AE1241 Physics
Chapter 18 Kinetics Theory of Gases
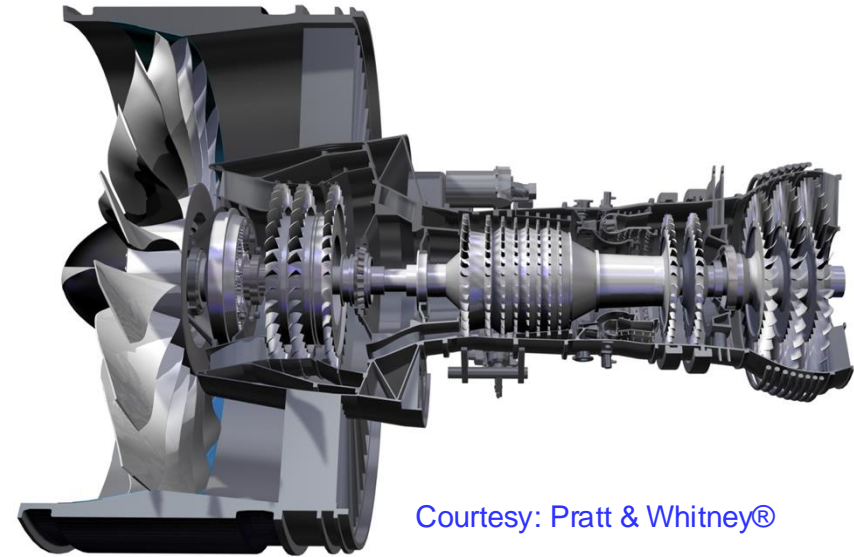
Dr. Feijia Yin

Operations and Environment

Faculty of Aerospace Engineering

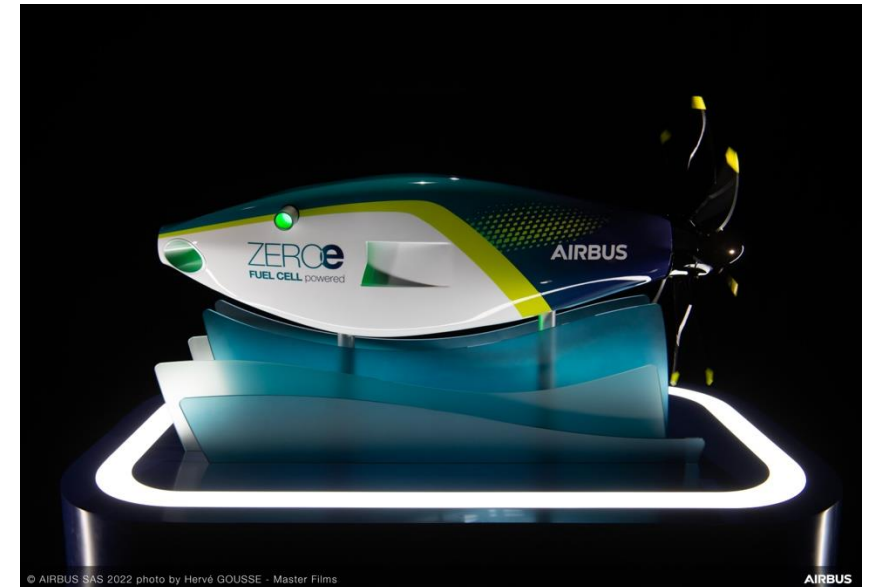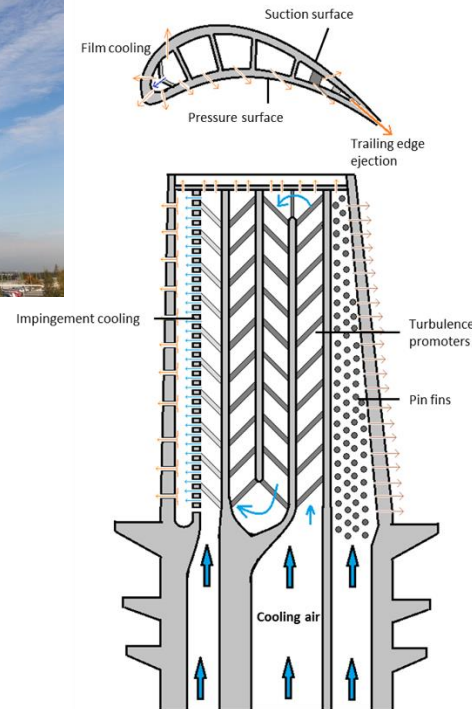**27th February, 2025**

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Relevance of thermodynamics to aerospace

Courtesy: Pratt & Whitney®

Link to video

Suction surface
Film cooling
Pressure surface
Trailing edge ejection
Impingement cooling
Turbulence promoters
Pin fins
Cooling air

ZEROe
FUEL CELL powered
AIRBUS

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Example: Radiation and climate change

Figure source: Kiehl and Trenberth, Earth's Annual Global Mean Energy Budget, 1997.

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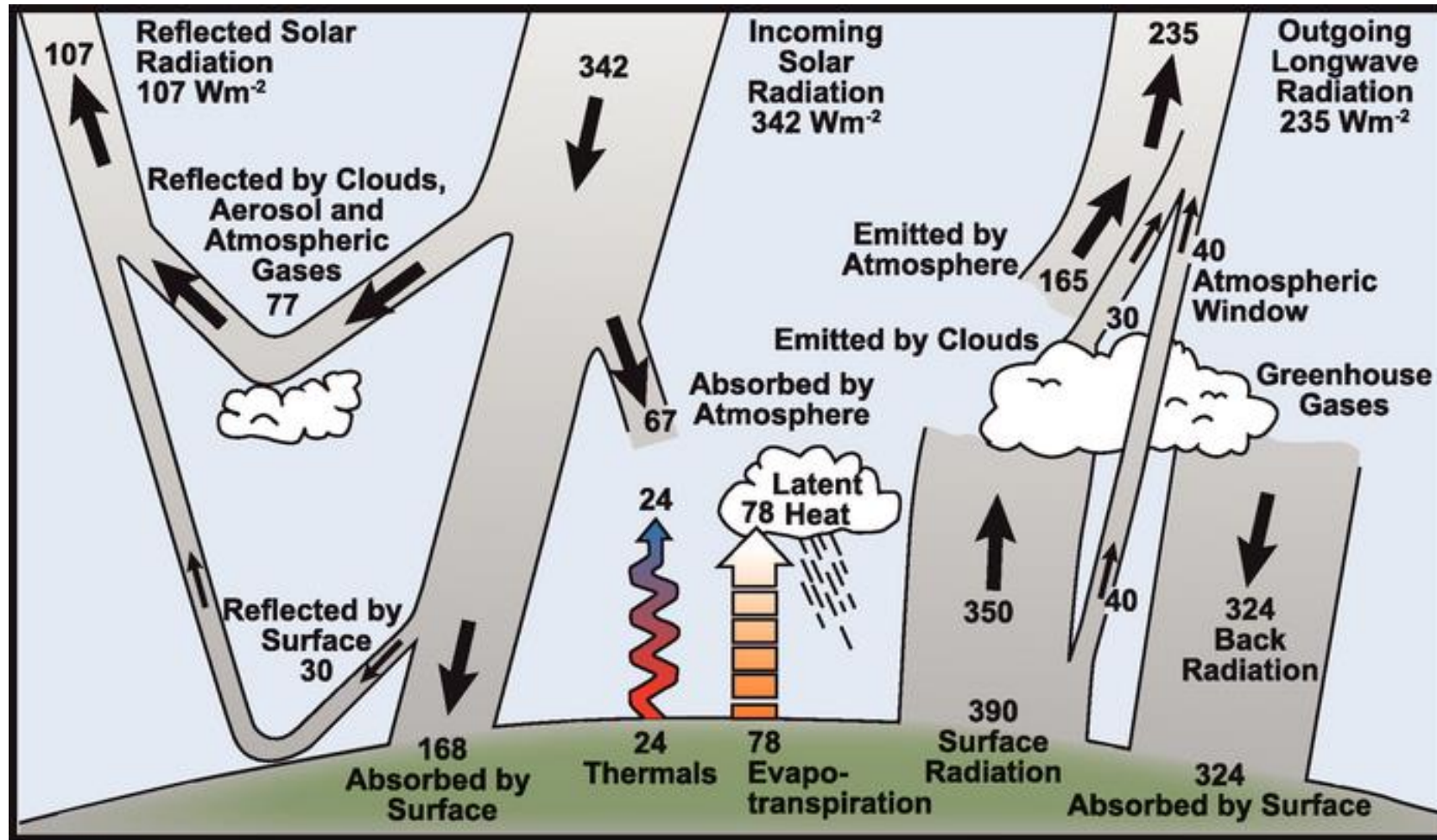
What do we focus on?
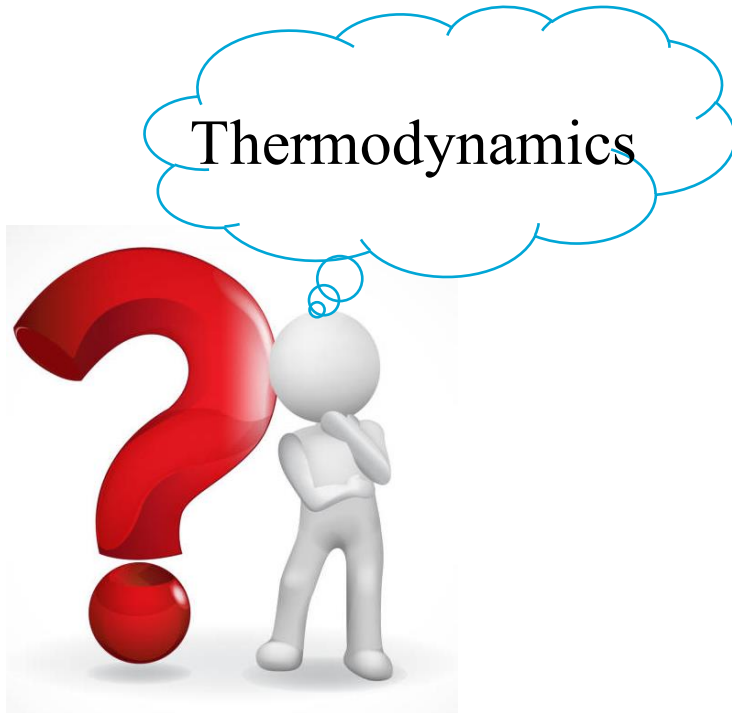
Thermodynamics

