

PHYSICS PHYS1121 – HIGHER PHYSICS 1131

3. THERMODYNAMICS

3.1 Temperature

3.1.1 Temperature Scales

The temperature scale has a lowest limit:

$$0\text{ K} = -273.15^\circ\text{C}, \quad \text{where } 1\text{ K} = 1\text{ Kelvin}$$

This is the so-called absolute zero temperature. It can never be reached. Even if a tremendous amount of energy is invested into cooling, the final temperature will always stay slightly above the absolute zero temperature.

The three temperature scales commonly used are: **Kelvin, Celsius and Fahrenheit.**

Kelvin scale

The temperature scale used in science is the Kelvin scale with the absolute zero temperature $T = 0\text{ K}$.

Celsius scale

Melting point of water ice 0°C at 1 atm

Boiling point of water 100°C at 1 atm

$$T_C = T - 273.15\text{ K}$$

Fahrenheit scale

Melting point of water ice $0^\circ\text{C} \hat{=} 32^\circ\text{F}$ at 1 atm

Boiling point of water $100^\circ\text{C} \hat{=} 212^\circ\text{F}$ at 1 atm

$$T_F = 9/5 T_C + 32^\circ\text{F}$$

It should be noted that the melting temperature of water ice and the boiling temperature of water changes with pressure. The above given values correspond to the values at a pressure of one atmosphere (1 atm), where:

$$1\text{ atm} = 1.013\text{ bar} = 1.013 \cdot 10^5\text{ Pa}$$

$$1\text{ Pa} = 1\text{ Pascal} = 1 \frac{\text{N}}{\text{m}^2}, \quad \text{and} \quad 1\text{ mbar} = 100\text{ Pa} = 1\text{ hPa}$$

Various physical properties depend on temperature:

- melting point of solids
- boiling point of liquids
- pressure of a gas in a closed container
- thermal expansion of a solid, a liquid or a gas
- electrical resistance
- even the colour of a flame changes with its temperature.

3.1.2 The 0th Law of Thermodynamics

The 0th Law of Thermodynamics

If the objects **A** and **B** are each in thermal equilibrium with a third object **C**, then **A** and **B** are in thermal equilibrium with each other.

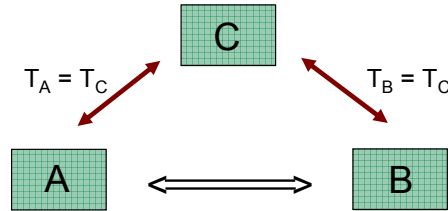


Figure 3.1: Illustration of the 0th Law of Thermodynamics.

To measure the temperature of an object or a liquid, a thermometer has to be brought into contact with the object. Be aware that this can change the temperature of the object, especially if the object is small compared to the size of the thermometer.

There are various types of thermometers:

1. The standard thermometer uses the thermal expansion of a liquid, e.g. alcohol or liquid mercury. Upon increasing temperature the liquid rises in the capillary.
2. Electronic thermometers use the fact that the electrical resistance increases with temperature. In the range between $0^{\circ}C$ and $100^{\circ}C$ the electrical resistance typically increases linearly with increasing temperature.
3. The constant volume gas thermometer uses the increase in pressure when a gas is heated.

For the calibration of a thermometer, fixed points are needed. An important requirement is that they have to be easily reproducible. The boiling point of water and the melting point of water ice (or other liquids such as ethanol or acetone) seem to be a good choice. However, both the boiling point and melting point depend on the external pressure. Precisely $0.0^{\circ}C$ and $100.0^{\circ}C$ for the melting and boiling temperature of water only hold for a pressure of exactly 1 atm. Therefore other fixed points are required. The triple-point of water would be one of them since it can be reached easily with a vacuum pump and is perfectly reproducible (see page 4).

State of Matter: Solid – Liquid – Gas

In general, matter can exist in three states: **Solid** — **Liquid** — **Gas**.

All elements of the periodic table of elements possess these three states. At ambient pressure only Helium is an exemption. It becomes liquid at 4.2 K and remains a liquid down to the lowest possible temperatures at a pressure of 1 atm. However, Helium can become a solid at low temperature and under pressure (e.g. at a temperature of 0.75 K and a pressure of 25.3 bar).

