

Introduction to Physics I

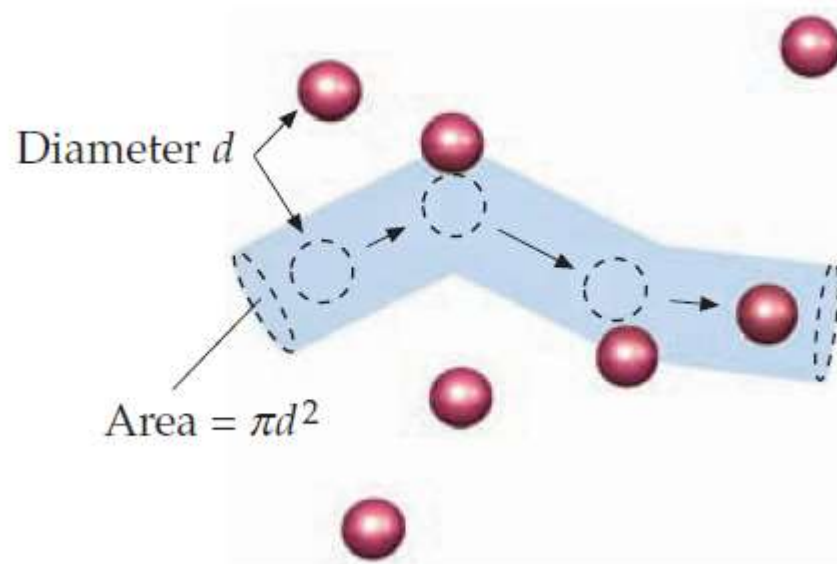
Kinetic gas theory

- equipartition, degrees of freedom
- mean free path
- Maxwell-Boltzmann distribution
- Brownian motion

Ideal gas examples: adiabatic processes

Real gas law: van der Waals equation

mean free path collisions for a moving molecule



mean free path, ideal gas at STP

STP

standard pressure
& temperature

$P = 100\text{kPa}$ (1bar)

$T = 273.15\text{ K}$ (0C)

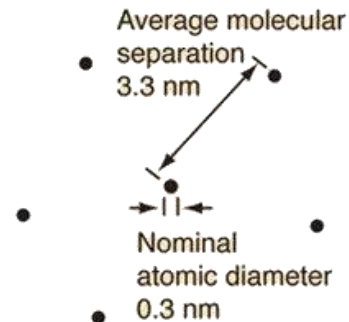
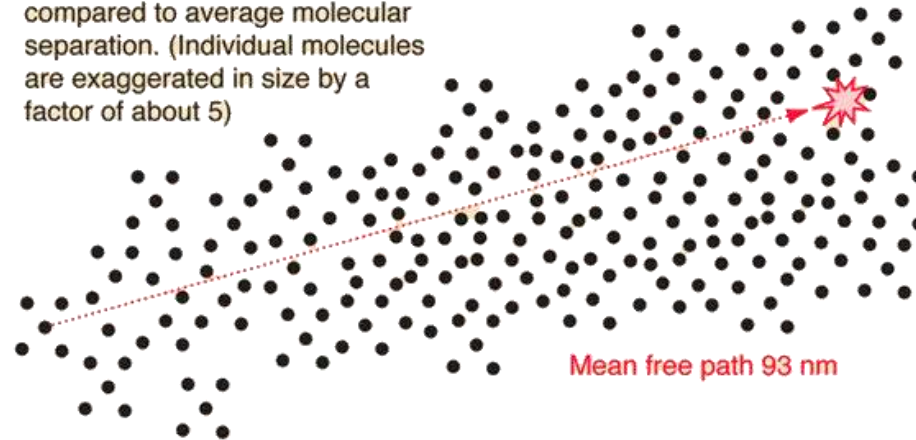
Atomic diameter

assumed here

0.3nm

The mean free path is 310 times the nominal atomic diameter and 28 times the average molecular separation.

Perspective of mean free path compared to average molecular separation. (Individual molecules are exaggerated in size by a factor of about 5)



Perspective of molecular size compared to average molecular separation.

The average molecular separation is about 10x the atomic diameter.

