The Boltzmann Factor & Equipartition

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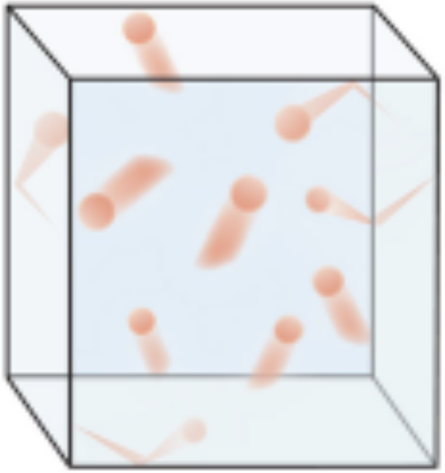
2.4 Summary

Not all molecules in a gas have the same speed.



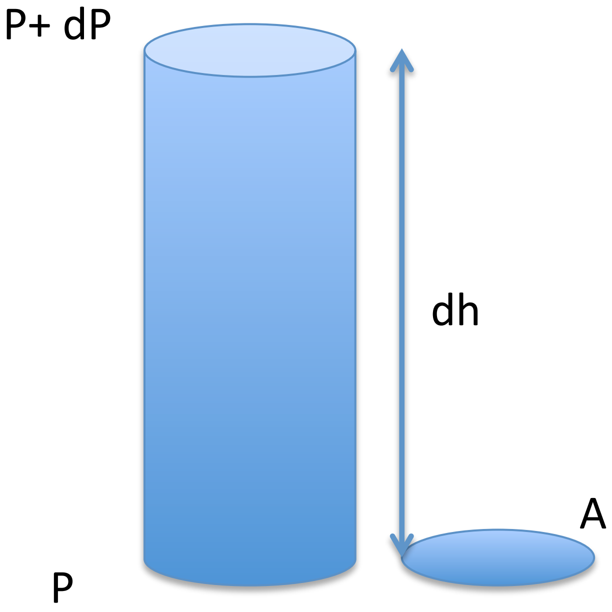
What is the probability of finding a molecule with a certain speed?

What factors determine the speed of a molecule?

2.1 Hydrostatic equilibrium

Consider a slab of gas of vertical thickness dh, density ρ, area A, in a gravitational field g, at equilibrium.

The weight of the slab is $\rho A g \, \mathrm{d}h$



Remembering that the pressure is
a force per unit area,
we can write the difference of force on the two surfaces as:

$$PA - (P + \mathrm{d}P)A = -A\,\mathrm{d}P.$$

$$\Downarrow$$

$$-A\,\mathrm{d}P = \rho A g \, \mathrm{d}h \Rightarrow \boxed{\frac{\mathrm{d}P}{\mathrm{d}h} = -\rho g}$$

equation of
hydrostatic equilibrium
it applies to any fluid
static under gravity

For an ideal gas we have $P = nkT_I$ and $\rho = nm$

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}h} = -\rho g}$$

can be written as

$$\frac{\mathrm{d}n}{\mathrm{d}h} = -\frac{mg}{kT_\mathrm{I}}n$$

In isothermal condition
(T_I is constant with h)

$$\int_{n_0}^{n} \frac{\mathrm{d}n'}{n'} = -\frac{mg}{kT_\mathrm{I}} \int_0^h \mathrm{d}h'$$

$$\ln \frac{n}{n_0} = -\frac{mgh}{kT_\mathrm{I}}$$

$$\frac{n}{n_0} = \frac{P}{P_0} = e^{-mgh/kT_\mathrm{I}}$$

in an isothermal atmosphere under hydrostatic equilibrium,
pressure and number density drop exponentially with height

