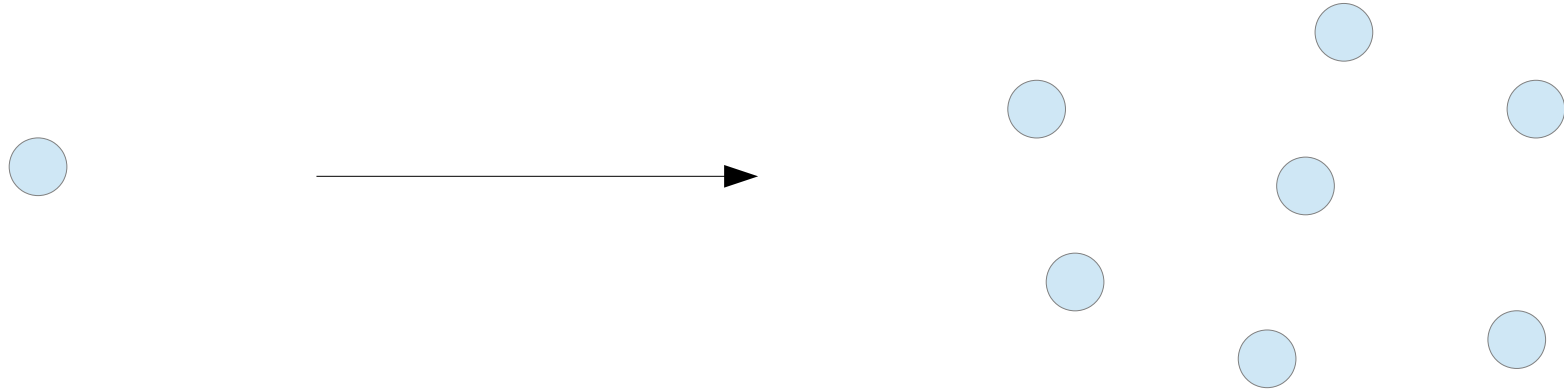# Elements of Statistical Physics

and

Heat Capacity of Gases

Agenda

1. Introduction

2. Fundamental Ideas in Statistical Physics

3. Equipartition Principle

4. Specific Heat of Gases

Introduction

Introduction

single particle

system of particles
(in general interacting – huge complication;
if non-interacting: *a gas of particles*)

Classically

in principle – given forces and initial conditions, one can use equations of motion to find trajectories of particles
practically – intractable; needs to solve a system of ~10^{23} equations of motion to describe ~1g of matter
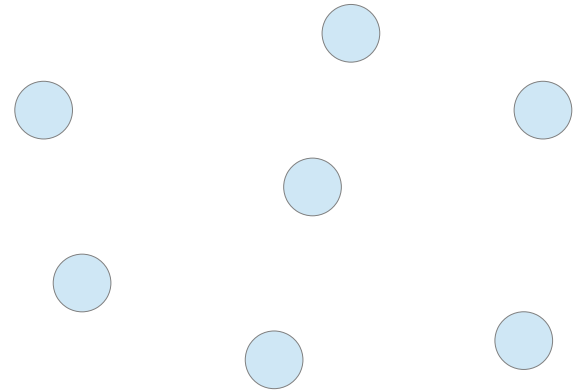(recall the difficulties we run into in the three body problem)

Quantum-mechanically

many-body problem with indistinguishable particles;
again – very complicated

Introduction

Idea: Infer about *macroscopic* properties of the system without keeping track of individual particles.

Statistical Physics (Statistical Mechanics)

laws of physics
(such as conservation laws) applied to **large systems** (*ensembles*) of particles

$\longrightarrow$

probable behavior
of the system
[e.g. probability that a state with a given energy is occupied]

$\downarrow$

macroscopic properties
of the system
[thermodynamical/ensemble averages]