measuring the speed distribution of molecules

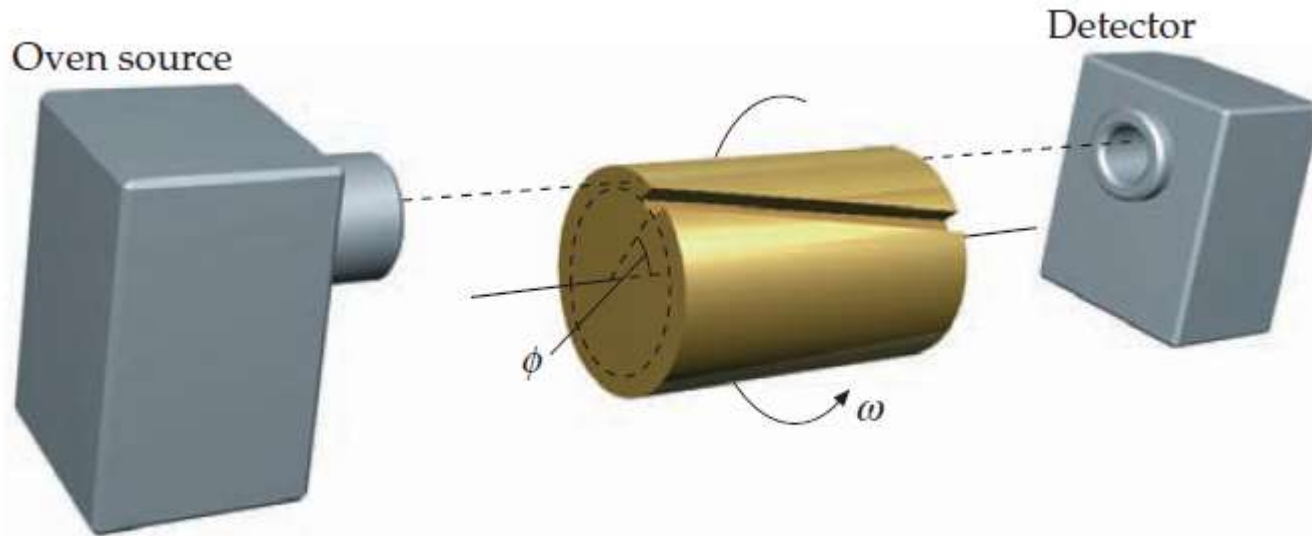


FIGURE 17-16 Schematic diagram of the apparatus for determining the speed distribution of the molecules of a gas. A substance is vaporized in an oven and the vapor molecules are allowed to escape through a hole in the oven wall into a vacuum chamber. The molecules are collimated into a narrow beam by a series of slits (not shown). The beam is aimed at a detector that counts the number of molecules that are incident on it in a given period of time. A rotating cylinder stops most of the beam. Small slits in the cylinder (only one of which is depicted here) allow the passage of molecules that have a narrow range of speeds that is determined by the angular speed of the rotating cylinder. Counting the number of molecules that reach the detector for each of a large number of angular speeds, gives a measure of the number of molecules in each range of speeds.

Maxwell-Boltzmann distribution

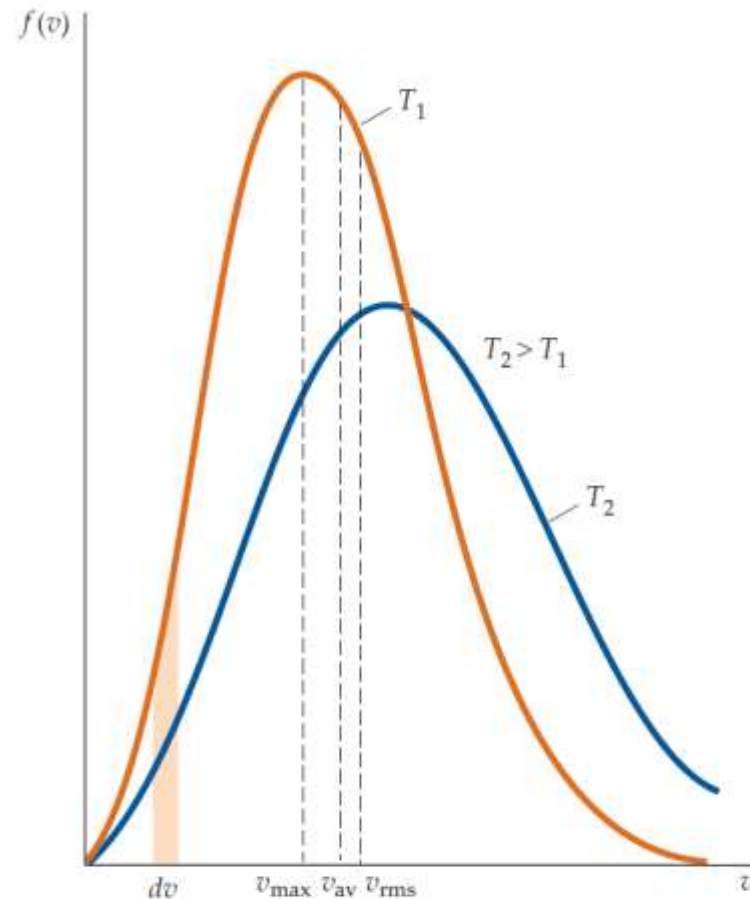





FIGURE 17-17 Distributions of molecular speeds in a gas at two temperatures, T_1 and $T_2 > T_1$. The shaded area $f(v) dv$ equals the fraction of the number of molecules having a particular speed in a narrow range of speeds dv . The mean speed v_{av} and the rms speed v_{rms} are both slightly greater than the most probable speed v_{\max} .

equipartition theorem

degrees of freedom & molar heat capacity

Molekül	Beispiel	$C_V(\text{J/mol}\cdot\text{K})$
eiatomig 	ideal	$3 R/2 = 12.5$
	He	12.5
	Ar	12.6
zweiatomig 	ideal	$7 R/2 = 29.0$
	N ₂	20.7
	O ₂	20.8
dreiatomig (gestreckt) 	ideal	$13 R/2 = 54.0$
	CO ₂	29.7