2.2 Boltzmann factor

The potential energy of a molecule E = mgh

We can thus rewrite $\frac{n}{n_0} = \frac{P}{P_0} = e^{-mgh/kT_1}$

as $n \propto e^{-E/kT}$

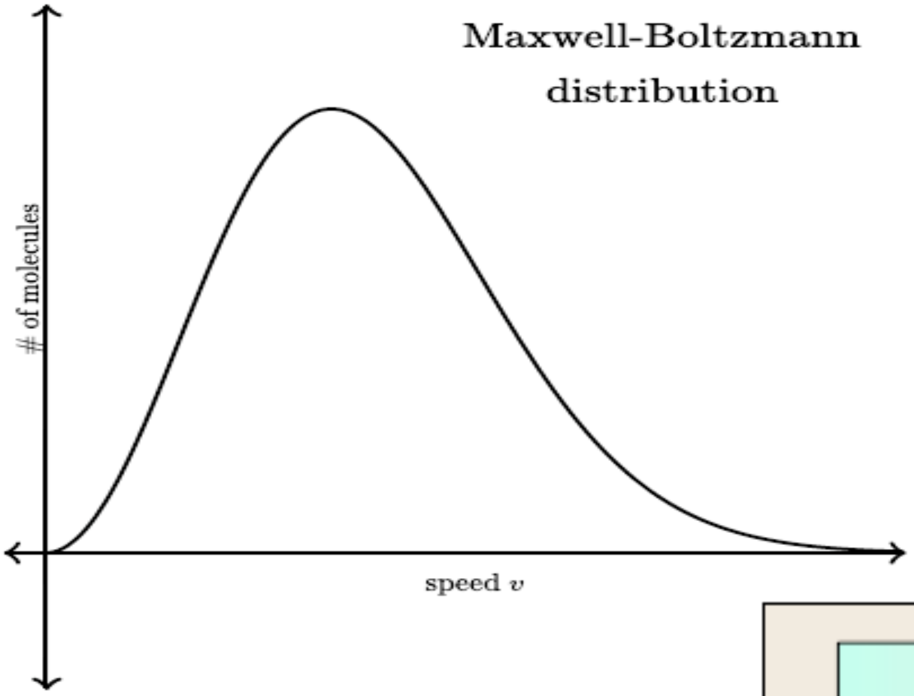
For each particle, the probability of finding it at height h, where the potential energy is E = mgh, is proportional to $e^{-E/kT}$

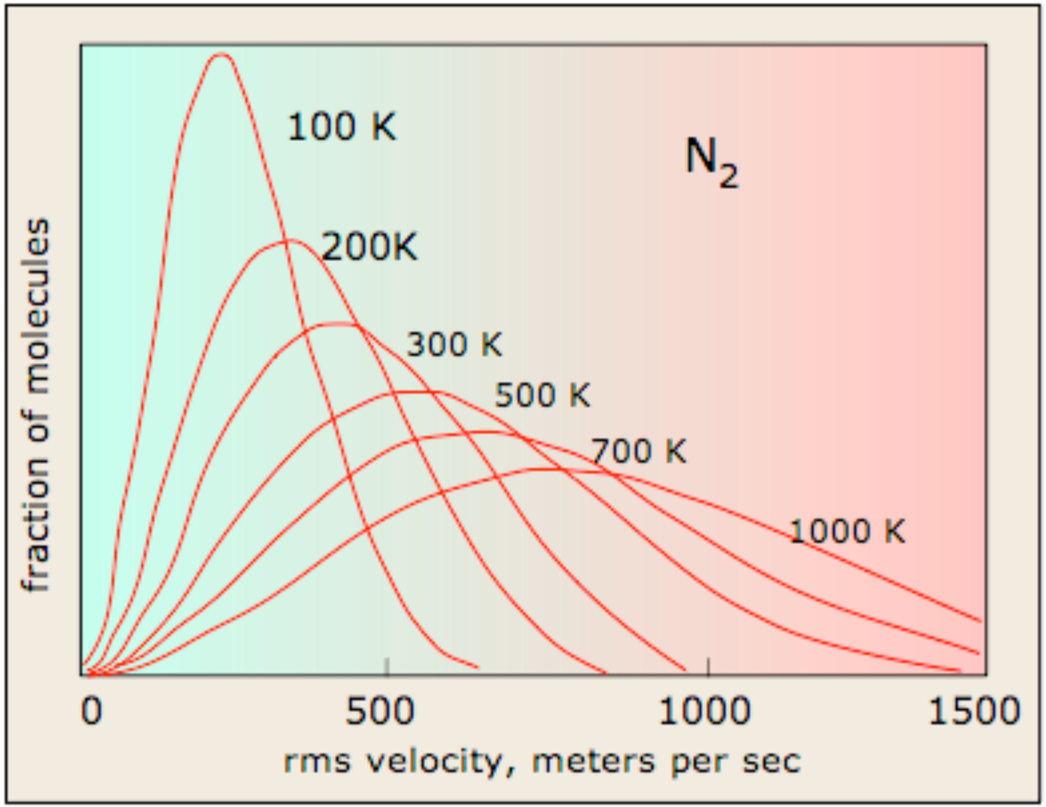
Generalising, the probability of finding a system, with energy E when in thermal equilibrium at temperature T is

