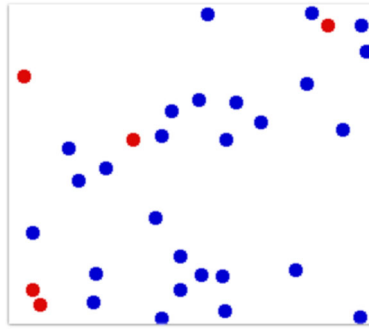# Chapter 18

Thermal Properties of Matter

楊 本 立 副教授

Outline

1. Equations of state

2. Microscopic interpretation of pressure and temperature in an ideal gas system

3. Degree of freedom and theorem of equipartition of energy

4. Specific heat of an ideal gas and a solid

5. Boltzmann distribution law

6. Mean free path

1. Equations of State

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Macroscopic state of matter

State variables: P, V, n, T

Equations of state in terms of the state variables.

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Equation of state for solids

Thermal expansion: $\Delta V_1 = \beta V_0 \Delta T$

Bulk modulus: $B = -\dfrac{\Delta P}{\Delta V_2 / V_0}$

$\Delta V = \Delta V_1 + \Delta V_2 = \beta V_0 \Delta T - k V_0 \Delta P$ $\qquad$ $k = \dfrac{1}{B}$ compressibility

$\Rightarrow V = V_0 \left[1 + \beta (T - T_0) - k(P - P_0) \right]$

An Ideal Gas

o For gases, the interatomic forces within the gas are very weak.

o The molecular volume is negligible compared with the volume of the container.

The law of Charles and Gay-Lussac : $V \propto T$

Boyle's law : $P \propto \dfrac{1}{V}$

Equation of state of an ideal gas

$$PV = nRT = Nk_BT$$

n : number of moles

Avogadro's number (the number of moleucles in a mole),

$N_A = 6.02 \times 10^{23}$ molecules/mol.

$R = 8.314$ J/mol·K, gas constant.

$k_B = \dfrac{R}{N_A} = 1.38 \times 10^{-23}$ J/molecule·K, Boltzmann constant

$$m_{total} = nM, \quad M : \text{molar mass}$$

$$\rho = \frac{m_{total}}{V}$$

$$\Rightarrow \quad \rho = \frac{PM}{RT}$$

Figure A bottle of champagne is shaken and opened. Liquid spews out of the opening. A common misconception is that the pressure inside the bottle is increased by the shaking.

Ex. Variation of atmospheric pressure with elevation.

Find the variation of atmospheric pressure with elevation in the earth's atmosphere, assuming that the temperature is 0 $^{\circ}$C at all elevations. Ignore the variation of g with elevation.

Ans:

$$\Delta P = -\rho g \Delta y \quad \Rightarrow \quad \frac{dP}{dy} = -\rho g$$

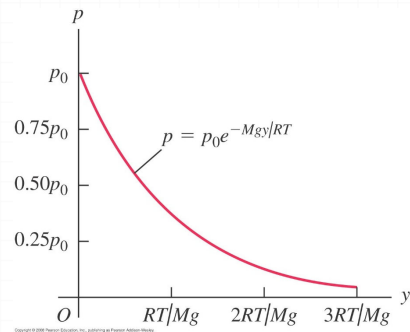$$\rho = \frac{PM}{RT} \quad \Rightarrow \quad \frac{dP}{dy} = -\frac{PM}{RT}g$$

$$\frac{dP}{P} = -\frac{Mg}{RT}dy$$

$$\int_{P_1}^{P_2}\frac{dP}{P} = -\int_{y_1}^{y_2}\frac{Mg}{RT}dy$$

$$\ln\frac{P_2}{P_1} = -\frac{Mg}{RT}(y_2 - y_1)$$

$$\frac{P_2}{P_1} = e^{-\frac{Mg}{RT}(y_2-y_1)}$$
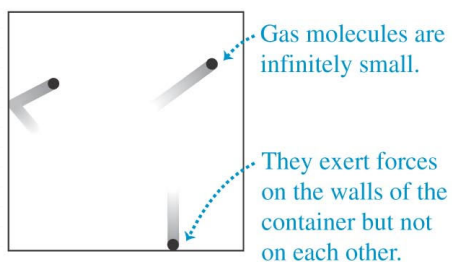
$$\Rightarrow \quad P = P_0 e^{-\frac{Mgy}{RT}}$$

p

p₀
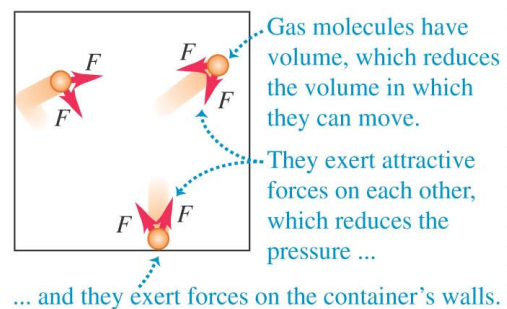
$0.75p_0$

$p = p_0 e^{-Mgy/RT}$

$0.50p_0$

$0.25p_0$

O   *RT/Mg*   *2RT/Mg*   *3RT/Mg*   *y*

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The van der waals equation

(a) An idealized model of a gas

Gas molecules are infinitely small.