equipartition theorem

degrees of freedom

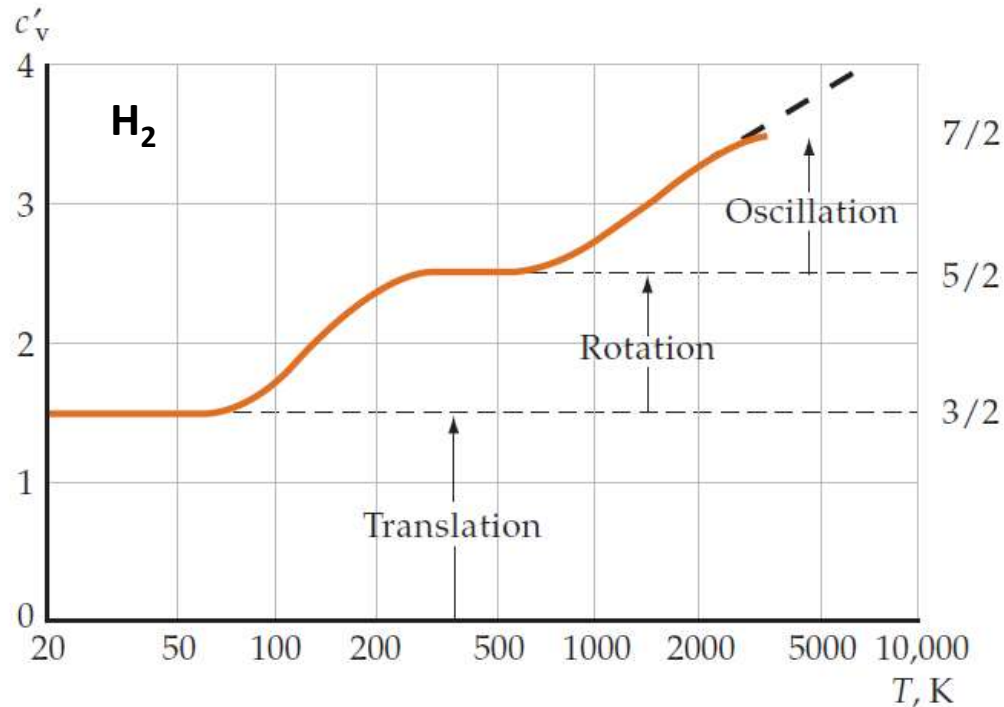


FIGURE 18-17 Temperature dependence of the molar heat capacity of H_2 . (The curve is qualitative in those regions where c'_v is changing.) Ninety-five percent of H_2 molecules are dissociated into atomic hydrogen at 5000 K.

equipartition theorem

heat capacity of a solid

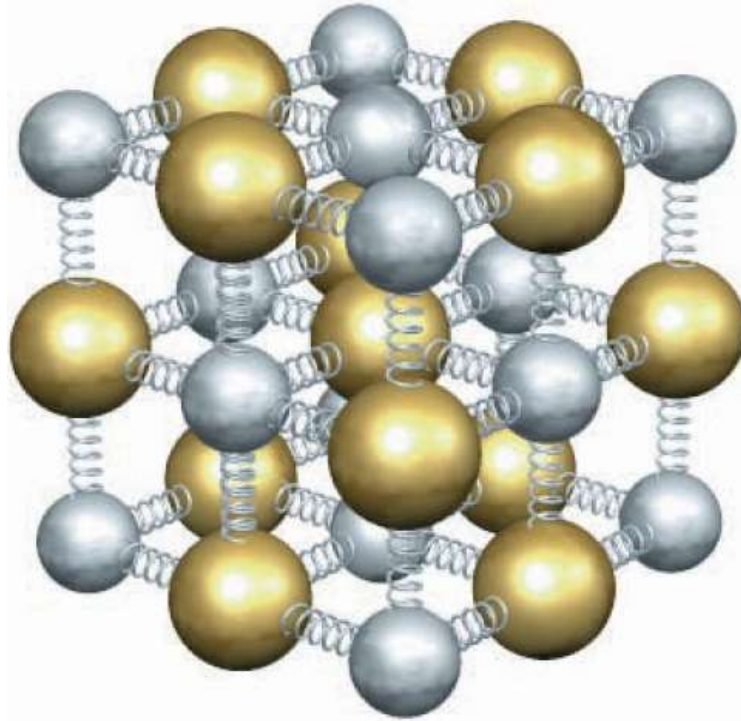


FIGURE 18-16 Model of a solid in which the atoms are connected to each other by springs. The internal energy of the molecule consists of the kinetic and potential energies of vibration.

(Makro-)Mechanik



Temperaturschwankungen:

$$x_{\text{th}} = 0.2 \text{ pm} = 2 \times 10^{-13} \text{ m}$$

$$T = 21 \text{ }^\circ\text{C}$$

Nanomechanik



Temperaturschwankungen:

$$x_{\text{th}} = 8 \text{ nm} = 8 \times 10^{-9} \text{ m}$$

$$T = 21 \text{ }^{\circ}\text{C}$$

adiabatic process

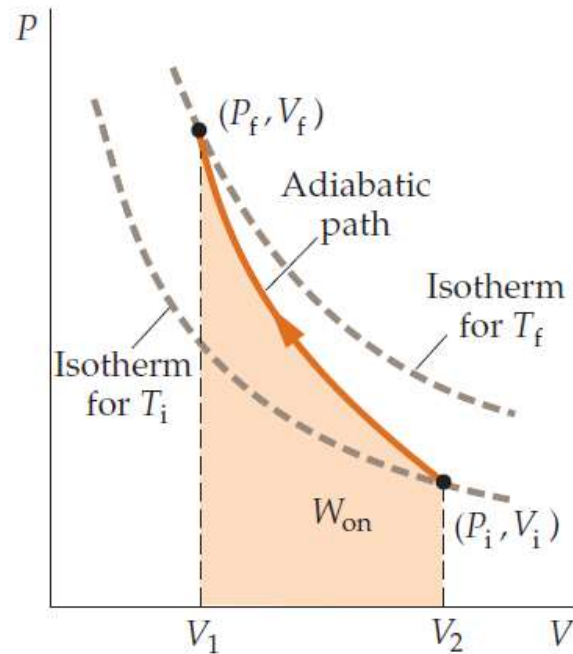


FIGURE 18-20 Quasi-static adiabatic compression of an ideal gas. The dashed lines are the isotherms for the initial and final temperatures. The curve connecting the initial and final states of the adiabatic compression is steeper than the isotherms because the temperature increases during the compression.