- 0th law of thermodynamics (temperature) – Chapter 17
- Kinetic Theory of Gases (temperature) – Chapter 18
- 1st law of thermodynamics (energy) – Chapter 19
- 2nd law of thermodynamics (entropy) – Chapter 20
- 3rd law of thermodynamics (absolute 0 K) – Chapter 20

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Structure of today's lecture

- The Ideal Gas Law and the Molecular Interpretation of Temperature

- Distribution of Molecular Speeds

- Real Gas and Changes of Phase

- Vapor Pressure and Humidity

- Van der Waals Equation of State

- Mean Free Path

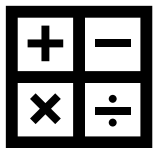- Diffusion

Learning objectives

After today's lecture, you should be able to:

- Explain **molecular kinetic theory** for ideal gases, including, average kinetic energy, average speed and speed distribution.
- Explain the difference of ideal and **real gas**, using van der Waals theory

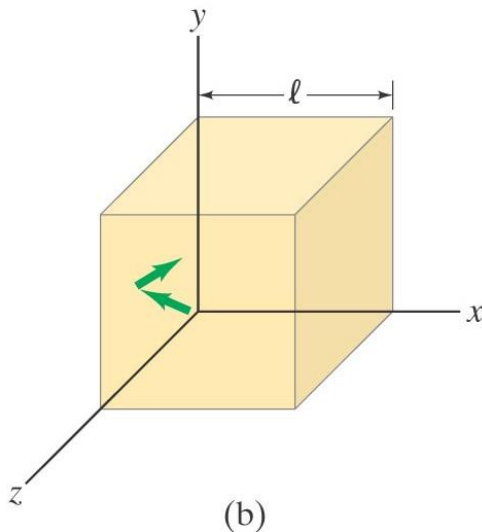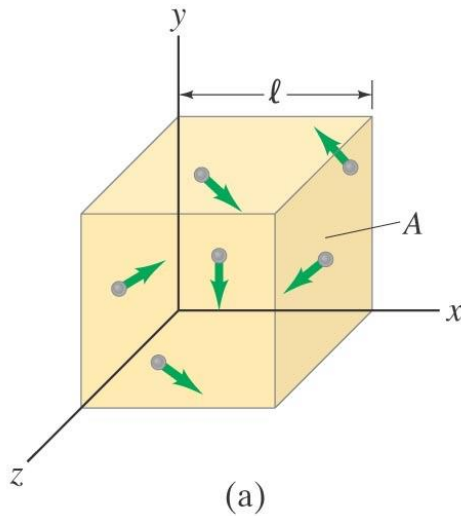- Analyze **phase changes** for given substances, using phase diagrams.

- Calculate **relative humidity** at given temperature.
- Calculate the **diffusion rate of molecules**

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Prior knowledge

- Basic mechanics (e.g., *Newton's law*)

- Calculus (e.g., *differential and integral*)

- Statistics (e.g., *distribution, probability*)

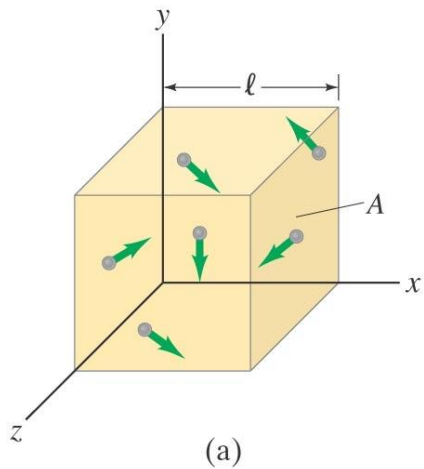**T**U Delft

18-1 Force of molecules

(a)

(b)

Pressure exerted on a wall of a container of gas is due to collisions of the molecules with the walls

<u>one</u> molecule striking wall (yz-plane):

$$\begin{cases} \Delta(mv) = mv_x - (-mv_x) \\ \Delta t = \dfrac{2l}{v_x} \end{cases}$$

➕

Newton's 2nd law:

$$F = \frac{\Delta(mv)}{\Delta t}$$

$$\boldsymbol{F} = \frac{\boldsymbol{mv_x^2}}{\boldsymbol{l}}$$

N molecules ⟹

$$\boldsymbol{F} = \frac{\boldsymbol{m(v_{x,1}^2 + v_{x,2}^2 + \cdots + v_{x,N}^2)}}{\boldsymbol{l}} = \frac{\boldsymbol{mN\overline{v_x^2}}}{\boldsymbol{l}}$$

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18-1 Average translational kinetic energy of molecules

(a)

$$F = \frac{mN\overline{v_x^2}}{l}$$

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2}$$

Energy is equally shared per degree of freedom

$$F = \frac{mN\overline{v^2}}{3l}$$

Average translational kinetic energy $\overline{K}$

N very large, P constant

$$P = \frac{F}{A} = \frac{1}{3}\frac{Nm\overline{v^2}}{V} \longrightarrow PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right) = \frac{2}{3}N\overline{K}$$

combine with ideal gas law $\quad PV = NkT$

$$\overline{K} = \frac{3}{2}kT$$

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Average translational energy

$$\overline{K} = \frac{3}{2}kT$$

Average translational kinetic energy, only depending on temperature.

T: Temperature in K

k: Boltzmann constant: $1.38 * 10^{-23}$ J/K

Q: what is the average kinetic energy of 40 molecules gas at 25°C.

$$\overline{K} = \frac{3}{2}kT = \frac{3}{2}(1.38 \times 10^{-23})(298K) = 6.17 \times 10^{-21} \, J/molecule$$

40 molecules will have a total translational kinetic energy of:

$$6.17 \times 10^{-23} \times 40 = 2.47 \times 10^{-19} J$$

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18-1 Root mean square speed

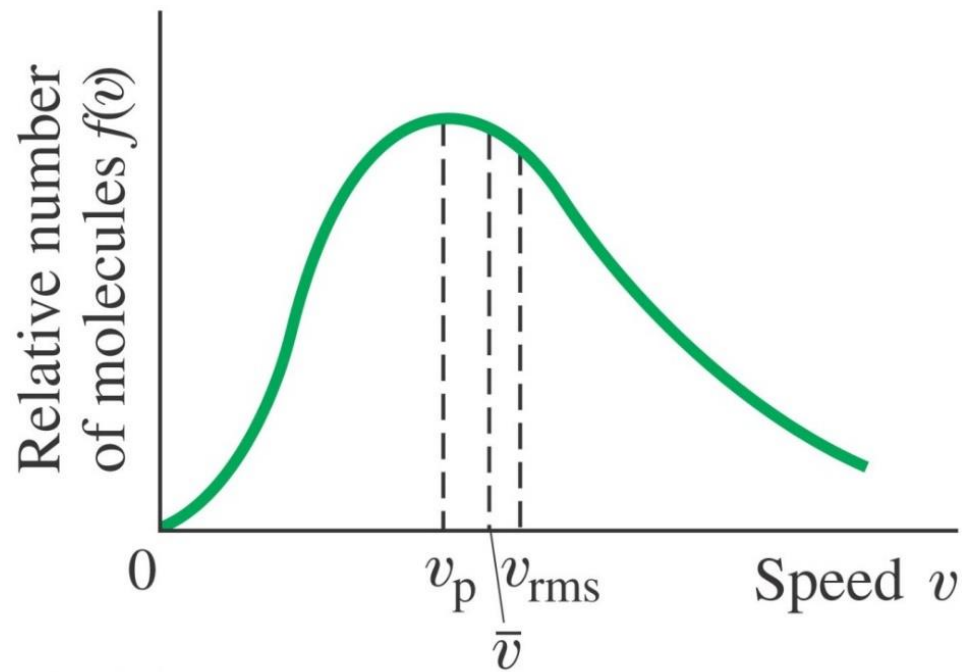$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3kT}{m}} \approx 1.73 \sqrt{\frac{kT}{m}}$$

Mass of one molecule O_2 (molecular mass = 32u) is: $m(O_2) = (32)(1.66 \times 10^{-27}) = 5.3 \times 10^{-26} \, kg$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} J/K)(293K)}{5.3 \times 10^{-26} kg}} = 481 m/s$$

Mass of one molecule He (molecular mass = 4u) is: $m(H_e) = (4)(1.66 \times 10^{-27}) = 6.6 \times 10^{-27} \, kg$

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3(1.38 \times 10^{-23} J/K)(293K)}{6.6 \times 10^{-27} kg}} = 1357 \, m/s$$
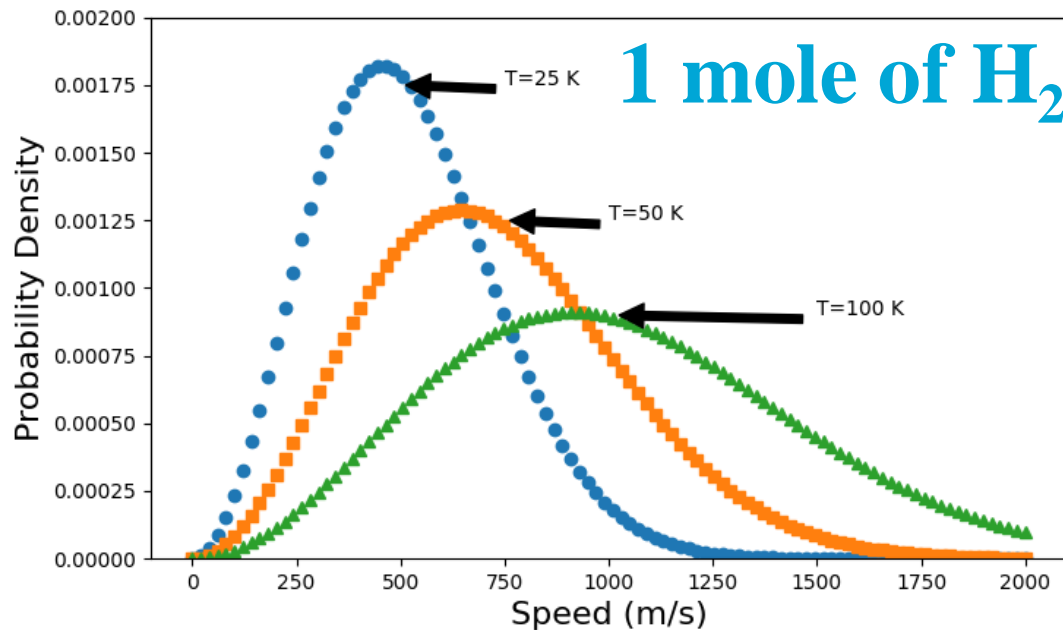
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18-2 Speed distribution

