Thermal Properties of matter II

Heat capacity of ideal gas

Recall: Molar heat capacity $= C = \dfrac{1}{n}\dfrac{dQ}{dT}$

Consider a gas with fixed V.

Heat transfer to the gas increases the kinetic energy of the gas.

$$\Delta Q = \Delta K \qquad \text{from kinetic theory} \quad K = \frac{3}{2}nRT.$$

$$\Rightarrow \quad \Delta Q = \frac{3}{2}nR\,\Delta T$$

Molar heat capacity at fixed V $= C_V = \dfrac{1}{n}\dfrac{\Delta Q}{\Delta T} = \dfrac{3}{2}R = 12.47 \;\text{J/mol}\cdot\text{K}.$

True for all kinds of ideal gas?

From experiment

Gas	C_V J/mol·K
Ne	12.47
Ar	12.47
H$_2$	20.42
O$_2$	20.85
N$_2$	20.76
CO	20.85

$\sim \dfrac{3}{2}R = 12.47$

$\sim \dfrac{5}{2}R = 20.78$

Seems to have some patterns

Recall how $K = \frac{3}{2} nRT$. is obtained.

for gas consisting of non-interacting point particles,

$$E_{tot} = K_{tr} = \sum_i \frac{1}{2} m |\vec{V_i}|^2$$

$$= \underbrace{\sum_i \frac{1}{2} m V_{ix}^2}_{\frac{1}{2} pV} + \underbrace{\sum_i \frac{1}{2} m V_{iy}^2}_{\frac{1}{2} pV} + \underbrace{\sum_i \frac{1}{2} m V_{iz}^2}_{\frac{1}{2} pV}$$

$$= \frac{3}{2} pV \qquad \therefore \text{ ideal gas law}$$
$$\qquad\qquad\qquad pV = nRT.$$

$$= \frac{3}{2} nRT$$

$$E_{tot} = \frac{3}{2} N k_B T.$$

every energy per particle/molecule $= \dfrac{E_{tot}}{N} = \dfrac{3}{2} k_B T = \underbrace{\frac{1}{2} k_B T}_{V_x} + \underbrace{\frac{1}{2} k_B T}_{V_y} + \underbrace{\frac{1}{2} k_B T}_{V_z}$

- each particle/molecule needs $\underline{3 \text{ parameters}}$ to specify
  (V_x, V_y, V_z)

  its energy:

  We refer this number of parameters as $\boxed{\text{degrees of freedom}}$

- each degree of freedom carries $\boxed{\frac{1}{2} k_B T}$ amount of

  energy per molecule. This principle is called

  $\boxed{\text{Principle of equipartition.}}$
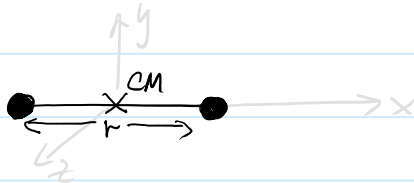
Applications of equipartition principle.

For a ideal gas consisting of

molecules with f degrees of freedom,

$$\text{Total energy of the gas} = E_{tot} = f \times \tfrac{1}{2} k_B T \times N$$

$$= \tfrac{f}{2} N k_B T \overset{or}{=} \tfrac{f}{2} n R T.$$

$$\Rightarrow \boxed{C_v = \tfrac{f}{2} R}$$

Example.   Diatomic ideal gas. e.g. H_2, N_2, O_2, $CO, \ldots$

Possible

Translation of CM $(\times 3)$
V_x, V_y, V_z.