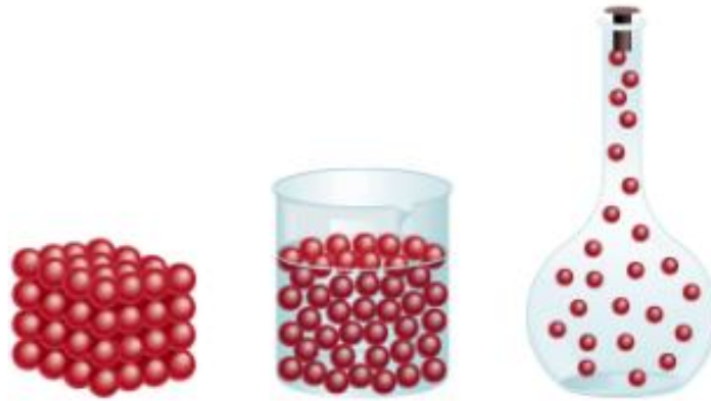


Figure 3.2: Solid – Liquid – Gas

The three states can be classified as:

- **Solid:** The atoms are in fixed positions, they do not move.
A solid material keeps its shape.
Solids are for example crystals where the atoms form a perfectly symmetric lattice.
Solids possess the lowest compressibility.
- **Liquid:** The atoms can move freely.
In a liquid the atoms fill out a closed container up to a certain filling level.
A liquid possesses a low compressibility.
It has a much higher density as compared to a gas.
- **Gas:** The atoms can move freely.
A gas fills out the entire closed container.
A gas can be easily compressed and possesses the lowest density.

Pressure – Temperature Phase Diagram of Water

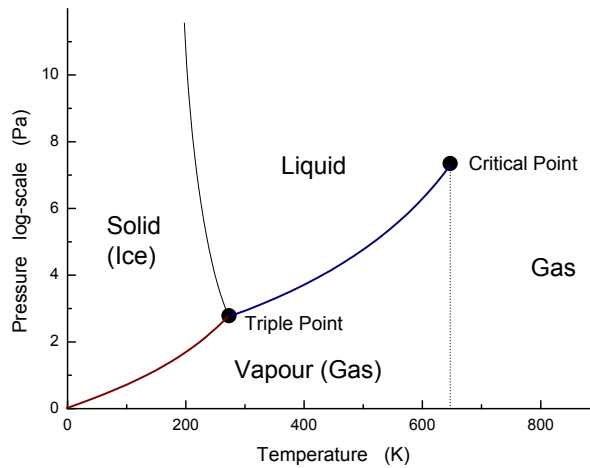


Figure 3.3: Pressure–Temperature phase diagram of water with the three phases: solid, liquid and gas. The triple-point and the critical point are given. Note that the pressure is plotted on a logarithmic scale.

Triple Point of Water:

$$T_{\text{tr.}} = 273.16 \text{ K}$$

$$P_{\text{tr.}} = 611.657 \text{ Pa}$$

Critical Point of Water:

$$T_{\text{tr.}} = 647 \text{ K}$$

$$P_{\text{tr.}} = 220.58 \text{ bar} = 220.58 \cdot 10^5 \text{ Pa}$$

3.1.3 Thermal Expansion

The linear thermal expansion of a material can be described by the following equation:

$$\Delta L = L_i \cdot \alpha \cdot \Delta T$$

where L_i is the initial length, L_f is the final length, and $\Delta L = L_f - L_i$. ΔT is the change in temperature and α is the linear thermal expansion coefficient.

Material (Solid)	linear expansion coefficient α [$^{\circ}C^{-1}$]	Material (Liquid, Gas)	linear expansion coefficient α [$^{\circ}C^{-1}$]
Aluminum	$23 \cdot 10^{-6}$	Acetone	$1.5 \cdot 10^{-4}$
Brass	$19 \cdot 10^{-6}$	Ethanol	$1.12 \cdot 10^{-4}$
Cooper	$17 \cdot 10^{-6}$	Benzene	$1.24 \cdot 10^{-4}$
Lead	$29 \cdot 10^{-6}$	Glycerine	$4.85 \cdot 10^{-4}$
Steel	$11 \cdot 10^{-6}$	Mercury	$1.82 \cdot 10^{-3}$
Concrete	$12 \cdot 10^{-6}$	Air at $0^{\circ}C$	$3.67 \cdot 10^{-3}$
Glass	$9 \cdot 10^{-6}$	Helium	$3.67 \cdot 10^{-3}$

Examples:

- Working principle of a thermometer.