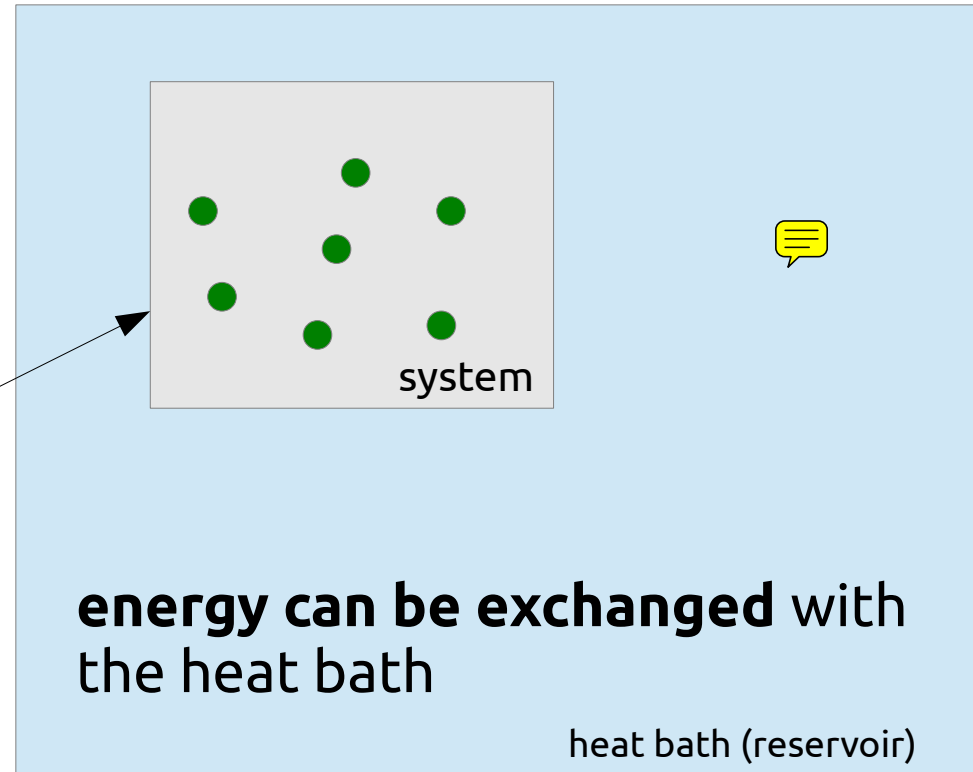# Fundamental Ideas
in Statistical Physics

Classical Statistical Physics. Canonical ensemble

canonical (or NVT) ensemble

"small" system in equilibrium with a (very large) heat bath

N (number of particles), V (volume), T (temperature) are all **fixed**

identical, distinguishable particles

system

energy can be exchanged with the heat bath

heat bath (reservoir)

The actual size of the "small" system can vary: it may be a single particle or a large number of particles, but it must be small compared to the heat bath.

Distinct states of the "small" system are called *microstates*.
At any instant the configuration of the system corresponds to a certain distribution among microstates occupied with some probability.

Boltzmann Distribution

Probability distribution (Boltzmann distribution)
gives the probability of finding the "small" system in a microstate with energy ε_i

$$f_B(\varepsilon_i) = \frac{1}{Z} \exp\left(-\frac{\varepsilon_i}{k_B T}\right)$$

normalization factor (*partition function*)

$$Z = \sum_i e^{-\varepsilon_i/k_B T}$$

Boltzmann's constant

$$k_B = 1.38 \times 10^{-23} \ \text{J/K}$$

Comments

- Some microstates may have the same energy – they are realized with the same probability.
- Microstates with lower energy are more likely to be occupied than microstates with higher energy.
- For a continuous distribution function $f_B(E)dE$ is the probability that the small system's energy is in (E, E+dE).

Example 1. Barometric Formula

Ideal gas (no interparticle interactions) in a uniform gravitational field

"small" system – a single particle; reservoir – other particles; microstate – state with a given $\mathbf{p}$ = (p_x, p_y, p_z) and z

$$E = E(\mathbf{p}, z) = K + U_{\mathrm{grav}} = \frac{|\mathbf{p}|^2}{2m} + mgz$$
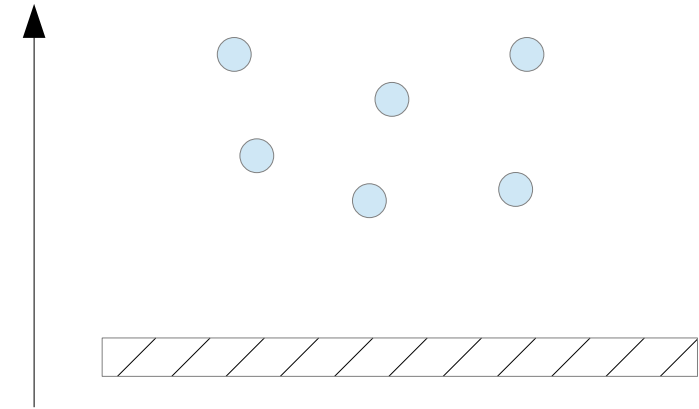
Probability that the particle has momentum in the region d³p around $\mathbf{p}$, and is at altitude (z, z+dz)

$$f_{\mathbf{p}z}(E(\mathbf{p}, z))\, d^3p\, dz = A \exp\left(-\frac{p^2}{2mk_BT}\right) \exp\left(-\frac{mgz}{k_BT}\right) d^3p\, dz$$