$$dN = \int_{v1}^{v1+dv} f(v)dv$$

The fraction of molecules that have the speed between v and v+dv

$$\int_{0}^{\infty} f(v)dv = N$$

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18-2 Maxwell distribution of speed

$$f(v) = 4\pi N \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{1}{2}\frac{mv^2}{kT}}$$
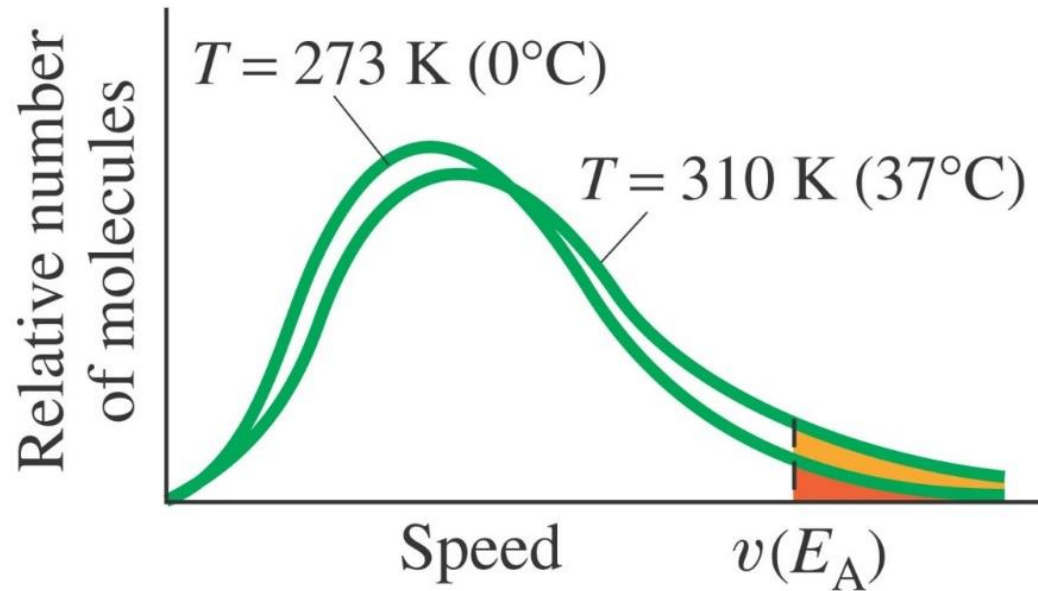
Temperature dependent, K

N: number of molecules

m: mass of a single molecule, kg

k: Boltzmann constant, J/K

1 mole of H$_2$
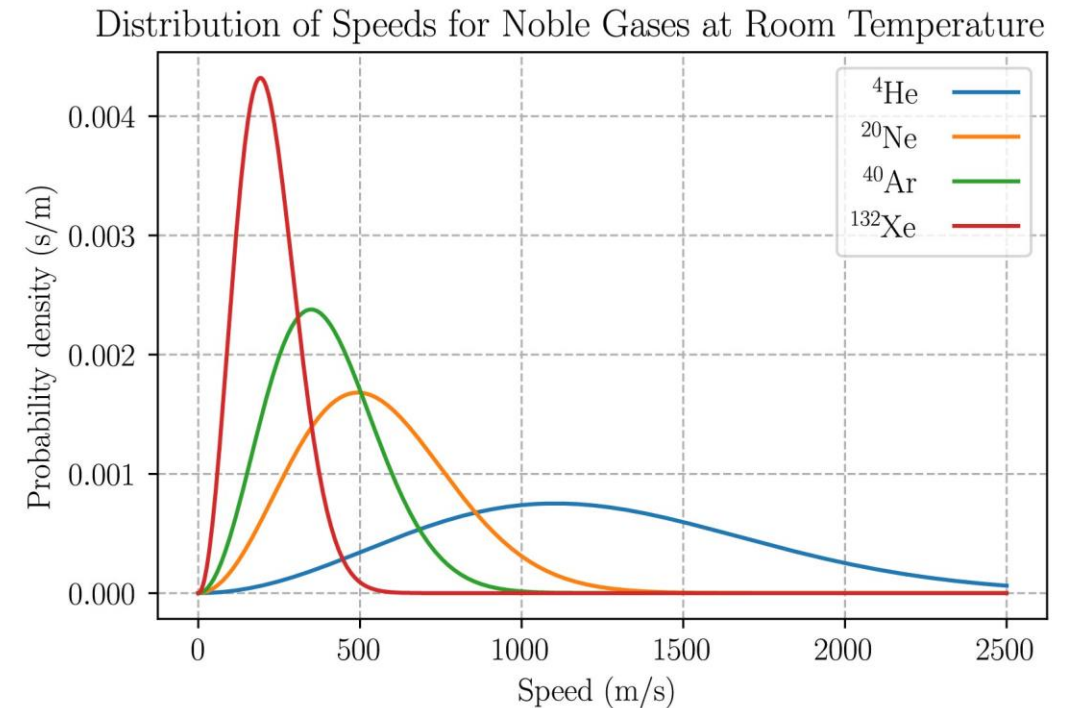
The speed distribution shifts towards high speed regime as increasing the temperature.

18-2 Maxwell distribution of speed

Chemical reactions take place more rapidly as T increases! (E_A activation energy)

For the same temperature, the lighter the molecule, the higher the speed.

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18-2 Calculation of different speeds

Average speed:

$$\bar{v} = \frac{\int_0^N v \, dN}{N} = \frac{\int_0^\infty v f(v) \, dv}{N}$$

$$= \sqrt{\frac{8kT}{\pi m}} \approx 1.6 \sqrt{\frac{kT}{m}}$$

Most probable speed:

$$\frac{df(v)}{dv} = 0 \longrightarrow v_p = \sqrt{\frac{2kT}{m}} \approx 1.41 \sqrt{\frac{kT}{m}}$$

$$v_{rms} > \bar{v} > v_p$$
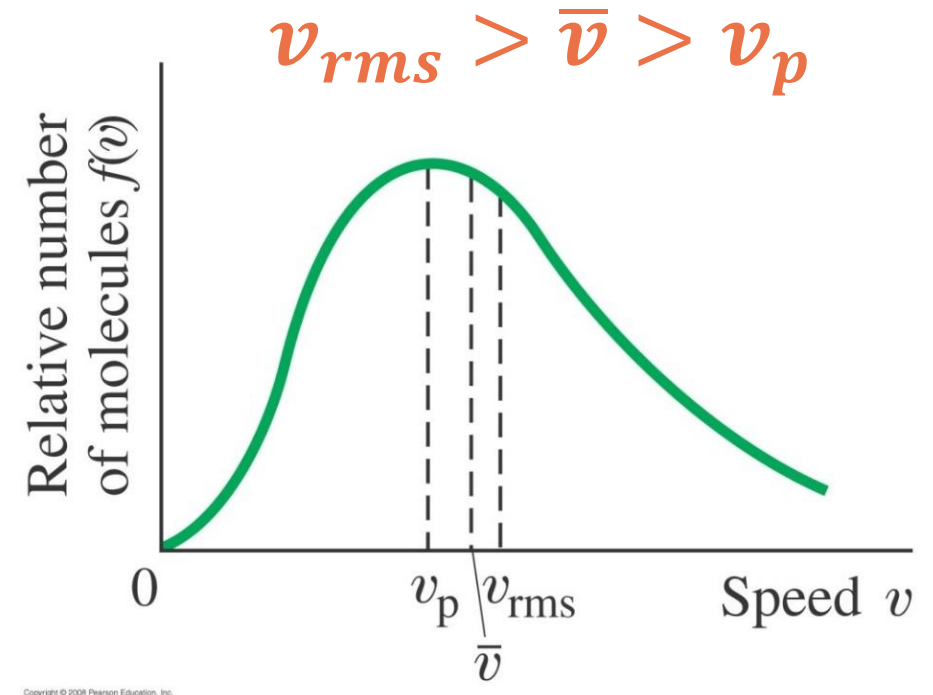
See derivation in Example 18-5

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Exercise

In outer space, the density of matter is about one atom per cm^3 (mainly hydrogen *atoms*). The temperature is about 2.7 K.

- What is the *rms* speed of the hydrogen atoms?
- What is the pressure in the atmosphere?

$$v_{rms} = \sqrt{\frac{3kT}{m}} = 259 \; m/s \qquad (m = 1.66 \text{ x } 10^{-27} \text{ kg})$$

$$P = \frac{1}{3}\frac{N}{V}m\overline{v^2} = \frac{1}{3}\frac{N}{V}mv_{rms}^2 = 3.7 \times 10^{-17} \; pa = 3.7 \times 10^{-22} \; atm$$

