_N \pi d^2}. \quad (19.51)$$

The factor $\sqrt{2}$ is therefore not a purely geometric factor. It belongs to this dilute identical hard-sphere equilibrium model.

(a) Two molecular spheres (b) Encounter disk in relative motion



A molecular centre passes within distance d of the other centre.
The encounter disk is not the physical surface of one molecule.

Figure 19.16: Hard-sphere collision geometry for identical molecular diameter d . The exclusion distance between two centres is d , so the disk swept in relative motion has radius d and area πd^2 . Panel (b) is a cross-sectional construction, rather than the projected physical size of one molecule.

19.5.2 Collision time and continuum scale

A characteristic time between collisions requires a specified characteristic speed. For example,

$$\tau_{\text{coll}} \approx \frac{\ell_{\text{mfp}}}{v_*}, \quad (19.52)$$

where v_* might be the mean or rms speed, as long as the choice is stated. The dimensionless ratio

$$\text{Kn} = \frac{\ell_{\text{mfp}}}{L} \quad (19.53)$$

compares molecular collision scale with a macroscopic length L . It is useful for judging whether a continuum description is plausible, though a full rarefied-gas theory is beyond this chapter.

Example 19.15: Collision scales in a stipulated gas

Take $n_N = 2.50 \times 10^{25} \text{ m}^{-3}$ and collision diameter $d = 3.70 \times 10^{-10} \text{ m}$ as stipulated model parameters. Then

$$\ell_{\text{mfp}} = \frac{1}{\sqrt{2}(2.50 \times 10^{25})\pi(3.70 \times 10^{-10})^2} = 6.58 \times 10^{-8} \text{ m}.$$

With a chosen characteristic speed $v_* = 500 \text{ m s}^{-1}$,

$$\tau_{\text{coll}} \approx 1.32 \times 10^{-10} \text{ s}.$$

For a vessel scale $L = 1.0 \text{ mm}$, $\text{Kn} = 6.6 \times 10^{-5}$. Doubling number density halves ℓ_{mfp} ; doubling the collision diameter divides it by four. These scalings are stronger evidence of correct use of Eq. (19.51) than a single numerical value.

19.5.3 A moving target and an ensemble collision frequency

The stationary-background cylinder is a useful geometric starting point, but an equilibrium gas contains moving targets. The relevant speed for a binary encounter is the relative speed $g = |\mathbf{v}_1 - \mathbf{v}_2|$, not the laboratory speed of either molecule. For independent identical Maxwellian molecules, each component of the difference has twice the variance of one component. Thus the relative velocity is itself Gaussian, with thermal scale larger by $\sqrt{2}$, and

$$\langle g \rangle = \sqrt{2} v_{\text{mean}}, \quad \nu_{\text{coll}} = n_N \sigma \langle g \rangle = \sqrt{2} n_N \pi d^2 v_{\text{mean}}. \quad (19.54)$$

Here ν_{coll} is the number of collision participations per molecule per unit time, averaged over the equilibrium population. The collision rate for the whole gas is $N\nu_{\text{coll}}/2$: each binary encounter has two participating molecules, so counting participations without dividing by two counts every event twice.

The usual mean-free-path convention is the total distance travelled by all molecules divided by the total number of collision participations during a long sampling time. It therefore gives

$$\ell_{\text{mfp}} = \frac{v_{\text{mean}}}{\nu_{\text{coll}}} = \frac{1}{\sqrt{2} n_N \pi d^2}.$$

Likewise the mean time per participation is $1/\nu_{\text{coll}} = \ell_{\text{mfp}}/v_{\text{mean}}$ in this ensemble convention. An individual fast molecule has a different collision rate from a slow one. Consequently the mean of its speed-conditioned flight time is not obtained by casually replacing every molecular speed with v_{rms} . The earlier ℓ_{mfp}/v_* estimate is a characteristic time; choosing $v_* \neq v_{\text{mean}}$ changes its meaning.

Figure 19.17 separates the geometric target from the motion that sets the rate. Relative velocity components add statistically in quadrature; this is the origin of the $\sqrt{2}$ correction. It is neither the diameter of a sphere nor an extra factor in the elastic impulse.

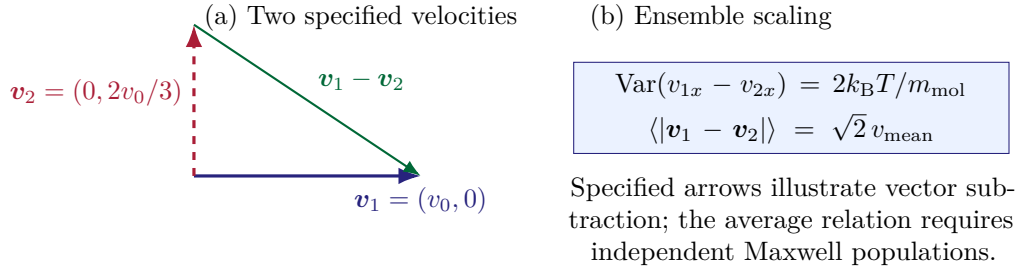


Figure 19.17: Relative motion for collisions. The left panel uses equal physical scales on both axes; the right panel concerns ensemble variances and is not an inference from those two selected arrows.

Example 19.16: Collision events versus participations

A stipulated equilibrium gas has $N = 1.00 \times 10^{20}$ molecules, $n_N = 2.50 \times 10^{25} \text{ m}^{-3}$, $d = 3.70 \times 10^{-10} \text{ m}$, and $v_{\text{mean}} = 500 \text{ m s}^{-1}$. Find the molecular collision frequency, ensemble collision time, and number of distinct binary collisions per second.

The collision cross-section is $\sigma = \pi d^2 = 4.301 \times 10^{-19} \text{ m}^2$. Its area, rather than its square root, enters the rate. Using Eq. (19.54),

$$\nu_{\text{coll}} = \sqrt{2}(2.50 \times 10^{25})(4.301 \times 10^{-19})(500) = 7.60 \times 10^9 \text{ s}^{-1}.$$

Thus $\tau = 1/\nu_{\text{coll}} = 1.32 \times 10^{-10} \text{ s}$. The distinct event rate is

$$\dot{N}_{\text{events}} = \frac{1}{2} N \nu_{\text{coll}} = 3.80 \times 10^{29} \text{ s}^{-1}.$$

As a check, $v_{\text{mean}} \tau = 6.58 \times 10^{-8} \text{ m}$, matching the independently obtained mean free path. The enormous event rate describes a population of many particles; it does not imply that one molecule collides 10^{29} times per second.

19.5.4 Diluteness, collision length, and device length

There are several different length scales in a gas. The particle diameter d is a collision-model parameter. The characteristic intermolecular separation is $a = n_N^{-1/3}$; it is the side of a cube whose expected particle count is one, not a regular lattice spacing. The mean free path ℓ_{mfp} is the distance accumulated between collision participations. The device length L might be a channel height, a vessel diameter, or a distance over which a flow changes appreciably. These quantities answer different questions.

The small parameter $n_N d^3$ is a useful dilute-packing indicator for the hard-sphere model. If it is small, the molecular size is small compared with the typical separation. The continuum question instead concerns ℓ_{mfp}/L . A gas may be dilute enough to obey the ideal-gas equation yet be too rarefied relative to a tiny channel for a conventional continuum boundary condition. Conversely, a large vessel can have a small Knudsen number even when molecular collisions occur extremely frequently.

At fixed absolute temperature, the ideal equation of state gives $n_N = p/(k_B T)$, hence

$$\ell_{\text{mfp}} = \frac{k_B T}{\sqrt{2} \pi d^2 p}. \quad (19.55)$$

This scaling assumes a fixed effective collision diameter. It is not a universal law for a real gas across arbitrary temperature ranges. The diagram in Fig. 19.18 shows exactly the stipulated model and separates the pressure dependence from the two choices of channel height.

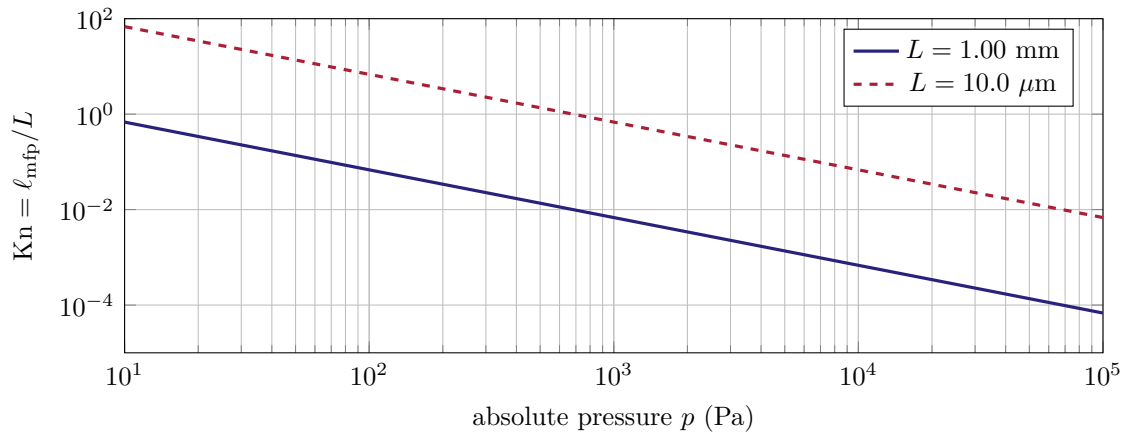


Figure 19.18: Mean-free-path to device-length ratio in a stipulated hard-sphere gas at $T = 300$ K and $d = 0.370$ nm. Both straight lines have logarithmic slope -1 ; reducing the device length by a factor of 100 raises the ratio by 100. No universal regime threshold is inferred from this plot.

Example 19.17: An ideal gas in two channel sizes

Take $T = 300$ K, $p = 100$ kPa and $d = 0.370$ nm. Find n_N , a , ℓ_{mfp} , and the Knudsen numbers for $L = 1.00$ mm and $L = 10.0$ μm . Explain which smallness test concerns packing and which concerns continuum scale.

The equation of state yields $n_N = p/(k_B T) = 2.414 \times 10^{25} \text{ m}^{-3}$. Therefore

$$a = n_N^{-1/3} = 3.46 \text{ nm}, \quad n_N d^3 = 1.22 \times 10^{-3}, \quad \ell_{\text{mfp}} = 68.1 \text{ nm}.$$

The small packing parameter is consistent with a dilute hard-sphere model. The mean free path is about $19.7a$; a molecule need not collide whenever it traverses one characteristic separation, because most neighbours are outside its collision cylinder. For the two devices,

$$\text{Kn}_{1\text{mm}} = 6.81 \times 10^{-5}, \quad \text{Kn}_{10\mu\text{m}} = 6.81 \times 10^{-3}.$$

The gas state and collision length have not changed. Only the distance over which a continuum description is being attempted has changed. At $p = 100$ Pa, both Knudsen numbers would be 1000 times larger under the same stipulated T, d model. This inverse-pressure scaling is a useful check on the logarithmic plot.

19.5.5 A limited transport estimate

Collisions redistribute momentum and energy, so kinetic theory motivates a simple estimate of diffusion. In an idealized random-flight model, suppose fixed-length steps ℓ occur every τ , with independent isotropic directions and no drift. After j steps the displacement is the vector sum of the steps. Cross terms average to zero, since independent directions have zero mean. Thus $\langle r^2 \rangle = j\ell^2$. At times $t = j\tau$, comparing with the diffusion definition $\langle r^2 \rangle = 6Dt$ gives $D = \ell^2/(6\tau)$.

This coefficient belongs to the fixed-step model. Molecular free paths have a distribution and correlated dynamics; the commonly used kinetic estimate $D \sim v_{\text{mean}}\ell_{\text{mfp}}/3$ involves different assumptions and must not be claimed as an exact consequence of the fixed-step calculation. The point of the estimate is the separation between fast microscopic speeds and slow macroscopic mixing. Net displacement grows like the square root of the number of random steps while path length grows in proportion to that number. This section is a qualitative transport connection, not a full derivation of gas viscosity or thermal conductivity.

19.6 Heat capacities and equipartition

Equation (19.24) accounts only for translation. Molecules can also rotate and vibrate. Classical equipartition provides a useful limiting model, but it must be used conditionally.

19.6.1 Quadratic energy terms

For a classical degree of freedom that appears quadratically in the energy and is thermally active, equipartition assigns a mean contribution $\frac{1}{2}k_B T$ per molecule. If f_q independent quadratic terms are active,

$$E_{\text{int}} = \frac{f_q}{2} N k_B T = \frac{f_q}{2} n R T. \quad (19.56)$$

If f_q is effectively constant over the temperature range of interest,

$$C_{V,m} = \frac{1}{n} \left(\frac{\partial E_{\text{int}}}{\partial T} \right)_V = \frac{f_q}{2} R. \quad (19.57)$$

Three translational kinetic terms give $f_q = 3$ for a monatomic classical ideal gas. A linear rigid molecule has two important rotational kinetic terms in the simplest classical model, raising f_q to 5. One harmonic vibrational mode contains both kinetic and potential quadratic contributions, so when that vibration is fully active it adds two more terms.

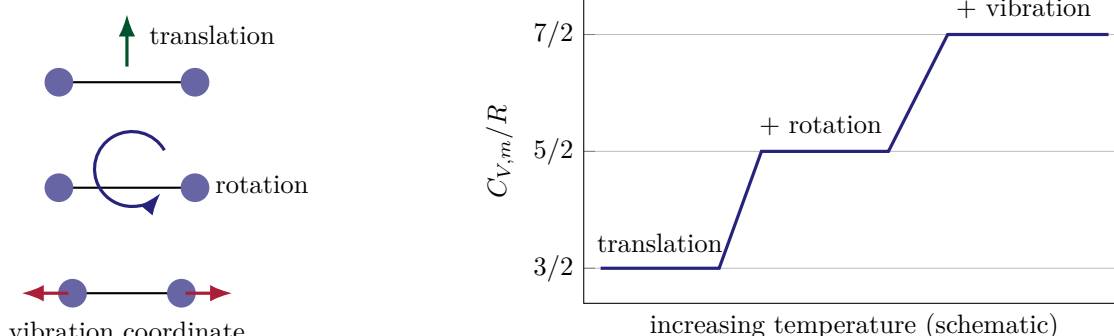


Figure 19.19: Molecular-mode bookkeeping and an idealised classical heat-capacity plateau model. The right panel is a schematic model, not measured data and not a universal temperature calibration. Quantum energy spacing can suppress rotational or vibrational contributions until the corresponding modes become thermally accessible.

19.6.2 Why $C_{p,m} - C_{V,m} = R$ for an ideal gas

For a quasi-static constant-pressure heating of a closed ideal gas, the first law gives

$$\delta Q = dE_{\text{int}} + p dV.$$

With $dE_{\text{int}} = nC_{V,m} dT$ and $p dV = nR dT$ at constant p ,

$$nC_{p,m} dT = nC_{V,m} dT + nR dT, \quad (19.58)$$

so

$$\boxed{C_{p,m} - C_{V,m} = R.} \quad (19.59)$$

The result is an ideal-gas relation; it is not a universal statement for condensed matter.

Example 19.18: Diagnose degree counting for model molecules

Use classical active-term counting to compare three model limits.

Model limit	f_q	$C_{V,m}/R$	$\gamma = C_{p,m}/C_{V,m}$
monatomic translation only	3	3/2	5/3
linear molecule, translation + rotation	5	5/2	7/5
linear molecule + one fully active vibration	7	7/2	9/7

Numerically, with $R = 8.314462618 \text{ J mol}^{-1} \text{ K}^{-1}$, the corresponding $C_{V,m}$ values are 12.47, 20.79, and 29.10 $\text{J mol}^{-1} \text{ K}^{-1}$.

The calculation is a model diagnosis, not a rule for reading real-gas heat capacity directly from chemical formula. Quantum energy spacings determine whether rotation or vibration is appreciably populated at a given temperature. A “frozen” mode is a limitation of the classical equipartition prediction, not a claim that the classical term is merely a smaller fraction of $k_B T$.

19.6.3 Heat capacity is a derivative, not an energy count

A heat capacity describes how rapidly internal energy changes with temperature. It is therefore a local property: its value at one temperature need not describe a large interval. For a fixed amount of a classical ideal gas whose molecular composition stays unchanged,

$$\Delta E_{\text{int}} = n \int_{T_i}^{T_f} C_{V,m}(T) dT. \quad (19.60)$$

The subscript V identifies the derivative used to define $C_{V,m}$. It does not mean that the actual process between these temperatures must have constant volume. For an ideal gas, internal energy depends on temperature alone; the same integral gives its change during a piston motion. In a rigid vessel, however, boundary work vanishes and this energy change also equals the heat entering the gas, provided no other work mode is present.