They exert forces on the walls of the container but not on each other.

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(b) A more realistic model of a gas

F   *F*

F

F

F   *F*

Gas molecules have volume, which reduces the volume in which they can move.

They exert attractive forces on each other, which reduces the pressure ...

... and they exert forces on the container's walls.

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6

The van der waals equation:

$$(P + \frac{an^2}{V^2})(V - nb) = nRT$$

a, b are emperical constants.

$(P + \frac{an^2}{V^2})$: the effective pressure

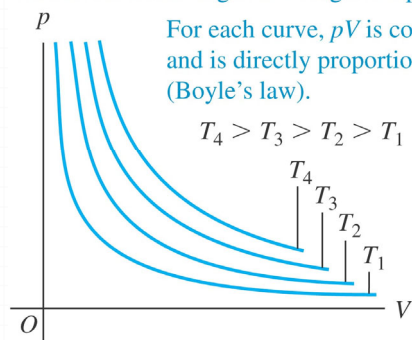a : the attractive intermoecular forces

$(V - nb)$: the effective volume
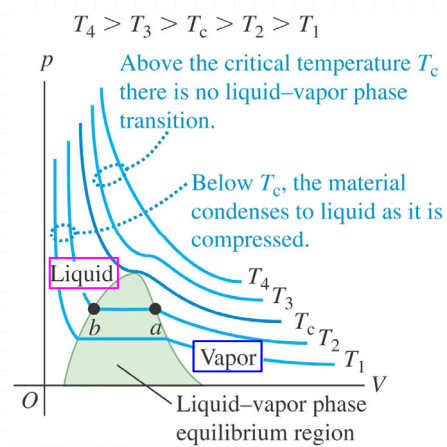
b : the volume of a mole of molecules.

Each curve represents pressure as a function of volume for an ideal gas at a single temperature.

p

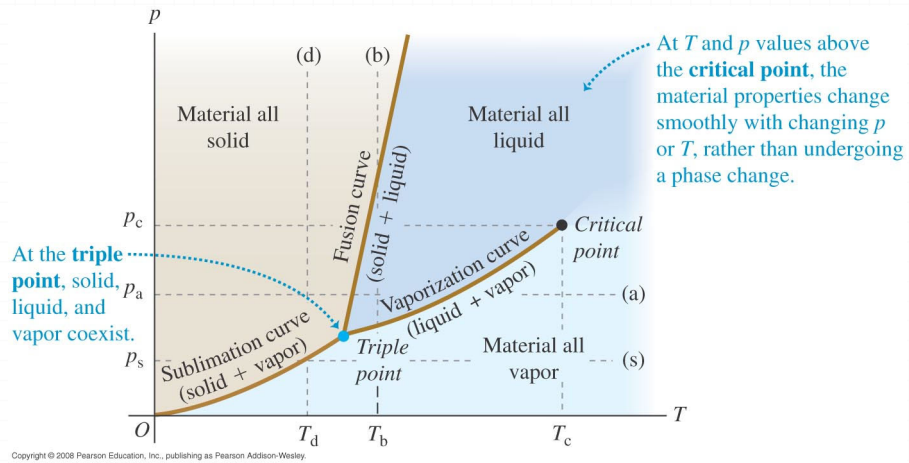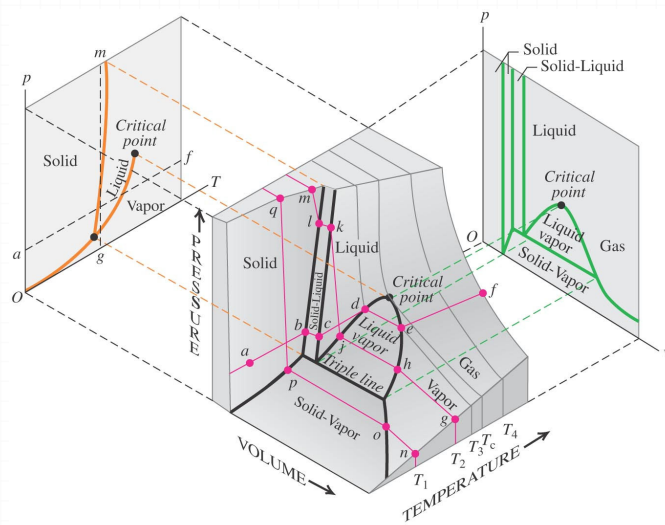For each curve, pV is constant and is directly proportional to T (Boyle's law).