Rotation about y and z axis. $(\times 2)$
ω_y, ω_z

Vibration of the two atoms $(\times 2)$
(each vibration needs 2
parameters to specify
the potential & kinetic
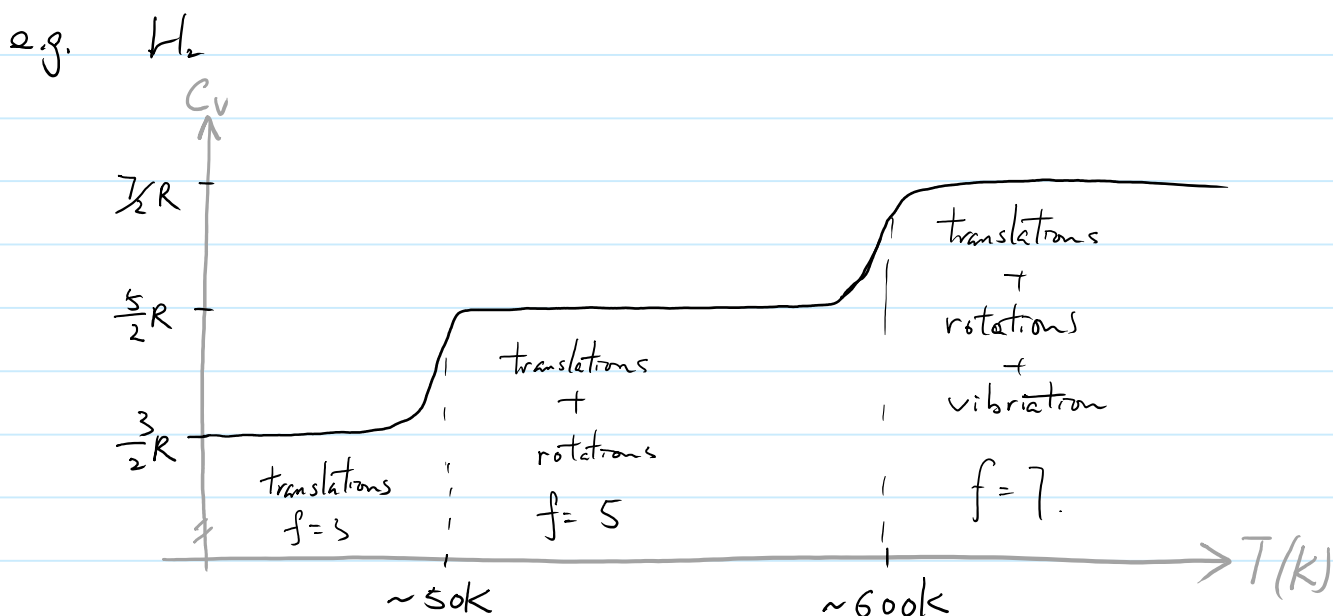energy).

Degree of freedom $= 3 + 2 + 2 = 7$.

for monoatomic gas, $f = 3$, $C_v = \frac{3}{2}R = 12.465 \frac{J}{mol \cdot k}$

(agree well with data
see table on p.2)

for diatomic gas, $f = 7$, $C_v = \frac{7}{2}R = 29 \frac{J}{mol \cdot k}$.

but most of them on the table have $C_v \approx 20 \frac{J}{mol \cdot k}$
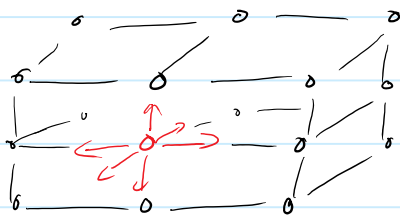what's wrong?

Temperature dependence of C_v

e.g. H_2

At room temperature, the vibration of diatomic molecules

is not probable. So, degrees of freedom equals 5.

$\Rightarrow$ $C_v = \frac{5}{2}R \sim 20.78 \ \frac{J}{mol \cdot K}$.

agree with experiments done in
room temperature.

In solid, molecules are located at a lattice site.
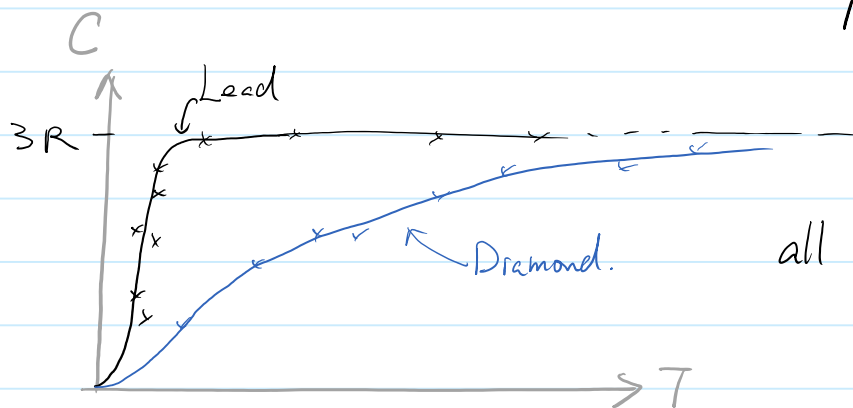
They can vibrate in 3 directions but not translate.