The constant- f_q result derived above follows by differentiating $nRTf_q/2$ while holding f_q fixed. The qualification matters near the activation of an internal molecular mode. Simply replacing f_q by a temperature-dependent “number of active terms” is not a derivation of the heat capacity. If someone proposes the heuristic energy expression $E_{\text{int}}(T) = nRTf(T)/2$, its actual derivative is

$$\frac{1}{n} \frac{dE_{\text{int}}}{dT} = \frac{R}{2} \left[f(T) + T \frac{df}{dT} \right], \quad (19.61)$$

including the second term. A partially activated quantum mode cannot generally be represented by a fractional classical term without specifying its energy model. For calculations in this chapter, either use a justified constant-capacity regime or prescribe $C_{V,m}(T)$ explicitly and integrate it.

Figure 19.20 illustrates why a sharp jump between classical plateaus is a teaching simplification. Molecular energies are quantized, and thermal populations change over a temperature interval. A low population of excited levels makes their contribution to the energy derivative small; it does not establish that every molecule has exactly zero energy in that mode. The classical limits remain useful, but an actual gas may liquefy, dissociate, or depart from ideal behavior before a proposed extreme-temperature limit can be reached. No molecular transition temperature is inferred from this schematic curve.

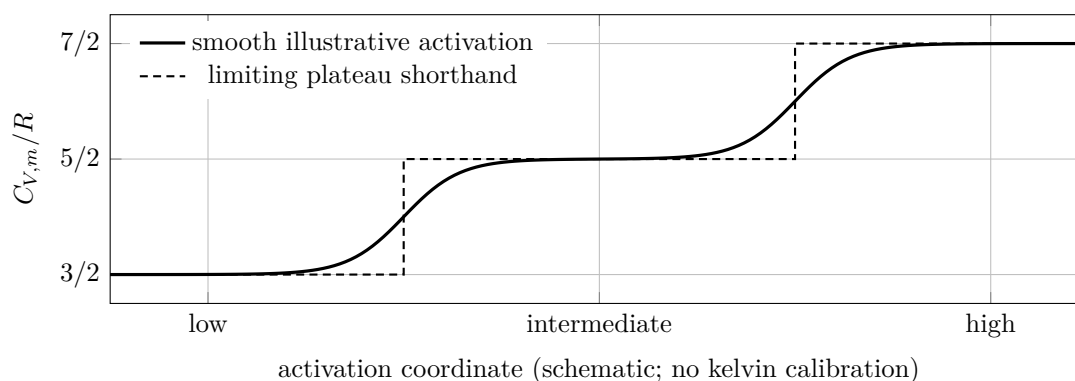


Figure 19.20: A smooth heat-capacity activation sketch compared with an abrupt plateau shorthand. The smooth curve is the explicitly chosen drawing function $3/2 + [1 + e^{-7(s-1)}]^{-1} + [1 + e^{-7(s-3)}]^{-1}$, with dimensionless coordinate s . It is neither a measured curve nor a molecular quantum calculation. Its purpose is to separate classical limiting values from the unspecified transition regions.

Example 19.19: Heating with a prescribed variable heat capacity

A sealed one-mole ideal-gas teaching model has

$$C_{V,m}(T) = R \left(\frac{5}{2} + \frac{T}{1500 \text{ K}} \right), \quad 300 \text{ K} \leq T \leq 600 \text{ K}.$$

Determine the internal-energy increase and the heat needed in a rigid vessel. Find the interval-average molar heat capacity, and compare constant-pressure heating through the same temperatures. The capacity formula is stipulated synthetic input, not a material-property fit.

Strategy and solution. Because the capacity changes, integrate it rather than choosing one endpoint:

$$\Delta E_{\text{int}} = nR \left[\frac{5}{2}(T_f - T_i) + \frac{T_f^2 - T_i^2}{3000 \text{ K}} \right].$$

The square-temperature term divided by kelvin has units of kelvin. With $n = 1.00 \text{ mol}$, the bracket is $750 \text{ K} + 90 \text{ K} = 840 \text{ K}$, giving

$$\Delta E_{\text{int}} = 6.984 \text{ kJ}, \quad Q_V = 6.984 \text{ kJ}.$$

The average capacity is $\Delta E_{\text{int}}/[n(T_f - T_i)] = 2.80R = 23.28 \text{ J mol}^{-1}\text{K}^{-1}$. Here the midpoint capacity happens to equal the average because the stipulated function is linear. The initial value $2.70R$ would underestimate the energy by 0.2494 kJ ; the final value $2.90R$ would overestimate it by the same amount.

For reversible constant-pressure heating, $C_{p,m}(T) = C_{V,m}(T) + R$ at every temperature. Thus

$$Q_p = \Delta E_{\text{int}} + nR(T_f - T_i) = 6.984 \text{ kJ} + 2.494 \text{ kJ} = 9.478 \text{ kJ}.$$

The additional heat supplies expansion work. Both processes connect temperatures with the same internal-energy change, while the heat differs because the volume constraint differs. An energy formula obtained by multiplying the endpoint capacity by temperature would fail this derivative-based check.

19.6.4 A closed piston, enthalpy, and the choice of units

At constant external pressure, a freely moving, frictionless piston gives a concrete meaning to the extra R in $C_{p,m} - C_{V,m}$. During a reversible quasi-static heating, mechanical balance keeps the gas pressure equal to the external pressure to the accuracy of the limiting model. The gas must both

increase its internal energy and lift the load. In contrast, a clamped piston lets the gas pressure increase without any piston displacement. Figure 19.21 makes the chosen system and the work direction explicit.

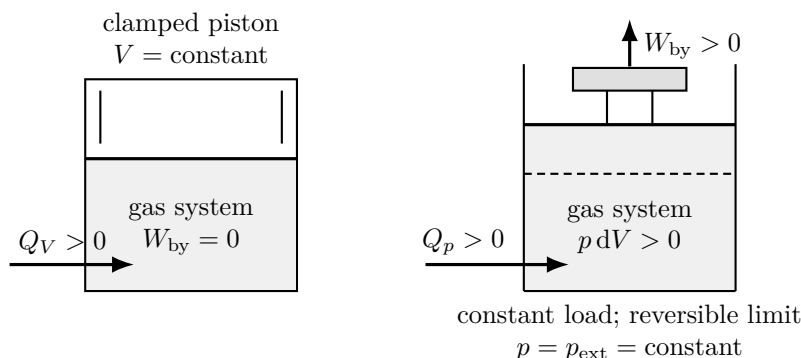


Figure 19.21: The same positive temperature change under two constraints. The gas is the closed system. The clamped piston gives zero boundary work; the constant-load piston moves upward, so work by the gas is positive. The dashed piston level on the right marks an earlier position, not a second boundary. Energy-flow arrows are schematic.

For the closed piston system, define the state function called enthalpy by $H = E_{\text{int}} + pV$. Its differential is

$$dH = dE_{\text{int}} + p dV + V dp.$$

When $dp = 0$ and reversible pressure-volume work is the only work mode, the first law makes $\delta Q_p = dH$. For an ideal gas, $pV = nRT$, so

$$H(T) = E_{\text{int}}(T) + nRT, \quad C_{p,m}(T) = \frac{1}{n} \frac{dH}{dT} = C_{V,m}(T) + R.$$

Enthalpy is useful bookkeeping for constant-pressure heat input; this derivation involves a closed gas sample, and does not assume flowing gas. Heating by an electrical element would require that electrical work be distinguished from heat transfer across the boundary. Neither $Q = \Delta H$ nor $Q = \Delta E_{\text{int}}$ should be applied without checking the relevant constraints and work modes.

The chapter's $C_{V,m}$ and $C_{p,m}$ are *molar* capacities. If the gas has molar mass M_m in kg mol^{-1} , its mass-specific capacities are

$$c_V = \frac{C_{V,m}}{M_m}, \quad c_p = \frac{C_{p,m}}{M_m}, \quad c_p - c_V = \frac{R}{M_m}. \quad (19.62)$$

Their units are $\text{J kg}^{-1} \text{K}^{-1}$. The ratio $c_p/c_V = C_{p,m}/C_{V,m}$ is unchanged by this conversion, whereas the difference is not numerically R . The total capacity of a sample is $nC_{V,m} = m_{\text{gas}}c_V$ and has units J K^{-1} . Keeping the amount, total mass, and one-molecule mass distinct prevents an otherwise plausible factor-of-a-thousand mistake.

Example 19.20: Molar and mass descriptions of a loaded piston

A closed ideal monatomic model gas has $n = 0.150$ mol and stipulated molar mass $M_m = 0.0400$ kg mol^{-1} . It warms reversibly from 280 to 360 K beneath a constant load maintaining $p = 120$ kPa. Find its mass-specific capacities, volume change, work, internal-energy increase, and heat input. Compare the heat with clamped-piston heating through the same temperature interval.

Model and method. Translation is the only active energy contribution; $C_{V,m} = 3R/2$ and

$C_{p,m} = 5R/2$ stay constant. The sample mass is $m_{\text{gas}} = nM_m = 0.00600$ kg. Therefore

$$c_V = 311.8 \text{ J kg}^{-1}\text{K}^{-1}, \quad c_p = 519.7 \text{ J kg}^{-1}\text{K}^{-1}.$$

The ideal-gas law gives $V_i = 2.910 \times 10^{-3} \text{ m}^3$ and $V_f = 3.742 \times 10^{-3} \text{ m}^3$. Hence

$$\Delta V = 8.314 \times 10^{-4} \text{ m}^3, \quad W_{\text{by}} = p\Delta V = nR\Delta T = 99.77 \text{ J},$$

$$\Delta E_{\text{int}} = nC_{V,m}\Delta T = 149.66 \text{ J}, \quad Q_p = \Delta E_{\text{int}} + W_{\text{by}} = 249.43 \text{ J}.$$

The mass calculation gives the same $\Delta E_{\text{int}} = m_{\text{gas}}c_V\Delta T$. Positive heat is split between increased internal energy and positive work by the gas, consistently with the right panel of Fig. 19.21. Clamping the piston changes the pressure history and gives $Q_V = 149.66 \text{ J}$, with no boundary work. Its final pressure would be $120(360/280) = 154.3 \text{ kPa}$, so the two final states have equal temperature but different volume and pressure.

19.7 Adiabatic ideal-gas processes

An adiabatic process has $Q = 0$. That statement alone does not imply a unique pressure–volume curve. The familiar power law requires a more specific model: a closed ideal gas, a reversible quasi-static change, and heat capacities treated as constant over the interval.

19.7.1 Derivation with the chapter sign convention

For the stated model, the first law in differential form is

$$dE_{\text{int}} = \delta Q - \delta W_{\text{by}}. \quad (19.63)$$

Adiabatic means $\delta Q = 0$, and reversible quasi-static boundary work gives $\delta W_{\text{by}} = p dV$. With $dE_{\text{int}} = nC_{V,m} dT$,

$$nC_{V,m} dT = -p dV. \quad (19.64)$$

Using $p = nRT/V$,

$$C_{V,m} \frac{dT}{T} = -R \frac{dV}{V}. \quad (19.65)$$

Since $R/C_{V,m} = \gamma - 1$ for an ideal gas,

$$\frac{dT}{T} = -(\gamma - 1) \frac{dV}{V}. \quad (19.66)$$

Integration gives

$$\boxed{TV^{\gamma-1} = \text{constant}.} \quad (19.67)$$

Combining with $pV = nRT$ gives

$$\boxed{pV^{\gamma} = \text{constant}.} \quad (19.68)$$

These equations inherit every condition used in the derivation.

19.7.2 Isothermal, reversible adiabatic, and free-expansion limits

For a reversible isothermal ideal-gas process,

$$W_{\text{by}} = nRT \ln \frac{V_f}{V_i}. \quad (19.69)$$

For the reversible adiabatic process with constant γ ,

$$W_{\text{by}} = \frac{p_i V_i - p_f V_f}{\gamma - 1}. \quad (19.70)$$

During compression $V_f < V_i$, both expressions are negative: the gas does negative work while the surroundings do positive work on it.

A free expansion into vacuum is a different adiabatic process. For a thermally insulated rigid outer container, $Q = 0$ and the boundary work on the vacuum is zero. For an ideal gas, $\Delta E_{\text{int}} = 0$ then implies no change in temperature. The initial and final equilibrium states can be plotted, but there is no justified equilibrium $p(V)$ curve connecting them during the irreversible expansion.

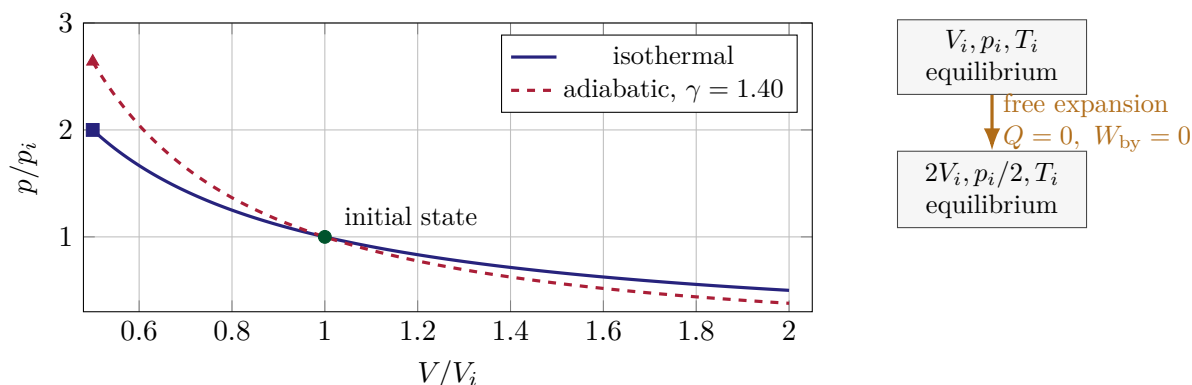


Figure 19.22: Two equilibrium compression paths from the same initial state and, separately, an irreversible free-expansion endpoint comparison. For compression to $V_f = V_i/2$, the reversible adiabatic pressure rises more steeply than the isothermal pressure. The free-expansion arrow is not a $p(V)$ process curve.

Example 19.21: Two compression limits from the same initial state

One mole of a stipulated ideal gas starts at $T_i = 300$ K and $p_i = 100$ kPa. Take $\gamma = 1.40$ with constant heat capacities and compress to $V_f = V_i/2$.

The initial volume is

$$V_i = \frac{RT_i}{p_i} = 2.494 \times 10^{-2} \text{ m}^3.$$

Isothermal reversible limit. $T_f = 300$ K and $p_f = 200$ kPa. The work by the gas is

$$W_{\text{by}} = RT_i \ln(1/2) = -1.73 \text{ kJ}.$$

For an ideal gas at fixed temperature, $\Delta E_{\text{int}} = 0$, so $Q = W_{\text{by}} = -1.73$ kJ: heat leaves the gas during the compression.

Reversible adiabatic limit.

$$T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1} = 395.9 \text{ K}, \quad p_f = p_i \left(\frac{V_i}{V_f} \right)^{\gamma} = 263.9 \text{ kPa}.$$

Here $Q = 0$. Since $C_{V,m} = R/(\gamma - 1) = 20.79 \text{ J mol}^{-1} \text{ K}^{-1}$,

$$\Delta E_{\text{int}} = nC_{V,m}(T_f - T_i) = +1.99 \text{ kJ}, \quad W_{\text{by}} = -1.99 \text{ kJ}.$$

The first-law residual $\Delta E_{\text{int}} - (Q - W_{\text{by}})$ is zero within rounding.

Free-expansion comparison. If the same ideal gas instead expands freely and adiabatically into vacuum to $2V_i$ inside an isolated outer container, $Q = 0$ and $W_{\text{by}} = 0$, so $T_f = T_i$ and $p_f = p_i/2$. The reversible power law is not used for that irreversible path.

Guided checks

Check 1. Why is the adiabatic compression temperature higher than the isothermal one? With no heat escape, positive work on the gas raises internal energy.

Check 2. Does $Q = 0$ imply $pV^\gamma = \text{constant}$? No. Additional reversible quasi-static ideal-gas and constant-heat-capacity assumptions were used.

Check 3. Why is a straight line between free-expansion endpoints misleading? Its area would suggest a process work that the nonequilibrium gas never followed.