As mentioned above, in a classical thermometer a liquid (alcohol or mercury) expands and its level rises in a glass capillary.

- Thermal expansion of a bridge; the joints.

With increasing temperature buildings or bridges expand. Therefore special joints are installed to compensate for this expansion.

The Sydney Harbor Bridge has a total length of 1,149 m. Throughout the year the temperature changes from e.g. $6^\circ C$ to $46^\circ C$. The temperature difference is $\Delta T = 40^\circ C$. The total thermal expansion of the Sydney Harbor Bridge is therefore 0.50 meter. Note that in the bright sun the steel of the bridge reaches even higher temperatures and cools down again over night.

- Bi-metal switch

A bi-metal consists of two metals with different linear thermal expansion coefficients. With changing temperature the bi-metal bends in one direction. This can be used to build a switch which regulates the temperature. For example radiators in a room are equipped with such thermostats, where bi-metal strips are used as circuit breakers.

A bi-metal can also be used to record the temperature over a longer time. A needle is attached to the bi-metal and touches a piece of paper on a slowly rotating drum.

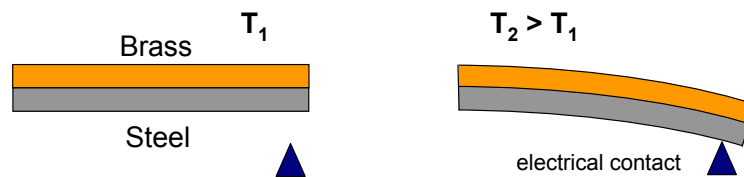


Figure 3.4: Schematic of a Bi-metal switch.

Volume Expansion:

$$\begin{aligned}
 V_i + \Delta V &= (l + \Delta l)(w + \Delta w)(h + \Delta h) \\
 &= (l + l\alpha\Delta T)(w + w\alpha\Delta T)(h + h\alpha\Delta T) \\
 &= lwh(1 + \alpha\Delta T)^3 = V_i(1 + \alpha\Delta T)^3 \\
 &= V_i(1 + 3(\alpha\Delta T) + \underbrace{3(\alpha\Delta T)^2}_{\text{small}} + \underbrace{(\alpha\Delta T)^3}_{\text{small}}) \\
 &= V_i(1 + 3\alpha\Delta T)
 \end{aligned}$$

$$\Delta V = 3\alpha V_i \Delta T = \beta V_i \Delta T$$

where β is the volume expansion coefficient with: $3\alpha = \beta$.

3.2 Kinetic Gas Theory and the Ideal Gas

3.2.1 Avogadro's Number

The amount of a gas can be expressed in moles 'n'.

$$n = \frac{m}{M}$$

where m is the mass of the gas in grams and M is the molar mass.

$$1 \text{ mole} = 1 N_A = 6.022 \cdot 10^{23} \text{ atoms or molecules}$$

N_A is the **Avogadro's number**.

$$n = \frac{N}{N_A} = \frac{\text{number of molecules}}{\text{Avogadro's number}}$$

1 mole corresponds to 12 g of the carbon isotope ^{12}C .

The molar mass is given in the periodic table of elements. It is typically not an integer number. This is caused by the fact that the elements possess different stable isotopes with a certain distribution. For example copper has a molar mass of $M = 63.546 \text{ g/mol}$ and possesses two stable isotopes: ^{63}Cu with a molar fraction of 0.6915(15) and ^{65}Cu with a molar fraction of 0.3085(15).

Most gasses appear as molecules such as H_2 , N_2 or O_2 . Exceptions are noble gases, i.e. Helium, Neon, Argon, Krypton, Xenon and Radon.

