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Thermal Properties of Matter

Equations of State

1662 Boyle's law $PV = P_0 V_0$ at constant temperature and numbers of gas molecules

1802 Gay Lussam law $V_t = V_0(1+\beta t)$ at constant pressure

1808 Dulong, Petitle $P_t = P_0(1+\beta t)$ at constant volume

Avogadro's law same number of molecules, N at constant temperature, pressure, and volume

$$\frac{PV}{T} \propto (N, \underset{\text{mole}}{n}) \qquad \frac{PV}{T} = nR \qquad \frac{PV}{T} = Nk$$

- constant volume gas

$$P_T V_0 = NkT$$

$$P_T = \frac{NkT}{V_0}$$

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

the ideal-gas equation

$m_{total} = nM$ M: molar mass

$PV = nRT$ works at very low pressures and heigh temperature

the van der Waals equation

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

b: the volume of a mole of molecules

a: depends one the attractive intramolecular force

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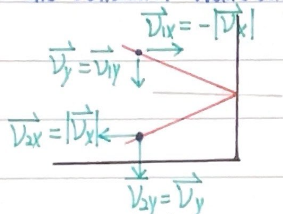
Kinetic-Molecular Model of an Ideal Gas

(1) a container with volume V contains a very large number N of identical molecules, each with mass m

(2) the molecules behave as point particles that are small compared to the size of the container and to the average distance between molecules

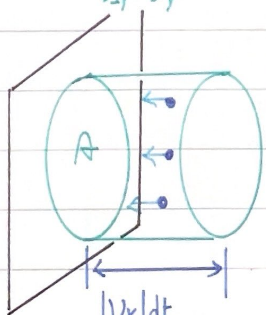
(3) the molecules are in constant motion, each molecule collides occasionally with a wall of the container, these collisions are perfectly elastic

(4) the container walls are rigid and infinitely massive and do not move



$$\Delta m\vec{v} = m|\vec{v_x}| - (-m|\vec{v_x}|) = 2m v_x \vec{e_x}$$

$$dP_x = \sum_{v_x>0} 2m\vec{v_x} A v_x \Delta t \frac{N}{V}$$



the number of collision with A $\frac{1}{2}\frac{N}{V}(A|v_x|dt)$

$$\frac{dP_x}{dt} = \frac{\sum_{v_x>0} 2m\vec{v_x} A v_x \Delta t \frac{N}{V}}{dt} = \sum_{v_x>0} 2m v_x^2 A \frac{N}{V} = F$$

$$\text{pressure} = \frac{F}{A} = \sum_{v_x>0} 2m v_x^2 \frac{N}{V} = \sum_{\text{all } v_x} m v_x^2 \frac{N}{V}$$

$$\text{pressure} = \sum_{\text{all}} m v_x^2 \frac{N}{V} = \frac{N}{V}\frac{1}{N}\sum N_{v_x} m v_x^2 = \frac{N}{V}\langle m v_x^2\rangle$$

$$\langle m v_x^2\rangle = \langle m v_y^2\rangle = \langle m v_z^2\rangle$$
$$= \frac{1}{3}\langle m(v_x^2+v_y^2+v_z^2)\rangle = \frac{2}{3}\langle \frac{1}{2}m(v_x^2+v_y^2+v_z^2)\rangle = \frac{2}{3}\langle KE\rangle$$

$\Rightarrow PV = N\langle m v_x^2\rangle = \frac{2}{3}N\langle KE\rangle = NkT$

$\Rightarrow \langle KE\rangle = \frac{3}{2}kT$

and $PV = \frac{2}{3}N\langle KE\rangle = \frac{2}{3}K = nRT$, $K = \frac{3}{2}nRT$

$$\frac{K}{N} = \frac{3nRT}{2N} = \frac{3RT}{2N_A} = \frac{3}{2}kT$$

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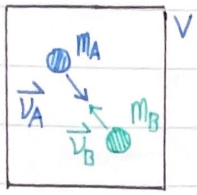
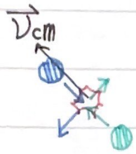


$$\left.\begin{aligned} P_A V &= N_A kT \\ P_B V &= N_B kT \end{aligned}\right] \quad (P_A+P_B)V = (N_A+N_B)kT$$