real gas law: van der Waals

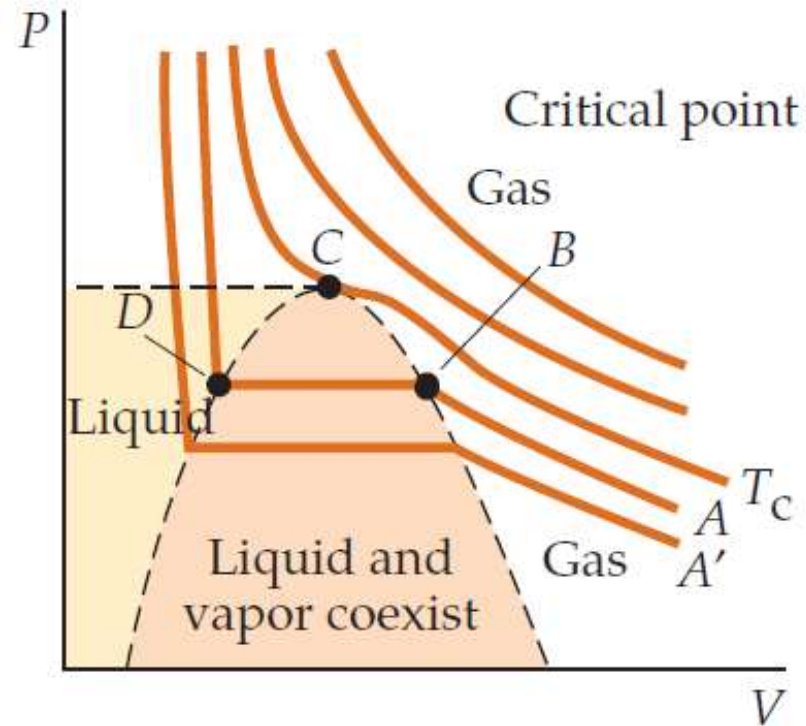
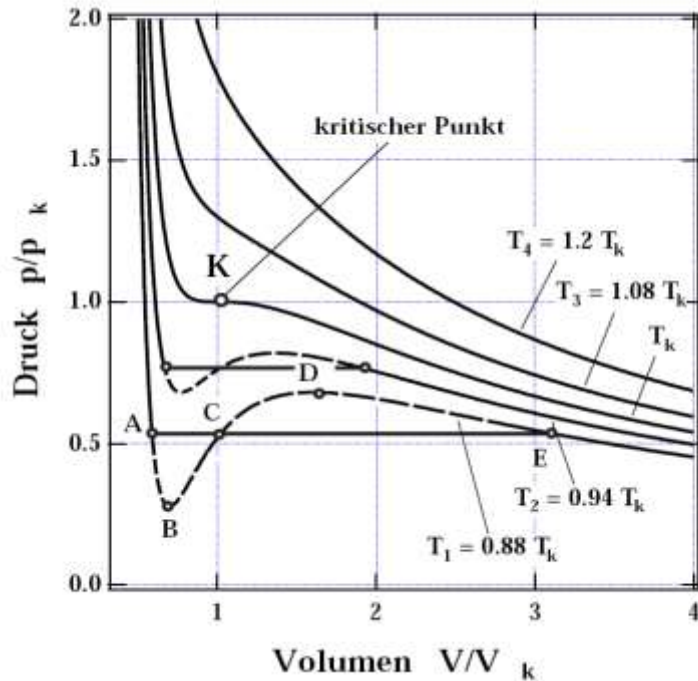
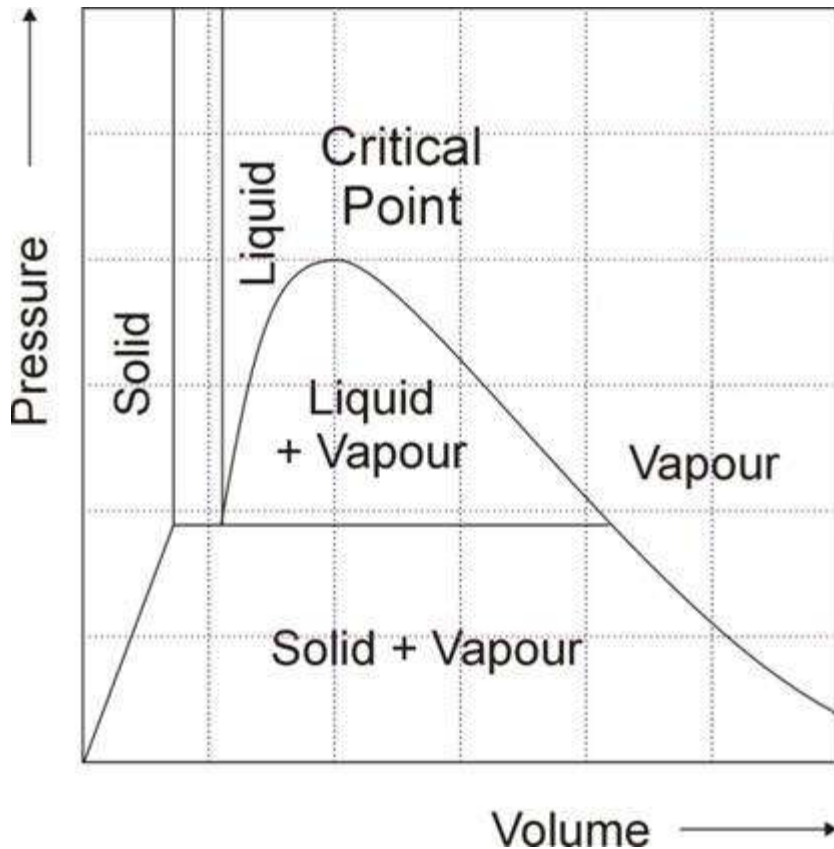