19.7.3 Adiabatic work as an area and as an energy change

The adiabatic work formula can be checked without trusting the final expression from memory. For the reversible constant-capacity model, substitute $p(V) = p_i(V_i/V)^\gamma$ into the boundary-work integral:

$$W_{\text{by}} = p_i V_i^\gamma \int_{V_i}^{V_f} V^{-\gamma} dV \quad (19.71)$$

$$= \frac{p_i V_i^\gamma}{1 - \gamma} (V_f^{1-\gamma} - V_i^{1-\gamma}) = \frac{p_i V_i - p_f V_f}{\gamma - 1}. \quad (19.72)$$

Since $\gamma > 1$, expansion lowers $pV = nRT$ and gives positive work. The independent first-law calculation, $W_{\text{by}} = -\Delta E_{\text{int}} = nC_{V,m}(T_i - T_f)$, agrees because $R = (\gamma - 1)C_{V,m}$. The equality connects the graph's area, the cooling of the gas, and the capacity model. For compression, reversing the integration limits changes the work sign; one must not use a positive unsigned area as W_{by} .

For instance, 0.750 mol of a model gas initially at 320 K and 200 kPa expands reversibly and adiabatically to $1.60V_i$ with $\gamma = 1.40$. The initial volume is $9.977 \times 10^{-3} \text{ m}^3$, the final temperature is 265.16 K, and

$$\frac{W_{\text{by}}}{p_i V_i} = \int_1^{1.6} r^{-1.4} dr = 0.42847, \quad W_{\text{by}} = +855.0 \text{ J}.$$

Thus $\Delta E_{\text{int}} = -855.0 \text{ J}$ although no heat crosses the boundary. The left panel of Fig. 19.23 shows the geometric meaning. The area of a normalized graph is dimensionless; multiplying by the axis scales $p_i V_i$ restores joules.

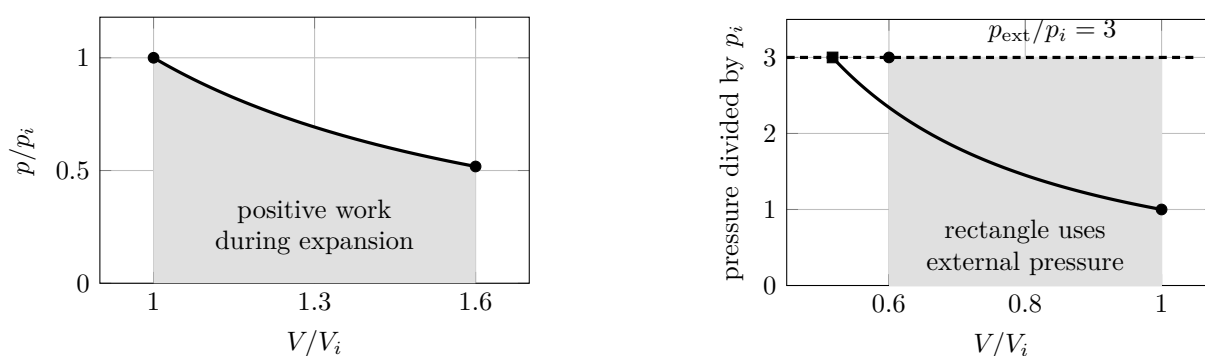


Figure 19.23: Work requires the appropriate pressure. Left: the equilibrium gas pressure determines reversible expansion work; shading represents $\int p dV$. Right: the constant external pressure in Example 19.23 determines irreversible compression work. Its shaded rectangle is not an equilibrium gas-pressure path. Circles mark the irreversible endpoints; the solid reversible comparison curve reaches the square at the same final pressure but a different volume.

19.7.4 What changes when the capacity varies?

A reversible adiabatic ideal gas still satisfies $nC_{V,m}(T) dT = -p dV$, even if its internal modes make the heat capacity vary. Dividing by nT and integrating gives the more general relation

$$\int_{T_i}^{T_f} \frac{C_{V,m}(T)}{T} dT = R \ln \frac{V_i}{V_f}. \quad (19.73)$$

The left side has units of molar heat capacity, just as R does. A logarithm must contain a dimensionless ratio. With constant $C_{V,m}$, the left side becomes $C_{V,m} \ln(T_f/T_i)$ and recovers the familiar power law. With varying $C_{V,m}$, using one universal constant γ discards information about the temperature interval.

There is still a local slope relation,

$$\frac{d \ln p}{d \ln V} = - \left[1 + \frac{R}{C_{V,m}(T)} \right] = -\gamma(T),$$

because $\ln p = \ln(nR) + \ln T - \ln V$. A slope that changes along a curve cannot be pulled outside an integral as a constant exponent. A constant-capacity approximation can be reasonable over a sufficiently narrow interval, but it should be tested against the prescribed capacity model rather than assumed.

Example 19.22: Reversible compression with variable capacity

Use the synthetic capacity in Example 19.19 for a closed ideal sample with $n = 0.400$ mol, $T_i = 300$ K, and $p_i = 100$ kPa. It is compressed reversibly and adiabatically to $V_f = V_i/2$. Find T_f , p_f , and work, and evaluate a constant-capacity approximation based on the initial temperature.

Method. The temperature follows from the integrated differential relation, not from a guessed exponent:

$$\frac{5}{2} \ln \frac{T_f}{300 \text{ K}} + \frac{T_f - 300 \text{ K}}{1500 \text{ K}} = \ln 2.$$

For $T_f > 0$, the derivative of the left side with respect to T_f is $5/(2T_f) + 1/(1500 \text{ K}) > 0$. There is therefore one physical root. The values at 386 and 387 K bracket the solution; bisection gives $T_f = 386.795$ K, within the model's specified range. The ideal-gas law then gives

$$p_f = p_i \frac{T_f}{T_i} \frac{V_i}{V_f} = 257.864 \text{ kPa}.$$

Integrating the capacity gives

$$\Delta E_{\text{int}} = nR \left[\frac{5}{2}(T_f - T_i) + \frac{T_f^2 - T_i^2}{3000 \text{ K}} \right] = 787.74 \text{ J}, \quad W_{\text{by}} = -787.74 \text{ J}.$$

Numerical integration of $p dV$ along the explicit path

$$\frac{V(T)}{V_i} = \left(\frac{T}{T_i} \right)^{-5/2} \exp \left[-\frac{T - T_i}{1500 \text{ K}} \right]$$

gives the same negative work. This check independently connects the first law with the boundary-work geometry.

At the initial temperature, $C_{V,m} = 2.70R$ gives $\gamma_i = 1.37037$. Freezing that capacity predicts $T_f = 300 \cdot 2^{1/2.7} = 387.805$ K, about 1.01 K higher than the variable-capacity result. The local final ratio is $\gamma_f = 1.36260$. The difference is modest here, but Fig. 19.24 shows how it grows with compression. The added capacity provides another place to store the work input and moderates the temperature rise.

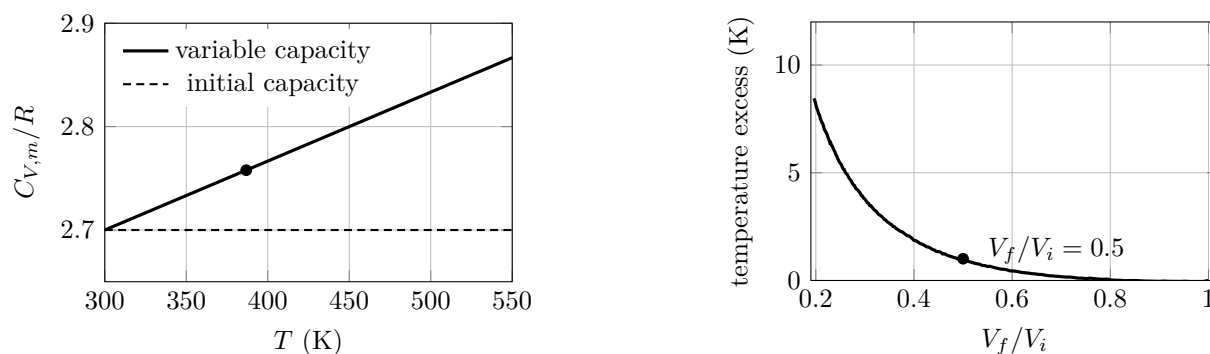


Figure 19.24: The stipulated capacity model and the error in freezing it at $T_i = 300$ K. The right ordinate is $T_{\text{fixed}} - T_{\text{variable}}$ for reversible adiabatic compression from the same initial state. The curve is computed from the explicit $V(T)$ relation in Example 19.22; no experimental heat-capacity values are implied.

19.7.5 Adiabatic does not mean reversible or fast

An insulated piston can move slowly and reversibly while transferring negligible heat. A fast compression may also transfer little heat, yet have pressure imbalances, temperature gradients, and viscous dissipation. The word “adiabatic” describes heat transfer; it does not determine the mechanical path. The first law remains valid for an irreversible process, but the equilibrium gas pressure generally cannot be used as a pressure history during it.

For a moving piston subject to a specified opposing pressure, boundary work is $\int p_{\text{ext}} dV$ under the usual piston-work model. During a sudden load change the gas can be out of mechanical equilibrium. It is permissible to compare its initial and final equilibrium states without assigning equilibrium (p, V, T) values to every intermediate configuration. The right panel of Fig. 19.23 deliberately plots the specified external loading and the endpoints separately.

Example 19.23: Sudden loading of an insulated piston

A closed 0.500-mol ideal monatomic sample begins at 300 K and 100 kPa. The externally applied pressure is abruptly raised to 300 kPa and then held constant. The insulated gas eventually reaches rest and mechanical equilibrium. Use a frictionless piston; neglect its weight and any net kinetic-energy change between the endpoints, and assume transient motion dissipates within the gas. Find the final temperature and volume and the work. Compare reversible adiabatic compression to the same final pressure.

Strategy. Use endpoint energy conservation and external-pressure work. With $V_i = nRT_i/p_i$, $V_f = nRT_f/p_{\text{ext}}$, and $Q = 0$,

$$nC_{V,m}(T_f - T_i) = -p_{\text{ext}}(V_f - V_i) = p_{\text{ext}}V_i - nRT_f.$$

Consequently,

$$T_f = T_i \frac{C_{V,m} + (p_{\text{ext}}/p_i)R}{C_{V,m} + R} = 300 \text{ K} \frac{3/2 + 3}{5/2} = 540 \text{ K}.$$

The endpoint volumes are $V_i = 1.2472 \times 10^{-2} \text{ m}^3$ and $V_f = 0.600V_i = 7.4830 \times 10^{-3} \text{ m}^3$. The work and energy change are

$$W_{\text{by}} = p_{\text{ext}}(V_f - V_i) = -1.4966 \text{ kJ}, \quad \Delta E_{\text{int}} = +1.4966 \text{ kJ}.$$

These signs match compression and the first law. The hypothetical reversible adiabatic comparison uses $\gamma = 5/3$ and gives

$$T_{f,\text{rev}} = 300 \cdot 3^{2/5} = 465.55 \text{ K}, \quad \frac{V_{f,\text{rev}}}{V_i} = 3^{-3/5} = 0.51728,$$

with $W_{\text{by}}^{(\text{rev})} = -1.0324 \text{ kJ}$. The final pressures match, but temperatures and volumes differ. Therefore neither the reversible curve nor its area describes the sudden-loading process. If piston friction dissipated energy into an external cylinder wall, or a piston retained kinetic energy at the final endpoint, the stated gas-only energy model would need additional terms.

19.8 Engineering, computation, and measurement connections

19.8.1 Fast and slow gas compression as model limits

Pneumatic and gas-storage calculations often begin by comparing two limiting thermal behaviours. A slowly compressed gas that remains close to thermal equilibrium with a large environment can approach an isothermal path. A rapid, well-insulated compression can approach an adiabatic limit over part of the process. Real devices may lie between these limits and may involve heat transfer, leakage, valve losses, turbulent flow, nonuniform temperature, and real-gas effects. The ideal curves in Fig. 19.22 are therefore screening models, not equipment ratings or safety specifications.

One useful comparison from Example 19.21 is that the same two-to-one volume compression requires different pressure and work histories depending on heat transfer. The difference is not a disagreement in the ideal-gas law; it reflects different process constraints.

19.8.2 A reproducible computational check

A molecular-speed simulation should reproduce a stated statistical model, not merely generate a cloud of random numbers. A transparent workflow is:

1. choose the dimensionless component model $u_x, u_y, u_z \sim \mathcal{N}(0, 1/2)$ independently;
2. declare the pseudorandom seed and sample size;
3. form $u = \sqrt{u_x^2 + u_y^2 + u_z^2}$;
4. compare the histogram with Eq. (19.32);
5. compare $\bar{u}$ and $\sqrt{u^2}$ with the analytic moments;
6. repeat at a larger sample size and distinguish sampling variation from a model error.

The final source package for this chapter includes a verification script, but the chapter PDF does not require that script to compile or to display Fig. 19.10.

19.8.3 A near-atmospheric pVT investigation with dead volume

A sealed gas sample can test an equation of state only if the three recorded quantities correspond to the same equilibrium state. Use absolute pressure, a volume calibration, and a temperature reading taken after adequate equilibration. If a piston moves quickly, the gas and sensor may initially have different temperatures. A smooth line drawn through such readings does not establish an equilibrium process. Leakage changes the amount of gas, and a pressure measured relative to atmosphere cannot be inserted into $pV = nRT$ without adding the atmospheric pressure.

A useful apparatus model separates the indicated piston volume V_s from a fixed unindicated volume V_d in connecting tubing or a sensor cavity. The total gas volume is $V = V_s + V_d$. At one controlled equilibrium temperature T , a sealed ideal sample obeys

$$p(V_s + V_d) = A, \quad A = nRT, \quad \frac{1}{p} = \frac{V_s}{A} + \frac{V_d}{A}. \quad (19.74)$$

Thus inverse pressure is linear in indicated volume, but need not pass through the origin. A nonzero intercept has a physical interpretation only after competing calibration offsets and thermal effects are considered. Fitting a line does not uniquely establish a dead volume, and a known temperature alone cannot separate n from R if both are treated as unknown.

The following worked investigation supplies every requested analysis as an exemplar. All numbers are synthetic. They are not readings from AGH equipment, and the chosen uncertainty model belongs to this exercise. An actual experiment needs equipment-specific limits and uncertainties. Choose equipment rated for the planned pressure and temperature range and follow the laboratory protocol.

Example 19.24: Synthetic inverse-pressure fit and residual diagnosis

At $T = 300.0$ K, define the dimensionless inverse-pressure ordinate $q = (1000 \text{ kPa})/p$. Six stipulated exact indicated volumes and synthetic q values are given below. The q values have independent equal standard uncertainty $u_q = 0.030$; the temperature has independent standard uncertainty $u_T = 0.5$ K. Pressure is calculated from q and is printed only for physical orientation.

V_s (mL)	q	p (kPa, calculated)
60	6.80	147.06
70	7.79	128.37
85	9.32	107.30
100	10.77	92.85
115	12.34	81.04
130	13.77	72.62

Fit $q = aV_s + b$, infer the amount and dead volume, quantify their uncertainties, examine residuals, and assess what happens if the line is forced through the origin. Use the listed q values, not reciprocals of rounded pressures.

Fit and parameters. For equal q uncertainties and exact V_s , ordinary least squares minimizes the sum of squared vertical residuals. With $\bar{V}_s = 93.3333$ mL, $\bar{q} = 10.13167$, and $S_{VV} = \sum(V_s - \bar{V}_s)^2 = 3583.333 \text{ mL}^2$,

$$a = \frac{\sum(V_s - \bar{V}_s)(q - \bar{q})}{S_{VV}} = 0.0998977 \text{ mL}^{-1}, \quad b = \bar{q} - a\bar{V}_s = 0.807884.$$

Comparing with Eq. (19.74) gives

$$A = \frac{1000 \text{ kPa}}{a} = 10010.24 \text{ kPa mL} = 10.01024 \text{ J}, \quad V_d = \frac{b}{a} = 8.087 \text{ mL}.$$

The unit conversion is $1 \text{ kPa mL} = 10^{-3} \text{ J}$. Therefore

$$n = \frac{A}{RT} = 0.00401319 \text{ mol}.$$

This analysis determines n conditional on the ideal-gas model and the accepted R . Figure 19.25 links these fitted parameters to the same six inputs.