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18-3 Phase change

Gas

Liquid

Solid

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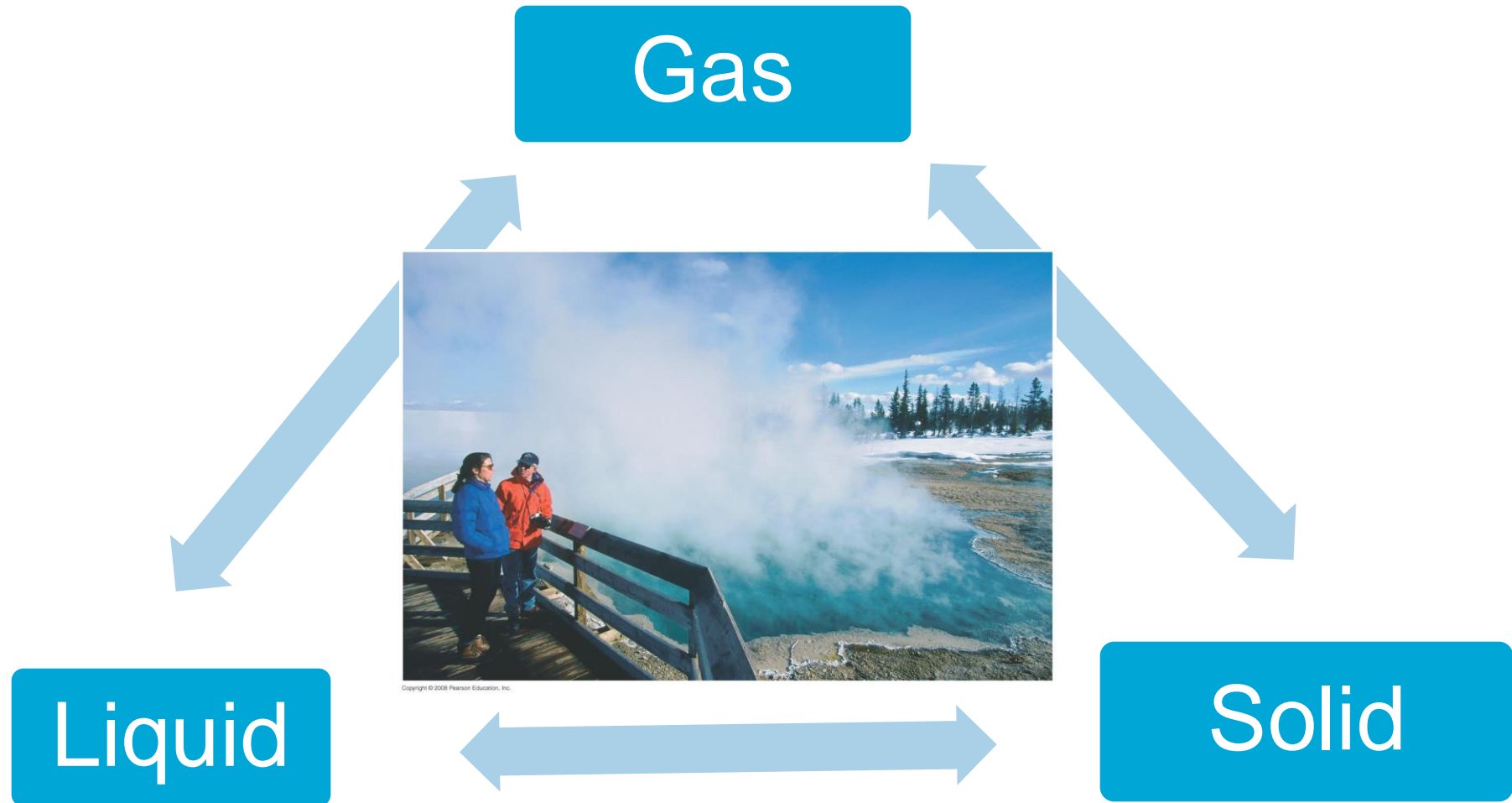
18-3 P-V diagram

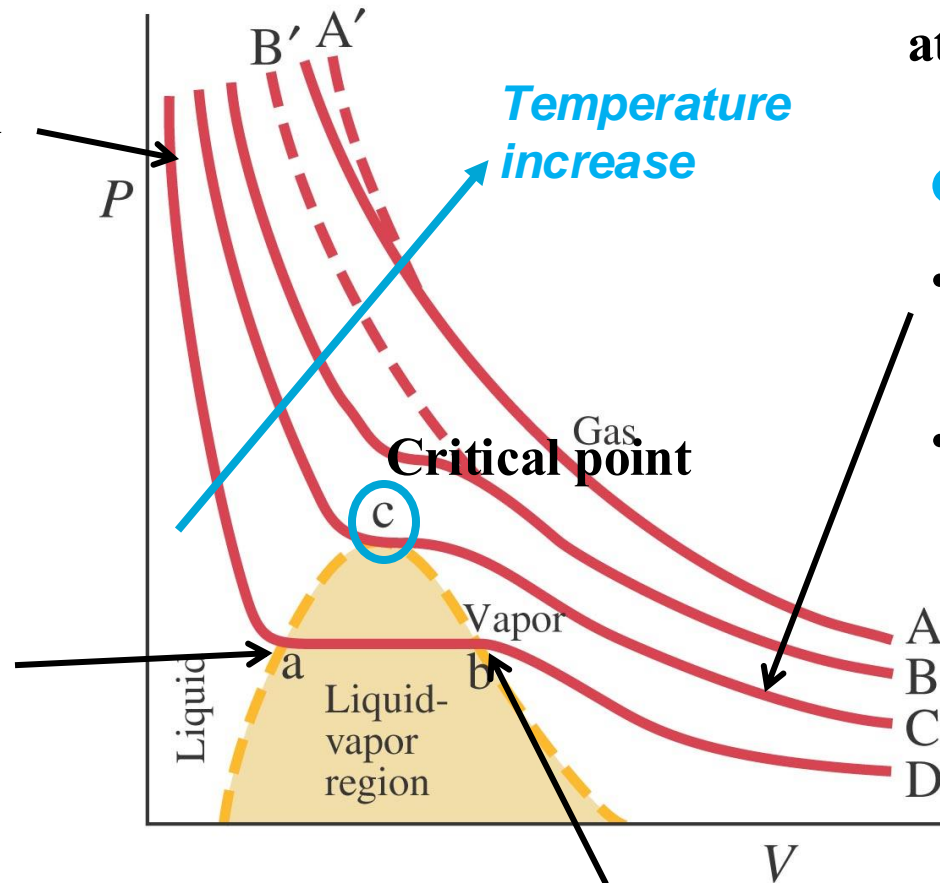Steep rise as liquids are nearly incompressible

All of the substance has become liquid

Liquefaction occurs: volume decreases with no change in pressure

- Dashed lines: ideal gas behavior: $PV = NkT$;

- Solid lines: real gas behavior driven by **attractive forces** (see 18-6 for details);
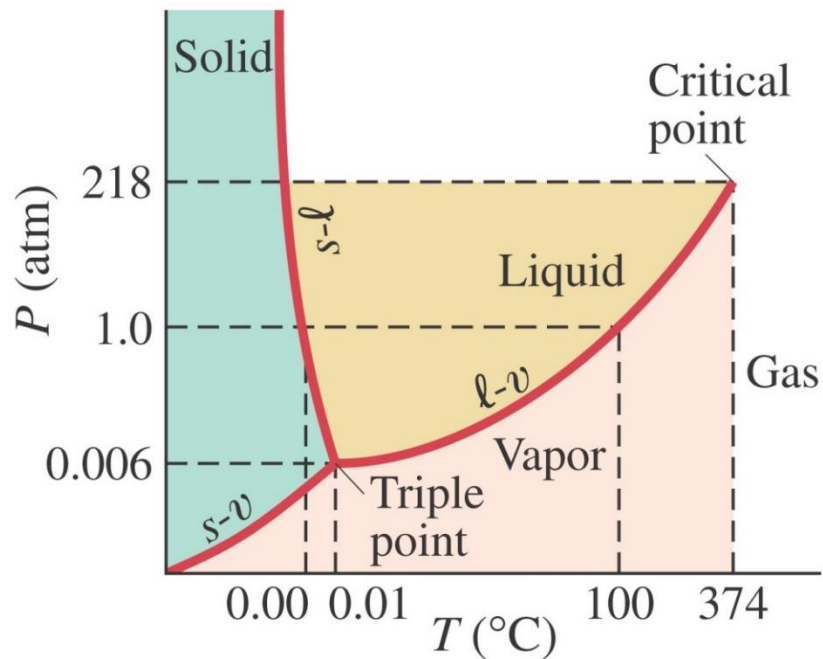
Critical temperature (T_C):

- $< T_C$: a gas changes to liquid with sufficient high pressure;

- $> T_C$: no phase change.

Substance	Critical temperature [K]	Critical pressure [atm]
Water	647	218
Nitrogen	126	33.5
Hydrogen	33.3	12.8

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18-3 P-T diagram
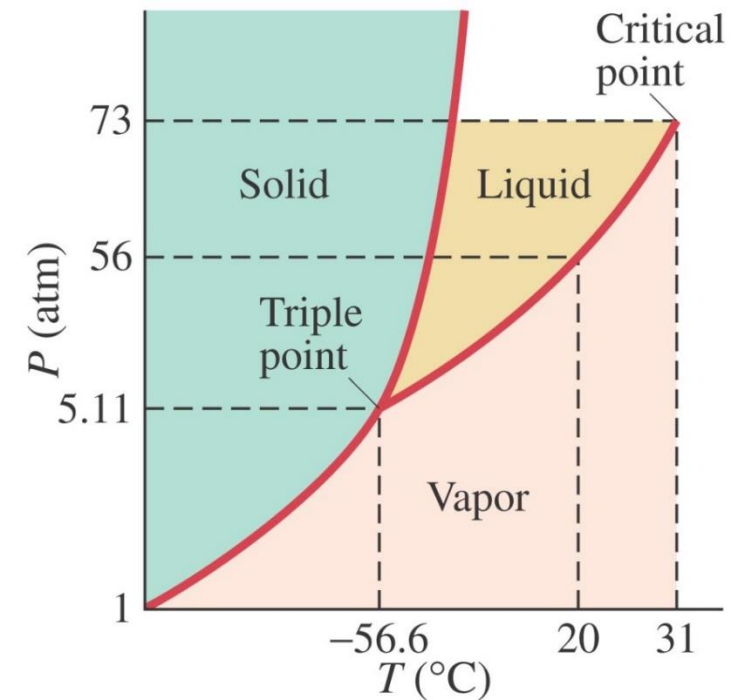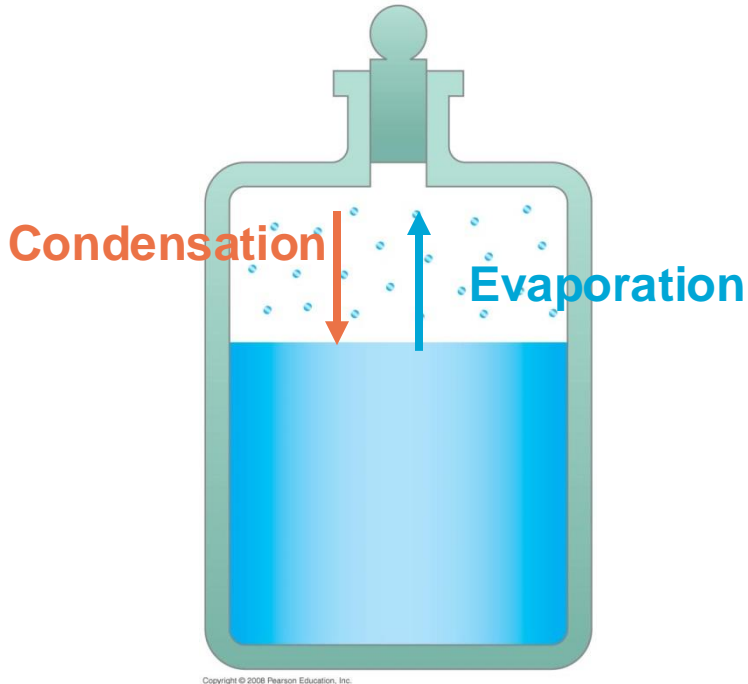
P-T diagram for water

- Curve (ℓ-v): liquid and vapour phase are in equilibrium (boiling point vs. pressure)

- Curve (s-ℓ): solid and liquid phase are in equilibrium (freezing point)

- Curve (s-v): Sublimation point

- Triple point: three phases coexist in equilibrium (unique value of P and T)

- Low pressure (< 0.006 atm): sublimation

P-T diagram for CO_2

18-4 Vapor Pressure

Condensation

Evaporation

- When equilibrium is reached, saturation occurs.