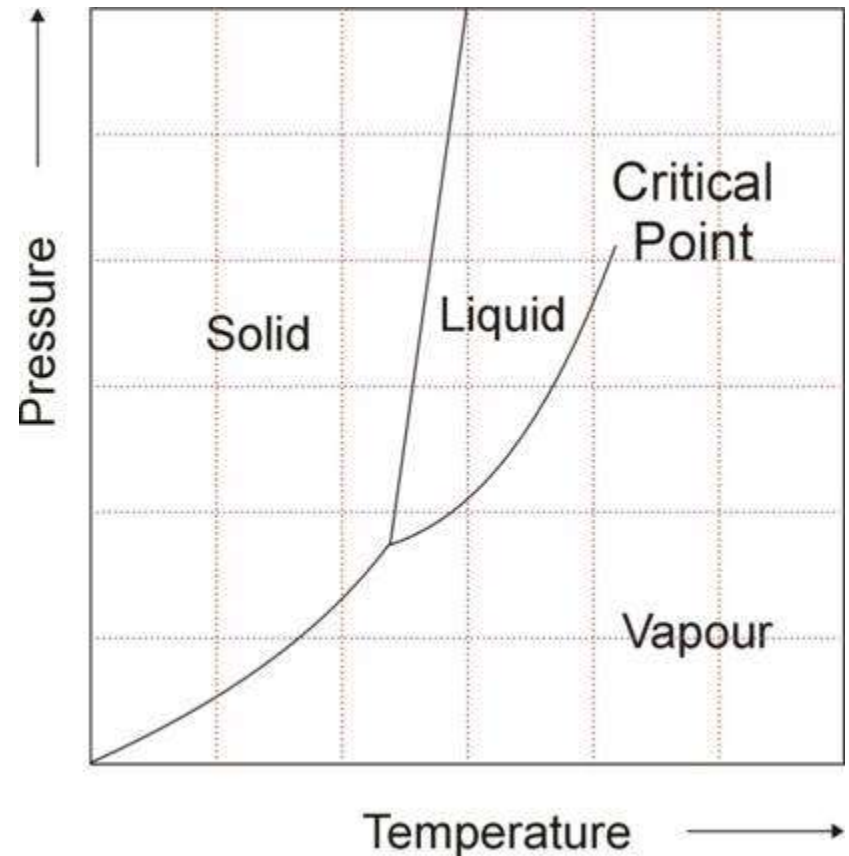
FIGURE 20-5 Isotherms on the PV diagram for a substance. For temperatures above the critical temperature T_c , the substance remains a gas at all pressures. Except for the region where the liquid and vapor coexist, these curves are described quite well by the van der Waals equation. The pressure for the horizontal portions of the curves in the shaded region is the vapor pressure which is the pressure at which the vapor and liquid are in equilibrium. In the region shaded yellow, to the left of the region shaded pink, the substance is a liquid and is nearly incompressible.

real gas law: van der Waals

PV diagram

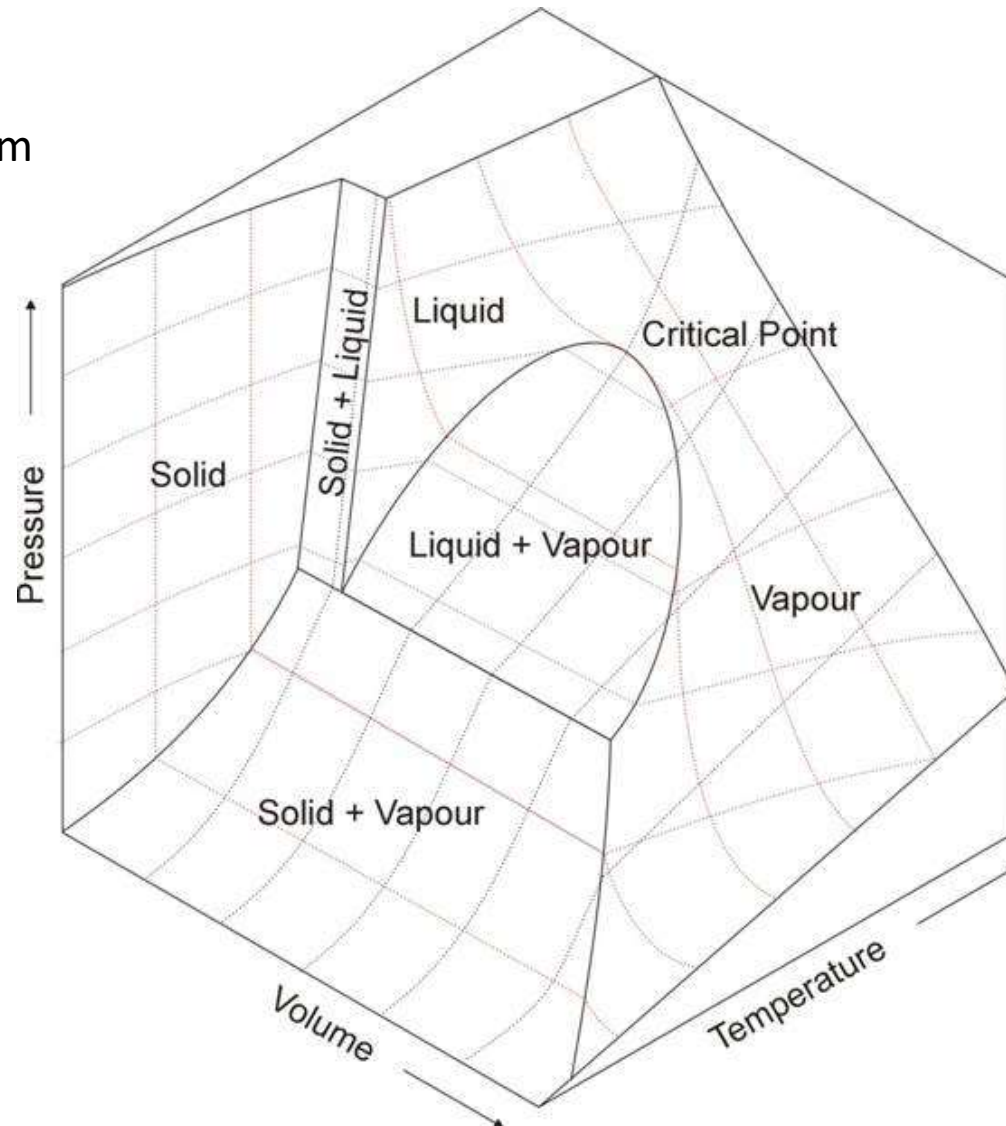


PT diagram



real gas law: van der Waals

PVT phase diagram



real gas law: van der Waals



Cloud forming behind an aircraft as it breaks the sound barrier. As the aircraft moves through the air, an area of low pressure forms behind it. When the pressure of this air parcel falls below the vapor pressure of gaseous water, the water in the air condenses to form the cloud. Different atmospheric conditions cause the phenomenon to occur at different aircraft speeds. (*U.S. Department of Defense/Photo Researchers, Inc.*)