Uncertainty. The declared u_q gives

$$u_a = \frac{u_q}{\sqrt{S_{VV}}} = 0.00050116 \text{ mL}^{-1}, \quad u_b = u_q \sqrt{\frac{1}{6} + \frac{\bar{V}_s^2}{S_{VV}}} = 0.048352,$$

$$\text{cov}(a, b) = -\frac{\bar{V}_s u_q^2}{S_{VV}} = -2.3442 \times 10^{-5} \text{ mL}^{-1}.$$

The slope and intercept are correlated because increasing the slope can be partially compensated by decreasing the intercept. To first order, independent temperature uncertainty gives

$$\frac{u_n}{n} = \sqrt{\left(\frac{u_a}{a}\right)^2 + \left(\frac{u_T}{T}\right)^2} = 0.005286,$$

so $n = (0.004013 \pm 0.000021)$ mol. For $V_d = b/a$, retaining the fit covariance gives

$$u_{V_d}^2 = \frac{u_b^2}{a^2} + \frac{b^2 u_a^2}{a^4} - \frac{2b \text{cov}(a, b)}{a^3}, \quad V_d = (8.09 \pm 0.52) \text{ mL}.$$

The uncertainties are standard uncertainties, not guaranteed bounds. These formulas follow by taking first derivatives of $n(a, T)$ and $V_d(a, b)$ and combining variances and covariance; they do not include unmodeled calibration errors.

Residuals and the forced-origin model. In increasing-volume order, the residuals $q - (aV_s + b)$ are -0.00174 , -0.01072 , $+0.02081$, -0.02765 , $+0.04388$, and -0.02458 . Their squared standardized sum is $\chi^2 = \sum (r_j/u_q)^2 = 4.27$ for six points and two fitted parameters. The alternating scatter has no evident monotonic volume trend, and its scale is compatible with the stated uncertainty model. This is a consistency check, not proof that all systematic effects are absent.

Forcing $b = 0$ instead gives $a_0 = \sum V_s q / \sum V_s^2 = 0.107998 \text{ mL}^{-1}$, implying $n_0 = 0.00371217$ mol, 7.50% below the two-parameter result. Its residuals drift from $+0.320$ at 60 mL to -0.270 at 130 mL, as Fig. 19.26 shows. The missing intercept therefore produces both parameter bias and visible residual structure.

Experimental interpretation. For real constant-pressure-resolution instruments, uncertainties in q would vary approximately as $1000u_p/p^2$, so the equal- u_q fit used here would usually be replaced by a weighted fit. Significant volume uncertainty also requires its propagation or an errors-in-variables analysis. Temperature equilibration should be checked by stable readings and repeats after different waiting times; heating or cooling correlated with piston position can imitate model deviations. Assess a real report by its absolute-pressure conversion, total-volume model, unit conversion, uncertainty assumptions, residual plot, and discussion of repeatability. A reasonable conclusion may be consistency within uncertainty rather than a claim of an exact law.

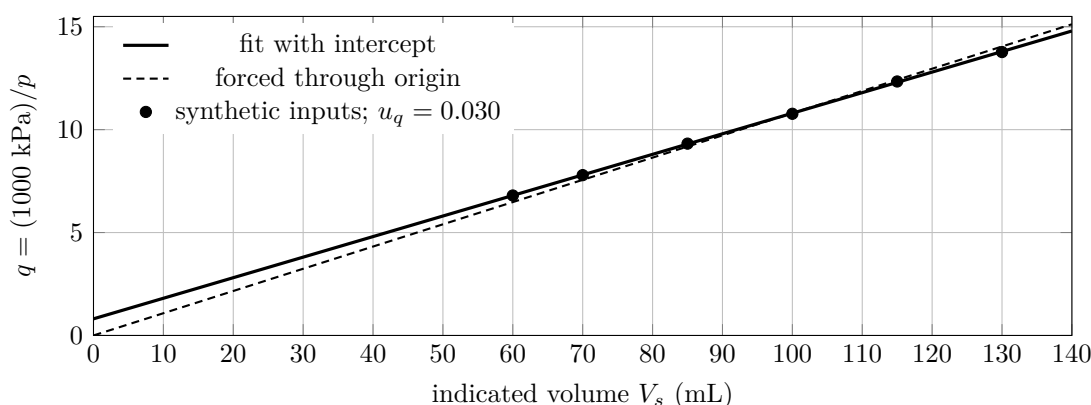


Figure 19.25: The six synthetic inputs in Example 19.24 and their inverse-pressure fits. The intercept is required by the prescribed dead-volume model. The uncertainty bars are small on this full ordinate range; the enlarged residual view in Fig. 19.26 carries the diagnostic comparison. The fit outside the sampled volume interval is an extrapolation.

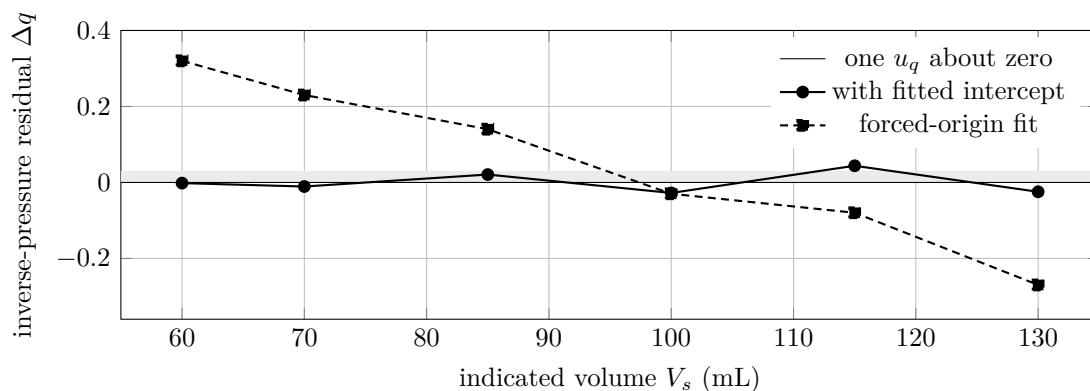


Figure 19.26: Residuals computed from the same inputs and coefficients as Fig. 19.25. The forced-origin constraint creates a systematic volume trend. The shaded band is the declared standard uncertainty of an individual q input, not a confidence interval for the fitted mean line. Connecting segments aid comparison and do not represent additional readings.

19.9 Chapter summary and working formula sheet

Summary

A dilute classical gas links macroscopic variables to molecular motion through a chain of carefully stated models. Moles and particles are connected by N_A ; wall momentum transfer produces pressure; isotropy supplies the factor $1/3$; the ideal-gas equation then identifies mean translational energy with $3k_B T/2$. The Maxwell distribution shows why one temperature corresponds to a range of molecular speeds. A hard-sphere collision model introduces mean free path. Classical equipartition predicts limiting heat capacities only for thermally active quadratic terms. Finally, a reversible quasi-static adiabatic ideal gas obeys $pV^\gamma = \text{constant}$, whereas an arbitrary adiabatic irreversible process need not.

Formula summary

Particle–mole conversion and ideal gas

$$N = nN_A, \quad m_{\text{mol}} = \frac{M_m}{N_A}, \quad R = N_A k_B, \quad pV = nRT = Nk_B T.$$

Kinetic pressure and translational energy

$$p = \frac{N}{V} m_{\text{mol}} \langle v_x^2 \rangle = \frac{1}{3} \frac{N}{V} m_{\text{mol}} \langle v^2 \rangle, \quad \langle K_{\text{trans}} \rangle = \frac{3}{2} k_B T, \quad v_{\text{rms}} = \sqrt{\frac{3RT}{M_m}}.$$

Maxwell speeds

$$f(v) = 4\pi \left(\frac{m_{\text{mol}}}{2\pi k_B T} \right)^{3/2} v^2 e^{-m_{\text{mol}} v^2 / (2k_B T)},$$

$$v_{\text{mp}} = \sqrt{\frac{2RT}{M_m}}, \quad v_{\text{mean}} = \sqrt{\frac{8RT}{\pi M_m}}, \quad v_{\text{rms}} = \sqrt{\frac{3RT}{M_m}}.$$

Collision model

$$\ell_{\text{mfp}} = \frac{1}{\sqrt{2} n_N \pi d^2}, \quad \tau_{\text{coll}} \approx \frac{\ell_{\text{mfp}}}{v_*}.$$

Classical active quadratic terms and ideal-gas heat capacities

$$E_{\text{int}} = \frac{f_q}{2} nRT, \quad C_{V,m} = \frac{f_q}{2} R, \quad C_{p,m} - C_{V,m} = R, \quad \gamma = \frac{C_{p,m}}{C_{V,m}}.$$

Reversible quasi-static adiabatic ideal gas, constant heat capacities

$$TV^{\gamma-1} = \text{constant}, \quad pV^{\gamma} = \text{constant}, \quad W_{\text{by}} = \frac{p_i V_i - p_f V_f}{\gamma - 1}.$$

19.10 Advanced Topics for Technical and Engineering Students

The advanced pathway deepens three ideas already encountered: where the Maxwell speed law comes from, how collision scale can be compared with device scale, and why rapid small disturbances in an ideal gas propagate with an adiabatic rather than isothermal stiffness. The added mathematics is introduced locally; none of these results is a hidden prerequisite for the core exercises.

19.10.1 Deriving the Maxwell speed density from Gaussian components

A fuller statistical derivation starts from the equilibrium probability density of one Cartesian velocity component,

$$g(v_x) = \sqrt{\frac{m_{\text{mol}}}{2\pi k_B T}} \exp\left(-\frac{m_{\text{mol}} v_x^2}{2k_B T}\right). \quad (19.75)$$

Rotational symmetry alone does not determine a Gaussian distribution or imply independent components. We use the classical equilibrium Gaussian component model, with independent Cartesian components, as an additional statistical premise. It is stronger than the isotropy assumption needed for the pressure moment. Under this premise the joint density is

$$G(v_x, v_y, v_z) = \left(\frac{m_{\text{mol}}}{2\pi k_B T}\right)^{3/2} \exp\left[-\frac{m_{\text{mol}}(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right]. \quad (19.76)$$

All velocity vectors whose magnitudes lie between v and $v + dv$ occupy a thin spherical shell in velocity space with volume $4\pi v^2 dv$. Multiplying the joint density by that shell volume produces Eq. (19.29).

In dimensionless form, the normalisation reduces to

$$\int_0^\infty \frac{4}{\sqrt{\pi}} u^2 e^{-u^2} du = 1,$$

using the Gaussian integral $\int_0^\infty u^2 e^{-u^2} du = \sqrt{\pi}/4$. The mode follows from

$$\frac{d}{du} (u^2 e^{-u^2}) = 2u(1 - u^2)e^{-u^2} = 0,$$

so the positive interior maximum is at $u = 1$. The first and second moments give $2/\sqrt{\pi}$ and $3/2$, respectively, reproducing the markers in Fig. 19.10.

Theoretical point 19.1: Density transformation matters

The factor $4\pi v^2$ is why the speed distribution does not peak at zero even though each Cartesian Gaussian component does. Many different velocity vectors correspond to the same nonzero speed. A component probability density and a speed probability density are different mathematical objects.

19.10.2 Synthetic sampling and the velocity-space derivation

The reproducible component-sampling algorithm and its complete sample analysis were developed in Section 19.4.8. The shell derivation explains why taking the norm of three independent Gaussian components gives the Maxwell speed law, rather than a one-dimensional Gaussian. Multiplying physical component variance by two multiplies every characteristic speed by $\sqrt{2}$; multiplying molecular mass by four halves the speed scale. The normalization, moments, and finite-tail checks remain essential. A declared seed fixes one realization, while the analytic distribution predicts a population and its sampling variability.

19.10.3 Collision scaling and the Knudsen viewpoint

Equation (19.51) reveals three dimensionless or scaling ideas useful in engineering models:

- at fixed d , $\ell_{\text{mfp}} \propto n_N^{-1}$;
- at fixed density, $\ell_{\text{mfp}} \propto d^{-2}$;
- comparison with a device length enters through $\text{Kn} = \ell_{\text{mfp}}/L$.

When $\text{Kn} \ll 1$, many collisions typically occur over the macroscopic scale L , making a continuum model plausible. As Kn grows, wall interactions and nonequilibrium effects can become increasingly important. The numerical thresholds used in specialist rarefied-gas engineering depend on the problem and are not imposed here.

19.10.4 Adiabatic gas stiffness and the speed of sound

Chapter 17 introduced sound as a mechanical wave whose speed is controlled by inertia and stiffness. For a fluid, the relevant small-disturbance relation has the form

$$c_w^2 = \left(\frac{\partial p}{\partial \rho} \right)_{\text{disturbance}}. \quad (19.77)$$

A small acoustic compression is usually rapid enough that heat transfer over one oscillation is negligible in the idealised model, so use the adiabatic relation rather than an isothermal one. With fixed gas mass, $\rho \propto 1/V$, and Eq. (19.68) becomes

$$p\rho^{-\gamma} = \text{constant}. \quad (19.78)$$

Differentiating,

$$\frac{dp}{d\rho} = \gamma \frac{p}{\rho}. \quad (19.79)$$

Writing $x = \rho/\rho_0$ and $y = p/p_0$, the local slope is $dy/dx = 1$ for the isothermal curve and γ for the adiabatic curve at $x = 1$. The dimensional derivative is $(p_0/\rho_0)dy/dx$, so a dimensionless graph slope alone is not a speed.

The adiabatic bulk modulus is therefore

$$B_{\text{ad}} = \rho \frac{dp}{d\rho} = \gamma p, \quad (19.80)$$

and

$$c_w = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{\gamma RT}{M_m}}. \quad (19.81)$$

No entropy notation was required: the result follows directly from the reversible adiabatic ideal-gas relation already derived.

For comparison, a hypothetical isothermal small compression would give $p \propto \rho$ and $B_T = p$, so

$$c_T = \sqrt{\frac{p}{\rho}} = \sqrt{\frac{RT}{M_m}}, \quad \frac{c_w}{c_T} = \sqrt{\gamma}. \quad (19.82)$$

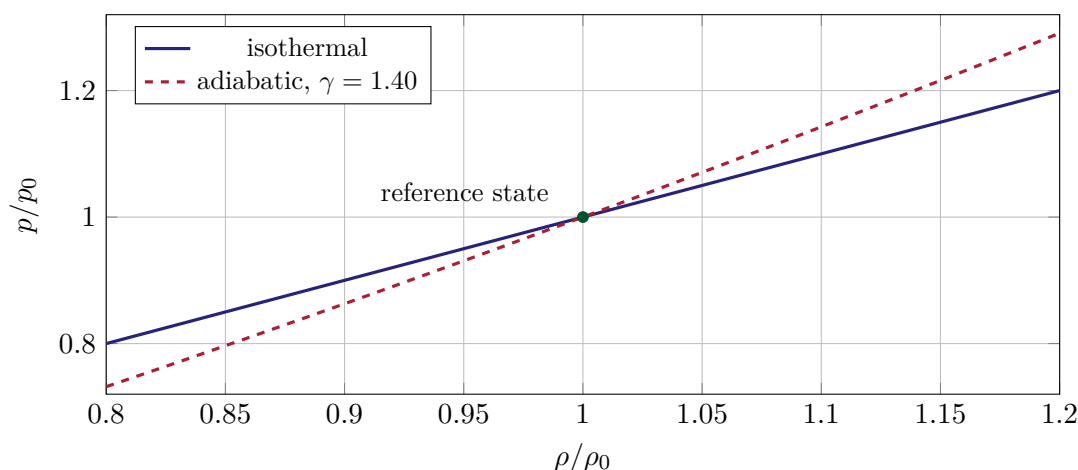


Figure 19.27: Local pressure–density stiffness for isothermal and reversible adiabatic ideal-gas models, normalised at the same state and shown for $\gamma = 1.40$. The different slopes at the reference point give $B_T = p_0$ and $B_{ad} = \gamma p_0$.

Example 19.25: Quantitative sound-speed preview

For a stipulated ideal gas with $M_m = 28.0 \times 10^{-3} \text{ kg mol}^{-1}$, $T = 300 \text{ K}$, and $\gamma = 1.40$,

$$c_T = \sqrt{\frac{RT}{M_m}} = 298.5 \text{ m s}^{-1},$$

whereas the adiabatic acoustic model gives

$$c_w = \sqrt{\gamma} c_T = 353.2 \text{ m s}^{-1}.$$

The ratio is $\sqrt{1.40} = 1.183$. The comparison explains why replacing the acoustic compression by an isothermal one underestimates the model wave speed. These are ideal-model values for the stipulated molar mass and heat-capacity ratio, not measured sound speeds for a named real gas.

Caution

The sound-speed derivation assumes a small disturbance about equilibrium, a locally ideal gas, negligible dissipative corrections, and an adiabatic constitutive response on the disturbance time scale. Viscosity, thermal conduction, real-gas behaviour, chemistry, humidity, and frequency-dependent relaxation can modify real acoustic propagation.