Probability that a particle is at altitude (*z, z+ dz*), regardless of its momentum (integrate out the momentum)

$$f_z(z)\, dz = \tilde{A} \exp\left(-\frac{mgz}{k_BT}\right) dz$$

$$\tilde{A} = mg/k_BT$$

Relative density

$$\frac{\varrho(h)}{\varrho(0)} = \frac{f_z(h)}{f_z(0)} \implies \boxed{p(h) = p(0)\exp\left(-\frac{mgh}{k_BT}\right)}$$

[from the ideal gas equation *p = RT(n/V)*, hence the pressure *p* is proportional to density n/V]
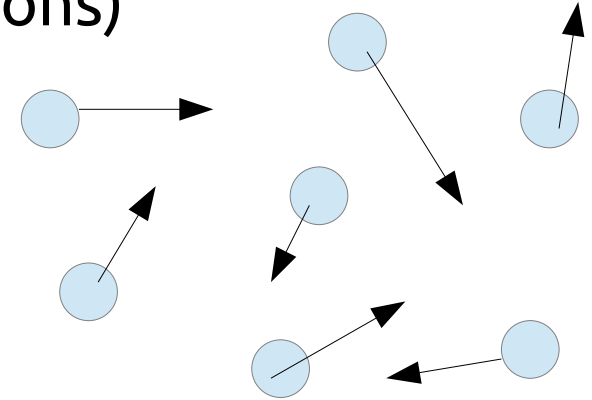
Example 2. Maxwell-Boltzmann Distribution

Ideal monoatomic gas (no interparticle interactions)

small system – single particle; reservoir – other particles;
microstate – state with a given $\mathbf{v} = (v_x, v_y, v_z)$

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

Probability that a single particle has velocity in the region d³v about **v**

$$f_{\mathbf{v}}(\mathbf{v})\, d^3v = A \exp\left[-\frac{\frac{1}{2}m(v_x^2 + v_y^2 + v_z^2)}{k_B T}\right] d^3v$$

Find A
[integrate in spherical coordinates]

$$\int_{R^3} f_{\mathbf{v}}(\mathbf{v})\, d^3v = 1 \implies \boxed{A = \left(\frac{m}{2\pi k_B T}\right)^{3/2}}$$

$$f_{\mathbf{v}}(E(\mathbf{v})) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m(v_x^2 + v_y^2 + v_z^2)}{2k_B T}\right)$$

Note. $\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle = 0$

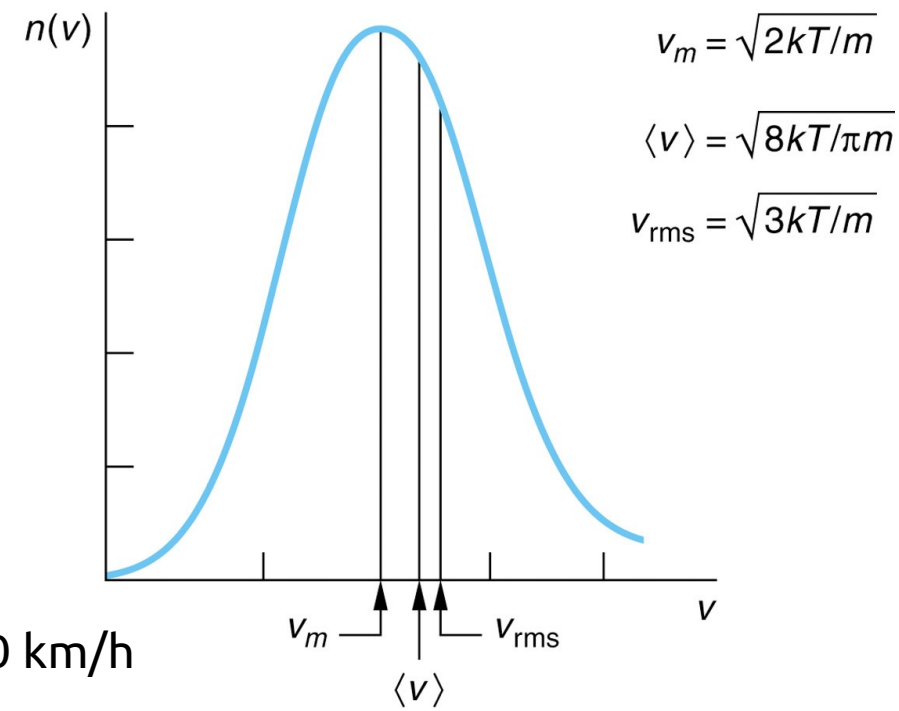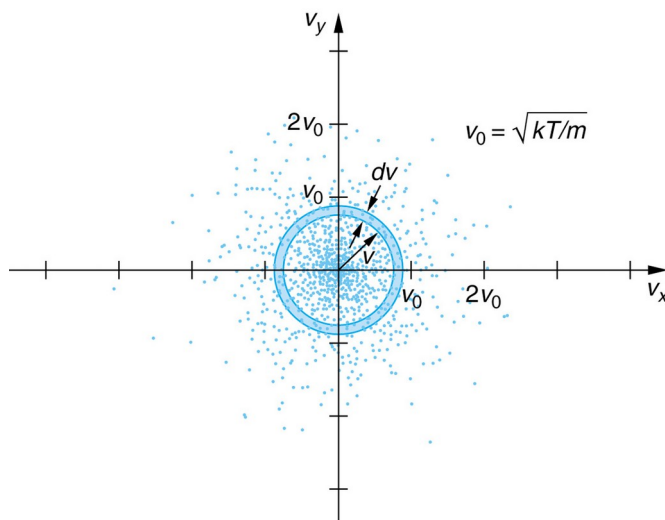# Example 2. Maxwell-Boltzmann Distribution