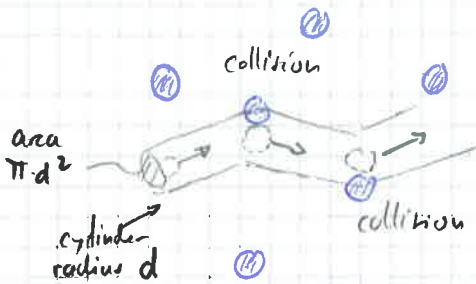
mean free path λ , $[d] = m$

λ : avg. distance between two collisions for a molecule

Consider 1 moving molecule (other, at rest) during time t ;

$\leftarrow d$, diameter

slide
drawing



if center of incoming molecule \odot is ~~the cylinder~~ closer or equal than d to other molecule: collision.

in time t , moving molecule (speed v) will collide with all molecules within cylinder with volume $\pi \cdot d^2 \cdot v \cdot t$
length of cylinder

nb collisions = $n_v \cdot \pi \cdot d^2 \cdot v \cdot t$, where $n_v = \frac{N}{V}$, nb molecules per unit volume

$$\parallel \text{mean free path (mfp)} = \frac{\text{total path}}{\text{nb collisions}} = \frac{v \cdot t}{n_v \cdot \pi \cdot d^2 \cdot v \cdot t} = \frac{1}{n_v \cdot \pi \cdot d^2} = \lambda$$

taking into account correction due to motion of other molecules (need to know speed distribution - function of later)

$$\parallel \lambda = \frac{1}{\sqrt{2}} \cdot \frac{1}{n_v \cdot \pi \cdot d^2} = \frac{1}{\sqrt{2}} \cdot \frac{k_B \cdot T}{P \cdot \pi \cdot d^2} \quad \text{example } \hookrightarrow \%$$

collision time $\bar{\tau}$
(avg time between collisions), $\tau = \frac{\lambda}{v_{avg}}$

$$* P \cdot V = n \cdot R \cdot T = n \cdot N_A \cdot k_B \cdot T, \text{ hence } \frac{N}{V} = \frac{P}{k_B T}$$

N , nb molecules

n : nb moles

$$N_A = 6.022 \cdot 10^{23} \frac{\text{molecules}}{\text{mole}}$$

example 1

for molecules with $d = 0.3 \text{ nm}$ at $T = 300 \text{ K}$ & $P = 100 \text{ kPa}$

$$\lambda \approx 10^{-7} \text{ m}$$

(26.85 °C) (1 bar)

$$= 0.1 \mu\text{m} = \underline{100 \text{ nm}}, \quad \sim 345 \times \text{molecule diameter}$$

avg dist. between
molecules $\approx 3.5 \text{ nm}$

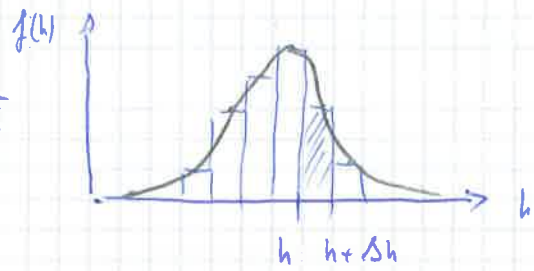
(slide) mfp for ideal gas

distribution function of gas velocities (Maxwell-Boltzmann)

(see Tipler ch 17-4, p 575 for example)

math: dist. function, e.g. $f(h)$: nb of persons with height h

1) histogram: count persons within $[h \text{ and } h+\Delta h]$



2) function $f(h)$

For N people, $N \cdot f(h) \cdot \Delta h$ is the nb of people whose height is between h and $h+\Delta h$
 ↑
 continuous function

Similarly, Maxwell-Boltzmann distribution function (dist. can be measured)
 c) Tipler ch 17-4

$$dN = N \cdot f(v) \cdot dv$$

N : gas molecules
 dN : nb gas molecules with speed between v and $v+dv$

Result from stat mech:

$$f(v) = \frac{4}{\sqrt{\pi}} \cdot \left(\frac{m}{2k_B T}\right)^{3/2} \cdot v^2 \cdot e^{-mv^2/(2k_B T)}$$

Boltzmann factor, $e^{-\text{Energy}/k_B T}$
 ↑
 relevant to probles here: kin energy molecules

slide

Maxwell-Boltz. distrib. function

• most probable speed v_{max} for $f(v)$ max

$$v_{max} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}}$$

M : molar mass
 $M = m \cdot N_A$

• root-mean square speed (see before)

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

Specific heat of gases

Leey

reminder : $\Delta Q = C \cdot \Delta T$
capital c

C : heat capacity $[C] = \frac{J}{K}$
 energy (heat) needed to warm a substance by 1 degree

$\Delta Q = c \cdot m \cdot \Delta T$
small c , $c = \frac{C}{m}$

c : specific heat (capacity)
 $[c] = \frac{J}{kg \cdot K}$, depend on substance

we have seen that the internal energy of a gas (monoatomic) consists of translational kinetic energy

$K_{trans} = N \cdot \left(\frac{1}{2} m v^2 \right)_{avg} = \frac{3}{2} \cdot N \cdot k_B T = \frac{3}{2} \cdot n \cdot R \cdot T = E_{int}$
3 deg. of freedom
nb. molecule , nb. mole

increasing T is equivalent to increase E_{int} , hence the heat capacity can be written ($\Delta T \rightarrow dT$)

$c_v = \frac{dQ}{dT} = \frac{dE_{int}}{dT} = \frac{3}{2} nR$

$C_v = \frac{3}{2} nR$ ~~total~~ ~~specific~~ heat capacity

(subscript "v" means at constant volume)

NB: why at const volume?