$T_4 > T_3 > T_2 > T_1$

T_4
T_3
T_2
T_1

O

V

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$T_4 > T_3 > T_c > T_2 > T_1$

p

Above the critical temperature T_c there is no liquid–vapor phase transition.

Below T_c, the material condenses to liquid as it is compressed.

Liquid

b a

Vapor

T_4
T_3
T_c T_2
T_1

O

V

Liquid–vapor phase equilibrium region

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Typical phase diagram in 2D

Typical phase diagram in 3D

Phase diagram of an Ideal gas
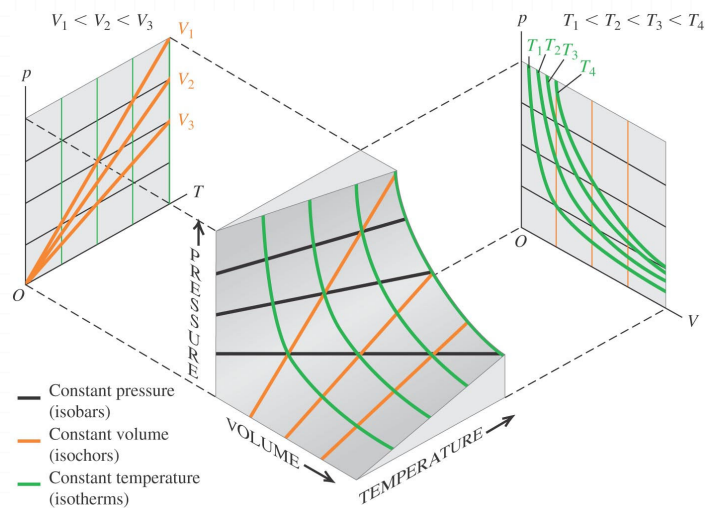
- Constant pressure (isobars)
- Constant volume (isochors)
- Constant temperature (isotherms)

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2. Microscopic interpretation of pressure and temperature in an ideal gas system

Kinetic Theory

O Model gas behavior using Newton's laws of motion to describe thermodynamic processes.

⇒ To understand "pressure" and "temperature"

Molecular Model of an Ideal Gas

O The number of molecules in the gas is large, and the average separation between the molecules is large compared with their dimensions. The volume of molecules is negligible.

O The molecules obey Newton's laws of motion, but as a whole they move randomly.

O The molecules interact only by short-range forces during elastic collisions.

O The molecules make elastic collisions with the walls.
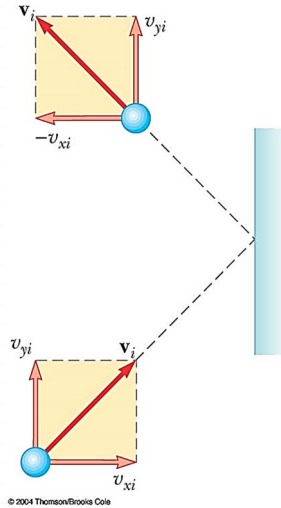
O All molecules are identical.

Pressure and Kinetic Energy
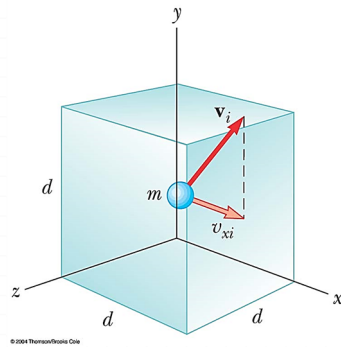
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Perfectly elastic collision:
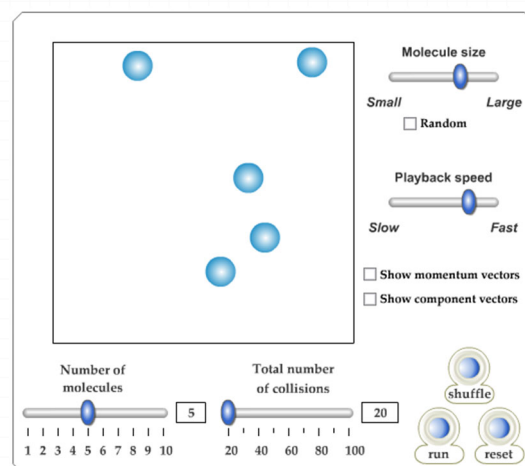
$$(1)\quad \Delta P_{xi} = \left(-mv_{xi}\right) - \left(mv_{xi}\right) = -2mv_{xi}$$