Periodic Table of Elements

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18																
1	H																		2	He															
3	Li	4	Be											10	Ne																				
11	Na	12	Mg											18	Ar																				
19	K	20	Ca	21	Sc	22	Ti	23	V	24	Cr	25	Mn	26	Fe	27	Co	28	Ni	29	Cu	30	Zn	31	Ga	32	Ge	33	As	34	Se	35	Br	36	Kr
37	Rb	38	Sr	39	Y	40	Zr	41	Nb	42	Mo	43	Tc	44	Ru	45	Rh	46	Pd	47	Ag	48	Cd	49	In	50	Sn	51	Sb	52	Te	53	I	54	Xe
55	Cs	56	Ba	57-71	72	Hf	73	Ta	74	W	75	Re	76	Os	77	Ir	78	Pt	79	Au	80	Hg	81	Tl	82	Pb	83	Bi	84	Po	85	At	86	Rn	
87	Fr	88	Ra	89-103	104	Rf	105	Db	106	Sg	107	Bh	108	Hs	109	Mt	110	Ds	111	Rg	112	Cn	113	Nh	114	Fl	115	Mc	116	Lv	117	Ts	118	Uuo	
																			For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.																
																			Design and Interface Copyright © 1997 Michael Dayah (michael@dayah.com). http://www.ptable.com/																
		57	58	59	60	61	62	63	64	65	66	67	68	69	70	71																			
		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu																			
		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr																			

C Solid

Hg Liquid

H Gas

Rf Unknown

Metals

Alkali metals

Alkaline earth metals

Lanthanoids

Actinoids

Transition metals

Poor metals

Nonmetals

Other nonmetals

Noble gases

Figure 3.5: Periodic Table of Elements. The molar mass is given under the name of the element.

3.2.2 The Ideal Gas

Definition of an ideal gas:

- The number of molecules in the gas is low, i.e. their separation is large.
- The molecules obey the Newton's law of motion.
- They move randomly.
- The molecules interact only by short-range forces, i.e. their radius can be neglected.
- Collisions between the molecules are only elastic processes, i.e. there is no energy transfer during collision.
- The molecules undergo only elastic collisions with the wall of the container.
- The gas is a pure substance, all molecules are identical.

Boyle's Law

At constant temperature the pressure is inversely proportional to the volume.

$$P = \frac{k_1}{V}$$

Charles's Law

At constant pressure the volume is proportional to the temperature.

$$V = k_2 \cdot T$$

Gay Lussac's Law

At constant volume the pressure is proportional to the temperature.

$$P = k_3 \cdot T$$

Ideal Gas Law

Combining these three gas law into one gives the ideal gas law:

$$P \cdot V = n \cdot R \cdot T$$

P is the absolute pressure in Pascal, T is the temperature in Kelvin and R is the ideal gas constant with:

$$R = 8.314 \text{ J}/(\text{mol} \cdot \text{K})$$

Alternatively the ideal gas law can be defined for single molecules:

$$P \cdot V = n \cdot R \cdot T = \frac{N}{N_A} R \cdot T = N \cdot k_B T$$

N is the number of atoms or molecules and

$$k_B = \frac{R}{N_A} = \frac{8.314 \text{ J}/\text{mol} \cdot \text{K}}{6.022 \cdot 10^{23} \text{ mol}^{-1}} = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{K}}$$

k_B is the **Boltzmann constant**.

From this rule an important identity can be derived:

$$\frac{P \cdot V}{T} = N \cdot k_B = n \cdot R = \text{constant}$$

therefore : $\frac{P_1 \cdot V_1}{T_1} = \frac{P_2 \cdot V_2}{T_2}$

3.2.3 Pressure, Temperature and RMS Speed of Gas Molecules

Consider an ideal gas which is confined in a box. The atoms or molecules are allowed to move freely in random direction. They undergo only elastic collisions with other molecules or

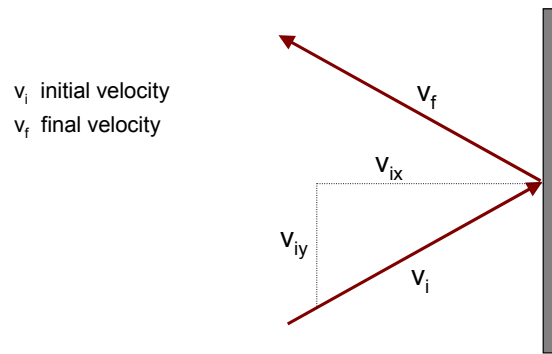


Figure 3.6: Elastic collision of a gas molecule at the wall of the container.