19.10.5 From the fluid equations to the acoustic speed

The stiffness derivative acquires a direct dynamical meaning by linearizing mass conservation and Newton’s law for a fluid element. Let $\rho = \rho_0 + \rho'$, $p = p_0 + p'$, and $w(x, t)$ be the small bulk velocity along x . Primes here denote disturbances, not derivatives. Products of disturbances are neglected. The linearized equations in a uniform stationary reference gas are

$$\frac{\partial \rho'}{\partial t} + \rho_0 \frac{\partial w}{\partial x} = 0, \quad \rho_0 \frac{\partial w}{\partial t} = -\frac{\partial p'}{\partial x}.$$

The first equation says that a converging velocity field compresses a fixed mass; the second balances force from the pressure gradient with fluid inertia. If the local constitutive response is $p' = c^2 \rho'$

with constant $c^2 = (\partial p / \partial \rho)_0$, differentiation and substitution eliminate w :

$$\frac{\partial^2 \rho'}{\partial t^2} = c^2 \frac{\partial^2 \rho'}{\partial x^2}. \quad (19.83)$$

This is the nondispersive wave equation recalled from Chapters 16–17. It shows why the square root of the stiffness-to-inertia ratio is a propagation speed, rather than merely a combination with the dimensions of speed.

For $\rho' = A_\rho \cos(k_w x - \omega t)$, substitution gives $\omega^2 = c^2 k_w^2$. Its progressive-wave bulk velocity amplitude is $w_{\text{amp}} = c A_\rho / \rho_0$ and pressure amplitude is $p_{\text{amp}} = c^2 A_\rho$. Consequently $p_{\text{amp}} = \rho_0 c w_{\text{amp}}$, linking microscopic gas modeling to the acoustic relations used earlier. Molecules travel in all directions; the much smaller coherent bulk velocity oscillates locally and the disturbance propagates at c . These three speeds have different definitions.

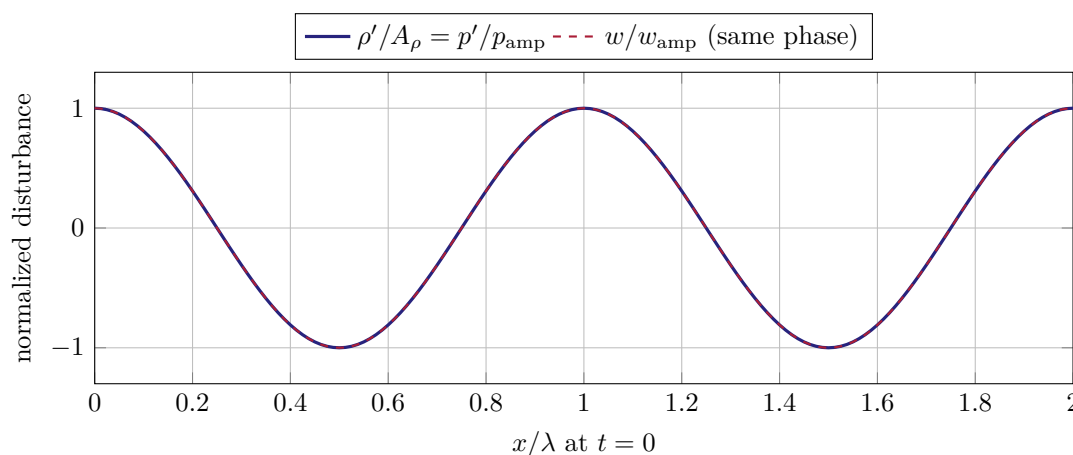


Figure 19.28: A right-moving, lossless plane sound wave has pressure, density, and longitudinal bulk-velocity disturbances in phase. The curves coincide after division by their own amplitudes; they have different physical units and sizes. This relation concerns a progressive wave, rather than a standing wave.

Example 19.26: Check the small-disturbance approximation

A stipulated ideal gas has $T = 300$ K, $M_m = 0.0280$ kg mol⁻¹, $p_0 = 100$ kPa, and $\gamma = 1.40$. A plane sound disturbance has pressure amplitude $p_{\text{amp}} = 10.0$ Pa and frequency $f = 1000$ Hz. Find the density, acoustic speed, wavelength, and bulk-velocity amplitude; compare that amplitude with the molecular rms speed.

The reference density is $\rho_0 = p_0 M_m / (RT) = 1.123$ kg m⁻³, and $c = \sqrt{\gamma RT / M_m} = 353.2$ m s⁻¹. Thus $\lambda = c / f = 0.3532$ m. The progressive-wave relation gives

$$w_{\text{amp}} = \frac{p_{\text{amp}}}{\rho_0 c} = 0.0252 \text{ m s}^{-1}.$$

The molecular rms speed is 517.0 m s⁻¹, so $w_{\text{amp}} / v_{\text{rms}} = 4.88 \times 10^{-5}$. Also $p_{\text{amp}} / p_0 = 10^{-4}$ and $A_\rho / \rho_0 = p_{\text{amp}} / (\gamma p_0) = 7.14 \times 10^{-5}$, consistent with linearization. These small amplitude tests establish the internal consistency of this ideal model; they do not measure dissipative or relaxation corrections in a real gas.

19.10.6 Timescales and the choice of acoustic stiffness

An acoustic model needs local equilibrium as well as limited heat exchange. Frequent molecular collisions should relax the velocity distribution much faster than one wave period, while heat conduction over the disturbance length should be slow enough that a compressed parcel retains

approximately its heat. These are different requirements. A small Knudsen number concerns spatial collisions; $\omega\tau_{\text{coll}} \ll 1$ concerns their timescale relative to forcing. Neither one alone proves negligible thermal conduction or complete equilibration of internal molecular modes.

If an explicitly stipulated thermal diffusivity is α , heat diffusion over a distance L_T has order-of-magnitude time $t_T \sim L_T^2/\alpha$. Thermal diffusion across a wavelength can be slow while diffusion to a nearby channel wall is fast. Consequently a wide gas volume can have an approximately adiabatic acoustic interior and a thermally influenced wall region. The scale $\delta_T = \sqrt{2\alpha/\omega}$ gives the penetration length in a simple harmonic diffusion model. A complete wall-boundary calculation is beyond this chapter, but this comparison prevents a misleading universal claim that every rapid gas oscillation must use the same γ .

The connection to Chapter 20 is now clear: local equilibrium, heat-transfer constraints, and reversibility are distinct modeling choices. The kinetic argument predicts a response under those choices; it does not erase their conditions.

19.11 Problems and complete solutions

Use $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$, $k_B = 1.380649 \times 10^{-23} \text{ J K}^{-1}$, and $R = 8.314462618 \text{ J mol}^{-1} \text{ K}^{-1}$ unless a problem states otherwise. Treat all numerical gas parameters as stipulated teaching inputs, not measured properties, unless explicitly identified. Use absolute temperature and absolute pressure in gas-state relations.

A. Particle, molar, and kinetic descriptions

1. A sample contains 3.00×10^{22} molecules. Find the amount of substance. If its total mass is 1.40 g, find the stipulated molar mass and single-molecule mass.
2. A 0.150 mol ideal-gas sample occupies 3.80 L at 290 K. Find its pressure using both nRT and $Nk_B T$ and show that the two numerical results agree.
3. Explain why replacing m_{mol} by M_m in $p = (N/V)m_{\text{mol}}\langle v_x^2 \rangle$ produces wrong dimensions. What conversion repairs it?
4. For one molecule in a cubic box, use the collision-free pedagogical model with specular walls and unchanged velocity components between wall encounters to derive the average force on a wall normal to x . Identify separately the factor of two from momentum reversal and the factor of two from the round-trip time.
5. A gas has $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$. Does this imply zero pressure? Use the correct velocity moment to justify the answer.
6. In a nonequilibrium state, $\langle v_x^2 \rangle = 2\langle v_y^2 \rangle = 2\langle v_z^2 \rangle$. Explain why the isotropic 1/3 replacement is invalid and which wall orientation feels the largest normal stress in the simple collision model.

B. Temperature and speed distributions

7. Two stipulated gases have molar masses 5.0 and 45.0 g mol⁻¹ at the same temperature. Find the ratio of their rms speeds and compare their mean translational energies per molecule. Use Fig. 19.8 to check the direction of the speed change.
8. At what temperature would a stipulated gas with $M_m = 32.0 \text{ g mol}^{-1}$ have $v_{\text{rms}} = 500 \text{ m s}^{-1}$ in the ideal model?

9. For the dimensionless Maxwell density $f_u = (4/\sqrt{\pi})u^2e^{-u^2}$, show that $u = 0$ is not the positive-speed maximum and find the nonzero mode. Relate your derivative test to the curve in Fig. 19.10.
10. Calculate u_{mp} , $\langle u \rangle$, and u_{rms} and order them. Which one is determined by the second moment? Locate the three markers in Fig. 19.10 and explain their order.
11. The analytic tail probability above $u = 3.2$ is 1.35×10^{-4} . In a sample of 8000 particles, estimate the expected number above that cutoff. Why can the actual integer differ? Explain why the omitted area beyond the plotting cutoff in Fig. 19.10 is a probability rather than the density at the cutoff.
12. A histogram is doubled in every bin height without changing the bin widths. What normalisation test detects the error? Why can the curve still look qualitatively Maxwell-like? Use Fig. 19.30 to illustrate the area test numerically.

C. Collisions and heat capacities

13. In the hard-sphere model, what happens to ℓ_{mfp} if number density is multiplied by 3 while d is unchanged? What if d is multiplied by 2 at fixed density?
14. Evaluate ℓ_{mfp} for $n_N = 1.00 \times 10^{25} \text{ m}^{-3}$ and $d = 4.00 \times 10^{-10} \text{ m}$. Then find Kn for $L = 0.50 \text{ mm}$.
15. The expressions πd^2 and $4\pi(d/2)^2$ have equal numerical values. Explain why the collision cross-section is physically the projected encounter disk of radius d , rather than the surface area of one molecule of radius $d/2$. Explain what d represents.
16. A monatomic classical ideal gas has $f_q = 3$. Derive $C_{V,m}$, $C_{p,m}$, and γ .
17. A linear-molecule model has translation and two rotational kinetic contributions active but vibration frozen. Find f_q , $C_{V,m}/R$, $C_{p,m}/R$, and γ .
18. A student assigns only one $\frac{1}{2}k_{\text{B}}T$ contribution to an active harmonic vibration. Diagnose the mistake by writing the kinetic and potential quadratic terms.
19. Explain why a measured temperature-dependent heat capacity can disagree with a fixed classical degree count without violating energy conservation.

D. Gas processes and energy accounting

20. Starting from $nC_{V,m}dT = -pdV$, derive $TV^{\gamma-1} = \text{constant}$ and list every physical condition used.
21. A reversible adiabatic ideal gas with $\gamma = 5/3$ expands from V_i to $2V_i$. Find T_f/T_i and p_f/p_i . Explain how the relative order of the expansion pressures agrees with the curves in Fig. 19.22, while noting the different stipulated value of γ .
22. One mole of ideal gas at 300 K expands isothermally and reversibly from 10.0 to 20.0 L. Find W_{by} , ΔE_{int} , and Q using the chapter sign convention.
23. The same ideal gas instead undergoes free expansion in a thermally insulated rigid outer container from 10.0 to 20.0 L. Find Q , W_{by} , ΔE_{int} , and T_f/T_i . Explain why Problem 22 and this problem have the same endpoints in volume but different work.
24. A proposed solution applies $pV^{\gamma} = \text{constant}$ to the free expansion in Problem 23. Identify the invalid assumption.

25. For the compression in Example 19.21, calculate the external work done on the gas in each limiting reversible model and state which requires the larger magnitude. Connect the work comparison to the areas beneath the curves in Fig. 19.22.

E. Measurement, computation, and engineering interpretation

26. Design a table for a pVT experiment that would allow pV/T to be checked. Which pressure must be recorded? What evidence would you require before treating each row as an equilibrium state?
27. A program samples Gaussian velocity components but uses standard deviation 1 instead of $1/\sqrt{2}$ in the dimensionless variable of Fig. 19.10. Predict the factor by which its rms speed marker is wrong.
28. A simulation gives a correct histogram shape but its reported $\overline{u^2} = 0.75$. Which analytic target should it approach, and what does the discrepancy indicate?
29. A stipulated vessel has $\ell_{\text{mfp}} = 2.0 \mu\text{m}$ and characteristic length $L = 0.20 \text{ mm}$. Compute Kn and explain what the ratio means without assigning a universal regime label.
30. Explain why isothermal and adiabatic compression curves can both satisfy the ideal-gas equation of state while giving different $p(V)$ relations. Identify these two distinct temperature constraints in Fig. 19.22.

F. Advanced challenges

31. Starting from the three-dimensional Gaussian density in Eq. (19.75), transform from velocity components to a speed shell and recover the $4\pi v^2$ factor in the Maxwell density. Check the units before and after the transformation.
32. For $p\rho^{-\gamma} = \text{constant}$, derive $B_{\text{ad}} = \gamma p$ and $c_w = \sqrt{\gamma p/\rho}$. Show that the isothermal and adiabatic model speeds merge as $\gamma \rightarrow 1$. Use the tangent slopes in Fig. 19.27 as a graphical check of your result.
33. At $T = 320 \text{ K}$, $M_m = 40.0 \text{ g mol}^{-1}$, and $\gamma = 5/3$, calculate c_T and c_w in the ideal model. State why these numbers are not automatically the measured speeds of sound in a named real gas.
34. The synthetic sample in Fig. 19.10 gives $\bar{u} = 1.12465$ and $u_{\text{rms}} = 1.22123$. Compute their fractional deviations from the analytic values. Explain whether these discrepancies alone demonstrate an implementation error. State a criterion that would distinguish finite-sample fluctuations from systematic error.
35. A device length is reduced by a factor of 10 at fixed gas state and molecular model. How does Kn change? Why can miniaturisation make molecular-scale effects more important even when the gas itself is unchanged?

G. Additional applied and experimental problems

These five problems use idealised or explicitly synthetic data. They test how a model is read, checked, and used, rather than supplying ratings for a real device.

36. A sealed ideal-gas model nominally contains $n_0 = 0.2000 \text{ mol}$. Five synthetic equilibrium-state rows are given below. Here p is absolute pressure and all volumes refer to the same gas amount. (a) Calculate $C_i = p_i V_i / T_i$ and the apparent amount $n_i = C_i / R$. (b) Plot or read the residual $r_i = 100(n_i / n_0 - 1)$ in Fig. 19.29. Each residual has a stipulated independent

standard uncertainty of 0.50%. Do these rows establish a departure from the ideal-gas model?
 (c) Describe one additional test that distinguishes leakage from a pressure calibration offset.

Row	T (K)	V (L)	p (kPa)
1	300	20	24.94339
2	315	18	29.21702
3	330	16	34.19427
4	345	14	41.06038
5	360	12	49.83689

- 37.** Figure 19.30 represents a synthetic probability-density histogram for a nonnegative dimensionless speed u . Its four bins have boundaries 0, 0.5, 1.0, 2.0, 3.0 and heights 0.40, 0.70, 0.30, 0.15. (a) Verify normalisation. (b) Find $P(0.5 \leq u < 2.0)$ and the expected number in that interval for 2000 independent samples. (c) A student calls the tallest bin's height 0.70 the probability of that bin. Explain the error. (d) Calculate the mean implied by treating the density as uniform within each bin; explain why this is a property of the histogram model rather than an exact Maxwell mean.
- 38.** A 0.200 mol classical monatomic ideal gas starts at $T_i = 300$ K and $V_i = 2.00$ L, then expands reversibly to 4.00 L. Compare the isothermal and adiabatic models in Fig. 19.31. (a) Find p_i , T_f , and p_f for each path. (b) Calculate work by the gas from the curve areas and determine Q and ΔE_{int} . (c) Both paths end at the same volume. Explain why their endpoint pressures and works differ.
- 39.** In the dilute hard-sphere model a gas has $T = (300 \pm 1)$ K, $d = (3.70 \pm 0.05) \times 10^{-10}$ m, and $\ell_{\text{mfp}} = (68 \pm 3)$ nm. Treat the uncertainties as independent standard uncertainties. (a) Infer the absolute pressure using the ideal equation of state and collision model. (b) Propagate uncertainty by linearising $\ln p$. (c) Identify the largest uncertainty contribution and explain why better temperature measurement alone has limited benefit. Do not interpret the inferred diameter as an exact molecular size.
- 40.** A dilute ideal mixture at 300 K and 100 kPa has mole fractions $x_A = 0.400$ and $x_B = 0.600$, with stipulated molar masses $M_A = 4.00$ and $M_B = 32.0$ g mol $^{-1}$. For each species, assume an equilibrium Maxwell distribution. (a) Find its partial pressure and rms speed. (b) Find the mixture mass density. (c) Use the equal-temperature reasoning of Fig. 19.8 to explain how different rms speeds coexist with equal mean translational energy per molecule. State why inserting the average molar mass into a single Maxwell curve does not reproduce both species distributions.