$$(2)\quad \overline{F}_{i,\text{on gas}}\Delta t = \Delta P_{xi} = -2mv_{xi}$$

$$(3)\quad \Delta t = \frac{2d}{v_{xi}}$$

$$\Rightarrow\quad \overline{F}_{i,\text{on gas}} = \frac{-2mv_{xi}}{\Delta t} = \frac{-mv_{xi}^2}{d}$$

$$\overline{F}_{i,\text{on wall}} = (-)\overline{F}_{i,\text{on gas}} = \frac{mv_{xi}^2}{d}$$

$$\overline{F}_{\text{on wall}} = \sum_{i=1}^{N}\frac{mv_{xi}^2}{d} = \frac{m}{d}\sum_{i=1}^{N}v_{xi}^2$$

Note, for small N, $\overline{F}_{\text{on wall}}$ would vary with time.

$$\overline{v_x^2} = \frac{\displaystyle\sum_{i=1}^{N}v_{xi}^2}{N} \quad\Rightarrow\quad \overline{F}_{\text{on wall}} = \frac{m}{d}N\overline{v_x^2}$$

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

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \quad\Rightarrow\quad \overline{v_x^2} = \frac{1}{3}\overline{v^2}$$

$$\overline{F}_{\text{on wall}} = \frac{N}{3}\left(\frac{m\overline{v^2}}{d}\right)$$

$$P = \frac{\overline{F}_{\text{on wall}}}{A} = \frac{\overline{F}_{\text{on wall}}}{d^2}$$

$$= \frac{N}{3}\left(\frac{m\overline{v^2}}{d^3}\right) = \frac{1}{3}\left(\frac{N}{V}\right)m\overline{v^2}$$

$$\Rightarrow \quad P = \frac{2}{3}\left(\frac{N}{V}\right)\left(\frac{1}{2}m\overline{v^2}\right) = \frac{2}{3}\frac{N}{V}\overline{E}_k$$

Molecular Interpretation of Temperature

$$PV = \frac{2}{3}N\left(\frac{1}{2}m\overline{v^2}\right)$$

compared with $PV = Nk_BT$

$$\Rightarrow \quad T = \frac{2}{3k_B}\underbrace{\left(\frac{1}{2}m\overline{v^2}\right)}_{\substack{\text{Average kinetic energy} \\ \text{per particle}}} \quad \text{(Only valid for monatomic gas)}$$

$\Rightarrow$ "Temperature" is a direct measure of average molecular kinetic energy.

😎 The velocity for the kinetic energy is measured with respect to the center of mass of the ideal gas. Therefore, the motion of the gas container doesn't change the gas temperature!

😎 For molecules, the rotational and vibrational motions can contribute to the pressure as well. The kinetic energy contain not just translational but also rotational and vibrational energies.

😎 在室溫金屬內的自由電子(Fermi gas)的平均動能 $\gg k_B T_{300K}$
⇒ 量子效應
(https://en.wikipedia.org/wiki/Fermi_energy)

VORTEX TUBE
https://en.wikipedia.org/wiki/Vortex_tube
https://www.youtube.com/watch?v=syu6SM7X8yU

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1. Equations of state
2. Microscopic interpretation of pressure and temperature in an ideal gas system
3. Degree of freedom and theorem of equipartition of energy
4. Specific heat of an ideal gas and a solid
5. Boltzmann distribution law
6. Mean free path

3. Degrees of freedom and theorem of equipartition of energy

Degrees of Freedom

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_BT$$

$$\overline{v^2_{x,y,z}} = \frac{1}{3}\overline{v^2} \quad \Rightarrow \quad \begin{cases} \frac{1}{2}m\overline{v^2_x} = \frac{1}{2}k_BT \\ \frac{1}{2}m\overline{v^2_y} = \frac{1}{2}k_BT \\ \frac{1}{2}m\overline{v^2_z} = \frac{1}{2}k_BT \end{cases}$$

- In general, a **degree of freedom** refers to an independent means by which a molecule can possess the energy.
- Each translational degree of freedom contributes an equal amount to the energy of the gas.

Theorem of Equipartition of Energy

- Each degree of freedom contributes $\frac{1}{2}k_BT$ to the energy of a system.

- The possible degrees of freedom, in addition to those associated with translation, could arise from rotation and vibration of molecules.

$$K_{\text{translation}} = N\left(\frac{1}{2}m\overline{v^2}\right) = N\left(\frac{1}{2}k_BT\right)\times 3 = \frac{3}{2}nRT$$

$$k_B = \frac{R}{N_A} \qquad n = \frac{N}{N_A}$$

The E_{int} of an ideal monatomic gas is the $K_{\text{translation}}$: $E_{\text{int}} = \frac{3}{2}nRT$

$\Rightarrow$ The internal energy of ideal gases depend only on temperature.