$$P(E) \propto e^{-E/kT}$$

the Boltzmann factor

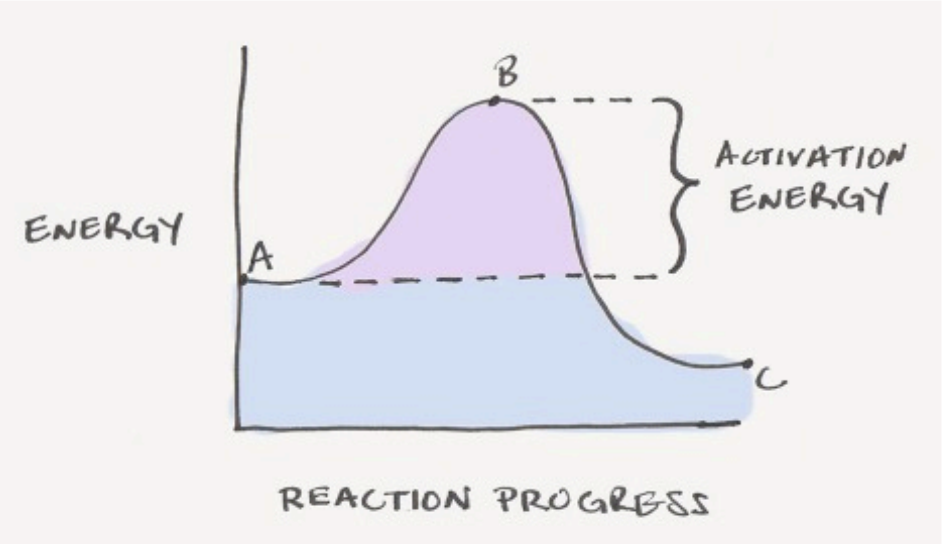
(not limited to ideal gases)


Maxwell-Boltzmann
distribution
# of molecules
speed v


N$_2$
100 K
200K
300 K
500 K
700 K
1000 K
fraction of molecules
0
500
1000
1500
rms velocity, meters per sec

2.2.1 Activation energies

The Boltzmann factor has
important consequences for
the rates of chemical
and other reactions.



Endothermic reactions
need external energy to occur.

Phase transitions can occur if a certain amount of energy,
called activation energy E_A, is provided to the system.

kT is the energy related to temperature of the system
If $E_A >> kT$, the reaction will not occur spontaneously.

Given that the Boltzmann factor is an exponential ($e^{-E/kT}$),
a small increase in temperature causes a dramatic increase in the Boltzmann factor.

Example:

- *If $E_A = 100\ kT$ and $T = 300K$ by how much does the Boltzmann factor change if T is raised by 20 K?*

Initial value is e^{-100}.

For $T = 320$ K, $E_A/kT = 100(300/320) = 93.75$
so the new value is $e^{-93.75}$.

The ratio is:

$$\frac{e^{-93.75}}{e^{-100}} = e^{100-93.75} = e^{6.25} = 518$$

2.3 The Equipartition of Energy and Heat Capacities

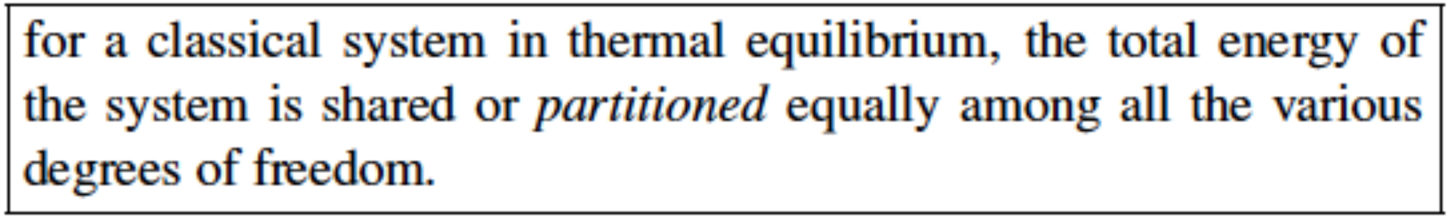
The Boltzmann factor also leads to an important theorem of classical physics called the equipartition theorem.

This theorem gives a simple rule-of-thumb for estimating heat capacities (… but it is wrong).

Let’s consider a monoatomic gas, like Helium, its kinetic energy will be:

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)$$

The equipartition theorem states that



for a classical system in thermal equilibrium, the total energy of the system is shared or *partitioned* equally among all the various degrees of freedom.

A degree of freedom is a variable needed to specify the state of a gas.

The temperature of a classical system in thermal equilibrium can be defined using this average energy per degree of freedom:

$$\frac{1}{2}kT = (\text{average energy in each degree of freedom})$$

Our helium atom has kinetic energy only and equipartition says that each squared term (x,y,z) has a mean thermal energy of kT/2, so that

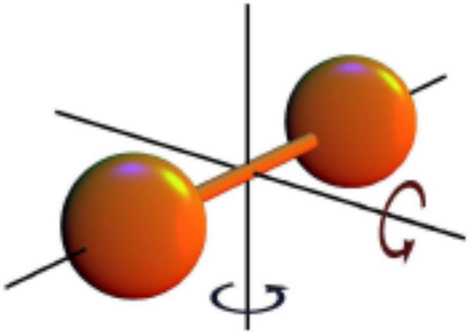
$$\frac{1}{2}m\bar{v}^2 = \frac{3}{2}kT.$$

For a mole of any ideal gas, the total energy
in thermal equilibrium at temperature T is 3RT/2.

This means that the internal energy of a monatomic gas is
U = 3RT/2 per mole, as already demonstrated.

2.3.2 Diatomic gases

Many gases are diatomic
for example H_2, O_2, N_2



They have translational motions (centre of mass motion), but they can also rotate and vibrate (motion relative to the centre of mass).