$$\vec{v}_{cm} = \frac{m_A\vec{v}_A + m_B\vec{v}_B}{m_A+m_B}$$



$$|\vec{v}_A' - \vec{v}_B'| = |\vec{v}_A - \vec{v}_B|$$

$$\vec{v}_{cm}\cdot(\vec{v}_A' - \vec{v}_B') = \frac{m_A\vec{v}_A + m_B\vec{v}_B}{m_A+m_B}\cdot(\vec{v}_A' - \vec{v}_B')$$

$$\langle \vec{v}_{cm}\cdot(\vec{v}_A' - \vec{v}_B')\rangle = \frac{1}{m_A+m_B}\left\langle \left[m_A\vec{v}_A\cdot\vec{v}_A' - m_B\vec{v}_B\cdot\vec{v}_B' + (m_B-m_A)\vec{v}_A'\cdot\vec{v}_B'\right]\right\rangle$$

$$= \langle \vec{v}_A'\cdot\vec{v}_B'\rangle = 0$$

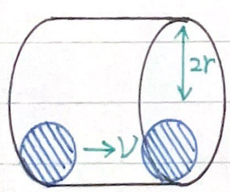
$$\frac{1}{2}(m_A+m_B)\langle \vec{v}_{cm}\cdot\vec{v}_{cm}\rangle = \frac{1}{2}(m_A+m_B)\frac{\langle (m_A\vec{v}_A' + m_B\vec{v}_B')^2\rangle}{(m_A+m_B)^2}$$

$$= \frac{1}{2}\frac{1}{m_A+m_B}\left(m_A^2\langle \vec{v}_A'\cdot\vec{v}_A'\rangle + m_B^2\langle \vec{v}_B'\cdot\vec{v}_B'\rangle + 2\langle m_A m_B\,\vec{v}_A'\cdot\vec{v}_B'\rangle\right)$$

$$= \frac{1}{2}\frac{1}{m_A+m_B}(m_A 3kT + m_B 3kT)$$

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

root-mean-square speed $v_{rms} = \sqrt{(v^2)_{av}} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$



$$dN = 4\pi r^2 v\,dt\,\frac{N}{V}$$

$$\frac{dN}{dt} = \frac{4\pi r^2 vN}{V}$$

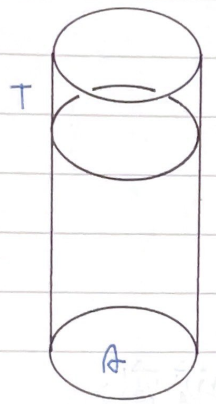
assume that only one molecule is moving $\frac{dN}{dt} = \frac{4\pi\sqrt{2}r^2vN}{V}$

mean free time : average time between collisions $t_{mean} = \frac{V}{4\pi\sqrt{2}r^2vN}$

mean free path $\lambda = vt_{mean} = \frac{V}{4\pi\sqrt{2}r^2N} = \frac{kT}{4\pi\sqrt{2}r^2p}$

Maxwell Distribution

First method



$z+dz$ $\quad p(z+dz)$

dz

$p(z) \qquad \rho(z) = \frac{N}{V}$

z

$$AP(z) = AP(z+dz) + mg\,\rho(z) A\,dz$$

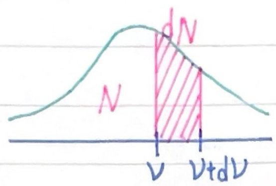
$$\Rightarrow -mg\,\rho(z)dz = P(z+dz) - P(z) = \frac{dP(z)}{dz}dz$$

$$\Rightarrow \frac{dP(z)}{dz} = -mg\rho(z) = -\frac{mg}{kt}P(z) \qquad \text{since } PV = NkT,\ P(z) = \rho(z)kT$$

$$\Rightarrow \int_0^z \frac{dP(z)}{P(z)} = \int_0^z -\frac{mg}{kt}\,dz, \quad \ln P(z) - \ln P(0) = -\frac{mg}{kt}(z-0)$$

$$\Rightarrow P(z) = P(0)e^{-\frac{mgz}{kt}}$$

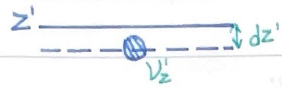
J. Perrin(1906) measure k by this way



$$\text{probability} = \frac{dN}{N} \propto dv$$

$$\frac{dN}{N} = f(v_z)\,dv_z$$

distribution function

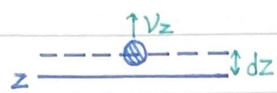


$$\frac{1}{2}mv_z^2 + mgz = \frac{1}{2}mv_z'^2 + mgz'$$

$\downarrow$ mgz, mgz' are fixed

$\downarrow$ differential

$$v_z\,dv_z = v_z'\,dv_z'$$

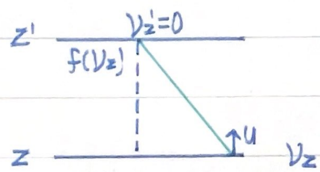


$$dz = v_z dt \qquad \frac{dz}{v_z} = \frac{dz'}{v_z'} = dt, \quad dz\,dv_z = dz'\,dv_z'$$
$$dz' = v_z' dt$$