For elastic scattering the following identity holds: $|\vec{V}_i| = |\vec{V}_f|$.

The force on the particle due to the collision with the wall is:

$$\begin{aligned} \vec{F} &= m_0(\vec{v}_{fx} - \vec{v}_{ix})/\Delta t_{\text{collision}} \\ &= 2 \cdot m_0 \vec{v}_{fx} / \Delta t_{\text{collision}} \end{aligned}$$

The time interval between two collisions with the same wall is:

$$\Delta t = 2d/\vec{v}_{ix}$$

where d is the average distance between two molecules.

Therefore, the force acting on the wall for one collision is:

$$\begin{aligned} \vec{F}_x &= 2 m_0 \vec{v}_{ix} / \Delta t \\ &= 2 m_0 \vec{v}_{ix}^2 / 2 d \\ &= m_0 \vec{v}_{ix}^2 / d \end{aligned}$$

The force in x-direction for all molecules is:

$$\vec{F}_x = \frac{m_0}{d} \sum_{i=1}^N \vec{v}_{ix}^2$$

The average squared velocity in x-direction is:

$$\bar{v}_{ix}^2 = \sum_{i=1}^N \vec{v}_{ix}^2 / N$$

The total force on the wall in x-direction is then:

$$\vec{F}_x = \frac{m_0}{d} N \cdot \vec{v}_{ix}^2$$

For the random motion in three dimensional space the following identity holds:

$$\begin{aligned}\vec{v}_i^2 &= \vec{v}_{ix}^2 + \vec{v}_{iy}^2 + \vec{v}_{iz}^2 \\ \vec{v}_i^2 &= \vec{v}_{ix}^2 + \vec{v}_{iy}^2 + \vec{v}_{iz}^2 = 3 \vec{v}_{ix}^2\end{aligned}$$

If averaged over a longer time, the mean square velocity is the the same for all three directions:

$$\begin{aligned}\bar{v}_i^2 &= 3 \bar{v}_{ix}^2 \\ F &= \frac{1}{3} N \cdot \frac{m_0 \bar{v}^2}{d} = \frac{2}{3} \frac{N}{d} \left(\frac{1}{2} m_0 \bar{v}^2 \right)\end{aligned}$$

The pressure on the wall caused by the collisions of the gas molecules is:

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3} N \cdot \frac{m_0 \bar{v}^2}{d^3} = \frac{1}{3} N \cdot \frac{m_0 \bar{v}^2}{V}$$

This is the precise expression of the **Boyle's law**:

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

or:

$$P \cdot V = \frac{2}{3} N \left(\frac{1}{2} m_0 \bar{v}^2 \right) = N k_B T$$

$$T = \frac{2}{3 k_B} \left(\frac{1}{2} m_0 \bar{v}^2 \right)$$

$$\vec{v}_{\text{rms}} = \sqrt{\frac{3 k_B T}{m_0}} = \sqrt{\frac{3 R T}{M}}$$

where \vec{v}_{rms} is the averaged velocity, to be precise the **rms (root-mean-square)** velocity of the molecules in the gas. M_0 is the mass of one molecule and M is the molar mass of the gas.

3.2.4 Degrees of Freedom

The average translation energy, i.e. the average kinetic energy of the molecules in the gas is:

$$E_{\text{kin,avg.}} = \left(\frac{1}{2} m_0 \bar{v}^2 \right)_{\text{avg.}} = \frac{1}{2} m_0 \bar{v}^2$$

$$E_{\text{kin,avg.}} = \frac{3 R T}{2 n M} = \frac{3 R T}{2 N_A} = \frac{3}{2} k_B T$$

This is the average translation energy for a gas molecule of an ideal, monoatomic gas moving randomly in three dimensional space.