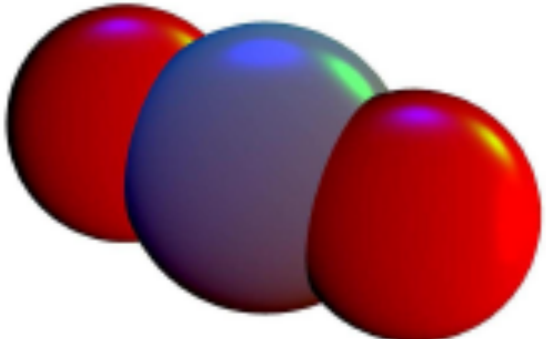
There are:

3 directions of translation (as before), $mv_x^2/2$ etc.
2 axes of rotation ($I\omega_x^2/2$ etc)
1 vibration ($mv^2/2 + kx^2/2$)

7 degrees of freedom, and so U = 7RT/2 per mole.

2.3.3 Triatomic molecules

Carbon dioxide, CO_2



3 translations

2 rotations

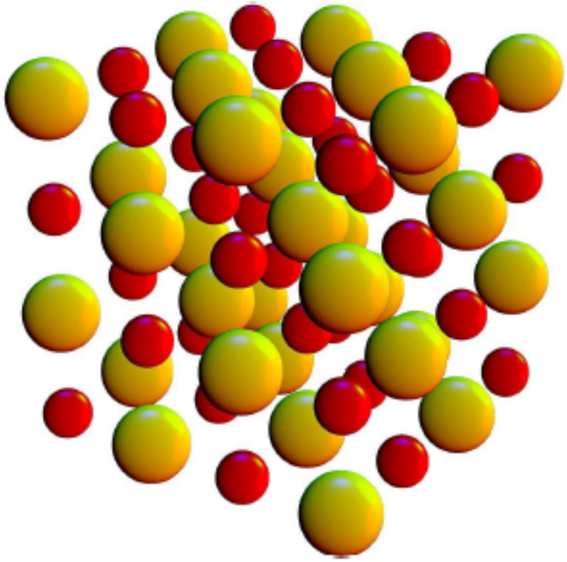
4 vibrations (2 along the bonds, 2 bending in perpendicular planes)

13 degrees of freedom

U = 13RT/2 per mole

2.3.4 Solids

a regular lattice of atoms



We need three coordinates to specify the position of each atom.
Each of these will have
a kinetic and potential energy term.

⇩

6 degrees of freedom per atom,
giving a total internal energy of
U = 3RT per mole
(Dulong and Petit's Law).

This is the maximum number of degrees of freedom we need since a position and velocity are enough to fully specify atoms.

Note that in terms of atoms the monatomic, diatomic, triatomic gases amount to 3RT/2, 7RT/4 and 13RT/6,
so none of them exceed 3RT (maximum internal energy).

2.3.5 Heat capacities

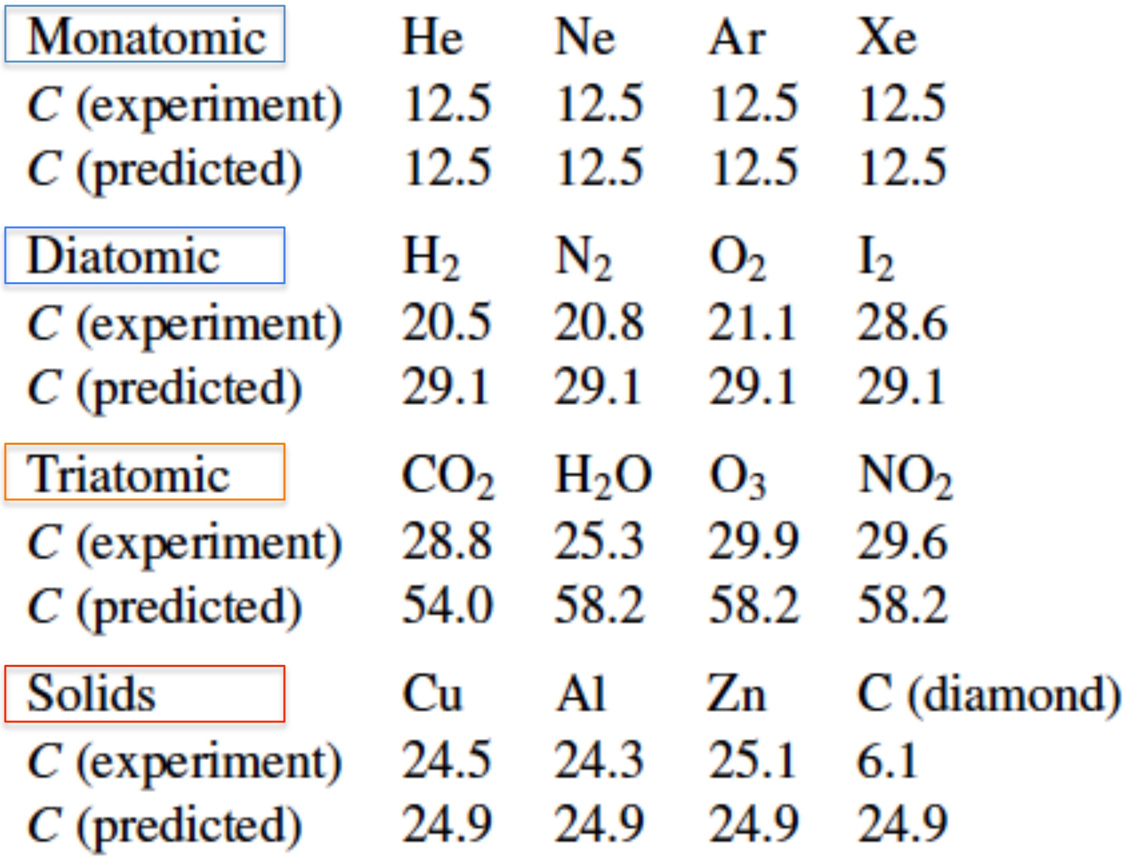
The rate of increase in internal energy of a substance with increasing temperature
or the increase in internal energy per unit rise in temperature
is called its heat capacity (SI units of JK^{-1}).