$$\rho(z) f(v_z)\,dz\,dv_z = \rho(z') f(v_z')\,dz'\,dv_z'$$

$$\rho(0)\, e^{-\frac{mgz}{kt}} f(v_z)\,dz\,dv_z = \rho(0)\, e^{-\frac{mgz'}{kt}} f(v_z')\,dz'\,dv_z'$$

$$e^{-\frac{mg(z-z')}{kt}} f(v_z)\,v_z\,dt\,dv_z = f(v_z')\,v_z'\,dt\,dv_z'$$



$$\frac{1}{2}mu^2 = mg(z'-z)$$

$$\rho(z)\int_u^\infty f(v_z)\,v_z\,dv_z = \rho(z')\int_0^\infty f(v_z')\,v_z'\,dv_z'$$

$$\frac{\rho(z)\int_u^\infty f(v_z)\,v_z\,dv_z}{\rho(z)\int_0^\infty f(v_z)\,v_z\,dv_z} = \frac{\int_u^\infty f(v_z)\,v_z\,dv_z}{\int_0^\infty f(v_z)\,v_z\,dv_z} = \frac{\rho(z')\int_0^\infty f(v_z')\,v_z'\,dv_z'}{\rho(z)\int_0^\infty f(v_z)\,v_z\,dv_z} = \frac{\rho(z')}{\rho(z)}$$

$$= e^{-\frac{mg(z'-z)}{kT}} = e^{-\frac{mu^2}{2kT}}$$

$$\int_u^\infty f(v_z)\,v_z\,dv_z = C\,e^{-\frac{mu^2}{2kT}}$$

$$\Rightarrow \frac{d}{du}\int_u^\infty f(v_z)\,v_z\,dv_z = -C\frac{mu}{kT}\,e^{-\frac{mu^2}{2kT}}$$

$$\Rightarrow -f(u)u = -\frac{Cmu}{kT}\,e^{-\frac{mu^2}{2kT}}$$

$$f(u) = C'\,e^{-\frac{mu^2}{2kT}}$$

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to normalization, $\int_{-\infty}^{\infty} f(v_z)dv_z = 1$

$\Rightarrow \int_{-\infty}^{\infty} C' e^{-\frac{mu^2}{2kT}} du = 1$

by Gaussian integral $\int_{-\infty}^{\infty} e^{-ax^2} dx$

let $I = \int_{-\infty}^{\infty} e^{-ax^2} dx$

$I^2 = \left(\int_{-\infty}^{\infty} e^{-ax^2} dx\right)\left(\int_{-\infty}^{\infty} e^{-ay^2} dy\right) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-a(x^2+y^2)} dxdy$

let $x^2+y^2=r^2 \quad dxdy = rdrd\theta$

$= \int_0^{2\pi}\int_0^{\infty} e^{-ar^2} rdrd\theta = 2\pi \int_0^{\infty} e^{-ar^2} rdr = \pi \int_0^{\infty} e^{-ar^2} d(r^2)$

let $R = ar^2$

$= \frac{\pi}{a}\int_0^{\infty} e^{-R} dR = \frac{\pi}{a}\left[-e^{-R}\right]_0^{\infty} = \frac{\pi}{a}$

$\Rightarrow I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}}$

thus $a = \frac{m}{2kT} \quad u = x$

$\int_{-\infty}^{\infty} C' e^{-\frac{m}{2kT}u^2} du = C' \sqrt{\frac{2\pi kT}{m}} = 1$

$\Rightarrow C' = \sqrt{\frac{m}{2\pi kT}}$

$\Rightarrow f(v_z)dv_z = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{mv_z^2}{2kT}} dv_z$, similarly,

$f(v_x)dv_x = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{mv_x^2}{2kT}} dv_x$

$f(v_y)dv_y = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{mv_y^2}{2kT}} dv_y$

the probability under $v_x \to v_x+dv_x \quad v_y \to v_y+dv_y \quad v_z \to v_z+dv_z$