Classification: Degrees of Freedom

Monoatomic Gas:

- A monoatomic gas consists of only single atoms, e.g. Helium, Neon, Argon, etc.
- The single atoms can move freely in three dimensional space, i.e. in x, y, and z-direction.
- The rotation of the atoms around the three corresponding axis can be neglected since the radius of the atomic core, which carries most of the mass, is tiny, i.e. in the femtometer range ($1 \text{ fm} = 1 \cdot 10^{-15} \text{ m}$). ($E_{\text{rot.}} = \frac{1}{2} I \omega^2$, where I is the momentum of Inertia, which is $I = \frac{2}{5} M R^2$ for a sphere. Since R is in the femtometer range, $E_{\text{rot.}}$ can be neglected).

The total degrees of freedom of a monoatomic gas is therefore: 3.

Diatomic Gas:

- A diatomic gas consists of two atoms, e.g. H₂, N₂, or O₂.
- The molecules can move freely in three dimensional space, i.e. in x, y, and z-direction.
- They can also rotate around the three corresponding axis. However, only two rotational axes are distinguishable: 2 rotational degrees of freedom.

The total degrees of freedom of a diatomic gas is: 5.

Note that at high temperatures the molecules can also vibrate and the number of degrees of freedom increases to 7.

Polyatomic Gas:

- A polyatomic gas consists of molecules with more than two atoms each.
- The molecules can move freely in three dimensional space, i.e. in x, y, and z-direction.
- They can also rotate around the three corresponding axis, x, y, and z.
- In addition various vibrations such as bending or stretching vibrations (in-phase and out-of-phase) are possible.

The total degrees of freedom of a polyatomic gas is 6.

At higher temperatures vibrations of the molecule become activated and the number of the degrees of freedom becomes larger than 6.

Single Crystal:

- A single crystal is a highly symmetric, periodic arrangement of atoms.
- The vibrations of the atoms in a crystal lattice are not random, but can be expressed rather as standing waves in the lattice. These lattice vibrations possess well defined frequencies.
- There are three propagation directions of the lattice vibrations, i.e. the x, y, and z-direction.
- In addition the waves can travel in the opposite directions, i.e. -x, -y, and -z.
- Rotations are not possible in a crystal lattice since the atoms are in fixed positions.

The total degrees of freedom of a crystal lattice is therefore 6.

Theorem of Equipartition of Energy

Theorem of Equipartition of Energy

Each degree of freedom f contributes $\frac{1}{2} k_B T$ to the energy of a system, where possible degrees of freedom are those which are associated with translations, rotations, and vibrations of atoms or molecules

Total energy of a gas:

$$E = \frac{1}{2} f N k_B T$$

The total energy of a monoatomic (ideal) gas is:

$$E = \frac{3}{2} N k_B T$$

3.2.5 Mean Free Path

Due to collisions, each gas molecule undergoes a zig-zag motion.

The mean free path is the average distance a molecule can travel between two collision.

The mean free path varies with the density of molecules, i.e. with N/V , the number of molecules per volume.

The mean free path is:

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 N/V}$$

where d is the interaction radius of the molecule, i.e. the characteristic radius of the molecule during the collision.

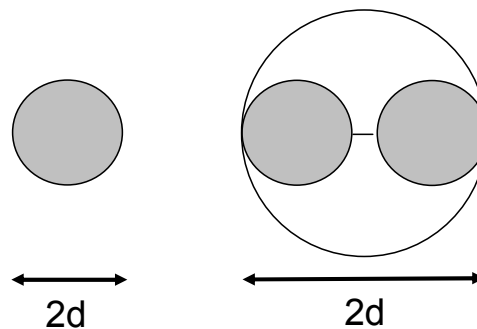


Figure 3.7: Schematic of the interaction radius of an atom and a diatomic molecule.

Calculation of the Mean Free Path

In the finite time interval Δt , the molecules travels a distance of $\vec{v}_{\text{rms}} \cdot \Delta t$.

Assume a cylinder with the radius corresponding to the characteristic interaction radius d and the length of the traveled distance of $\vec{v}_{\text{rms}} \cdot \Delta t$.

This is the volume where we can expect the next collision.