We can define a heat capacity per mole, per unit mass or per unit volume
it will be called specific heat capacity
and it will have units of $JK^{-1}mole^{-1}$, $JK^{-1}kg^{-1}$, $JK^{-1}\,m^{-3}$, …

For one mole of a monatomic gas, with $U = 3RT/2$, a rise of 1K causes U to increase by $3R/2$
and so the molar specific heat capacity C is given by:

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{3}{2}R = 12.5\,\mathrm{J\,K^{-1}\,mole^{-1}}$$

Experimental heat capacities vs theoretical values



Monatomic	He	Ne	Ar	Xe
C (experiment)	12.5	12.5	12.5	12.5
C (predicted)	12.5	12.5	12.5	12.5
Diatomic	H_2	N_2	O_2	I_2
C (experiment)	20.5	20.8	21.1	28.6
C (predicted)	29.1	29.1	29.1	29.1
Triatomic	CO_2	H_2O	O_3	NO_2
C (experiment)	28.8	25.3	29.9	29.6
C (predicted)	54.0	58.2	58.2	58.2
Solids	Cu	Al	Zn	C (diamond)
C (experiment)	24.5	24.3	25.1	6.1
C (predicted)	24.9	24.9	24.9	24.9

Good!

ok

bad

very bad (for C)

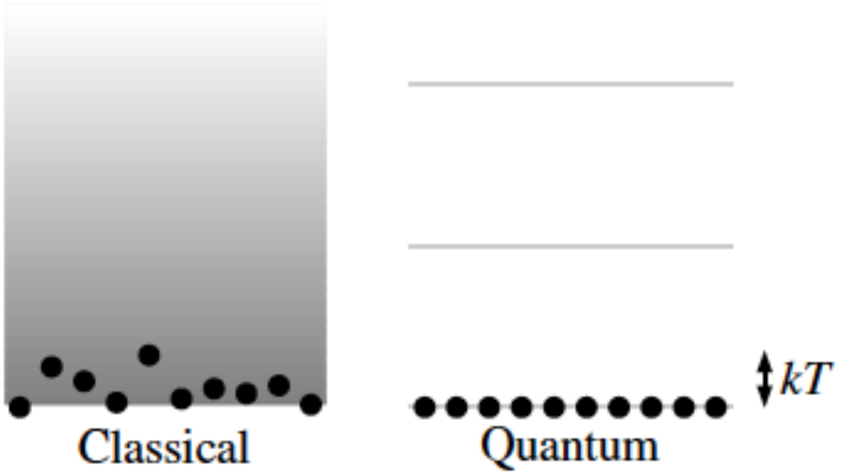
2.3.6 Why equipartition fails

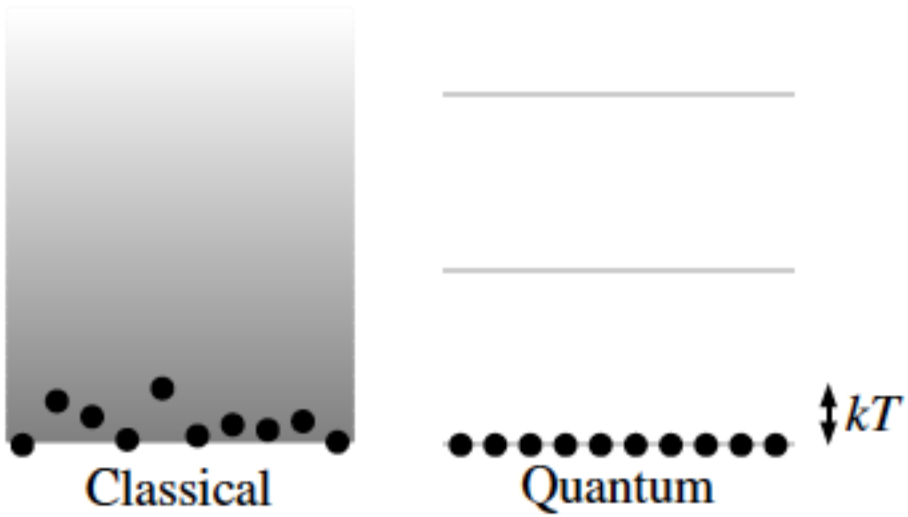
Classical physics assumes that there is a continuum of energy levels.

