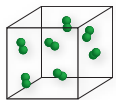
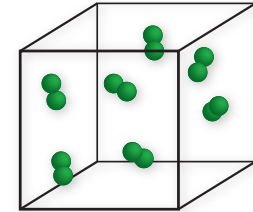


# Classical Mechanics & Properties of Gases

mark.wallace@chem.ox.ac.uk

## Properties of gases

- Ideal & real gases
- Kinetic theory of gases
- Maxwell-Boltzmann distribution
- Applications of kinetic theory

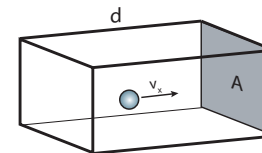


## Ideal gas assumptions

- The molecules obey Newton's law of motion
- There are no attractive or repulsive interactions between molecules
- The molecules undergo perfectly elastic collisions
- The volume occupied by the molecules is negligibly small in comparison to the size of the container

## Kinetic theory of gases

Consider a single collision



Momentum change of particle

$$\begin{aligned}\Delta p &= p_{\text{after}} - p_{\text{before}} \\ &= -mv_x - (mv_x) = -2mv_x\end{aligned}$$

Momentum imparted to wall

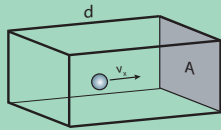
$$\Delta p = 2mv_x$$

Interval between collisions with the wall

$$\Delta t = \frac{2d}{v_x}$$

# Kinetic theory of gases

Consider many collisions



Momentum imparted to wall

$$\Delta p = 2mv_x$$

Interval between collisions

$$\Delta t = \frac{2d}{v_x}$$

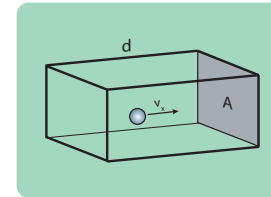
$$F = ma = \frac{d(p)}{dt} \approx \frac{\Delta p}{\Delta t} = \frac{2mv_x}{2d/v_x} = \frac{mv_x^2}{d}$$

$$p = \frac{F}{A} = \frac{mv_x^2}{Ad} = \frac{mv_x^2}{V}$$

$$p = \frac{Nm \langle v_x^2 \rangle}{V}$$

# Kinetic theory of gases

Consider many collisions in 3D



$$p = \frac{Nm \langle v_x^2 \rangle}{V}$$

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle$$

$$p = \frac{Nm \langle v^2 \rangle}{3V} \quad \text{or} \quad pV = \frac{1}{3} Nm \langle v^2 \rangle$$

c.f. Boyle's law

# Kinetic theory of gases

Apply classical equipartition

For each degree of freedom there is a  $\frac{1}{2}k_B T$  contribution to the internal energy

$$\frac{3}{2} k_B T = \frac{1}{2} m \langle v^2 \rangle$$

$$pV = \frac{1}{3} Nm \langle v^2 \rangle = \frac{1}{3} Nm \left( \frac{3k_B T}{m} \right)$$

$$pV = Nk_B T$$

$$pV = nRT$$

# Classical Equipartition

For each degree of freedom there is a  $\frac{1}{2}k_B T$  contribution to the internal energy

- The mean energy of each quadratic contribution to the total energy of a particle is the same, and equal to  $\frac{1}{2}k_B T$ .

A quadratic contribution to the energy is one that is proportional to the square of a particle's velocity or position.

# Contributions to the total energy

Total Energy = Kinetic + Potential Energy

$$U = K + V$$

$$H = K + V \quad \text{---} \quad -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V\psi = E\psi$$

$$\hat{H}\psi = E\psi$$

# Degrees of freedom

The total number of degrees of freedom is given by  $3N$ , where  $N$  is the number of atoms.