Probability that a single particle has <u>speed</u> (v, v +dv), regardless of direction

$$f_{\mathbf{v}}(E(\mathbf{v}))\, d^3 v = \underbrace{4\pi v^2 f_{\mathbf{v}}(E(\mathbf{v}))}_{f_v(v)}\, dv$$

Number of particles with speed (v, v +dv)

$$n(v)\, dv = N f_v(v)\, dv = N 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) dv$$

**The speed distribution
(*Maxwell-Boltzmann distribution*)**

$$v_m = \sqrt{2kT/m}$$

$$\langle v \rangle = \sqrt{8kT/\pi m}$$

$$v_{rms} = \sqrt{3kT/m}$$

E.g. for N_2 the average speed at $T = 300$ K is $\langle v \rangle = 1700$ km/h

Example 2. Maxwell Distribution for Kinetic Energy (Monoatomic Gas)

Using the relation between the kinetic energy and speed, we find

$$E(v) = \frac{1}{2}mv^2 \qquad \Longrightarrow \qquad dv = \frac{1}{mv}\,dE = \frac{1}{\sqrt{2mE}}\,dE$$

To find the distribution function for the energy f(E), look for the probability that a single particle has energy (E, E+dE)

$$f_v(v)\,dv = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right)\,dv =$$

$$= 4\pi \frac{2E}{m} \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{E}{k_B T}\right) \frac{1}{\sqrt{2mE}}\,dE =$$

$$= \underbrace{\frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right)}_{f(E)}\,dE = f(E)\,dE$$

Example 2. Maxwell Distribution for Kinetic Energy (Monoatomic Gas)

Maxwell distribution function for the energy

$$f(E) = \frac{2\pi}{(\pi k_B T)^{3/2}} \sqrt{E} \exp\left(-\frac{E}{k_B T}\right)$$

Having found the distribution function, we can calculate various characteristics of the monoatomic gas. In particular, the average kinetic energy (per particle) is

degrees of freedom
(monoatomic gas)

$$\langle E \rangle = \int_0^\infty E\, f(E)\, dE = \frac{3}{2}\, k_B T \qquad \Longrightarrow \qquad \langle E \rangle = 3 \times \frac{1}{2} k_B T$$

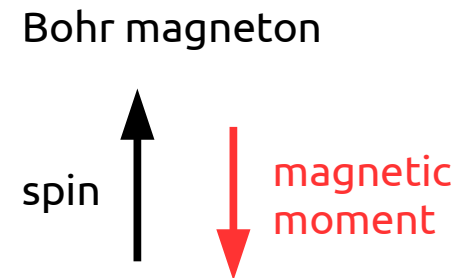# Example 3. Spin-1/2 Paramagnet

A spin-1/2 particle (e.g. electron) has two possible spin states, corresponding to two possible projections of the spin onto a certain direction (e.g. that of an external magnetic field).

If such a particle is placed in an external magnetic field, the two states are of different energy, because of the tendency of the spin-induced magnetic dipole moment to line up in the field direction.