This means that the total energy of a system can vary continuously and the equipartition theorem assumes this.

However, in the quantum world, energy levels are discrete.

In particular there is a finite step between the lowest energy level and the first excited state above it.



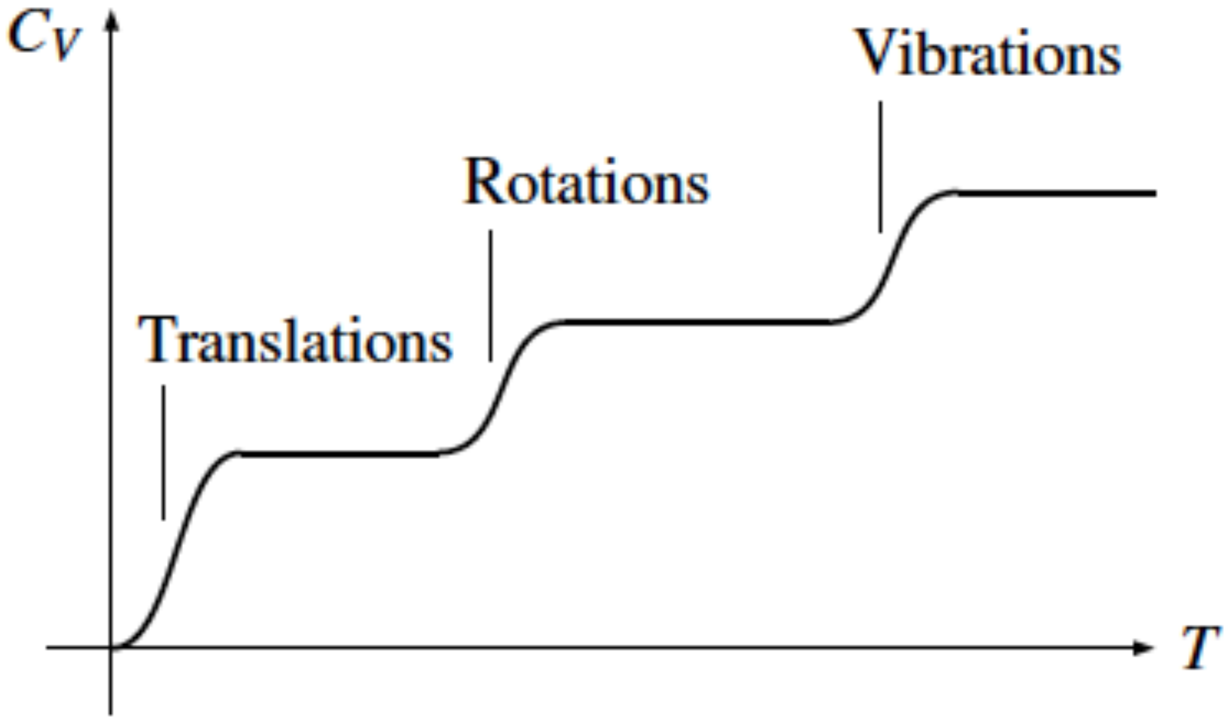


In a classical system it is always possible for some atoms to be excited above the lowest energy level.

In a real system, if kT is much less than the energy needed to get to the first excited state, there can be no excitation at all, and no contribution to the specific heat.

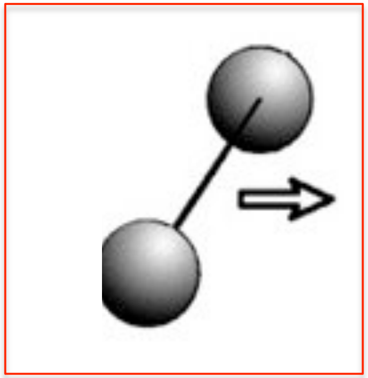
For typical molecules:

$$\Delta E_{\text{trans}} \ll \Delta E_{\text{rot}} \ll \Delta E_{\text{vib}}$$

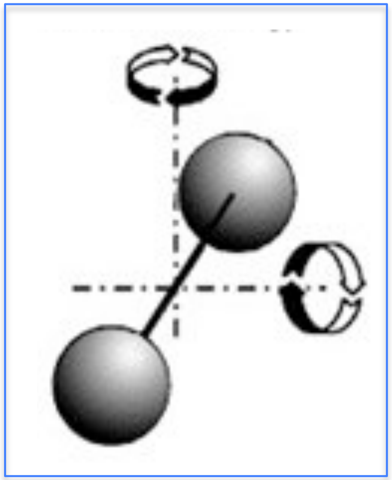


This means that, if we provide energy to the system, initially static:

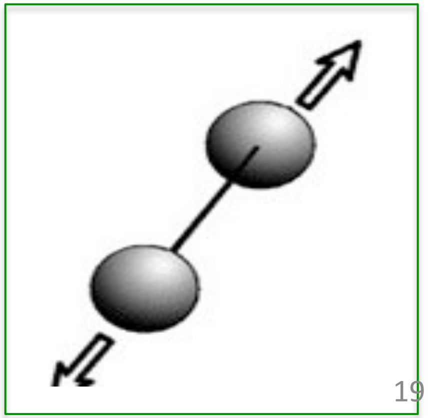
- Firstly, translational modes will be activated



- Secondly, rotational modes



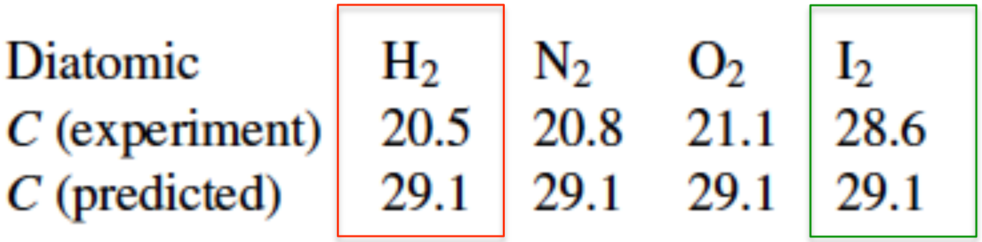
- Lastly, vibrational modes



Examples:

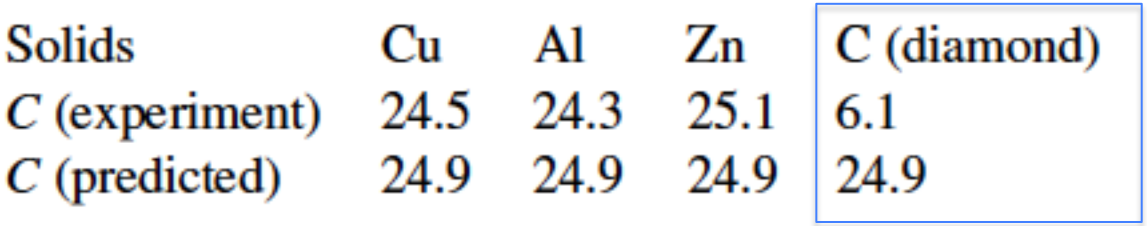
Iodine:

The frequency of vibrations is lower for more massive atoms, and so we can expect that a heavier molecule might match the equipartition value better than a light molecule.



Diatomic	H_2	N_2	O_2	I_2
C (experiment)	20.5	20.8	21.1	28.6
C (predicted)	29.1	29.1	29.1	29.1

Diamond:



Solids	Cu	Al	Zn	C (diamond)
C (experiment)	24.5	24.3	25.1	6.1
C (predicted)	24.9	24.9	24.9	24.9