The number of molecules in this cylinder corresponds to the number of expected collisions.

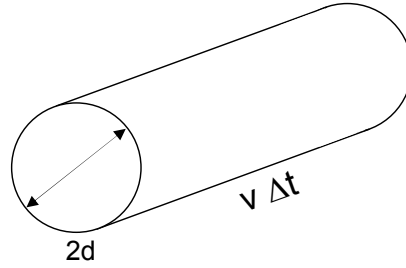


Figure 3.8: Cylindrical volume where the next collision will take place.

$$\begin{aligned}\lambda &= \frac{\text{length of the traveled path in } \Delta t}{\text{number of collisions in } \Delta t} \\ &= \frac{\vec{v}_{\text{rms}} \cdot \Delta t}{(N/V) \pi d^2 \vec{v}_{\text{rms}} \cdot \Delta t} \\ &= \frac{1}{\pi d^2 (N/V)}\end{aligned}$$

Note that the factor $\sqrt{2}$ is missing in the denominator. It has to be added since $v_{\text{rel.}} = \sqrt{2} v_{\text{avg.}}$.

Example:

Air at sea level	$\lambda = 0.1 \mu m$
Air at 100 km above sea level	$\lambda = 16 cm$

3.2.6 The Distribution of Molecular Speeds

The root-mean-square distribution \vec{v}_{rms} gives a general idea of the average speed of the molecules. However, every molecule has its own speed.

At a certain temperature there is a certain distribution of the velocities of the molecules.

Maxwell Distribution Function:

$$P(v) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT}\right)$$

$P(v)$ is the probability distribution function of the velocities

M : molar mass, R : universal gas constant, T : temperature of the gas.

If you consider 100 molecules, 20 of them might travel in the range around the maximum velocity ($\approx 400 m/s$ at a temperature of $300 K$) and 10 of them might travel with a speed around $\approx 700 m/s$.

By integrating over all velocities, i.e. from 0 to ∞ , all molecules are counted and the probability will be 100%:

$$\int_0^{\infty} P(v) dv = 100\% = 1$$

The number of molecules in a certain range of velocities from v_1 to v_2 is:

$$\int_{v_1}^{v_2} P(v) dv = \text{number of molecules with a speed between } v_1 \text{ and } v_2$$

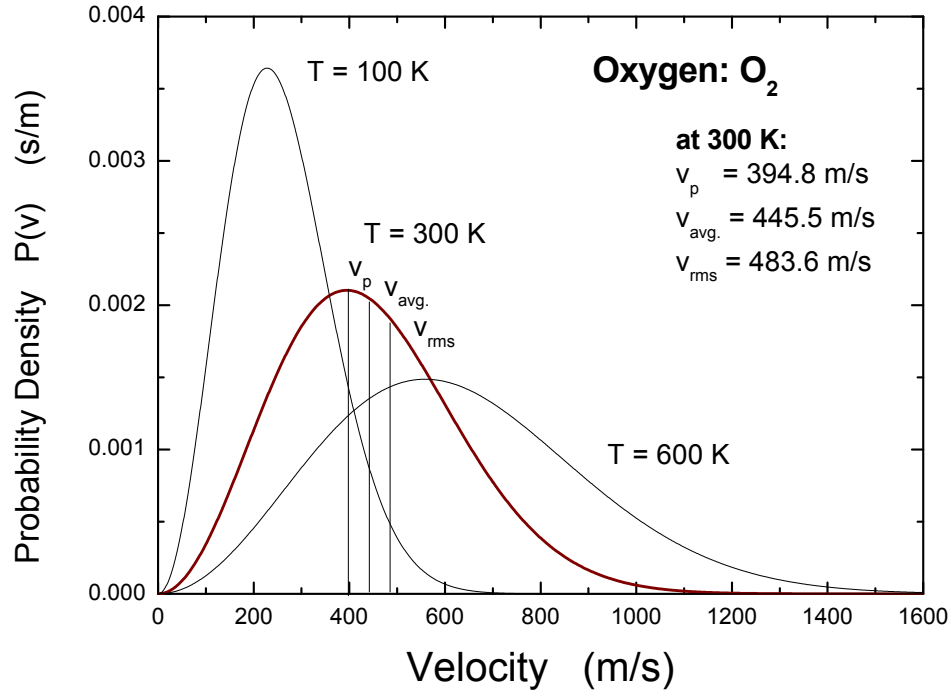


Figure 3.9: Maxwell distribution function, i.e. probability distribution function of the velocities of oxygen gas with a temperature of 100 K, 300 K, and 600 K.