- The pressure of the vapour when saturation occurs is called saturated vapor pressure

- Evaporation occurs when the vapor pressure < saturated vapor pressure

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TABLE 18–2 Saturated Vapor Pressure of Water

Temperature (°C)	Saturated Vapor Pressure	
	torr (= mm-Hg)	Pa (= N/m²)
−50	0.030	4.0
−10	1.95	2.60×10^2
0	4.58	6.11×10^2
5	6.54	8.72×10^2
10	9.21	1.23×10^3
15	12.8	1.71×10^3
20	17.5	2.33×10^3
25	23.8	3.17×10^3
30	31.8	4.24×10^3
40	55.3	7.37×10^3
50	92.5	1.23×10^4
60	149	1.99×10^4
70[†]	234	3.12×10^4
80	355	4.73×10^4
90	526	7.01×10^4
100[‡]	760	1.01×10^5
120	1489	1.99×10^5
150	3570	4.76×10^5

depends on T

[†]Boiling point on summit of Mt. Everest.
[‡]Boiling point at sea level.

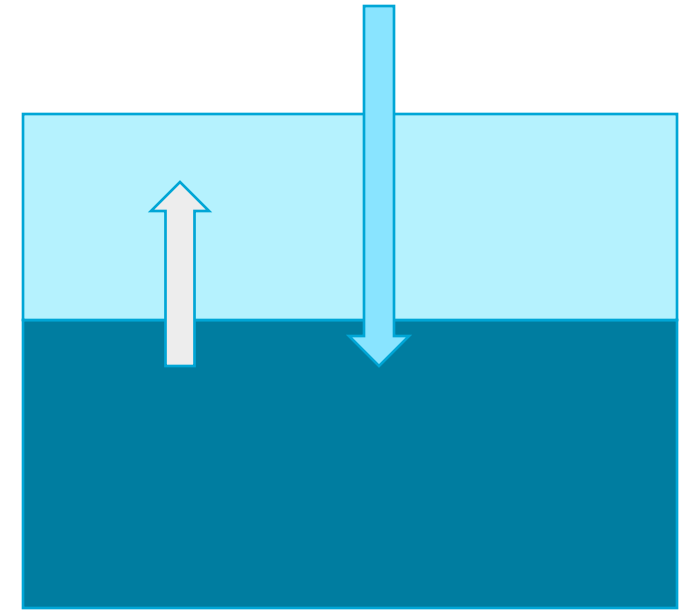Copyright © 2008 Pearson Education, Inc.

18-4 Evaporation vs. condensation
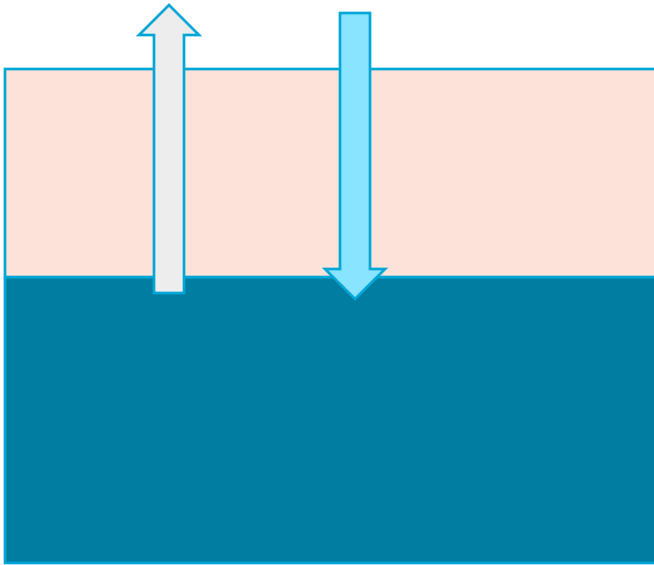
Equilibrium: saturation reached. Partial pressure = saturated vapour pressure
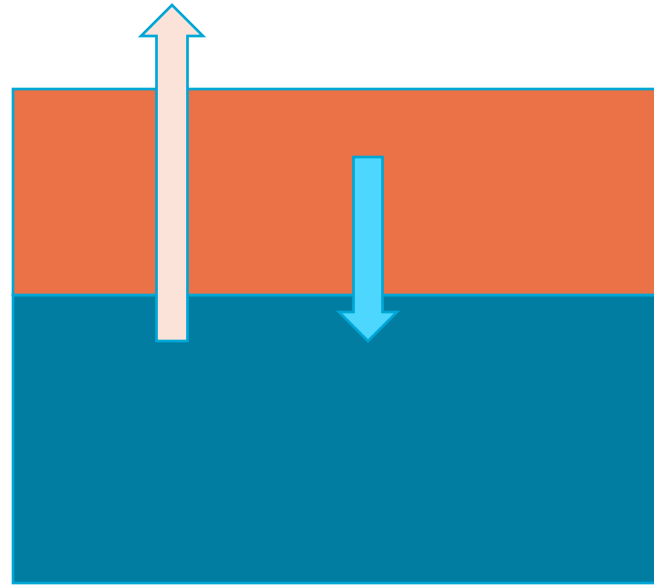
Temperature increase→ saturated vapor pressure increases → More evaporation

Temperature reduces→ saturated vapor pressure reduces → More condensation

18-4 Boiling

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Boiling: when saturated vapour pressure equals the external pressure.

Q: At top of Mt. Everest air pressure is 1/3 of that at the sea level.
Then at what temperature water boils?

70 °C

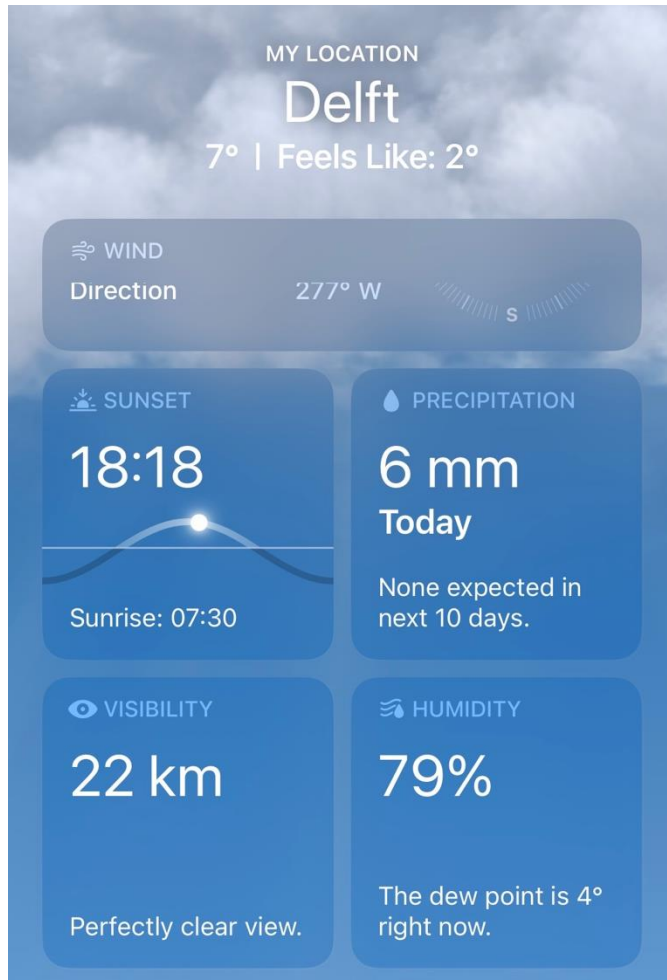**TABLE 18–2 Saturated Vapor Pressure of Water**

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[†]Boiling point on summit of Mt. Everest.
[‡]Boiling point at sea level.

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18-4 Relative Humidity

$$relative\ humidity = \frac{partial\ pressure\ of\ water}{saturated\ vapor\ pressure}$$

MY LOCATION
Delft
7° | Feels Like: 2°

≋ WIND
Direction   277° W
                              S

☀ SUNSET
18:18

Sunrise: 07:30

💧 PRECIPITATION
6 mm
Today

None expected in next 10 days.

👁 VISIBILITY
22 km

Perfectly clear view.

≋ HUMIDITY
79%

The dew point is 4° right now.

Exercise: 1) What is the water vapor partial pressure now in Delft?

2) Considering the same amount vapor pressure, if temperature increases to 10 °C, what would be the relative humidity?

TABLE 18–2 Saturated Vapor Pressure of Water

Temperature (°C)	Saturated Vapor Pressure	
	torr (= mm-Hg)	Pa (= N/m^2)
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[†]Boiling point on summit of Mt. Everest.
[‡]Boiling point at sea level.

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18-4 various phenomena: dew, frost, clouds

- **Dew point**: the temperature, at which, the air is saturated with water.
- If the temperature is below the dew point, water vapor condenses on surface to form dew drops.