$V = const$: all energy goes only to increasing the internal energy $\left(\frac{1}{2} m v^2 \right)_{avg}$
 if $V = const$ ($P \nearrow$), no work done

$V \neq const$: expansion (assume $P = const$), hence the heat dQ added to gas has to also produce work $[P \cdot V] = \frac{N}{m^2} \cdot m^3$

$dW = F \cdot ds = P \cdot A \cdot ds = P \cdot dV$
 only if $dV = 0$, is $dW = 0$.

$= \frac{N \cdot m}{m^2} \cdot m^3$
 $= N \cdot m = \int$
 energy, work

and $C_p \cdot dT - C_v \cdot dT = P \cdot dV$

Using the state eq. $PV = nRT$, $P \cdot dV = n \cdot R \cdot dT$

we get

$C_p - C_v = n \cdot R$ (for an ideal, monoatomic gas)
 $C_p = C_v + nR = \frac{5}{2} nR$, $C_v = \frac{3}{2} nR$

def. molar (specific) heat c'

$$c' = \frac{Q}{n} = \frac{m \cdot c}{n} = M \cdot c$$

Q : heat capacity
 n : no. of moles
 m : mass of sample (substance)
 M : molar mass $[M] = \frac{kg}{mol}$

and $C'_v = \frac{3}{2} R$

We only accounted for translational modes here; ok for monoatomic gas

Rem. equipartition theorem: if N atoms > 1 (a molecule), rot + vibrat total $3N$ modes (deg. freedom)

slides equip theorem

2) c' for various molecules compare measured value to ideal gas

remember vibration modes contribute to kin and pot energy

c_p 10' last lecture

$$E_{int} = \sum_i E_{kin}^{trans} + \sum_i E_{kin}^{rot} + \left(\sum_i E_{kin}^{vibr} + \sum_i E_{pot}^{vibr} \right)$$

"weight 2"

(for He, monoatomic 3 deg. freedom (trans))

$$C'_v = 3 \cdot \frac{1}{2} R = \frac{3}{2} R$$



for H_2 , diatomic 3 trans, 2 rot, 1 vibr (= 6 = 3x2) atoms

$$C'_v = \left(\underset{\substack{\uparrow \\ \text{kin}}}{3} + \underset{\substack{\uparrow \\ \text{pot}}}{2} + \overset{\text{vibr}}{1+1} \right) \cdot \frac{1}{2} R = \frac{7}{2} R$$



for CO_2 3 trans, 2 rot, 4 vibr (= 9 = 3x3)

$$C'_v = \left(3 + 2 + 4 + 4 \right) \frac{1}{2} R = \frac{13}{2} R$$

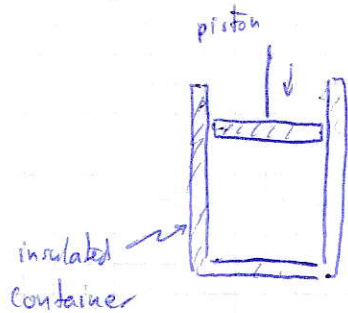
slide c'_v for H_2 : excitation of rotation modes and vibration modes as $T \nearrow$
note: molecule start dissociating above 700K

adiabatic process

process in which no heat transfers in or out of a system
 \overline{Q}

0%

(e.g. very well insulated system)



slide
 adiabatic
 process,
 PV diagram

seen previously:
 (L20 - L21)

~~slowly~~ compression of gas,
 (insulated container, $\Delta Q = 0$)

→ Eq. of state : $P \cdot V = n \cdot R \cdot T$
 (ideal gas)

→ first law thermo : $dE_{int} = dQ_{in} + dW_{on}$
 $= 0$, adiabatic process

$$dE_{int} = C_V \cdot dT$$

↑ heat capacity at const V.

$$dW_{on} = -P \cdot dV$$

work done on gas

$dQ = 0$, adiabatic process

$$C_V \cdot dT = 0 + P \cdot dV$$

$$\left(P \cdot V = nRT, \quad P = \frac{nRT}{V} \right)$$

$$C_V dT + \frac{n \cdot R \cdot T}{V} dV = 0$$

$$\frac{dT}{T} + \frac{n \cdot R}{C_V} \cdot \frac{dV}{V} = 0$$

integrate

$$\ln T + \frac{n \cdot R}{C_V} \cdot \ln V = \text{const}$$

$$\ln V^{nR/C_V}$$

and

$$\ln \left(T \cdot V^{nR/C_V} \right) = \text{const}$$

thus

$$T \cdot V^{nR/C_V} = \text{const}$$

Using

$$\gamma = \frac{C_p}{C_v}$$

and

$$C_p - C_v = nR$$

C_p : specific heat at const P.