## Translation

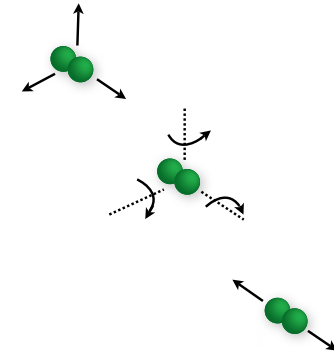
$$H = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$

## Rotation

$$H = \frac{1}{2}(I_x\omega_x^2 + I_y\omega_y^2 + I_z\omega_z^2)$$

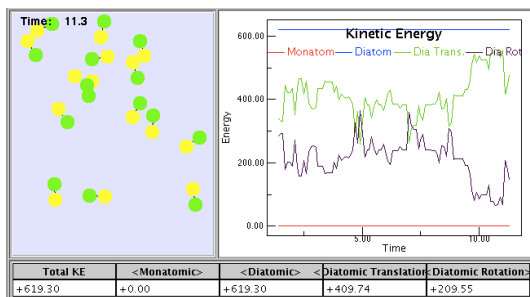
## Vibration in one dimension

$$H = \frac{1}{2}mv^2 + \frac{1}{2}kx^2$$



# Demo simulation

<http://tinyurl.com/equipartition>



# Classical Equipartition

Mathematical formulation (not required)

$$\left\langle x_n \frac{\partial H}{\partial x_n} \right\rangle = k_B T \quad \text{for all } n$$

$$\left\langle x_m \frac{\partial H}{\partial x_n} \right\rangle = 0 \quad \text{for all } n \neq m$$

## Translation

$$H = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)$$



$$\langle H_x \rangle = \left\langle \frac{1}{2}mv_x^2 \right\rangle = \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{1}{2}k_B T$$

$$\left\langle p_x \frac{\partial H}{\partial p_x} \right\rangle = \left\langle p_x \frac{\partial \frac{p_x^2}{2m}}{\partial p_x} \right\rangle = \left\langle p_x \frac{2p_x}{2m} \right\rangle = \left\langle \frac{p_x^2}{m} \right\rangle = k_B T$$

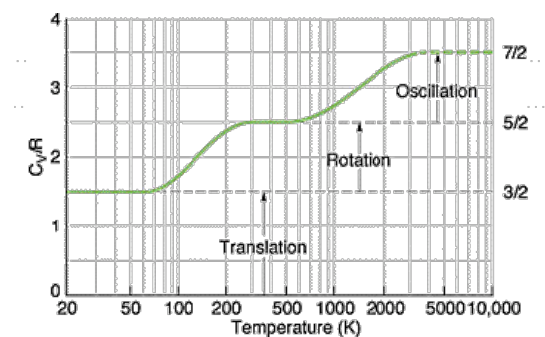
$$\left\langle \frac{1}{2} \frac{p_x^2}{m} \right\rangle = \frac{1}{2}k_B T$$

## Contributions to $C_v$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V$$

	trans.	rot.	vib.
monatomic	$3/2 R$	-	-
diatomic	$3/2 R$	$2/2 R$	$R$
linear	$3/2 R$	$2/2 R$	$(3N-5)R$
non-linear	$3/2 R$	$3/2 R$	$(3N-6)R$

## $C_v$ for $O_2$



## An example

Prelim 2007

3 (a) State the *equipartition theorem*.

[2]

(b) Show how the theorem may be used to estimate the molar constant-pressure heat capacities,  $C_{p,m}$ , of (i)  $Ar(g)$ , (ii)  $CO_2(g)$ , (iii)  $CH_4(g)$ , (iv)  $Pb(s)$ . Express your results as a multiple of the gas constant  $R$ .

[3]

$$C_p = C_v + R$$

$$\frac{3}{2}R + R$$

$$\frac{3}{2}R + \frac{2}{2}R + (3 \times 3 - 5)R + R$$

$$\frac{3}{2}R + \frac{3}{2}R + (3 \times 5 - 6)R + R$$

$$3R$$

(c) The experimental values of these heat capacities at 298 K are as follows:

Substance	$Ar(g)$	$CO_2(g)$	$CH_4(g)$	$Pb(s)$
$C_{p,m}/(J K^{-1} mol^{-1})$	20.8	37.1	35.3	26.4

Suggest reasons for the deviation of these values from the values you have calculated.

[3]

## Lecture Summary

- Kinetic Theory of Gases
  - Derivation of  $pV=nRT$
- Classical Equipartition
  - The mean energy of each quadratic contribution to the total energy of a particle is the same, and equal to  $\frac{1}{2}k_B T$ .