- **Frost point**: If the temperature is below **freezing**, the dew point is called the frost point.
- If the temperature falls below the frost point, water vapor deposits on surface to form crystals known as frost

- If the air temperature cools below the dew point, water vapor condenses to form cloud/fog drops

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18-4 Clouds formation
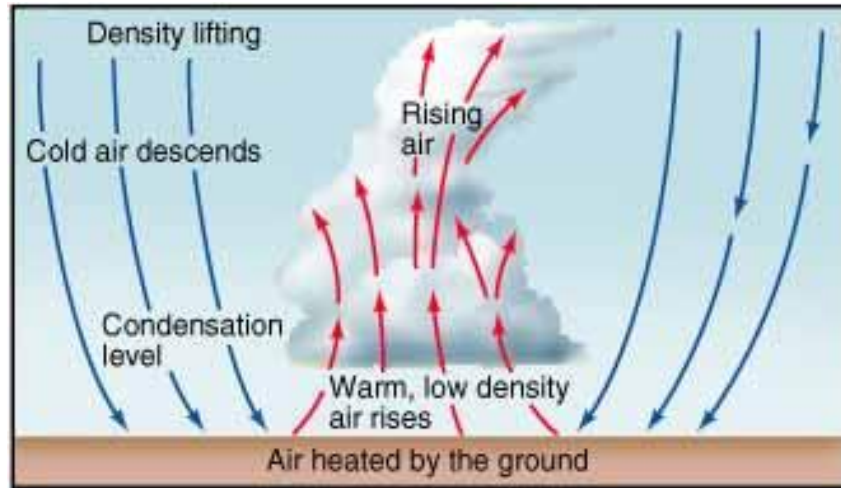
https://laulima.hawaii.edu/access/content/group/dbd544e4-dcdd-4631-b8ad-3304985e1be2/book/chapter_6/lifting.htm
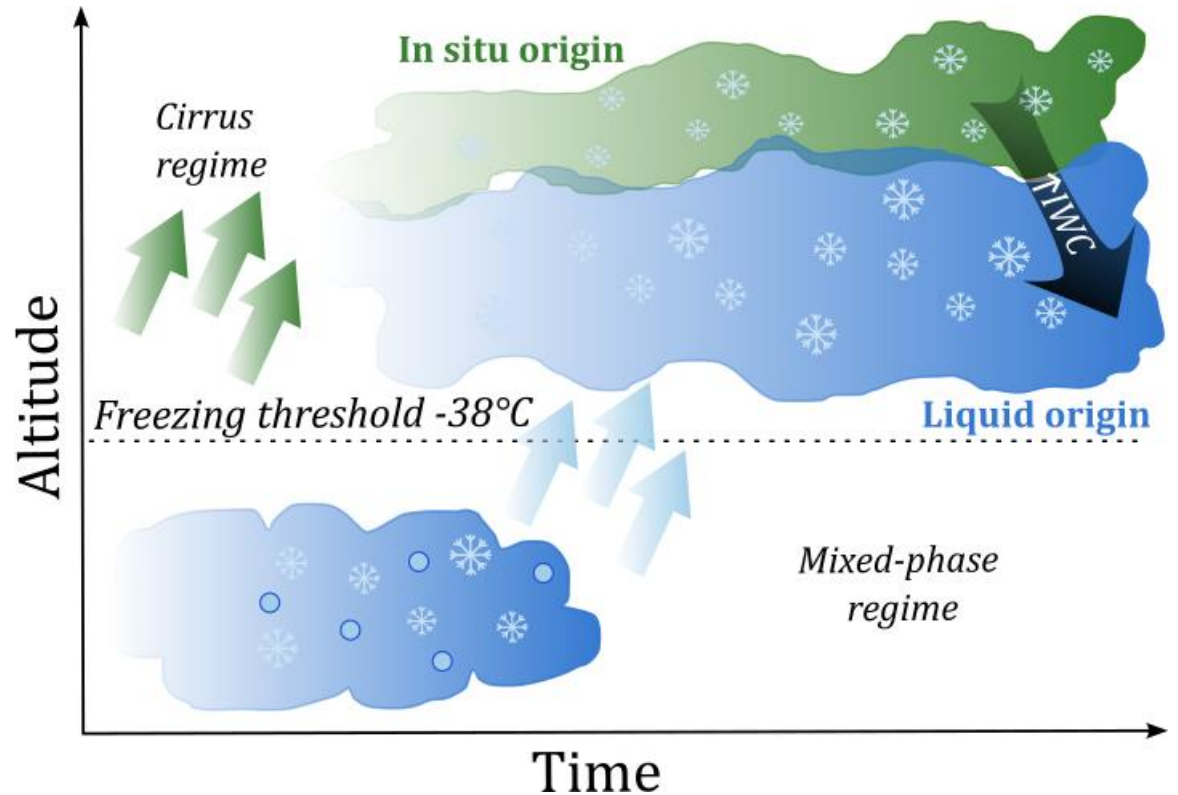

Figure source: De la Torre Castro, 2025

- If the partial pressure of water exceeds the saturated vapour pressure, the air is **supersaturated;**
- Drop formation occurs on particles known as cloud condensation nuclei (CCN)
- Without particles clouds would not form in the Atmosphere

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Exercise

What is the mass of water in a closed room of 5.0 m x 3.0 m x 2.5 m when the temperature is 25 °C and the relative humidity is 65 %?

$$V = 5 \times 3 \times 2.5 = 37.5 \, m^3$$

$$p_{H2O} = 65\% \times (3.17 \times 10^3) \, pa = 2.06 \times 10^3 pa = 0.020 \, atm$$

$$n = \frac{PV}{RT} = \frac{(0.020 \times 10^5) pa \times 37.5 \, m^3}{8.314 \frac{J}{mol \, K} \times (25 + 273)K} = 30.27 \, mol$$

$$m = n \times M = 30.27 \, mol \times 18g/mol = 544.86g$$

Temp-erature (°C)	Saturated Vapor Pressure	
	torr (= mm-Hg)	Pa (= N/m²)
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0	4.58	6.11×10^2
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150	3570	4.76×10^5

TABLE 18–2 Saturated Vapor Pressure of Water

[†]Boiling point on summit of Mt. Everest.
[‡]Boiling point at sea level.

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Problem 33 pressure cooker

Weight (mass *m*)

m

←|→ Diameter *d*

Steam

Water

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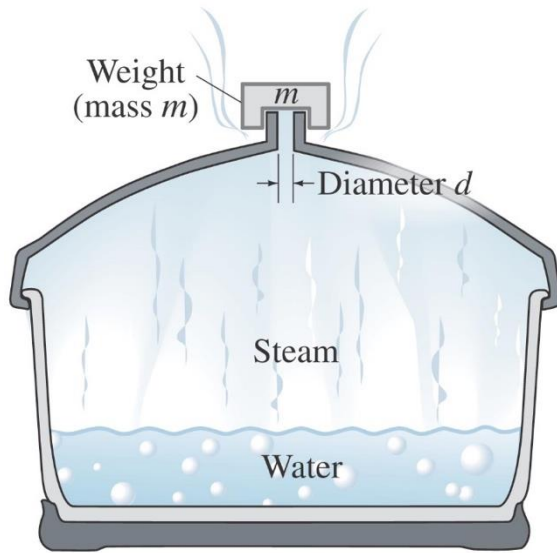
- A pressure cooker is a sealed pot designed to cook food with the steam produced by boiling water above 100 °C.
- It uses a weight of mass *m* to allow steam to escape at a certain pressure through a small hole in the lid.
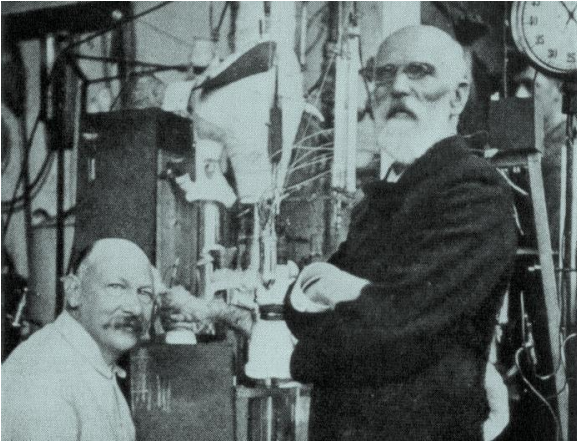 The diameter of the hole is *d* equal to 3.0 mm.

What should *m* be in order to cook food at 120 °C? (assume atmospheric pressure outside the cooker is 1 atm)

$$mg = (Pin - Pa_{tm})A = \Delta P \frac{\pi d^2}{4} \qquad m = \frac{\Delta P \pi d^2}{4g}$$

Saturated vapor pressure at 120 °C = 1.99*10^5 pa, the ambient pressure of 1 atm is 1.0 * 10^5 pa

$$m = \frac{(0.99 \times 10^5)pa \times \pi \times (0.003 \, m)^2}{4 \times 9.8 \, m^2/s} = 0.071 \, kg$$

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18-6 Van der Waals Equation of State

Nobel prize in physics 1910

Van der Waals forces
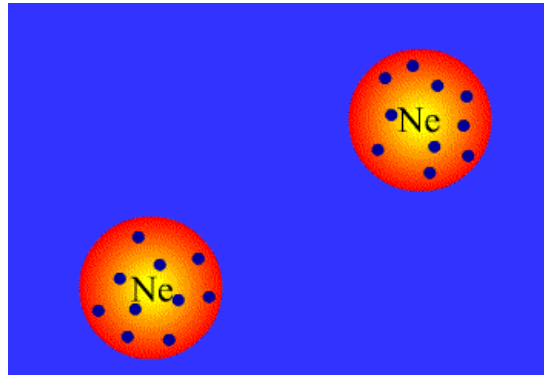
Animation from:
http://www.chm.bris.ac.uk/webproject
s2003/swinerd/forces/forces.htm
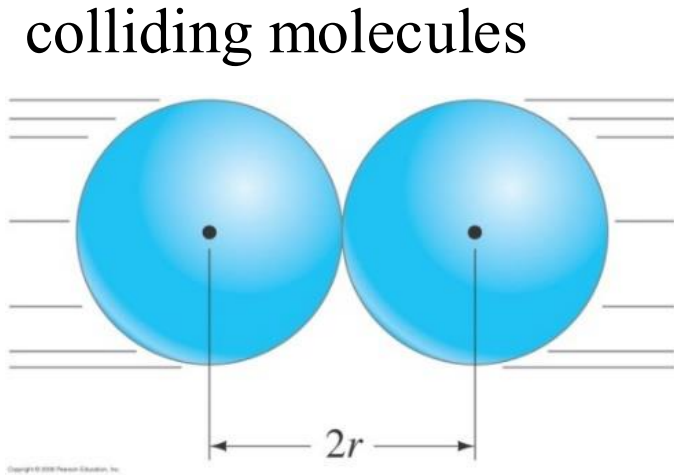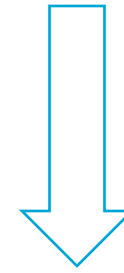
- Based on kinetic theory
- Non-negligible volume of molecules
- Range of attractive forces larger than size of molecules
- The actual volume in which the molecules can move is smaller than the volume of container.