Distribution of Molecular Velocities

The average speed can be calculated as follows:

$$\begin{aligned} v_{\text{avg.}} &= \int_0^{\infty} v P(v) dv \\ &= \int_0^{\infty} v 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} v^2 \exp\left(-\frac{Mv^2}{2RT}\right) dv \\ &= 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \cdot \left(\frac{1}{2\left(\frac{M}{2RT}\right)^2} \right) \\ &= \sqrt{\frac{8RT}{\pi M}} \end{aligned}$$

The integral was calculated using the following equation:

$$\left(\int_0^{\infty} x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}, \quad a > 0 \right)$$

In a similar way v_{rms} can be calculated:

$$v_{\text{rms}} = \sqrt{(v^2)_{\text{avg.}}} = \left(\int_0^{\infty} v^2 P(v) dv \right)^{1/2} = \sqrt{\frac{3RT}{M}}$$

Note that this is the same result as we had calculated before for the root-mean-square velocity (see page 9).

v_p **ist the most probable speed**, i.e. the speed at the maximum of the Maxwell distribution function. It can be determined by calculation the first derivative of the Maxwell distribution function.

$$v_p \longrightarrow \frac{dP}{dv} = 0$$

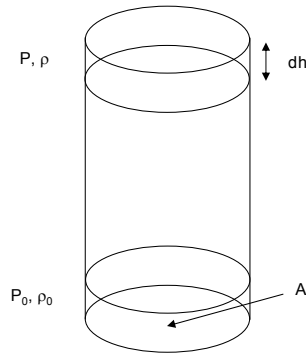
$$4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} \left(2v_p \exp\left(-\frac{Mv_p^2}{2RT}\right) + v_p^2 \left(-\frac{M}{2RT}\right) \cdot 2v_p \exp\left(-\frac{Mv_p^2}{2RT}\right) \right) = 0$$

$$2v_p - 2v_p^3 \frac{M}{2RT} = 0$$

$$v_p^2 = \frac{2RT}{M} \quad v_p = \sqrt{\frac{2RT}{M}}$$

Derivation of the Boltzmann Factor

Density of air in a column at various altitudes.



The potential energy of the gas is:

$$E_{\text{pot.}} = -\varrho g \cdot dV = -\varrho g A \cdot dh$$

$$dP = -\varrho g dh = -\frac{\varrho_0}{P_0} g P \cdot dh$$

$$\frac{dP}{P} = -\frac{\varrho_0}{P_0} g \cdot dh$$

where P_0 and ϱ_0 are the pressure and density at the lowest level (ground level), respectively.

By integration one obtains:

$$\int \frac{1}{P} dP = -\int \frac{\varrho_0}{P_0} g dh$$

$$\ln p = -\frac{\varrho_0}{P_0} g \cdot h$$

$$P(h) = P_0 \exp\left(-\frac{\varrho_0}{P_0} g \cdot h\right)$$

$$\varrho(h) = \varrho_0 \exp\left(-\frac{\varrho_0}{P_0} g \cdot h\right)$$

$$\varrho(h) = \varrho_0 \exp\left(-\frac{mgh}{k_B T}\right), \quad \text{using } P \cdot V = N k_B T$$

$$\varrho(h) = \varrho_0 \exp\left(-\frac{E}{k_B T}\right)$$

The density of the gas gets reduced with increasing height. The reduction corresponds to an exponentially decreasing function.

If we replace the potential energy with the kinetic energy ($mgh = E_{\text{pot.}} = E_{\text{kin.}}$) the Boltzmann factor is obtained:

$$\varrho(h) = \varrho_0 \exp\left(-\frac{E_{\text{kin.}}}{k_B T}\right) = \varrho_0 \exp\left(-\frac{mv^2}{2k_B T}\right)$$