E.g. for the electron

$$\mu_z = -m_s g \mu_B = \pm \mu_B$$

Bohr magneton

$$E = -\mu_z B_z = \mp \mu_B B_z$$

spin

magnetic moment

The energies of these two distinct states are

$$\varepsilon_1 = E_\uparrow = \mu_B B_z \qquad\qquad \varepsilon_2 = E_\downarrow = -\mu_B B_z$$

spin "up"

"small" system – a single particle; reservoir – other particles;
microstate – state with a given m_s (i.e. projection of the spin on the direction of **B**)

Example 3. Spin-1/2 Paramagnet

Distribution function $\quad f(\varepsilon_i) = \dfrac{1}{Z} \exp\left(-\dfrac{\varepsilon_i}{k_B T}\right), \qquad i = 1, 2$

Partition function

$$Z = \sum_i e^{-\varepsilon_i/k_B T} = e^{\mu_B B_z/k_B T} + e^{-\mu_B B_z/k_B T} = 2\cosh(\mu_B B_z/k_B T)$$

Now, as the distribution function is known completely,

$$f(\varepsilon_i) = \frac{\exp\left(-\dfrac{\varepsilon_i}{k_B T}\right)}{2\cosh(\mu_B B_z/k_B T)}$$

other quantities can be found, e.g. the average energy

$$\langle E \rangle = \sum_i \varepsilon_i f(\varepsilon_i) = \frac{1}{2\cosh(\mu_B B_z/k_B T)}\left[\mu_B B_z e^{-\frac{\mu_B B_z}{k_B T}} + (-\mu_B B_z)e^{\frac{\mu_B B_z}{k_B T}}\right]$$

$$= -\mu_B B_z \frac{\sinh(\mu_B B_z/k_B T)}{\cosh(\mu_B B_z/k_B T)} = -\mu_B B_z \tanh(\mu_B B_z/k_B T)$$

Note that this can be found also from $\qquad \langle E \rangle = -\dfrac{\partial \ln Z}{\partial (k_B T)^{-1}}$

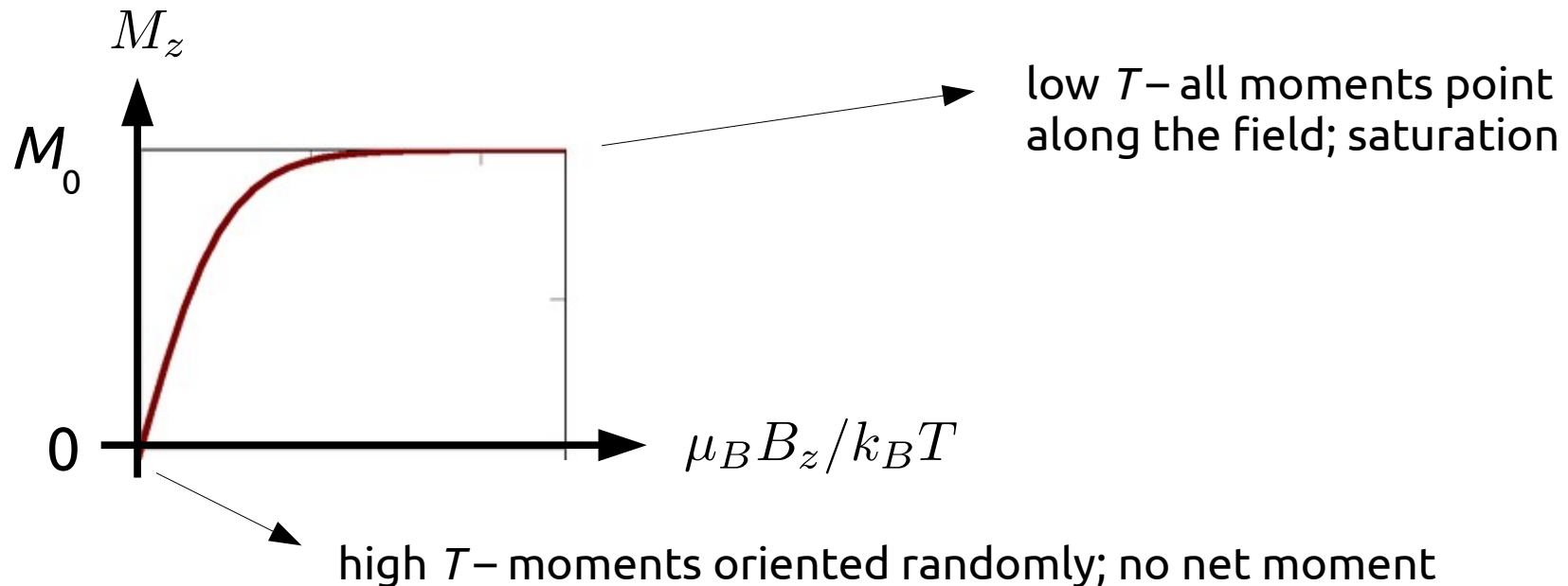# Example 3. Spin-1/2 Paramagnet

The average magnetic moment of a single particle can be found in a similar manner