H. Additional advanced challenges

The necessary mathematical or modelling extension is stated in each problem. These problems enrich the core rather than change the assumptions of the earlier exercises.

- 41.** Define $\text{erfc}(a) = (2/\sqrt{\pi}) \int_a^\infty e^{-s^2} ds$. For the Maxwell speed density $f_u = (4/\sqrt{\pi})u^2 e^{-u^2}$, (a) integrate by parts to derive the exact probability $P(u > a)$. (b) Evaluate it at $a = 2$, taking $\text{erfc}(2) = 0.004677735$. (c) In 1000 independent samples, find the expected tail count and its standard deviation using the binomial relation $\text{Var}(K) = NP(1 - P)$. Explain why a count of 46 is not a mandatory result.
- 42.** A hypothetical ideal gas has temperature-dependent molar heat capacity $C_{V,m}(T) = R[1.50 + bT]$ with $b = 0.00200$ K $^{-1}$. One mole expands reversibly and adiabatically from $T_i = 300$ K to $V_f = 2V_i$. (a) Integrate the first law to obtain an implicit equation for T_f without imposing a constant γ . (b) Find T_f by trial, bisection, or another stated numerical method, and then find

- p_f/p_i . (c) Calculate W_{by} from the internal-energy change and compare T_f with a calculation that incorrectly freezes γ at its initial value. Explain the source and direction of the discrepancy.
- 43.** A thin small aperture samples molecules from a dilute equilibrium reservoir into vacuum without intermolecular collisions in the aperture. At fixed speed, the number crossing is proportional to speed, after angular integration over the outward hemisphere. Thus the speed density among crossing molecules is $g(u) = uf_u(u)/\langle u \rangle$. (a) Normalise g explicitly. (b) Find its mode and mean speed. Use $\int_0^\infty u^3 e^{-u^2} du = 1/2$ and $\int_0^\infty u^4 e^{-u^2} du = 3\sqrt{\pi}/8$ if needed. (c) Explain why a measured escaping sample can be faster on average than the reservoir molecules without violating the common reservoir temperature.
- 44.** For independent Maxwell samples, $\langle u \rangle = 2/\sqrt{\pi}$ and $\langle u^2 \rangle = 3/2$. (a) Derive the variance of u and the standard error of a mean from $N = 8000$ samples. (b) For the synthetic mean 1.12465 in Problem 34., calculate its deviation in standard-error units. Does this alone provide compelling evidence of incorrect sampling? (c) Explain how serial correlation in a simulation changes the interpretation and propose an empirical check of independence.
- 45.** Two idealised stiffness measurements at the same gas state give an isothermal model speed $c_T = 250 \text{ m s}^{-1}$ and an adiabatic model speed $c_w = 300 \text{ m s}^{-1}$. (a) Infer γ , $C_{V,m}$, and $C_{p,m}$ assuming a calorically ideal gas. (b) Use Fig. 19.27 to interpret the speed ratio as a tangent-slope ratio; distinguish slopes from the speeds themselves. (c) If both speed measurements have independent 1% standard uncertainty, estimate the relative uncertainty of γ and discuss the sensitivity of the inferred $C_{V,m}$. Explain why inferred noninteger effective degrees of freedom need not contradict thermodynamics.

19.12 Complete reasoned solutions

Answers use the chapter convention $\Delta E_{\text{int}} = Q - W_{\text{by}}$: $Q > 0$ enters the gas and $W_{\text{by}} > 0$ is work done by the gas. Extra digits are retained only where they help audit a calculation. A model result and evidence that a real gas follows that model are different conclusions.

1. Count, amount, and two mass descriptions

The amount is a particle count divided by the number of particles per mole:

$$n = \frac{N}{N_A} = \frac{3.00 \times 10^{22}}{6.02214076 \times 10^{23}} = 0.0498 \text{ mol.}$$

The sample mass is $1.40 \text{ g} = 1.40 \times 10^{-3} \text{ kg}$. Its stipulated molar mass and molecular mass are therefore

$$M_m = \frac{1.40 \text{ g}}{0.0498162 \text{ mol}} = 28.1 \text{ g mol}^{-1}, \quad m_{\text{mol}} = \frac{1.40 \times 10^{-3}}{3.00 \times 10^{22}} = 4.67 \times 10^{-26} \text{ kg.}$$

The independent bookkeeping check is $M_m/N_A = m_{\text{mol}}$, with M_m first converted to kg mol^{-1} . The result does not identify a chemical species: a stipulated average mass could describe several samples or a mixture.

2. Two state descriptions

First convert $V = 3.80 \text{ L}$ to $3.80 \times 10^{-3} \text{ m}^3$. In molar form,

$$p = \frac{nRT}{V} = \frac{(0.150)(8.314462618)(290)}{3.80 \times 10^{-3}} = 9.52 \times 10^4 \text{ Pa.}$$

The count is $N = nN_A = 9.03321 \times 10^{22}$, so the particle form gives

$$p = \frac{Nk_B T}{V} = \frac{(9.03321 \times 10^{22})(1.380649 \times 10^{-23})(290)}{3.80 \times 10^{-3}} = 9.52 \times 10^4 \text{ Pa.}$$

Both numerators have energy units; energy per volume is pressure. Their agreement follows from $R = N_A k_B$ and is a conversion check rather than two independent tests of ideal-gas behaviour.

3. Dimensional diagnosis

A molecular count has no mole unit. Thus $(N/V)m_{\text{mol}}\langle v_x^2 \rangle$ has units $(\text{m}^{-3})(\text{kg})(\text{m}^2\text{s}^{-2}) = \text{Pa}$. Replacing molecular mass by molar mass leaves Pa mol^{-1} , an extra inverse mole. Repair the expression with $m_{\text{mol}} = M_m/N_A$:

$$p = \frac{N}{V} \frac{M_m}{N_A} \langle v_x^2 \rangle = \frac{n}{V} M_m \langle v_x^2 \rangle.$$

The second form uses amount density rather than number density. A symbol named “mass” is not sufficient to choose the correct formula; its physical definition and unit must agree with the density multiplying it.

4. One molecule and repeated wall encounters

In the stated collision-free pedagogical model, a molecule preserves $|v_x|$ between encounters with specular walls. A collision reverses its normal momentum from $+m_{\text{mol}}|v_x|$ to $-m_{\text{mol}}|v_x|$. The opposite impulse delivered to the wall is $2m_{\text{mol}}|v_x|$. To hit that same wall again it travels to the opposite wall and back; the recurrence time is $2L/|v_x|$. Consequently

$$\overline{F}_x = \frac{2m_{\text{mol}}|v_x|}{2L/|v_x|} = \frac{m_{\text{mol}}v_x^2}{L}.$$

The numerator’s two comes from momentum reversal; the denominator’s two comes from the round trip. The units are kg m s^{-2} . For $v_x = 0$, the limiting force is zero. Intermolecular collisions invalidate this particular recurring fixed- v_x trajectory; the ensemble pressure in a collisional equilibrium gas instead follows the velocity-flux derivation in the core text.

5. Zero mean velocity and positive pressure

Oppositely directed velocities cancel in a first moment but add in a second moment. For example, equal populations moving at $+a$ and $-a$ along x have $\langle v_x \rangle = 0$ but $\langle v_x^2 \rangle = a^2$. The wall momentum transfer therefore gives

$$p_x = n_N m_{\text{mol}} \langle v_x^2 \rangle > 0$$

when thermal motion is nonzero. Equilibrium pressure uses this second moment, with equal component second moments under isotropy. The vanishing first moments describe no bulk flow in the chosen frame; they do not describe motionless molecules. The model has zero pressure only in the limiting state where all relevant velocity components vanish.

6. Anisotropic normal stresses

Set $\langle v_y^2 \rangle = \langle v_z^2 \rangle = a$. Then $\langle v_x^2 \rangle = 2a$ and $\langle v^2 \rangle = 4a$. Replacing every component moment by $\langle v^2 \rangle/3 = 4a/3$ contradicts those given values. The wall-normal stresses are

$$p_x = 2n_N m_{\text{mol}} a, \quad p_y = p_z = n_N m_{\text{mol}} a.$$

The x -normal wall feels twice the other two normal stresses. A single equilibrium scalar pressure cannot encode this anisotropic state without an additional averaging prescription. Zero mean velocities alone would not restore isotropy; equal second moments are the missing condition.

7. Equal temperature, unequal speeds

At common T , $v_{\text{rms}} = \sqrt{3RT/M_m}$, so for the lighter and heavier stipulated gases,

$$\frac{v_{\text{rms}}(5.0)}{v_{\text{rms}}(45.0)} = \sqrt{\frac{45.0}{5.0}} = 3.0.$$

Their mean translational energies are both $\langle K_{\text{tr}} \rangle = 3k_B T/2$. The energy relation multiplies squared speed by mass; the heavier molecule's speed is smaller just enough to preserve the common energy. Figure 19.8 should therefore place the lighter gas's rms speed farther to the right. A diagram showing equal rms speeds at the same temperature for these two masses would fail that check.

8. Temperature inferred from rms speed

Invert the second-moment relation and use $M_m = 0.0320 \text{ kg mol}^{-1}$:

$$T = \frac{M_m v_{\text{rms}}^2}{3R} = \frac{(0.0320)(500)^2}{3(8.314462618)} = 320.726 \text{ K} \simeq 321 \text{ K}.$$

The numerator has units J mol^{-1} , so division by R yields kelvin. Substituting the unconverted value 32.0 would give a thousandfold error. This temperature is inferred from an equilibrium translational model; a directed molecular beam with the same speed magnitude need not have that thermal temperature.

9. Locating the Maxwell mode

Differentiate the stated density:

$$\frac{df_u}{du} = \frac{8}{\sqrt{\pi}} u(1 - u^2)e^{-u^2}.$$

For $0 < u < 1$ the derivative is positive, while for $u > 1$ it is negative. Thus $u = 1$ is the positive-speed maximum. The derivative also vanishes at $u = 0$, but $f_u(0) = 0$ and the density rises immediately to its right; this endpoint is not the positive maximum. The rise, crest, and decaying tail of Fig. 19.10 provide a graphical check. The density peaks at nonzero speed even though each Cartesian velocity component has its Gaussian maximum at zero.

10. Three characteristic speeds

The preceding derivative gives $u_{\text{mp}} = 1$. The moments are

$$\langle u \rangle = \frac{4}{\sqrt{\pi}} \int_0^\infty u^3 e^{-u^2} du = \frac{2}{\sqrt{\pi}} = 1.12838, \quad \langle u^2 \rangle = \frac{4}{\sqrt{\pi}} \int_0^\infty u^4 e^{-u^2} du = \frac{3}{2}.$$

For the first integral put $t = u^2$, so it becomes $\frac{1}{2} \int_0^\infty t e^{-t} dt = 1/2$. Integration by parts gives the second integral as $3\sqrt{\pi}/8$. Hence $u_{\text{rms}} = \sqrt{3/2} = 1.22474$ and

$$u_{\text{mp}} < \langle u \rangle < u_{\text{rms}}.$$

The rms speed is determined by the second moment, not the position of the peak. Figure 19.10 must display the markers in that order. The long high-speed tail draws the mean above the mode, and squaring speeds increases the weight of that tail still further.

11. Rare-tail counts

The expected number above the cutoff is $\mathbb{E}[K] = NP = 8000(1.35 \times 10^{-4}) = 1.08$. It is an average over repeated samples and can be noninteger even though each observed count is an integer. Independent sampling permits zero, one, two, or more tail particles; their probabilities are binomial. The omitted area beyond $u = 3.2$, the plotting cutoff in Fig. 19.10, is the probability. The density's value at the cutoff is a height and has to be integrated over an interval to become a probability. A small tail height alone is insufficient to count particles.

12. Histogram normalisation

For density heights h_j and widths Δu_j , the required test is $\sum_j h_j \Delta u_j = 1$ when all samples are included. Doubling every height doubles the area to two, although the peak location and relative heights remain unchanged. In Fig. 19.30 the original areas are 0.20, 0.35, 0.30, 0.15, summing to one; doubled heights give $0.40 + 0.70 + 0.60 + 0.30 = 2$. For a display with a stated tail cutoff, the plotted area can be slightly below one, but that declared truncation does not justify doubling. Visual resemblance cannot replace this area test.

13. Collision-length scaling

The stipulated dilute identical-hard-sphere model gives $\ell_{\text{mfp}} = (\sqrt{2}n_N\pi d^2)^{-1}$. Multiplying number density by three multiplies the denominator by three, so $\ell_{\text{mfp}} \rightarrow \ell_{\text{mfp}}/3$. At fixed density, doubling d quadruples the collision cross-section, so $\ell_{\text{mfp}} \rightarrow \ell_{\text{mfp}}/4$. This quadratic dependence arises from an area, not a circumference. These comparisons hold with the same collision model and fixed remaining parameters; changing pressure at fixed temperature can supply the density change through $n_N = p/(k_B T)$.

14. Mean free path and device length

Using SI units throughout,

$$\ell_{\text{mfp}} = \frac{1}{\sqrt{2}(1.00 \times 10^{25})\pi(4.00 \times 10^{-10})^2} = 1.40674 \times 10^{-7} \text{ m}.$$

The denominator has units m^{-1} , so the inverse is a length. With $L = 0.50 \text{ mm} = 5.0 \times 10^{-4} \text{ m}$,

$$\text{Kn} = \frac{\ell_{\text{mfp}}}{L} = 2.81 \times 10^{-4}.$$

Thus the mean collision distance is about 0.028% of this chosen device length. That comparison supports a continuum scale separation but does not itself validate every boundary condition, local-equilibrium approximation, or continuum prediction.

15. A collision target is an area

Each molecule has radius $d/2$, so the two centres collide when their closest separation reaches d . Holding one centre fixed and following the relative motion of the other therefore gives a disk of allowed impact parameters with radius d and area πd^2 . The expression $4\pi(d/2)^2$ is a sphere's surface area; it happens to have the same numerical value but describes a different geometric object. The cylinder in Fig. 19.16 counts trajectories intercepted by a projected disk, not molecules touching an entire spherical surface. For unequal diameters, the collision distance is half their sum, reinforcing the need to define d carefully.

16. Monatomic heat capacities

Three active translational quadratic terms give $E_{\text{int}} = n(3/2)RT$ up to a temperature-independent reference constant. At fixed amount,

$$C_{V,m} = \frac{1}{n} \left(\frac{\partial E_{\text{int}}}{\partial T} \right)_V = \frac{3}{2}R = 12.47 \text{ J mol}^{-1}\text{K}^{-1}.$$

For an ideal gas, $H = E_{\text{int}} + pV = E_{\text{int}} + nRT$, so $C_{p,m} = C_{V,m} + R = 5R/2 = 20.79 \text{ J mol}^{-1}\text{K}^{-1}$ and $\gamma = C_{p,m}/C_{V,m} = 5/3$. The additional R accounts for expansion work during constant-pressure heating. It is not an extra molecular kinetic mode.

17. Translation and rotation

Three translational and two rotational kinetic quadratic terms give $f_q = 5$. With vibration frozen,

$$C_{V,m} = \frac{5}{2}R, \quad C_{p,m} = \frac{7}{2}R, \quad \frac{C_{V,m}}{R} = 2.50, \quad \frac{C_{p,m}}{R} = 3.50, \quad \gamma = \frac{7}{5} = 1.40.$$

The heat capacities are 20.79 and 29.10 J mol⁻¹K⁻¹, respectively. Only thermally active modes enter this count. Figure 19.19 provides a model of such plateaus, but a real linear molecule does not possess these same heat capacities at all temperatures or pressures.

18. Two quadratic terms per harmonic vibration

For a normal coordinate q with effective mass μ and stiffness κ , the oscillator energy is

$$E_{\text{vib}} = \frac{p_q^2}{2\mu} + \frac{1}{2}\kappa q^2.$$

Both terms are quadratic, one kinetic and one potential. Classical equipartition assigns $k_B T/2$ to each, so one fully active harmonic vibration contributes $k_B T$ per molecule and R to molar $C_{V,m}$. Assigning only one half omits stored potential energy. This conclusion requires the classical thermally active regime; quantum freeze-out can suppress the oscillator contribution and is not corrected by counting only its kinetic term.