(monatomic gas, cf L20, L21)

$$\frac{nR}{C_v} = \frac{C_p}{C_v} - 1 = \gamma - 1$$

We have $\parallel T \cdot V^{\gamma-1} = \text{const}$

Using $PV = nRT$, $T = \frac{P \cdot V}{nR}$

$$\frac{P \cdot V}{nR} \cdot V^{\gamma-1} = \frac{P \cdot V^{\gamma}}{nR} = \text{const}$$

and ~~also~~ also

$$\parallel P \cdot V^{\gamma} = \text{const} \quad (\text{at } n = \text{const})$$

$$\gamma = \frac{C_p}{C_v}$$

adiabatic process
(quasi-static)

exp adiabatic

6%

gas mixtures (ideal gases)

e.g. air ~21% oxygen, 75% nitrogen

diving: oxygen-enriched air (nitrox) → longer dive

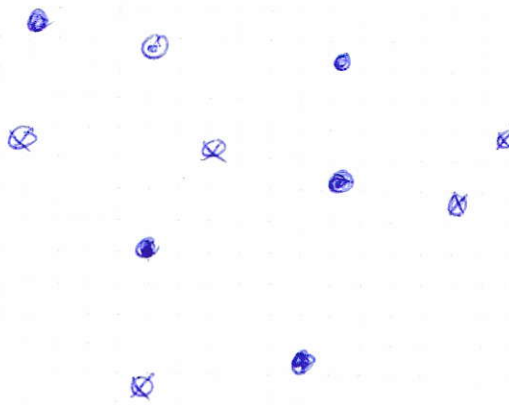
deep diving: oxygen + helium (heliox) -
(avoid nitrogen narcosis)

if mixture sufficiently dilute (in confined volume V),
each gas occupies the whole volume V
(Vol. of gas molecules negligible as compared to V)

then $P_{\text{mixture}} = \sum_i P_i$, sum of individual pressures
or partial pressures

$$= \frac{1}{V} \cdot \sum_i n_i \cdot R \cdot T$$

↑
nb of mole individual gases



Brownian motion : random movement of microscopic particles suspended in a liquid or gas

(Robert Brown 1827)
botanist

explanation: Einstein, 1905 / Jean Perrin: quantitative observation 1905-1910, Nobel 1926; ended skepticism about atoms/molecules

exp: Rauchhammer - smoke particle in air
~ 10um - 1um

(L) discontinuous structure of matter

origin of brownian motion: jittering of particles in a gas/liquid
due to repeated collisions with molecules of gas

→ hypothesis/explanation: Einstein: brownian motion as evidence for the existence of atoms (molecules)

(NB: 1st observation of atoms: 1980's STM, AFM)
1st of electrons ~ 2010

diffusion of particle, D : diffusion constant, $[D] = \frac{m^2}{s}$

avg particle motion: $\langle r^2 \rangle_{avg} \sim \begin{matrix} D \cdot t \\ \uparrow \quad \uparrow \\ \text{diffusion} \quad \text{time} \\ \text{constant} \end{matrix}$

Einstein
(Sutherland-Einstein)
of APAC, Subtle in the
Lord

$$D = \frac{k_B \cdot T}{f} = \frac{k_B T}{6\pi\eta R}$$

$f = 6\pi\eta R$ Stokes friction coefficient
particle radius R
 η viscosity of liquid

$$\langle r^2 \rangle_{avg}^{1/2} \sim \sqrt{\frac{k_B T \cdot t}{6\pi\eta R}}$$

and $\left(\frac{1}{2} m \overline{v^2}\right)_{avg} = \frac{3}{2} k_B T$
 $\uparrow \quad \uparrow$
mass of atom avg speed of atom

relationship between a macroscopic diffusion constant and the atomic nature/properties of matter

(like considering the motion of an iceberg due to penguin jumping on it)

slides - macro mechanics
- nanomechanics

example: Brownian motion

gas, normal / standard condition

$$n = \frac{N_A}{V} = \frac{6.02 \cdot 10^{23}}{0.0224} \frac{\text{particle}}{\text{m}^3}$$

density of gas molecule

for 1 mol in std condition

$$P = 100 \text{ kPa}, T = 273.15 \text{ K}, V = 22.4 \text{ L}$$

typ. mean free path for gas molecule

$$\lambda = \frac{1}{\sqrt{2}} \cdot \frac{1}{n \cdot \pi \cdot d^2}$$

assume

$$d = 1 \text{ \AA} = 10^{-10} \text{ m} \quad (\sim \text{atom size})$$

$$\approx 8.4 \cdot 10^{-7} \text{ m} = 0.84 \mu\text{m}$$

assuming $\langle v^2 \rangle_{\text{avg}}^{1/2} = 10^3 \text{ m/s}$

(Hydrogen estimate $\sim 480 \text{ m/s}$)

$$\lambda = \left(\langle v^2 \rangle_{\text{avg}} \right)^{1/2} \cdot \tau$$

$$= \tau \approx 8.4 \cdot 10^{-10} \text{ s} \quad \text{time between collision}$$

$$\text{hence } \frac{1}{\tau} \sim 10^9 \text{ s}^{-1} \quad \text{nb collisions per second}$$

real gas law - van der Waals equation of state

~~12/11/18~~
12/11/18

• at high pressure P or low temperature T : breakdown of ideal gas law

and $P \cdot V = n \cdot R \cdot T$ requires correction:

$$\left\| \left(P + \frac{a \cdot n^2}{V^2} \right) \cdot (V - b \cdot n) = n \cdot R \cdot T \right. \quad n \text{ moles of gas}$$

Van der Waals eq. of state

Correction, because 1) molecules have a finite (non zero) volume b for one mole of gas

2) force F between gas molecules:

• F attracts gas molecule approaching wall container
(\rightarrow remember how we calculated P)

$F \propto \frac{n}{V}$, density of molecules pulling back

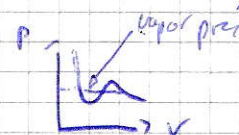
• nb of molecules hitting container wall per unit time
 $\propto \frac{n}{V}$

hence correction to pressure $P \propto \left(\frac{n}{V}\right)^2$

constant a : small for inert gases (Ar, Ne)
(low reactivity)

$\left(\frac{a n^2}{V^2}, b \cdot n \right)$ small for large V
 \rightarrow ideal gas law

slide
phase diag.

• isotherms  shape \rightarrow \exists critical point T_c

• v.d Waals eq. describes isotherms outside shaded region
where liquid & vapor coexist \rightarrow 2 different states gas & liquid

\Rightarrow gas can condense when $P \& V \downarrow$

- phase diag. PV, PT, PT
- condensation cloud behind aircraft

exp %