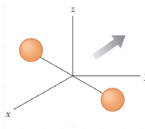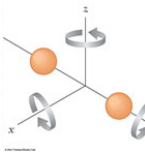The root mean square (rms) speed is the square root of the average of the squares of the speeds. (M is the molar mass and $M = mN_A$)

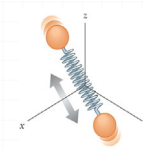$$v_{\text{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}$$

For diatomic molecules, the possible degrees of freedom are

Translational:

$$\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$
$$= \left(\frac{1}{2}k_BT\right) + \left(\frac{1}{2}k_BT\right) + \left(\frac{1}{2}k_BT\right) \Rightarrow \left(\frac{1}{2}k_BT\right)\times 3$$

Rotational:

$$\frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$
$$\approx \left(\frac{1}{2}k_BT\right) + 0 + \left(\frac{1}{2}k_BT\right) \Rightarrow \left(\frac{1}{2}k_BT\right)\times 2$$

Vibrational:

$$\frac{1}{2}mv^2 + \frac{1}{2}kx^2$$
$$= \left(\frac{1}{2}k_BT\right) + \left(\frac{1}{2}k_BT\right) \Rightarrow \left(\frac{1}{2}k_BT\right)\times 2$$

$$\Rightarrow E_{\text{int}} = \left(\frac{7}{2}k_BT\right)N$$

Complex Molecules

0 For molecules with more than two atoms, the vibrations are more complex.

> ➤ The number of degrees of freedom is larger.

> ➤ The more degrees of freedom available to a molecule, the more "ways" there are to store energy. This results in a higher molar specific heat.

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1. Equations of state
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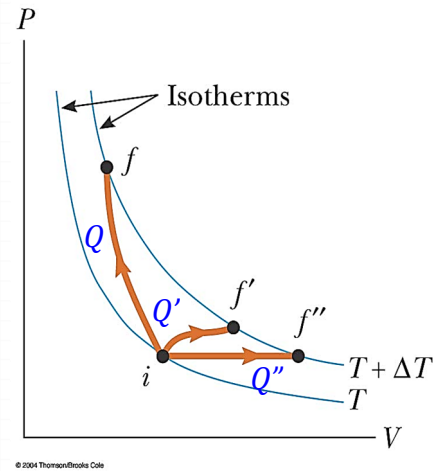5. Boltzmann distribution law
6. Mean free path

4. Specific heat of an ideal gas and a solid

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Molar Specific Heat of an Ideal Gas

- *O* Several processes can change the temperature of an ideal gas.
- *O* Since ΔT is the same for each process, ΔE_{int} is also the same.
- *O* The heat is different for the different paths.

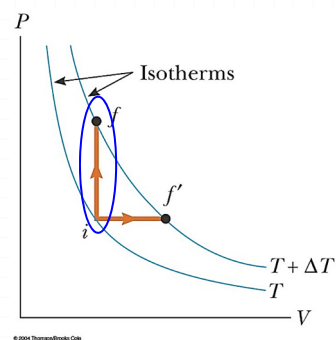© 2004 Thomson/Brooks Cole

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(1) For constant volume:

$$Q = nc_v \Delta T$$

$$W = 0$$

$$\Rightarrow \ \Delta E_{\text{int}} = Q + W = nc_v \Delta T$$

$$\Rightarrow \ \begin{cases} E_{\text{int}} = nc_v T \\ c_v = \dfrac{1}{n}\dfrac{dE_{\text{int}}}{dT} \end{cases}$$

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For monatomic gases, $E_{\text{int}} = \dfrac{3}{2}nRT \ \Rightarrow \ c_v = \dfrac{3}{2}R$

For diatomic gases, $E_{\text{int}} = \dfrac{7}{2}nRT \ \Rightarrow \ c_v = \dfrac{7}{2}R$

(2) For constant pressure:
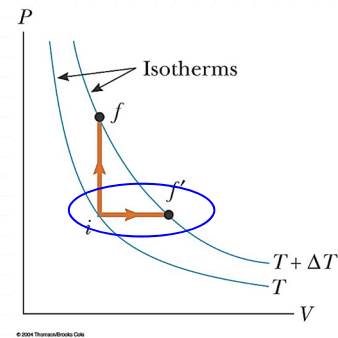
$$Q = nc_p \Delta T$$

$$W \neq 0$$

$$\Rightarrow \ \Delta E_{\text{int}} = Q + W$$

$$\Rightarrow \ nc_v \Delta T = nc_p \Delta T + (-\underbrace{P\Delta V}_{=nR\Delta T})$$