3 vibrations

$$\Rightarrow f = 6$$

$$\Rightarrow C = \frac{6}{2} R = 3R.$$

when all 3 vibrations are probable.

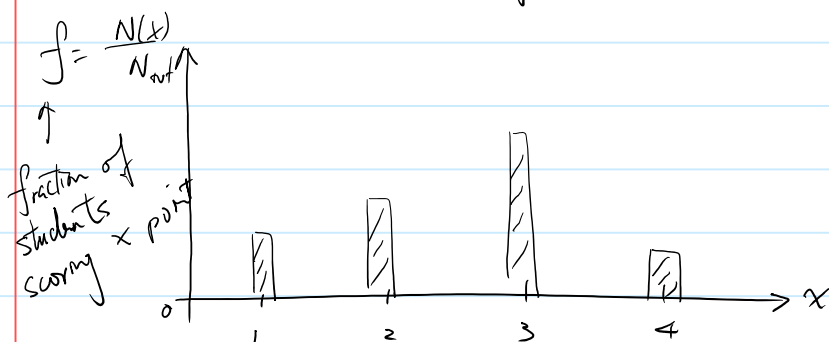all saturate at $C = 3R$. at high T.

Molecular speed of gas

Speed distribution in a gas. (histogram of a continuous value)

Analogy: score distribution in class
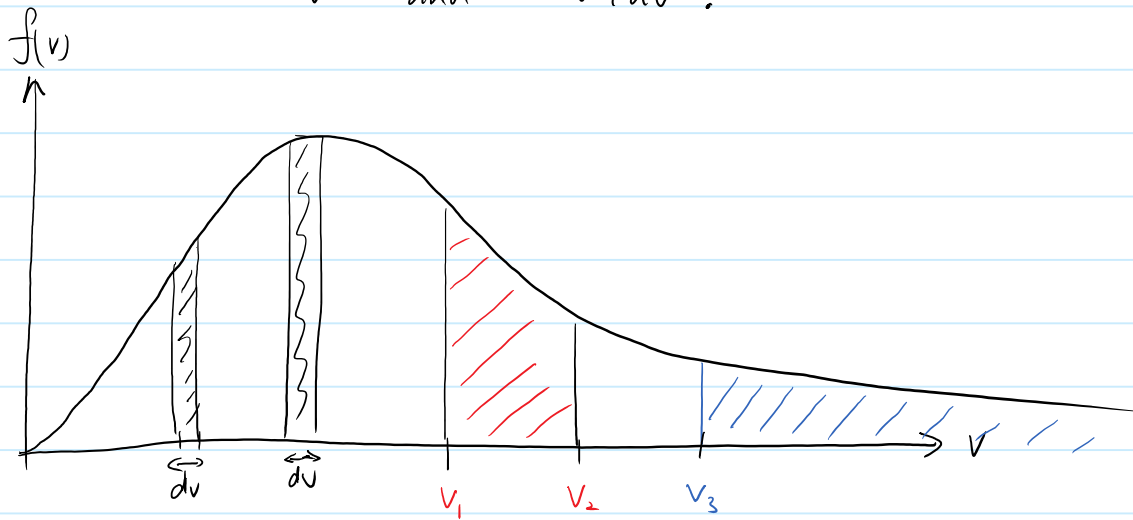
$N(x) = \#$ of students score x point

$N_{tot} = $ total $\#$ of students in the class

$f = \frac{N(x)}{N_{tot}}$

fraction of students scoring x point

what if the x is continuous?

V = speed of gas molecule

$f(v)\,dv$ = fraction of gas molecules having a speed between
V and $V+dv$.