$$\langle \mu_z \rangle = \sum_i \mu_i f(\varepsilon_i) = \frac{1}{2\cosh(\mu_B B_z / k_B T)} \left[\mu_B e^{\frac{\mu_B B_z}{k_B T}} + (-\mu_B) e^{-\frac{\mu_B B_z}{k_B T}} \right] =$$

$$= \mu_B \tanh(\mu_B B_z / k_B T)$$

Hence, the magnetization (total magnetic moment of *N* electrons)

$$M_z = N\langle \mu_z \rangle = \underbrace{\mu_B N}_{M_0} \tanh(\mu_B B_z / k_B T)$$

low *T* − all moments point along the field; saturation

high *T* − moments oriented randomly; no net moment

The Equipartition Principle

The Equipartition Principle

Observation

For a monoatomic gas, each degree of freedom contributes $(k_B T)/2$ to the average energy per particle.

In general (the Equipartition Principle)

==Each quadratic== term in the expression for one-particle energy, contributes $(k_B T)/2$ to the average energy per particle.
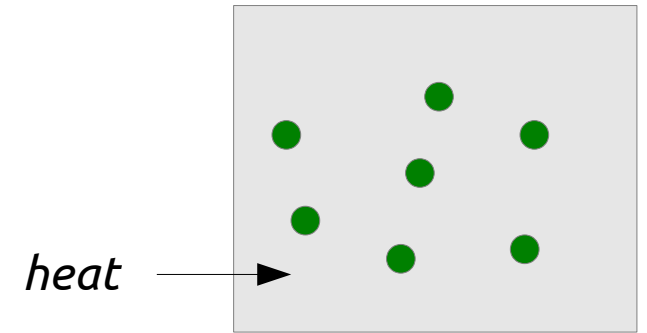
Heat Capacity of Gases

Heat Capacity of Gases

GASES

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

(internal) energy per mole

heat capacity at constant volume

volume kept constant

heat →

Specific heat: the amount of heat needed to be delivered to the system to change its temperature by 1 K

monoatomic gas (one mole)

$$E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{translational DoF}} \Longrightarrow \frac{\partial}{\partial T}\left(\frac{3}{2}RT\right) = \frac{3}{2}R$$
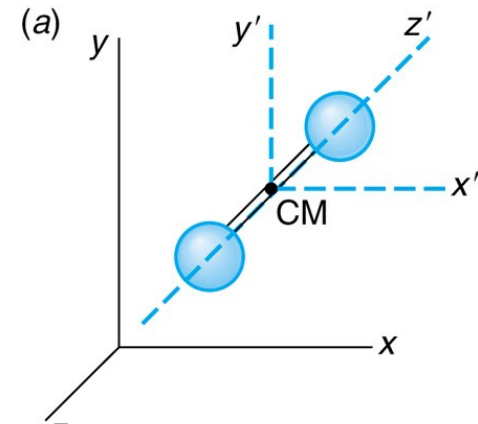
gas constant

$$R = k_{\mathrm{B}} N_{\mathrm{Avogadro}}$$

Heat Capacity of Gases

diatomic; rigid (per mole)

$$E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{translational DoF}} + \underbrace{\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2}_{\text{rotational DoF}} \implies \frac{\partial}{\partial T}\left(\frac{5}{2}RT\right) = \frac{5}{2}R$$

(a)

diatomic; non- rigid (per mole)

$$E = \underbrace{\frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2}_{\text{translational DoF}} + \underbrace{\frac{1}{2}I_1\omega_1^2 + \frac{1}{2}I_2\omega_2^2}_{\text{rotational DoF}} + \underbrace{\frac{p^2}{2\mu} + \frac{1}{2}\mu\omega^2 s^2}_{\text{vibrational DoF}}$$

$$\implies \frac{\partial}{\partial T}\left(\frac{7}{2}RT\right) = \frac{7}{2}R$$