19. Temperature-dependent heat capacity

Heat capacity measures how the equilibrium internal energy changes with temperature. If a mode's quantum energy spacing is large compared with $k_B T$, raising T may populate it very little; its heat-capacity contribution is then small. As more levels become accessible, the contribution grows toward the classical result. The fixed equipartition degree count is therefore an approximation to a particular thermal regime. Energy conservation still holds as $\Delta E_{\text{int}} = Q - W_{\text{by}}$, but ΔE_{int} must be calculated by integrating the actual $C_{V,m}(T)$ rather than assuming a constant value. A changing derivative of internal energy does not imply missing energy.

20. Reversible adiabatic temperature law

Insert $p = nRT/V$ into the given balance and cancel the fixed amount:

$$C_{V,m} \frac{dT}{T} = -R \frac{dV}{V}.$$

For constant heat capacities, $R/C_{V,m} = \gamma - 1$, so integration gives

$$\ln \frac{T_f}{T_i} = -(\gamma - 1) \ln \frac{V_f}{V_i}, \quad TV^{\gamma-1} = \text{constant}.$$

The conditions are a closed ideal gas of fixed composition; no heat transfer; reversible quasi-static mechanical work so the working pressure equals the gas equilibrium pressure; equilibrium states along the path; and effectively constant heat capacities. The balance also neglects changes in macroscopic kinetic and potential energy. Adiabaticity alone is insufficient: removing a partition into vacuum satisfies $Q = 0$ while violating the required reversible path.

21. Doubling volume adiabatically

With $\gamma = 5/3$ and $V_f/V_i = 2$,

$$\frac{T_f}{T_i} = 2^{-(\gamma-1)} = 2^{-2/3} = 0.630, \quad \frac{p_f}{p_i} = 2^{-\gamma} = 2^{-5/3} = 0.315.$$

The equation of state checks the result: $(p_f/p_i)(V_f/V_i) = 0.315(2) = 0.630 = T_f/T_i$. For an isothermal expansion to the same volume, $p_f/p_i = 1/2$. The adiabatic pressure is smaller because expansion work cools the gas. This is the ordering shown in Fig. 19.22, whose illustrative $\gamma = 1.40$ gives a different numerical endpoint; its curve should not be read as a numerical plot for $5/3$.

22. Isothermal expansion

Reversibility permits using equilibrium pressure in the work integral:

$$W_{\text{by}} = \int_{V_i}^{V_f} \frac{nRT}{V} dV = RT \ln 2 = 1728.94 \text{ J} = +1.73 \text{ kJ}.$$

The logarithm takes a ratio of volumes, so either litres or cubic metres give the same ratio. Ideal-gas internal energy depends on temperature, which is unchanged; therefore $\Delta E_{\text{int}} = 0$. The first law then requires $Q = W_{\text{by}} = +1.73 \text{ kJ}$. Heat must enter while the gas does positive work. Setting $Q = 0$ merely because temperature is fixed would violate the first law for this path.

23. Free expansion into vacuum

Thermal insulation gives $Q = 0$. The external pressure against the expanding gas is zero, so $W_{\text{by}} = \int p_{\text{ext}} dV = 0$. The rigid outer container performs no additional boundary work. Hence

$$\Delta E_{\text{int}} = Q - W_{\text{by}} = 0, \quad T_f/T_i = 1$$

for an ideal gas after it re-equilibrates. The same volume endpoints as Problem 22 do not fix work or heat: that reversible path pushes a resisting boundary and draws heat from a reservoir. Free expansion has neither interaction. Its intermediate state is not represented by an equilibrium $p(V)$ curve; drawing and integrating a line between its endpoints would invent work.

24. Misapplying the adiabatic power law

The invalid assumption is reversible quasi-static expansion. During free expansion the gas is not a sequence of uniform equilibrium states whose pressure can be used as the opposing boundary pressure. Substituting its own p into $dW = pdV$ therefore fails. Although $Q = 0$, the correct work is zero because the receiving space is vacuum. The ideal-gas equation can still relate the initial and final equilibrium states, giving $p_f/p_i = V_i/V_f$ at unchanged temperature. This endpoint relation does not create a reversible isothermal path between them.

25. Work done on the compressed gas

For the stipulated one-mole example with $T_i = 300 \text{ K}$, $\gamma = 1.40$, and $V_f = V_i/2$, work on the gas is $W_{\text{on}} = -W_{\text{by}}$. In the isothermal limit,

$$W_{\text{on},T} = RT_i \ln 2 = +1.72894 \text{ kJ}.$$

In the reversible adiabatic limit, $T_f = 300(2^{0.40}) = 395.852 \text{ K}$ and $C_{V,m} = R/0.40$, giving

$$W_{\text{on},\text{ad}} = \Delta E_{\text{int}} = \frac{R}{0.40}(395.852 - 300) = +1.99240 \text{ kJ}.$$

Both signs are positive because compression transfers mechanical energy into the gas. Throughout compression below V_i , the adiabatic curve lies above the isothermal curve in Fig. 19.22. Its area magnitude is larger, agreeing with the calculation. The plotted area represents work by the gas with a negative integration direction, so comparing positive geometric areas here compares work on the gas.

26. A worked experimental design and rubric

One valid design uses a sealed sample in a calibrated piston cylinder with pressure and gas-temperature probes. Record run and timestamp, absolute p , calibrated gas volume V , temperature T in kelvin, their uncertainties, and the derived $C = pV/T$. Also record piston position, direction of the preceding change, waiting time, and evidence that the amount remained fixed. A suitable table structure is

Run/time	$p \pm u_p$ (Pa)	$V \pm u_V$ (m ³)	$T \pm u_T$ (K)	$C \pm u_C$ (J K ⁻¹)
1, stable	recorded	recorded	recorded	calculated
2, stable	recorded	recorded	recorded	calculated

Absolute pressure is required. A gauge reading must be corrected using the measured atmospheric reference: $p_{\text{abs}} = p_{\text{gauge}} + p_{\text{atm}}$. The gas volume must include relevant tubing and sensor dead volume. Absolute temperature is required; a temperature in Celsius cannot be substituted into the state relation.

For each row, require pressure and temperature to plateau within the stated resolution over several instrument response times, negligible piston motion during recording, and no sustained drift suggesting leakage. A second temperature probe or agreement after longer waiting helps detect gradients. A single stationary probe reading does not establish thermal uniformity. Compression and decompression revisits to the same target state help test hysteresis and incomplete equilibration. Limit the range so the ideal model remains a defensible starting point.

For independent small measurement uncertainties, a useful reported uncertainty is

$$\frac{u_C}{C} \simeq \sqrt{(u_p/p)^2 + (u_V/V)^2 + (u_T/T)^2}.$$

Compare the rows with a common $C = nR$ within these uncertainties; do not require identical displayed last digits. As a worked exemplar, the synthetic table in Problem 36 yields amounts close to 0.2000 mol and residuals smaller than their stipulated uncertainties. This supports consistency, while a calibration check and leak test remain separate evidence.

A ten-point rubric can award two points for absolute pressure and kelvin; two for a complete table with units and uncertainties; two for equilibrium criteria and sufficient waiting; two for fixed amount, calibration, and dead-volume control; and two for an uncertainty-aware common- C test with a limitation stated. Other sound apparatus and designs earn equivalent credit if they meet those physical requirements. Listing p, V, T alone without a method to establish their state meaning is incomplete.

27. Incorrect Gaussian component scale

The required dimensionless components each have variance 1/2. Sampling standard deviation one instead gives variance one. Since $u^2 = u_x^2 + u_y^2 + u_z^2$, its mean becomes 3 instead of 3/2. The rms marker is therefore too large by

$$\frac{\sqrt{3}}{\sqrt{3/2}} = \sqrt{2} \simeq 1.414.$$

The entire speed distribution is rescaled, so its outline can still resemble a Maxwell curve. A correct-looking peak is not a moment check. Examining the variance of each generated component would identify the error before the components are combined into speed.

28. A second-moment audit

The analytic target is $\langle u^2 \rangle = 3/2 = 1.50$. The reported 0.75 is half of this target. A persistent value near 0.75 under repeated large samples indicates incorrect scaling, normalisation, or calculation of the second moment. For example, components with variance 1/4 would produce this value. One isolated

sample must still be judged using its size and variability, but such a factor-of-two discrepancy for a well-sampled simulation is qualitatively different from the small stochastic deviations in Problem 34. Check component variances, the definition of u , and the divisor used when accumulating sample moments.

29. A Knudsen number without a universal label

Convert the lengths to the same units: $\ell_{\text{mfp}} = 2.0 \times 10^{-6}$ m and $L = 2.0 \times 10^{-4}$ m. Then

$$\text{Kn} = \ell_{\text{mfp}}/L = 0.010.$$

The mean collision distance is one hundredth of the chosen device length. This dimensionless comparison helps assess whether molecular transport lengths can be neglected, but its implications depend on geometry, local gradients, boundaries, and the required accuracy. Naming a universal regime from the number alone would ignore that context. A smaller local length, such as a narrow opening, can yield a larger relevant Knudsen number in the same vessel.

30. Equation of state and path constraints

The equation $pV = nRT$ relates each equilibrium state but does not specify how a process changes temperature. Isothermal contact with a reservoir imposes $T = T_i$, giving $p/p_i = V_i/V$. Reversible adiabatic expansion or compression with constant heat capacities imposes $T/T_i = (V_i/V)^{\gamma-1}$, giving $p/p_i = (V_i/V)^\gamma$. Both substitutions satisfy the same state equation. Figure 19.22 shows these distinct curves through the same initial point. Their separation encodes different temperature histories and therefore different energy transfers, not a contradiction between two gas equations of state.

31. Velocity-space shell transformation

Write the isotropic three-component density as

$$F(\mathbf{v}) = \left(\frac{m_{\text{mol}}}{2\pi k_B T} \right)^{3/2} \exp \left[-\frac{m_{\text{mol}}(v_x^2 + v_y^2 + v_z^2)}{2k_B T} \right].$$

The probability in a velocity-space element is $F dv_x dv_y dv_z$. In spherical velocity coordinates that element is $v^2 \sin \theta dv d\theta d\phi$. Because F depends only on v , angular integration gives

$$f(v)dv = F(v)v^2 dv \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta = 4\pi v^2 F(v)dv.$$

The factor $4\pi v^2$ counts the shell area, not a spatial area in the container. The density F has units $(\text{m s}^{-1})^{-3}$, while $f(v)$ has units $(\text{m s}^{-1})^{-1}$; multiplying by dv gives dimensionless probability. Omitting the shell factor would confuse a component distribution with a speed distribution and would incorrectly place the speed maximum at zero.

32. Adiabatic stiffness and speed

For constant γ , write $p = C\rho^\gamma$. Differentiation along the reversible adiabatic family gives

$$\left(\frac{\partial p}{\partial \rho} \right)_{\text{rev ad}} = \gamma C \rho^{\gamma-1} = \gamma \frac{p}{\rho}.$$

The bulk modulus is $B_{\text{ad}} = \rho(\partial p/\partial \rho)_{\text{rev ad}} = \gamma p$, hence the small-disturbance model speed is $c_w = \sqrt{B_{\text{ad}}/\rho} = \sqrt{\gamma p/\rho}$. At fixed state the isothermal derivative is p/ρ , so $c_T = \sqrt{p/\rho}$. The normalised curves in Fig. 19.27 have slopes γ and one at their common reference point; the speed ratio is the square root of the slope ratio. As $\gamma \rightarrow 1$, these derivatives and speeds coincide. This is a mathematical limit of the two model relations, not a statement that a typical gas literally has $C_{V,m} = \infty$.

33. Stipulated acoustic speeds

Use $M_m = 0.0400 \text{ kg mol}^{-1}$ and $p/\rho = RT/M_m$:

$$c_T = \sqrt{\frac{(8.314462618)(320)}{0.0400}} = 257.906 \text{ m s}^{-1}, \quad c_w = \sqrt{\frac{5}{3}} c_T = 332.956 \text{ m s}^{-1}.$$

To three significant figures these are 258 and 333 m s^{-1} . The dimensions inside the root are $\text{m}^2 \text{s}^{-2}$. Identifying a real gas requires composition, a valid equation of state and heat capacity, and the relevant disturbance time scale and thermal relaxation. Stipulated mass and γ alone do not constitute measured material data.

34. Finite-sample moment discrepancies

Using the analytic markers of Fig. 19.10, the signed relative deviations are

$$\frac{1.12465 - 1.128379167}{1.128379167} = -0.00330489 = -0.330489\%,$$

$$\frac{1.22123 - 1.224744871}{1.224744871} = -0.00286988 = -0.286988\%.$$

Both sample moments lie slightly below their analytic targets. Their mere inequality to the targets does not prove an implementation error: finite random samples do not reproduce ensemble integrals exactly. A useful criterion is agreement with expected sampling fluctuations across independent seeds and increasing sample sizes. A persistent offset large compared with the standard error, a wrong component variance, or failed exact normalisation would instead indicate an implementation problem. Problem 44 quantifies the mean's fluctuation scale rather than classifying a small discrepancy by appearance alone.

35. Miniaturisation at fixed gas state

At unchanged gas state and collision model, ℓ_{mfp} is unchanged. If $L' = L/10$,

$$\text{Kn}' = \frac{\ell_{\text{mfp}}}{L/10} = 10 \text{ Kn}.$$

Molecules consequently travel a larger fraction of the device dimension between collisions. Wall interactions, nonlocal transport, and departures from a locally equilibrated continuum can become more influential. The gas itself need not change: the altered ratio results from geometry. For a device with several distinct length scales, the length relevant to the process must be chosen rather than using the overall device size automatically.

36. Synthetic state-consistency residuals

(a) Because $1 \text{ kPa} \times 1 \text{ L} = 1 \text{ J}$, the table's numerical pV/T directly has units J K^{-1} . The calculation gives

Row	$C_i \text{ (J K}^{-1}\text{)}$	$n_i \text{ (mol)}$	$r_i \text{ (\%)}$
1	1.662893	0.200000	0.0000
2	1.669544	0.200800	+0.4000
3	1.657904	0.199400	−0.3000
4	1.666218	0.200400	+0.2000
5	1.661230	0.199800	−0.1000

(b) Figure 19.29 shows that every residual's stipulated 0.50% standard-uncertainty bar includes zero. There is no compelling evidence of a departure in these five rows. For an illustrative goodness-of-fit

check with fixed n_0 , $\sum (r_i/0.50)^2 = 0 + 0.64 + 0.36 + 0.16 + 0.04 = 1.20$ for five residuals. Such a small value does not demonstrate ideal behaviour at all states; it only shows that this synthetic data set is consistent with its model and declared uncertainty.

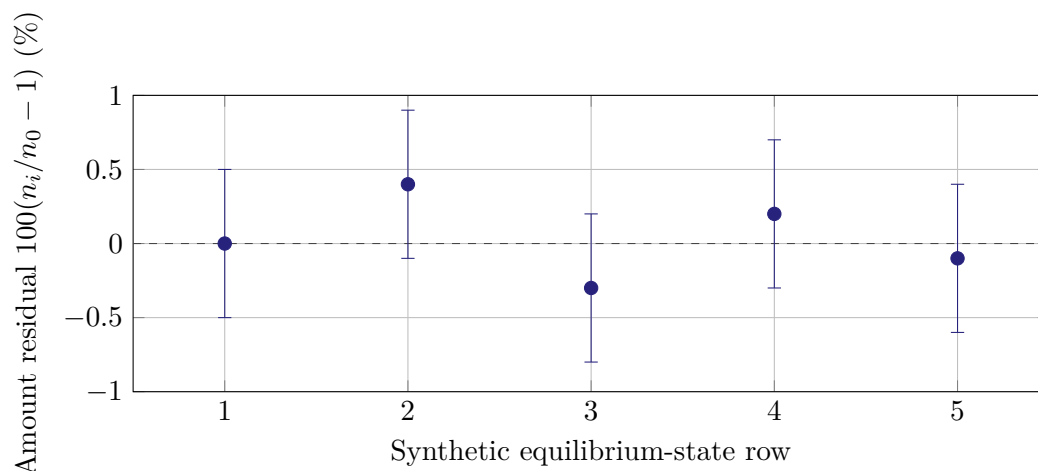


Figure 19.29: Residuals calculated from the declared synthetic pVT table. Bars are stipulated standard uncertainties of 0.50% in each residual, not measured confidence intervals. The data scatter is compatible with the reference amount $n_0 = 0.2000$ mol.