Probability / fraction of molecules having speed between V_1 & V_2

$$= \int_{V_1}^{V_2} f(v)\,dv \qquad = \text{Area under the curve from } V_1 \text{ to } V_2.$$

Probability / fraction of molecules having speed larger than V_3

$$= \int_{V_3}^{\infty} f(v)\,dv.$$

By definition, probability / fraction of molecules having speed
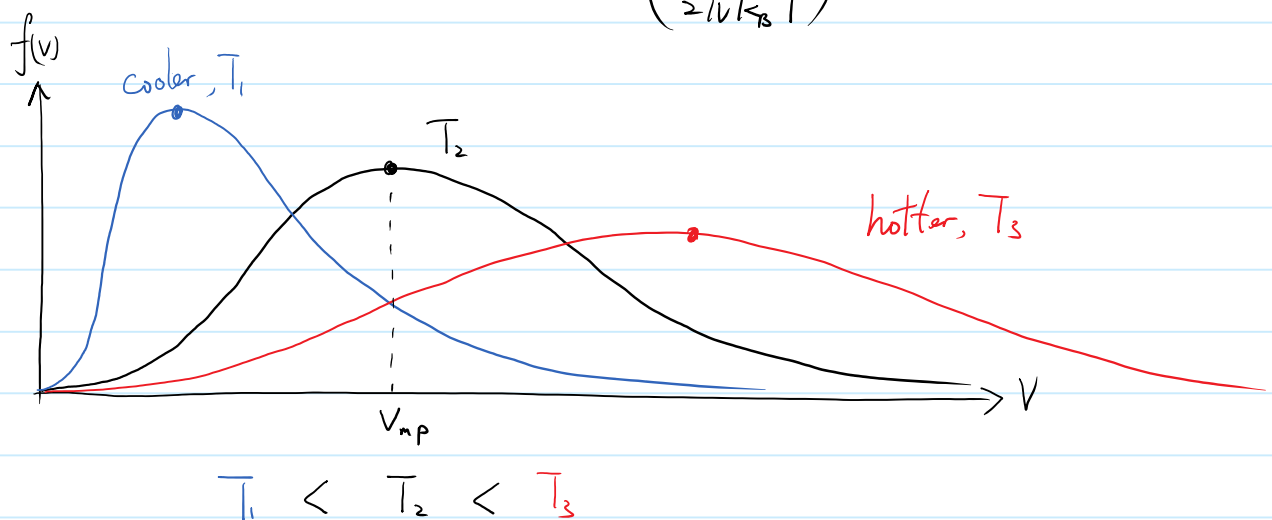
from 0 to ∞ $= 100\% = 1$

$$\Rightarrow \int_{0}^{\infty} f(v)\,dv = 1$$

Average speed $= \int_0^{\infty} v \cdot f(v) \cdot dv$

$$V_{rms} = \left[\overline{(V^2)_{avg}} \right]^{1/2} = \left[\int_0^{\infty} v^2 f(v) \, dv \right]^{1/2}$$

Maxwell - Boltzmann Distribution.

for ideal gas: $\quad f(v) = 4\pi \left(\dfrac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-\frac{\frac{1}{2}mv^2}{k_B T}}$

$T_1 < T_2 < T_3$

The area under the curve must be 1.

$\Rightarrow$ longer the tail, lower the peak.

Most populated speed $= V_{mp}$

To find V_{mp} : $\quad \dfrac{df}{dV}\bigg|_{V=V_{mp}} = 0$

$$\Rightarrow \quad 2V e^{-\frac{\frac{1}{2}mv^2}{k_B T}} + v^2 e^{-\frac{\frac{1}{2}mv^2}{k_B T}} \cdot (-mV)/k_B T = 0$$

$$\Rightarrow \quad 2V = \frac{mv^3}{k_B T} \quad \Rightarrow \quad V_{mp} = \sqrt{\frac{2k_B T}{m}}$$

The fact that at any temperature there are always some fraction of molecules which have very high speed is the reason why evaporation could occur.

Imagine a cup of water at room temperature. The water molecules could have a wide range of speeds. Some of the molecules will have enough speed to escape from the inter-molecular force holding them together. Those molecules will fly away from the water. In principle, the water becomes cooler due to the loss of the high energy molecules. But the temperature will be equilibrate by the environment and, practically remains at room temperature. So, there will be the same fraction of molecules which could evapourate. The process will continue until, in principle, only infinitesimal amount of water left in the cup given long enough times.