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18-6 Clausius equation of state−effects of molecule size

colliding molecules

$$PV = nRT$$

b represents the
unavailable volume
per mole of gas

$$P(V - nb) = nRT$$

$$P\left(\frac{V}{n} - b\right) = RT$$

$$P_{real} < P_{ideal}$$

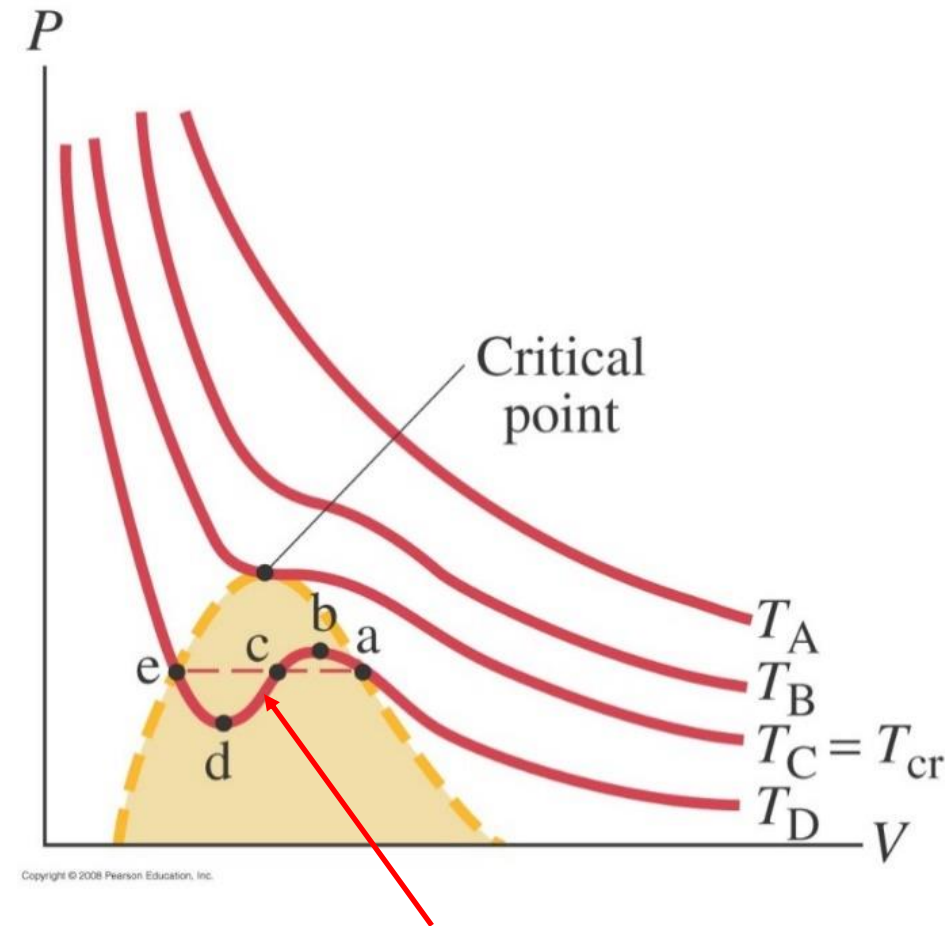for given
temperature
and volume

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18-6 Van der Waals equation of state

- Molecules towards wall are slowed down
- The corresponding reduced pressure is proportional to density of molecules in layer of gas at the surface (and to density in next layer)

- Actual forces exerted on the wall is less due to attractive forces;

- We expect the pressure to be reduced is proportional to the density squared $(n/V)^2$

$$P = \frac{nRT}{V - nb} - \frac{a}{(V/n)^2}$$
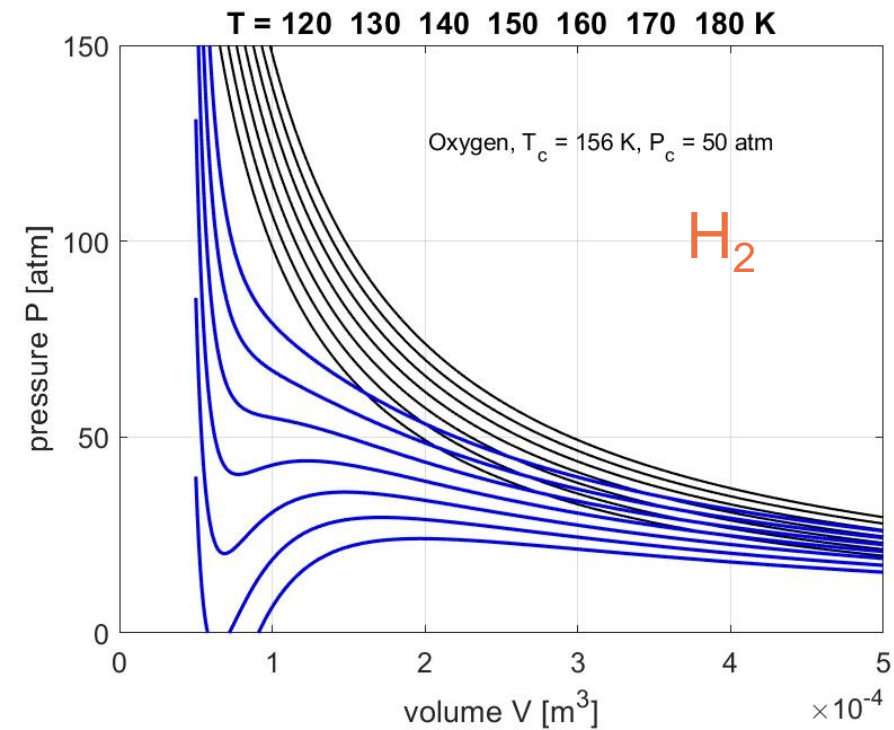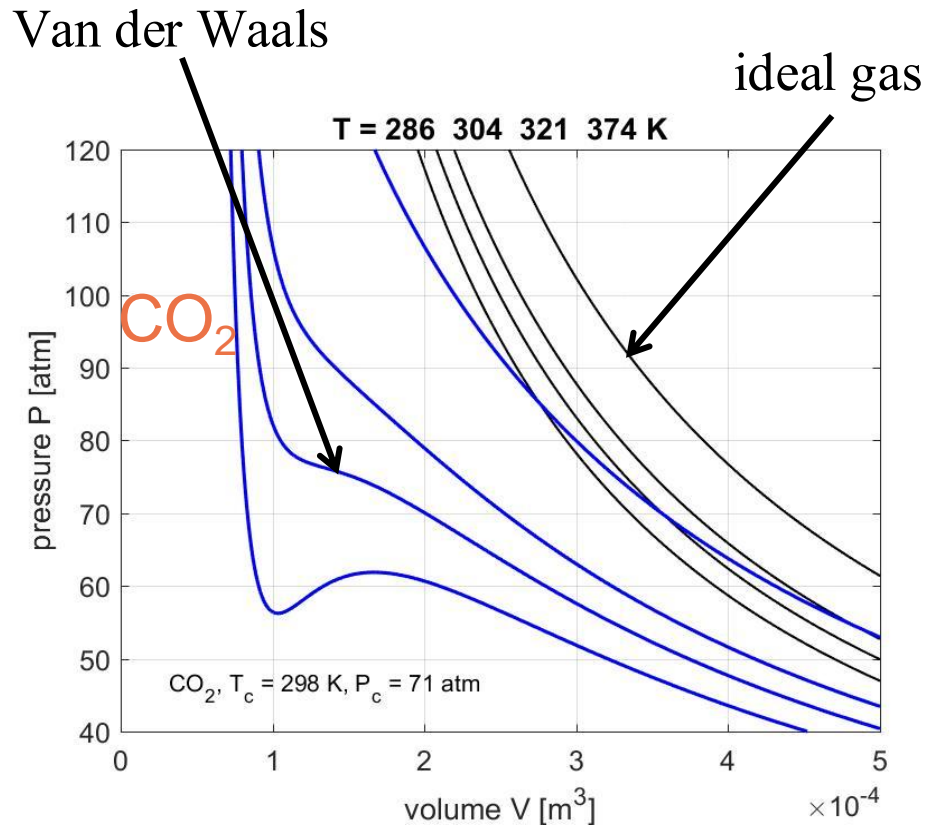
Constant a, b differ per gas
Determined by experiments

Critical point

T_A
T_B
$T_C = T_{cr}$
T_D

$$T_{cr} = \frac{8a}{27bR} \qquad P_{cr} = \frac{a}{27b^2}$$

Was not observed in experiment.

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18-6 Van der Waals Equation of State—comparison

Van der Waals

ideal gas

Changes with the type of gas!

CO_2

H_2

18-7 Mean Free Path
---average distance molecule travels between collisions

- If molecules were true point particles, they would never collide with one another.

- **Mean free path distance** is the average distance a molecule travels between collisions.

- Greater molecule, greater air density → shorter mean free path distance

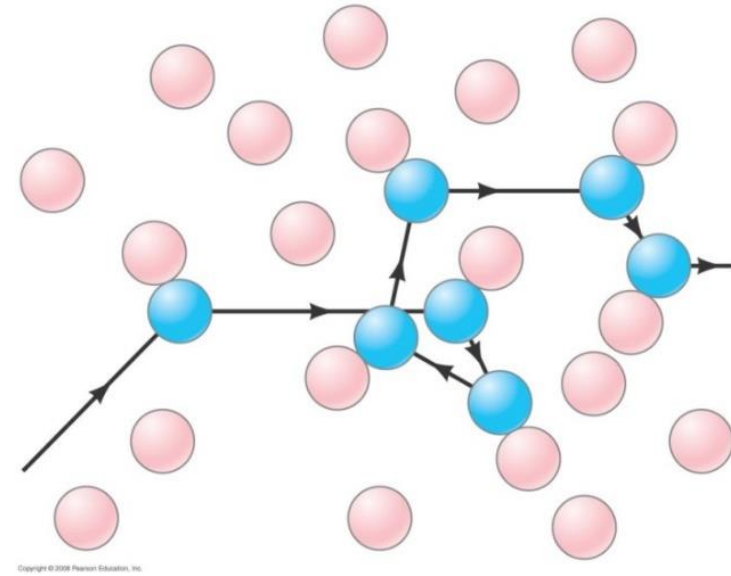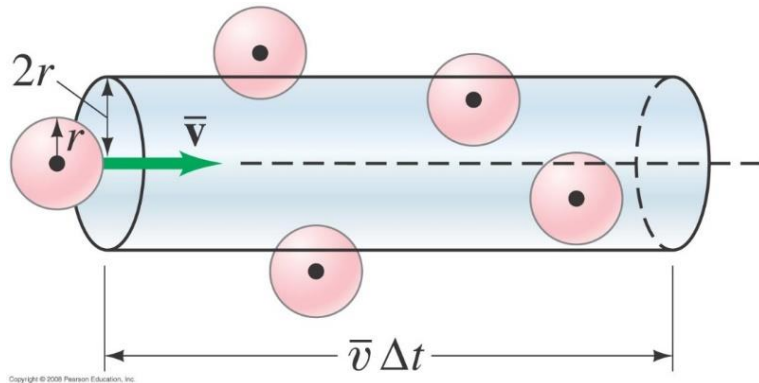Figure 18-12 Zigzag path of a molecule colliding with other molecules.