$$\Rightarrow \ c_p - c_v = R, \qquad \gamma \equiv c_p / c_v$$
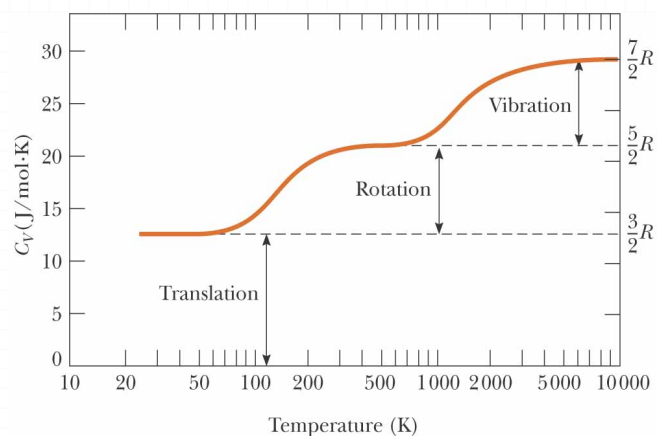
Note: For solids and liquids, $c_p \approx c_v$.

😎 If neither P or V is constant, there will be infinite number of possible specific heat.

P

Isotherms

f

f'

i

$T + \Delta T$

T

V

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The molar specific heat of hydrogen

C_V (J/mol·K) vs Temperature (K)

Translation — $\frac{3}{2}R$

Rotation — $\frac{5}{2}R$

Vibration — $\frac{7}{2}R$

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It requires quantum mechanics to explain the temperature dependence of the specific heat.

DuLong-Petit Law

- *o* At high temperatures, the molar specific heat of solids approaches the value of $3R$.

- *o* The molar specific heat of a solid at high temperature can be explained by the equipartition theorem.

  - ➤ Each atom of the solid has six degrees of freedom.

  - ➤ The internal energy is $6 \times (1/2)nRT$ and $C_v = 3R$.

In solids,

$$E_{\text{int}} = \left(\frac{1}{2}mv_x^2 + \frac{1}{2}kx^2\right) + \left(\frac{1}{2}mv_y^2 + \frac{1}{2}ky^2\right) + \left(\frac{1}{2}mv_z^2 + \frac{1}{2}kz^2\right)$$

$$= N(\frac{1}{2}k_B T) \times 6$$

$$= 3nRT$$

$$\Rightarrow \quad c_v = \frac{1}{n}\frac{dE_{\text{int}}}{dT} = 3R$$
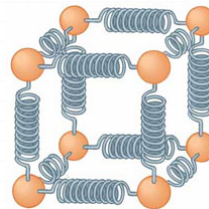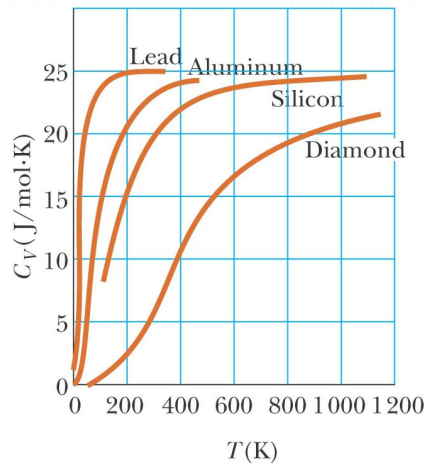
Molar Specific Heat of Solids

- As T approaches 0, the molar specific heat approaches 0.
- At high temperatures, C_V becomes a constant at $\sim 3R.$

Energy Quantization – energy levels

- This energy level diagram shows the rotational and vibrational states of a diatomic molecule.
- The lowest allowed state is the ground state.
- The vibrational states are separated by larger energy gaps than are rotational states.
- At low temperatures, the energy gained during collisions is generally not enough to raise it to the first excited state of either rotation or vibration.
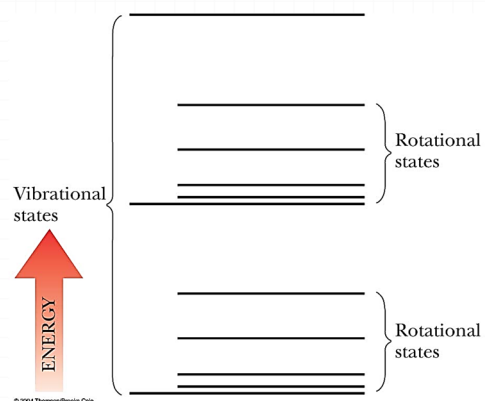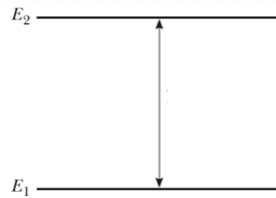
5. Boltzmann distribution law

Boltzmann Distribution Law

- The motion of molecules is extremely chaotic.