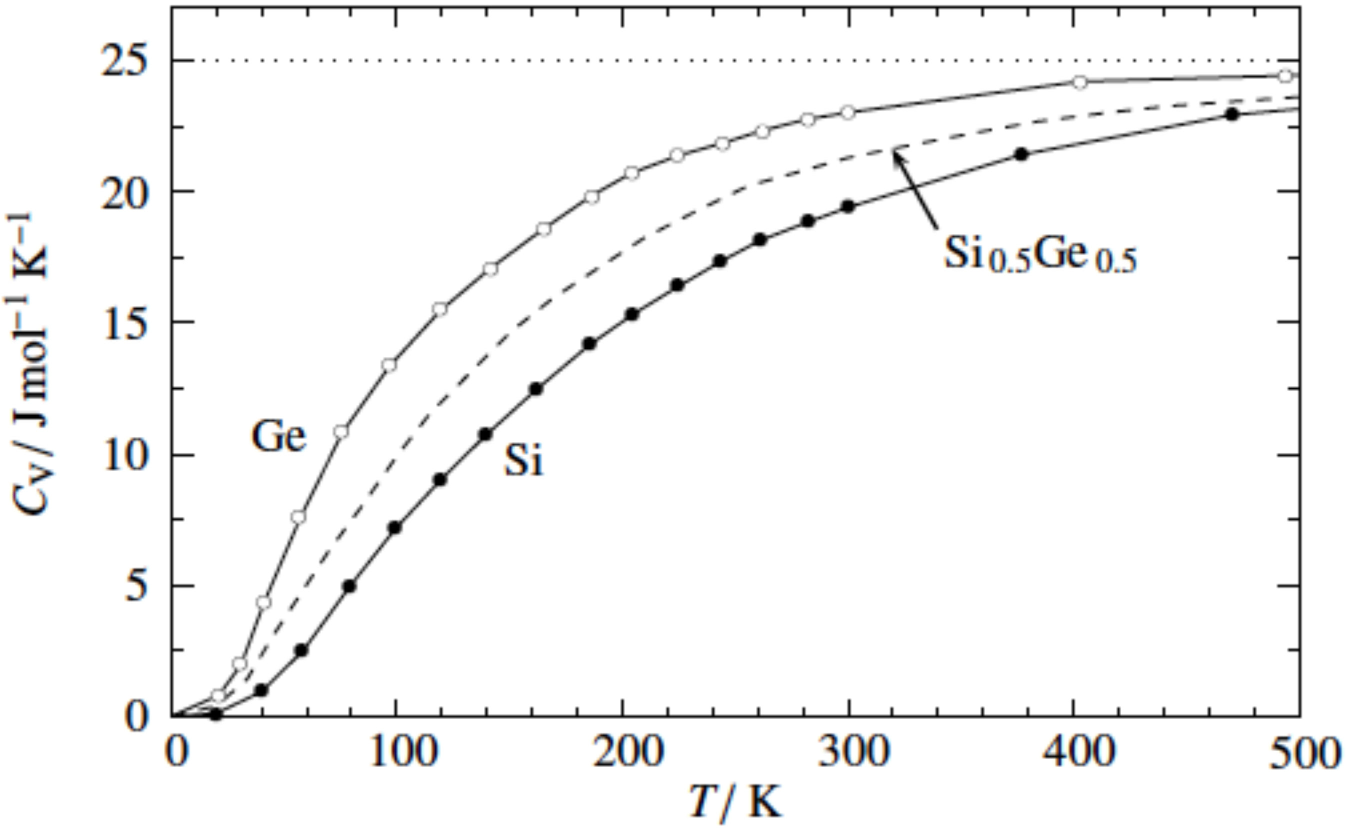
very rigid structure with strong bonds and relatively light atoms

Vibration frequencies are high

and not fully excited at room temperature.

Hence its heat capacity
is only 1/4 of the value predicted by equipartition.

Ge, Si and their alloy:



the equipartition value of 3R (dashed line) is only approached at temperatures of hundreds of kelvin,
when the translational, rotational and vibrational mode discrete energies are activated.

Theories based on quantum mechanics are needed to explain, in particular, the behaviour of solids.

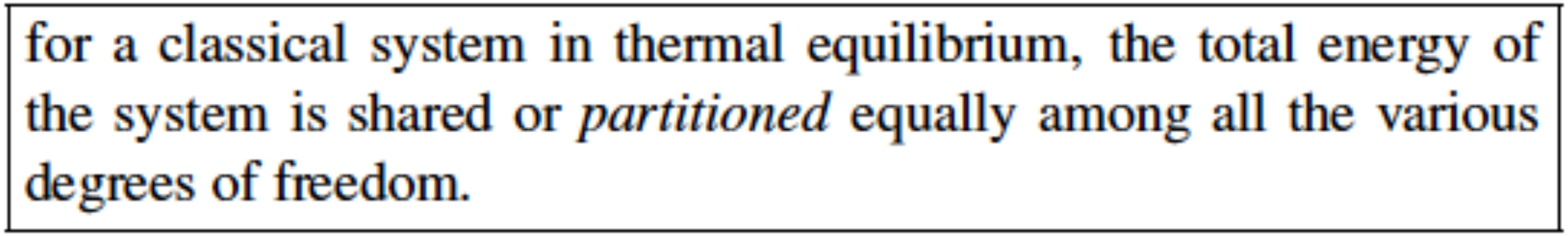
Equipartition theory, for instance, does not describe well systems with:

- conduction electrons (like metals)
- non-rigid molecules

2.4 Summary

- Boltzmann factor $$P(E) \propto e^{-E/kT}$$

- The equipartition theorem states that



for a classical system in thermal equilibrium, the total energy of the system is shared or *partitioned* equally among all the various degrees of freedom.

This means that the internal energy is

U = 3RT/2 per mole for a monatomic gas

U = 7RT/2 per mole for a diatomic gas

U = 13RT/2 per mole for a triatomic gas

U = 3RT per mole for solids

- The rate of increase in internal energy of a substance with increasing temperature

  or the increase in internal energy per unit rise in temperature

  is called its heat capacity (SI units of JK^{-1}).

Specific heat capacity per mole

$$C = \frac{dU}{dT} = \frac{3}{2}R = 12.5\,\mathrm{J\,K^{-1}\,mole^{-1}}$$

- Equipartition failure:

In a classical system it is always possible for some atoms to be excited above the lowest energy level.

In a real system, if kT is much less than the energy needed to get to the first excited state, there can be no excitation at all, and no contribution to the specific heat.