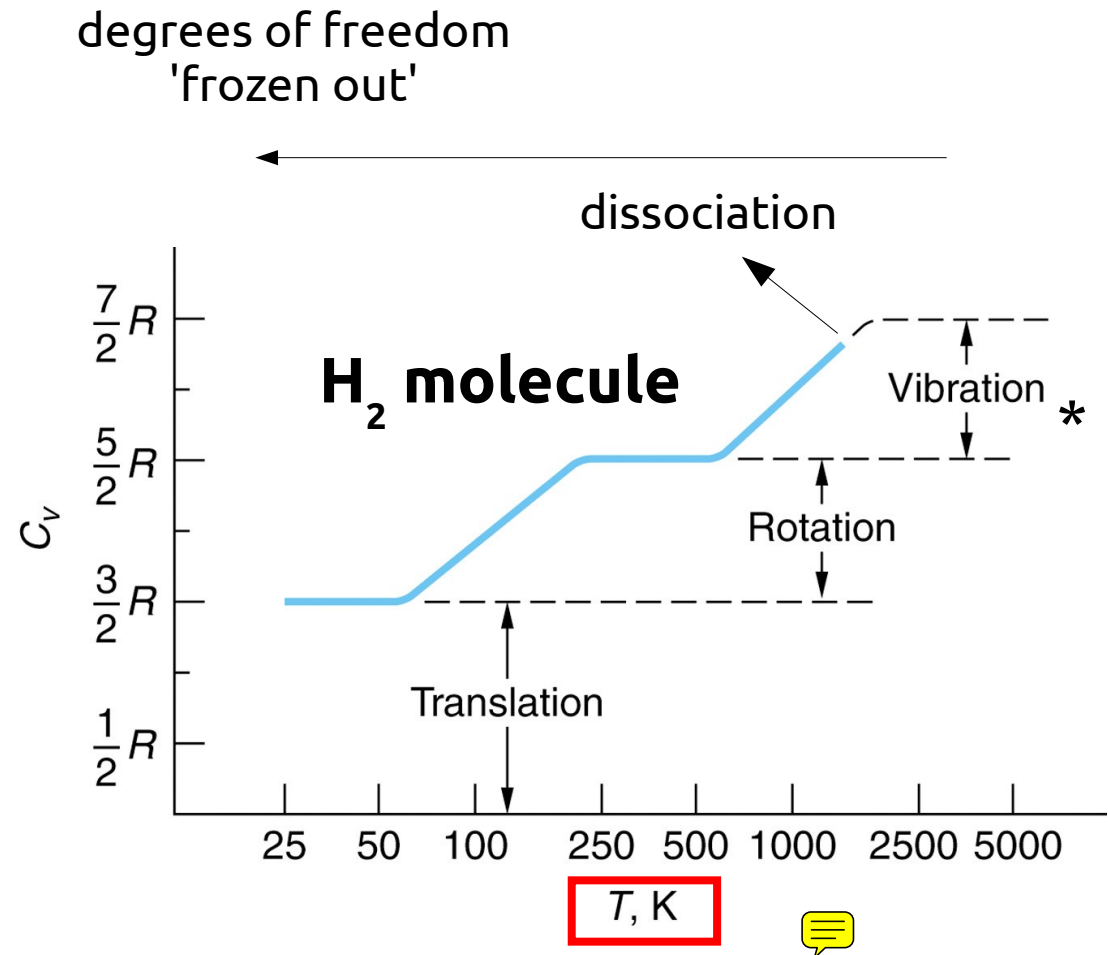# Heat Capacity (Specific Heat) of Gases

Gas	C_V (cal/mol-deg)	C_V/R
Ar	2.98	1.50
He	2.98	1.50
CO	4.94	2.49
H_2	4.87	2.45
HCl	5.11	2.57
N_2	4.93	2.49
NO	5.00	2.51
O_2	5.04	2.54
Cl_2	5.93	2.98
CO_2	6.75	3.40
CS_2	9.77	4.92
H_2S	6.08	3.06
N_2O	6.81	3.42
SO_2	7.49	3.76

Table 8-1 C_V for some gases at 15°C and 1 atm

$R = 1.987$ cal/mol-deg

From J. R. Partington and W. G. Shilling, *The Specific Heats of Gases* (London: Ernest Benn, Ltd., 1924).

degrees of freedom 'frozen out'

dissociation

H_2 molecule

Vibration *

Rotation

Translation

Observation: For diatomic molecules contributions to the heat capacity due to different kinds of degrees of freedom are being gradually 'activated' as the temperature increases – unexplainable with the equipartition principle.

Heat Capacity of Gases

degrees of freedom
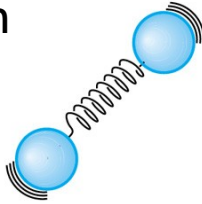- *translational*
- *rotational*
- *vibrational*

Table 8-1 C_V for some gases at 15°C and 1 atm

Gas	C_V (cal/mol-deg)	C_V/R
Ar	2.98	1.50
He	2.98	1.50
CO	4.94	2.49
H_2	4.87	2.45
HCl	5.11	2.57
N_2	4.93	2.49
NO	5.00	2.51
O_2	5.04	2.54
Cl_2	5.93	2.98

Characteristic temperatures of activation of different kinds of degrees of freedom