- From statistical mechanics, the probability density or the distribution function for classical particles is a function of energy and temperature, $n(E) \propto e^{-\frac{E}{k_B T}}$, known as the Boltzmann distribution law.

  ➤ $n(E)dE$ is the number of molecules per unit volume with energy between E and $E + dE$.

  ➤ The distribution shows that states with lower energy will always have a higher probability of being occupied.

Ex. Determine the ratio of the number of atoms in the higher energy level to the number of atoms in the lower energy level.

E_2 ———————

↕

E_1 ———————

Ans:

$$\frac{n(E_2)}{n(E_1)} = \frac{e^{-\frac{E_2}{k_BT}}}{e^{-\frac{E_1}{k_BT}}} = e^{-\frac{E_2-E_1}{k_BT}}$$
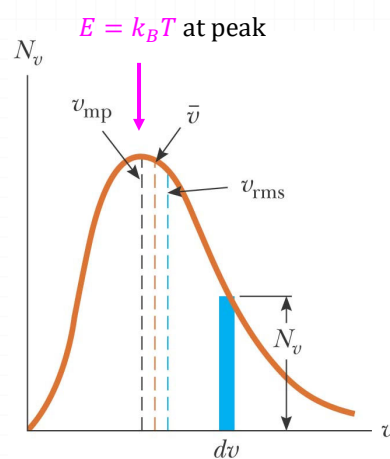

Distribution of Molecular Speeds

o $N(v)$ is called the Maxwell-Boltzmann speed distribution function:

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

with $N = \int_0^\infty N(v)dv$

$$E = \frac{1}{2}mv^2 \quad \Rightarrow \quad N(E) = \frac{8\pi}{m} \left(\frac{m}{2\pi k_B T} \right)^{3/2} E e^{-E/k_BT}$$
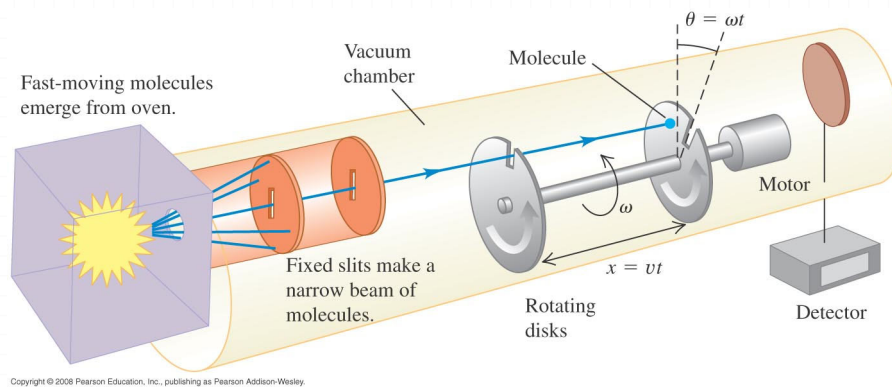
Distribution depends on $E / k_B T$.

$E = k_B T$ at peak

N_v

v_{mp} $\bar{v}$

v_{rms}

N_v

v

dv

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Most probable speed : $v_{mp} = \sqrt{\dfrac{2k_B T}{m}}$ (By $\dfrac{\partial N(v)}{\partial v} = 0$)

Root mean square speed : $v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\dfrac{3k_B T}{m}}$ $\qquad \left[\sqrt{\overline{v^2}} = \left(\int_0^\infty v^2 N_v dv \right)^{1/2} \right]$

Average speed : $\overline{v} = \sqrt{\dfrac{8k_B T}{\pi m}}$ $\qquad \left[\overline{v} = \int_0^\infty v N_v dv \right]$

$\Rightarrow$ $v_{rms} > \overline{v} > v_{mp}$

(This can explain why lighter gas molecules such as H_2, can escape easier from the Earth than the heavier molecules N_2.)

😎 Sound speed = ?

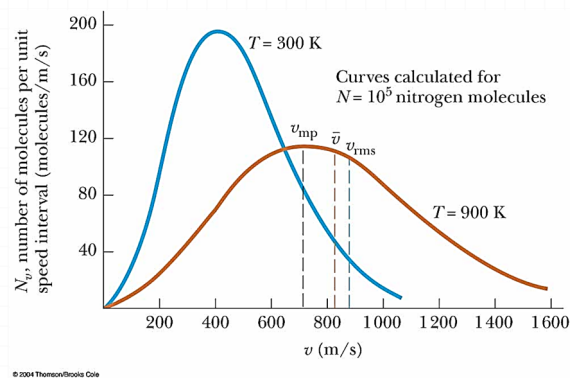$$v = \sqrt{\dfrac{\gamma k_B T}{m_0}}, \quad m_0 : \text{ mass of one molecule}$$

Speed Distribution at different temperature

O The peak shifts to the right as *T* increases.