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18-7 Mean Free Path
## ---average distance molecule travels between collisions

- Molecules are hard spheres with radius *r;*
- Dashed line: molecule moves from left to right with speed $\bar{v}$ without collision;
- Assuming the other molecules are still;
- Concentrations of molecules (#/volume) are *N/V;*
- Number of Collison = concentration * volume

Mean free distance: $\quad l_M = \dfrac{\bar{v}\Delta t}{\pi(2r)^2 \bar{v}\Delta t(N/V)} = \dfrac{1}{4\pi r^2 (N/V)}$

We expect mean free path to be inversely proportional to density *N/V* and size ($\sim r^2$) of the molecules

18-7 Mean Free Path

---average distance molecule travels between collisions
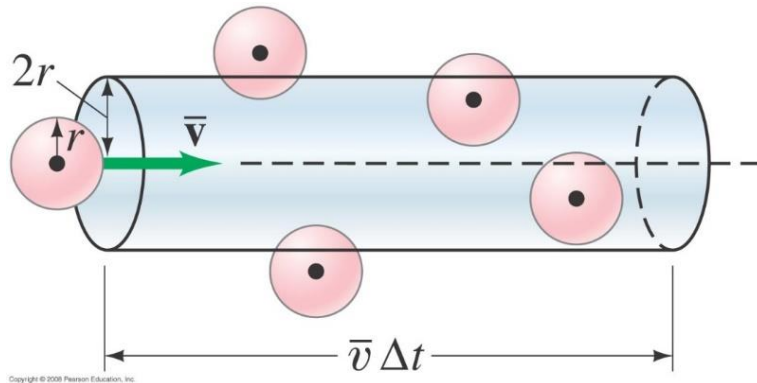
- Assuming the other molecules are still

$$l_M = \frac{\bar{v}\Delta t}{\pi(2r)^2\bar{v}\Delta t(N/V)}$$

Not true!

- Relative speed matters:

$$v_{rel} = \sqrt{2}\bar{v}$$

Mean free distance: $$\boldsymbol{l_m = \frac{1}{4\pi\sqrt{2}r^2(N/V)}}$$

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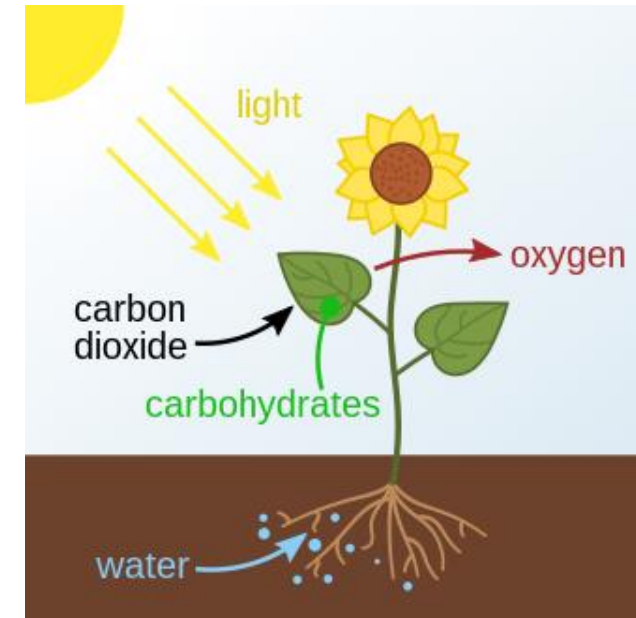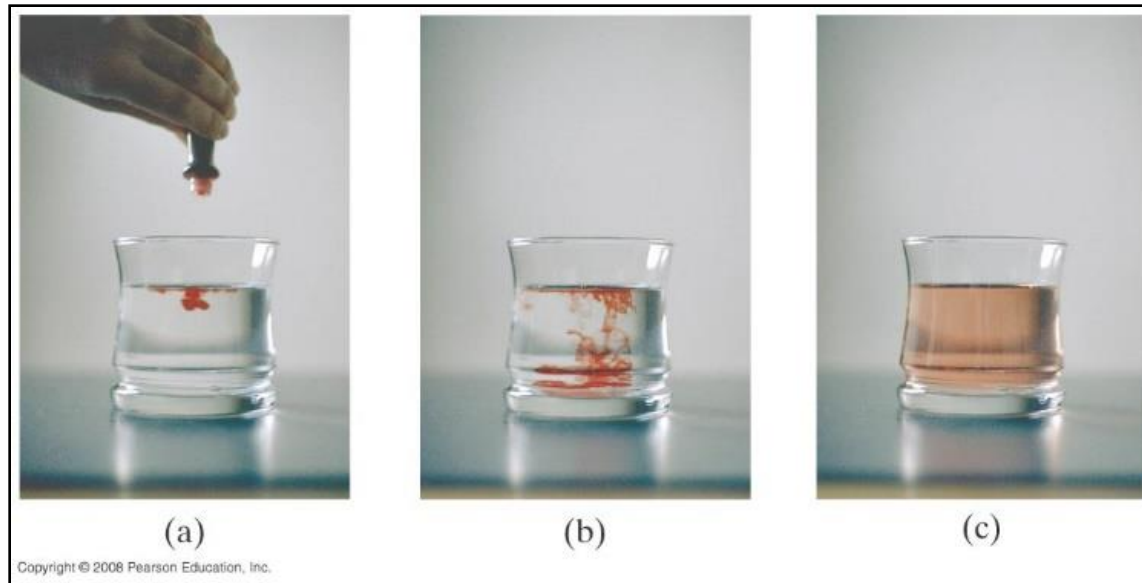# Example 18-8 Mean free path of air molecules at STP

Estimate the mean free path of air molecules at STP, standard temperature and pressure (0°C, 1atm). The diameter of O_2 and N_2 molecules is about 3×10^{-10} m.

Knowing 1 mol of an ideal gas occupies a volume of 22.4×10^{-3} m³ at STP.

$$\frac{N}{V} = \frac{6.02 \times 10^{23}}{22.4 \times 10^{-3}} = 2.69 \times 10^{25} \ \#/m^3$$

$$l_M = \frac{1}{4\pi\sqrt{2}(1.5\times10^{-10})^2(2.7\times10^{25}m^{-3})} = {\sim}9\times10^{-8} \text{ m.}$$

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18-8 Diffusion

- Takes place because of the random motion of molecules
- Diffusion depends on concentrations (#/mol; #/m^3)
- Diffusing direction: high concentration region → low concentration region

18-8 Fick's law

- often convection (moving air currents) plays a greater role than diffusion
- diffusion can be understood on the basis of kinetic theory

Region 1; concentration = C_1 $\leftarrow \Delta x \rightarrow$ Region 2; concentration = C_2
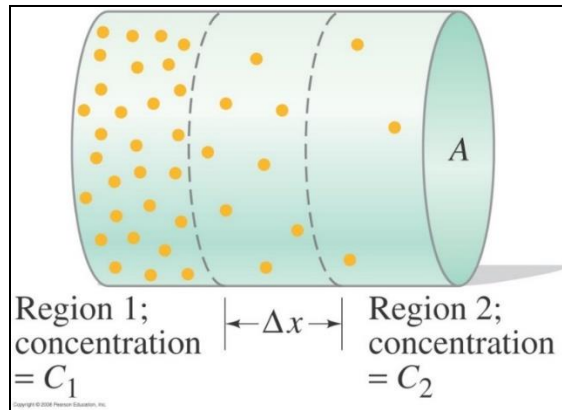
- more molecules cross into central region from region 1 than from region 2 →
- net flow of molecules from left to right

TABLE 18–3 Diffusion Constants, D (20°C, 1 atm)

Diffusing Molecules	Medium	D (m²/s)
H_2	Air	6.3×10^{-5}
O_2	Air	1.8×10^{-5}
O_2	Water	100×10^{-11}
Blood hemoglobin	Water	6.9×10^{-11}
Glycine (an amino acid)	Water	95×10^{-11}
DNA (mass 6×10^6 u)	Water	0.13×10^{-11}

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$$J = DA \frac{C_1 - C_2}{\Delta x} \implies J = DA \frac{dC}{dx}$$

Diffusion gets faster when temperature increases!

Rate of diffusion in mol/s

Diffusion factor

Concentration gradient in mol/m⁴

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Wrap up: learning objectives

- Explain **molecular kinetic theory** for ideal gases, including, average kinetic energy, average speed and speed distribution. (**Maxwell distribution**)

$$\overline{K} = \frac{3}{2}kT \qquad \overline{v} = \sqrt{\frac{8kT}{\pi m}} \qquad v_p = \sqrt{\frac{2kT}{m}} \qquad v_{rms} = \sqrt{\frac{3kT}{m}}$$
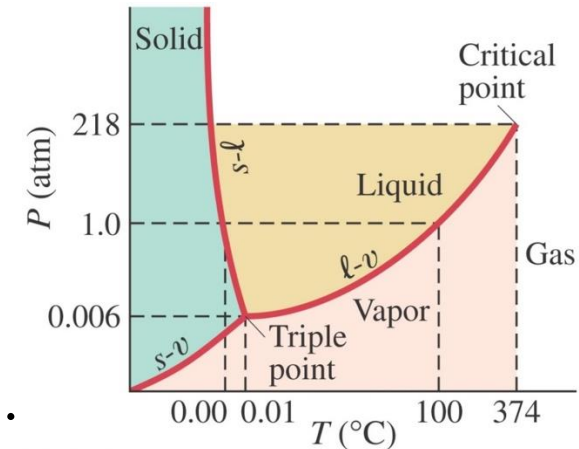
- Explain the **real gas behaviors**, using van der Waals theory

$$P = \frac{nRT}{V - nb} - \frac{a}{(V/n)^2}$$

- Analyze **phase changes** for given substances, using phase diagrams.

- Calculate **relative humidity** at given temperature. $RH = \dfrac{p_{H2O}}{p_{saturated,\ H2O}}$

- Calculate the **diffusion rate of molecules** $J = DA\dfrac{dC}{dx}$

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Thank you for your attention!

Feijia Yin

f.yin@tudelft.nl

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