(c) Revisit the same p, V, T state after several waiting times. Leakage tends to change inferred amount with elapsed time, whereas an additive pressure calibration offset gives $C_{\text{app}} = nR + \delta p V/T$ and therefore a reproducible state-dependent pattern. An independent pressure calibration plus a timed leak test can separate them. The five rows alone, with no timing or instrument information, cannot identify either mechanism.

37. Bin area, probability, and approximate mean

(a) Density must be multiplied by each bin's width. The four areas are

$$(0.40)(0.5) = 0.20, \quad (0.70)(0.5) = 0.35, \quad (0.30)(1.0) = 0.30, \quad (0.15)(1.0) = 0.15.$$

Their sum is one. (b) The interval includes the second and third bins, so its probability is $0.35 + 0.30 = 0.65$ and the expected count is $2000(0.65) = 1300$. A particular sample need not contain exactly 1300. (c) The tallest bin's probability is $0.70(0.5) = 0.35$, not 0.70; height and probability differ because width matters.

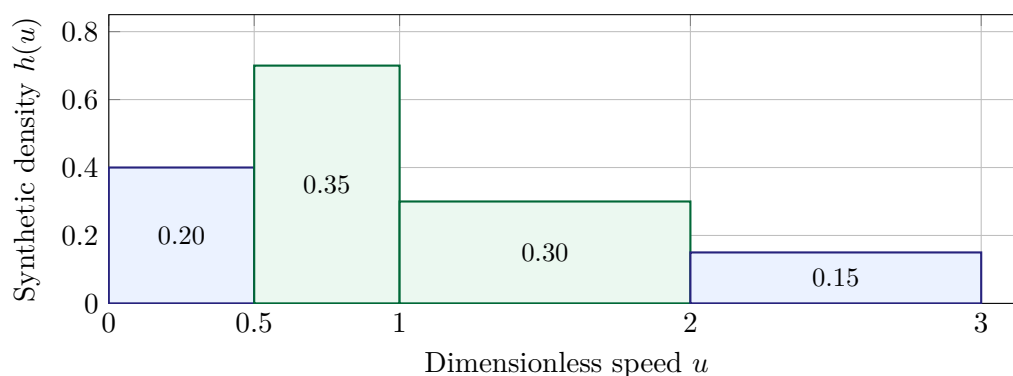


Figure 19.30: Unequal-width synthetic density bins. Labels are bin probabilities, equal to height times width. The two green bins cover $0.5 \leq u < 2.0$ and contain probability 0.65. This teaching histogram is a declared piecewise-constant model, not Maxwell sample data.

(d) A uniform bin's mean is its midpoint, so the model mean is

$$\langle u \rangle_h = (0.20)(0.25) + (0.35)(0.75) + (0.30)(1.5) + (0.15)(2.5) = 1.1375.$$

This is exact for the displayed piecewise-constant density. It is not the exact Maxwell mean because those bin heights were stipulated independently and replace any within-bin structure by a constant. If derived from measurements, the same midpoint procedure would be a binning approximation to the underlying sample mean.

38. Work as curve area

(a) The shared initial pressure is

$$p_i = \frac{nRT_i}{V_i} = \frac{(0.200)(8.314462618)(300)}{0.00200} = 249.434 \text{ kPa}.$$

The isothermal endpoint has $T_f = 300 \text{ K}$ and $p_f = 124.717 \text{ kPa}$. With $\gamma = 5/3$, the adiabatic endpoint has $T_f = 300(2^{-2/3}) = 188.988 \text{ K}$ and $p_f = p_i 2^{-5/3} = 78.5667 \text{ kPa}$.

(b) Put $x = V/V_i$. Work is $p_i V_i$ times the area under p/p_i against x . The two integrals are

$$W_{\text{by,T}} = nRT_i \int_1^2 x^{-1} dx = nRT_i \ln 2 = +345.789 \text{ J},$$

$$W_{\text{by,ad}} = nRT_i \int_1^2 x^{-5/3} dx = \frac{nRT_i}{2/3} (1 - 2^{-2/3}) = +276.901 \text{ J}.$$

The isothermal gas has $\Delta E_{\text{int}} = 0$ and $Q = +345.789 \text{ J}$. The adiabatic gas has $Q = 0$ and $\Delta E_{\text{int}} = -276.901 \text{ J}$. Directly using $nC_{V,m}(T_f - T_i)$ with $C_{V,m} = 3R/2$ reproduces the latter value.

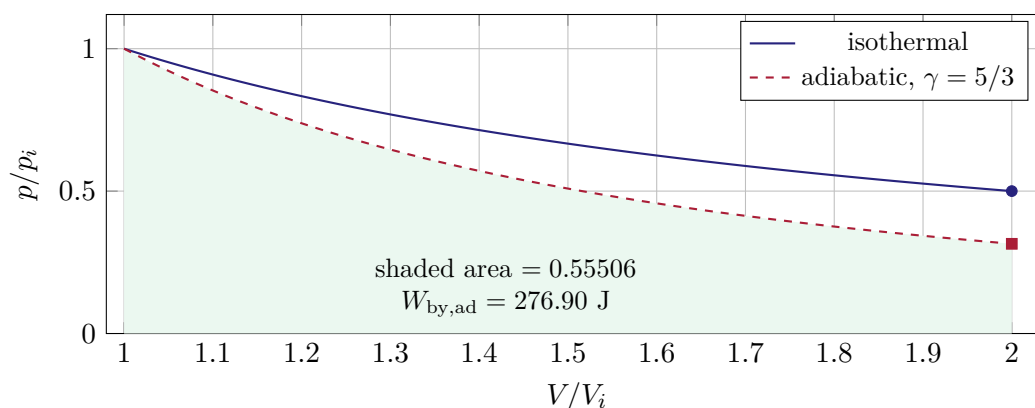


Figure 19.31: Reversible expansion paths for Problem 38. The green area is the integral under the adiabatic curve from V_i to $2V_i$, with the integration baseline at zero pressure. The isothermal area is $\ln 2 = 0.69315$ and is larger. Dimensionless areas must be multiplied by $p_i V_i = nRT_i$ to obtain joules.

(c) Along the adiabatic expansion, work draws energy from the gas and lowers its temperature; heat entering from a reservoir prevents that cooling in the isothermal path. Consequently its pressure remains higher at every expanded volume and its work integral is larger. Volume alone does not determine an equilibrium state or an energy transfer.

39. Collision model as an inverse measurement

(a) Combine $\ell_{\text{mfp}} = (\sqrt{2}n_N\pi d^2)^{-1}$ with $n_N = p/(k_B T)$:

$$p = \frac{k_B T}{\sqrt{2}\pi d^2 \ell_{\text{mfp}}} = \frac{(1.380649 \times 10^{-23})(300)}{\sqrt{2}\pi(3.70 \times 10^{-10})^2(68 \times 10^{-9})} = 100.145 \text{ kPa}.$$

(b) The logarithmic differential is $dp/p = dT/T - 2dd/d - d\ell_{\text{mfp}}/\ell_{\text{mfp}}$. Squaring independent standard-uncertainty contributions gives

$$\frac{u_p}{p} = \sqrt{\left(\frac{1}{300}\right)^2 + \left(\frac{2(0.05)}{3.70}\right)^2 + \left(\frac{3}{68}\right)^2} = 0.05185.$$

The inferred result is approximately $p = (100.1 \pm 5.2)$ kPa with a standard uncertainty. **(c)** The fractional contributions are 0.33% from temperature, 2.70% from diameter, and 4.41% from mean free path, making the last largest. Temperature improvement alone barely changes their quadrature total. The uncertainty calculation describes the stated model and inputs; model inadequacy or an ambiguous effective collision diameter introduces additional uncertainty beyond these instrument-like terms.

40. An ideal mixture at equilibrium

(a) Each species contributes its own number-density pressure, so $p_A = x_A p = 40.0$ kPa and $p_B = x_B p = 60.0$ kPa. At the common temperature,

$$v_{\text{rms,A}} = \sqrt{\frac{3RT}{0.00400}} = 1367.76 \text{ m s}^{-1}, \quad v_{\text{rms,B}} = \sqrt{\frac{3RT}{0.0320}} = 483.574 \text{ m s}^{-1}.$$

Their ratio $\sqrt{8}$ checks the inverse square-root mass scaling. **(b)** The average mass per mole of mixture is $\bar{M} = 0.400(0.00400) + 0.600(0.0320) = 0.0212 \text{ kg mol}^{-1}$. Therefore

$$\rho = \frac{p\bar{M}}{RT} = 0.849925 \text{ kg m}^{-3}.$$

(c) Multiplying each species' mean squared speed by its molecular mass gives the same $3k_B T/2$ translational energy. This is the equal-temperature interpretation of Fig. 19.8. The mixture speed density is $x_A f_A(v) + x_B f_B(v)$; a single Maxwell curve formed using $\bar{M}$ cannot generally reproduce that weighted sum because its two mass-dependent scales differ. The average mass is suitable for total mass density, but it does not erase the identity of the component distributions.

41. Exact Maxwell tail and count fluctuations

(a) Integrate $I(a) = \int_a^\infty u^2 e^{-u^2} du$ by taking one factor u with the differential $u e^{-u^2} du = -\frac{1}{2} d(e^{-u^2})$. The boundary term at infinity vanishes, giving

$$I(a) = \frac{a}{2} e^{-a^2} + \frac{1}{2} \int_a^\infty e^{-u^2} du.$$

Multiplication by $4/\sqrt{\pi}$ yields

$$P(u > a) = \text{erfc}(a) + \frac{2a}{\sqrt{\pi}} e^{-a^2}.$$

At $a = 0$ this becomes one, and as $a \rightarrow \infty$ both terms vanish, checking the limits. **(b)** At $a = 2$ the probability is $0.004677735 + (4/\sqrt{\pi})e^{-4} = 0.0460117$, or 4.60%. **(c)** With $N = 1000$, the count mean is 46.0117 and its standard deviation is

$$\sigma_K = \sqrt{1000(0.0460117)(1 - 0.0460117)} = 6.63.$$

A result near 46 is typical, but individual samples vary substantially. The expected count is neither a forced integer output nor an exact prediction of a particular simulation seed.

42. Adiabatic cooling with variable heat capacity

(a) Reversible adiabatic work gives $C_{V,m}(T)dT/T = -RdV/V$. Insert the stipulated function and integrate:

$$1.50 \ln \frac{T_f}{300} + b(T_f - 300) = -\ln 2.$$

This logarithmic-plus-linear equation replaces a constant- γ power law. (b) Its left side has derivative $1.50/T_f + b > 0$ at positive temperature, so there is at most one positive root. Bisection between 200 and 220 K gives $T_f = 212.402$ K. Then

$$\frac{p_f}{p_i} = \frac{T_f}{T_i} \frac{V_i}{V_f} = \frac{212.402}{600} = 0.354004.$$

(c) For one mole, integrate the heat capacity directly:

$$\Delta E_{\text{int}} = R \left[1.50(T_f - 300) + \frac{b}{2}(T_f^2 - 300^2) \right] = -1465.69 \text{ J}.$$

Thus $W_{\text{by}} = +1465.69$ J since $Q = 0$. Freezing γ initially gives $\gamma_i = 1 + 1/(1.50 + 0.00200 \times 300) = 1.47619$ and the incorrect power-law value $T_f = 300(2^{1-\gamma_i}) = 215.662$ K. During cooling, the actual $C_{V,m}$ decreases, so the same incremental expansion removes a larger fractional thermal energy than the frozen-capacity model predicts; the actual final temperature is lower. No energy-conservation rule has changed; only the constitutive relation being integrated differs.

43. Effusive speed selection

(a) Since $\langle u \rangle = 2/\sqrt{\pi}$,

$$g(u) = 2u^3 e^{-u^2}, \quad \int_0^\infty g(u) du = 2 \left(\frac{1}{2} \right) = 1.$$

This is a density among crossing molecules; it is not the bulk density f_u . (b) Differentiate:

$$g'(u) = 2u^2 e^{-u^2} (3 - 2u^2).$$

Its positive maximum is at $u_{\text{mp,eff}} = \sqrt{3/2} = 1.22474$. The escaping mean is

$$\langle u \rangle_{\text{eff}} = 2 \int_0^\infty u^4 e^{-u^2} du = \frac{3\sqrt{\pi}}{4} = 1.32934,$$

which exceeds the bulk mean 1.12838. (c) Faster molecules meet and cross the aperture more often, so flux weighting preferentially samples them. The reservoir's temperature determines both distributions; selecting crossing events changes the sampled population, not the underlying equilibrium temperature. A finite isolated reservoir can cool as energetic molecules escape, whereas the stipulated maintained equilibrium reservoir is treated as unchanged during sampling. Intermolecular collisions in a thick aperture or outside it would require a different model.

44. Sampling fluctuations and independence

(a) The single-sample variance is

$$\sigma_u^2 = \langle u^2 \rangle - \langle u \rangle^2 = \frac{3}{2} - \frac{4}{\pi} = 0.226760.$$

For independent samples, variances of the sum add. Dividing the sum by N yields $\text{Var}(\bar{u}) = \sigma_u^2/N$, so

$$\text{SE}(\bar{u}) = \sqrt{0.226760/8000} = 0.00532401.$$

(b) The observed mean's deviation is $1.12465 - 1.128379167 = -0.00372917$. In standard-error units it is $z = -0.70044$, well within an ordinary one-standard-error fluctuation. It does not alone provide compelling evidence of a sampling error. A systematic bias could still evade a single such test, which is why component and normalisation checks remain valuable.

(c) Serially correlated values do not make variances of successive samples add as though they were independent. Positive correlation usually enlarges the mean's uncertainty and reduces the effective sample size. Inspect a speed or component autocorrelation versus lag, or compare variance among long independent blocks with the independent-sample prediction. Use separate seeds for replicate runs. A numerically large count of stored values is not sufficient evidence of an equally large number of independent observations.

45. Inverting acoustic stiffness for heat capacity

(a) At the same state, $\gamma = c_w^2/c_T^2 = (300/250)^2 = 1.44$. The ideal-gas relation $C_{p,m} - C_{V,m} = R$ then gives

$$C_{V,m} = \frac{R}{\gamma - 1} = 18.8965 \text{ J mol}^{-1}\text{K}^{-1}, \quad C_{p,m} = C_{V,m} + R = 27.2110 \text{ J mol}^{-1}\text{K}^{-1}.$$

(b) The two tangent derivatives of $p(\rho)$ are c_w^2 and c_T^2 . Thus their slope ratio is 1.44, while their speed ratio is 1.20. Figure 19.27 checks this square-root relation; reading its illustrative slope 1.40 as either a speed or as the stipulated value here would be incorrect.

(c) From $\ln \gamma = 2 \ln c_w - 2 \ln c_T$, independent 1% speed uncertainties give

$$u_\gamma/\gamma = \sqrt{(2\%)^2 + (2\%)^2} = 2.83\%.$$

Hence $u_\gamma \simeq 0.0407$. Linearising $C_{V,m} = R/(\gamma - 1)$ gives

$$\frac{u_{C_V}}{C_{V,m}} \simeq \frac{u_\gamma}{\gamma - 1} = \frac{0.0407}{0.44} = 9.26\%,$$

about $1.75 \text{ J mol}^{-1}\text{K}^{-1}$. The inverse becomes increasingly sensitive as γ approaches one. Formally $f_{\text{eff}} = 2C_{V,m}/R = 4.54545$, a noninteger value. It can describe an effective mixture average, or a local value when quantum modes are partly active. Over a wider temperature range those modes can make heat capacity vary, limiting the calorically ideal assumption; a strict integer count belongs to a single-species fully classical plateau approximation. All inferences also require the two measurements to probe the stipulated thermal responses at the same state.

19.13 Bridge to Chapter 20

Kinetic theory explains how many-particle motion can generate pressure, temperature-linked energy scales, collision rates, and process-dependent gas stiffness. Yet the chapter also exposes a deeper question. If molecular motion is reversible at the microscopic level, why do macroscopic gas processes have a preferred direction? Why does a freely expanding gas not spontaneously return to one side of its container, even though energy conservation alone does not forbid the reverse movie?

In an equilibrium macroscopic ideal-gas sample, vastly more molecular arrangements occupy the expanded volume than confine every molecule to one region. Spontaneous return to the confined state is extraordinarily improbable; microscopic reversibility does not make these two macrostates equally probable.

Chapter 20, *Entropy and the Second Law of Thermodynamics*, introduces the thermodynamic quantity and principles needed to answer those questions. The distinction made here between a reversible comparison path and an irreversible actual process becomes central there.

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