Evaporation

○ Some molecules in the liquid are more energetic than others.

➢ This occurs even before the boiling point is reached.

○ The molecules that escape are those that have enough energy to overcome the attractive forces of the molecules in the liquid phase.

➢ Evaporation is a cooling process.

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6. Mean free path

Mean Free Path

- The average velocity of air molecules is ~340 m/s. Why don't we smell perfume immediately when the bottle is just opened?

- A molecule moving through a gas collides with other molecules in a random fashion, sometimes referred to as a *random-walk process.*

- The average distance between collisions is called the mean free path.

- The mean free path increases as the number of molecules per unit volume decreases.
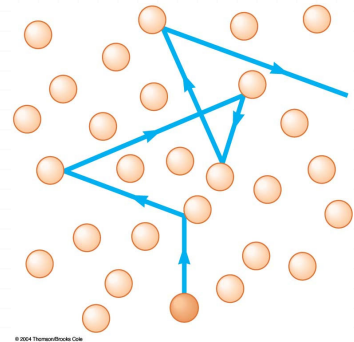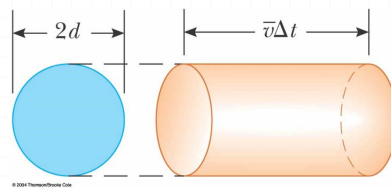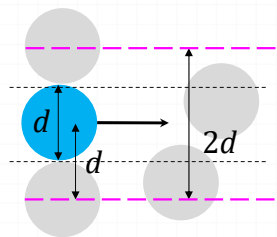
The number of collisions # in Δt is equivalent to the number of molecules in the cylinder.

$$\# = (\pi d^2 \bar{v} \Delta t) \times n$$

n: number of molecules per unit volume

o The number of collisions per unit time is the collision frequency:

$$f = \frac{\#}{\Delta t} = \pi d^2 \bar{v} n$$

➤ The inverse of the collision frequency is the collision mean free time $= 1 / f$.

o The mean free path, ℓ, equals the average distance $v\Delta t$ traveled in a time interval Δt divided by the number of collisions that occur in that time interval:

$$\ell = \frac{\bar{v}\Delta t}{\#} = \frac{\bar{v}\Delta t}{\left(\pi d^2 \bar{v}\Delta t\right)n} = \frac{1}{\pi d^2 n} \qquad \Rightarrow \quad f\ell = \bar{v}$$

o Ideal gas : $\ell = \infty$

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o In reality, the molecules are not fixed in space, so the correction is

$$f = \sqrt{2}\pi d^2 \bar{v} n,$$

$$\ell = \frac{1}{\sqrt{2}\pi d^2 n} = \frac{k_B T}{\sqrt{2}\pi d^2 P}$$

$$\bar{v} = f\ell$$

Ex. Approximate the air around you as a collection of nitrogen molecules, each having a diameter of 2.00×10^{-10} m.

(A) How far does a typical molecule move before it collides with another molecule?

(B) On average, how frequently does one molecule collide with another?

Ans:

(A)

$$n = \frac{N}{V} = \frac{P}{k_B T} = \frac{1.01 \times 10^5 \text{ N/m}^2}{(1.38 \times 10^{-23} \text{ J/K})(293 \text{ K})} = 2.5 \times 10^{25} \text{ molecules/m}^3$$

Mean free path:

$$\ell = \frac{1}{\sqrt{2}\pi d^2 n} = \frac{1}{\sqrt{2}\pi (2 \times 10^{-10} \text{ m})^2 (2.5 \times 10^{25} \text{ molecules/m}^3)}$$
$$= 2.25 \times 10^{-7} \text{ m}$$

Average separation: $D = \dfrac{1}{n^{1/3}} = \dfrac{1}{(2.5 \times 10^{25})^{1/3}} = 3.4 \times 10^{-9} \text{ m}$

Molecule diameter d = 2 x 10^{-10} m

Average separation D = 3.4 x 10^{-9} m

Mean free path ℓ = 2.25 x 10^{-7} m

$\Rightarrow$ $d < D < \ell$ for 1-atm air at room temperature

(B)

$$f = \frac{\bar{v}}{\ell} = \frac{473 \text{ m/s}}{2.25 \times 10^{-7} \text{ m}} = 2.10 \times 10^{9} \text{ /s}$$

https://fb.watch/hx4Rlilfhi/
https://youtu.be/Xw_Nb_dyi3A