* rotations

$$T_r \sim \frac{E_r}{k_B} \sim \frac{\frac{\hbar^2 l(l+1)}{2I}}{k_B} \sim \frac{\hbar^2}{2I k_B}$$ recall rigid rotor
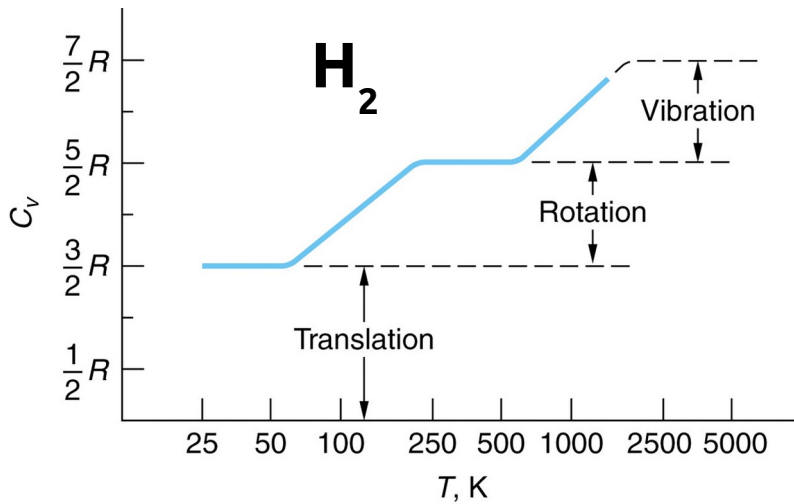
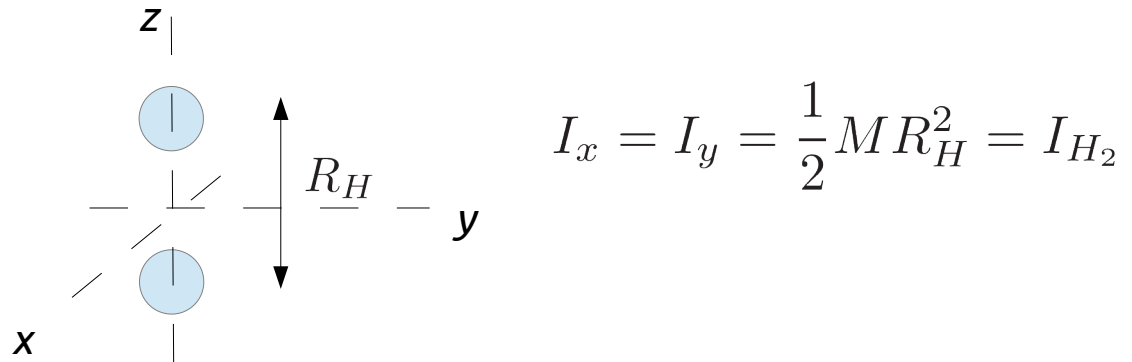For T above T_r rotational degrees of freedom are expected to contribute.

* vibrations

$$T_v \sim \frac{E_v}{k_B} \sim \frac{\hbar\omega}{k_B}$$

characteristic angular frequency of vibrations

For T above T_v vibrational degrees of freedom are expected to contribute.

Note, for all diatomic molecules (except Cl_2) listed in the table $T_v >$ 288 K (15° C).

Heat Capacity of Gases. Examples

$$I_x = I_y = \frac{1}{2}MR_H^2 = I_{H_2}$$

(1) Hydrogen H$_2$

$$R_H = 0.08 \text{ nm}, M_H = 940 \text{ MeV}/c^2$$
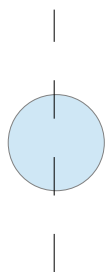
$$T_r \sim 74 \text{ K}$$

cf. figure on the previous slide

(2) Oxygen O$_2$

$$R_O \approx R_H, \ M_O = 16 \times M_H$$

$$T_r \sim \frac{74}{16} \text{ K} \approx 4.6 \text{ K}$$

rotational degrees of freedom always contribute (in the temperature range where O$_2$ is a gas)

(3) Monoatomic Hydrogen H

moment of inertia mainly due to the electron at distance R_H from the proton

$$I_H \approx \frac{1}{2000}I_{H_2}$$

$$T_r \sim 2000 \times 74 \text{ K} \approx 1.5 \times 10^5 \text{ K}$$

no contribution due to rotations

Summary

Statistical Physics (Statistical Mechanics)

- allows to analyze systems of many particles without the need of tracing individual particles

- offers unified approach; very efficient in explaining properties of various systems of classical and quantum particles

- fundamental tool in analysis of temperature-dependent properties of matter