$f(v_x)dv_x f(v_y)dv_y f(v_z)dv_z = f(v_x)f(v_y)f(v_z)\, dv_x dv_y dv_z$

$= \left(\sqrt{\frac{m}{2\pi kT}}\right)^3 e^{-\frac{m(v_x^2+v_y^2+v_z^2)}{2kT}} dv_x dv_y dv_z$

the probability under $v \to v+dv$

$\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}\, 4\pi v^2 dv = \frac{8\pi}{m}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \varepsilon\, e^{-\frac{\varepsilon}{kT}}, \quad \varepsilon = \frac{1}{2}mv^2$

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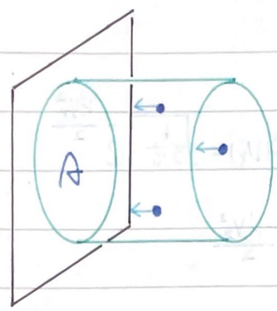
second method



the number of collision with A, $N = \rho A \Delta t \sum_{v_x>0} v_x f(v_x)$

$$\Delta p = N 2 m v_x = 2 m \rho A \Delta t \sum_{v_x>0} v_x^2 f(v_x)$$

$$\text{pressure} = \frac{F}{A} = \frac{\Delta P_x}{A \Delta t} = 2 m \rho \sum_{v_x>0} v_x^2 f(v_x)$$

$$= m \rho \sum_{v_x} v_x^2 f(v_x)$$

$$\frac{nRT}{V} = m\rho \sum_{v_x} v_x^2 f(v_x) = m\rho \langle v_x^2 \rangle = m \frac{N}{V} \langle v_x^2 \rangle \quad , \quad nRT = mN \langle v_x^2 \rangle = mn N_A \langle v_x^2 \rangle$$

$$\Rightarrow \langle v_x^2 \rangle = \frac{RT}{M} \quad \text{and} \quad \langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \, , \quad \langle v^2 \rangle = \frac{3RT}{M} = v_{rms} = \frac{3kT}{m}$$

$$\Rightarrow \langle E \rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{m}{2} \frac{3kT}{m} = \frac{3kT}{2}$$

let a distributive function $g_v dv = f(v_x) f(v_y) f(v_z) dv_x dv_y dv_z$ $\quad \frac{1}{2}(v^2)^{-\frac{1}{2}} 2v_x$

$$\frac{\partial g_v}{\partial v_x} = \frac{dg}{dv} \frac{\partial v}{\partial v_x} = \frac{dg}{dv} \frac{\partial}{\partial v_x} \sqrt{v_x^2 + v_y^2 + v_z^2} = \frac{dg}{dv} \frac{v_x}{v} \, , \quad \frac{1}{v_x} \frac{\partial g_v}{\partial v_x} = \frac{1}{v} \frac{dg}{dv}$$

$$\frac{1}{v_x} \frac{\partial}{\partial v_x} \left[f(v_x) f(v_y) f(v_z) \right] = \frac{1}{v} \frac{dg}{dv} \, , \quad \frac{f(v_y) f(v_z)}{v_x} \frac{\partial f(v_x)}{\partial v_x} = \frac{1}{v} \frac{dg}{dv}$$

similarly,

$$\frac{f(v_x) f(v_z)}{v_y} \frac{\partial f(v_y)}{\partial v_y} = \frac{1}{v} \frac{dg}{dv}$$

$$\frac{f(v_x) f(v_y)}{v_z} \frac{\partial f(v_z)}{\partial v_z} = \frac{1}{v} \frac{dg}{dv}$$

$$\Rightarrow \frac{1}{v_x f(v_x)} \frac{\partial f(v_x)}{\partial v_x} = \frac{1}{v_y f(v_y)} \frac{\partial f(v_y)}{\partial v_y} = \frac{1}{v_z f(v_z)} \frac{\partial f(v_z)}{\partial v_z} = \frac{1}{gv} \frac{dg}{dv} = -K'$$

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$$\Rightarrow \frac{\partial f(v_x)}{f(v_x)} = -k' v_x \partial v_x$$

$$\Rightarrow \int \frac{\partial f(v_x)}{f(v_x)} = \int -k' v_x \partial v_x \ , \quad f(v_x) = C e^{-\frac{k' v_x^2}{2}}$$

to normalization

$$C \int_{-\infty}^{\infty} e^{-\frac{k' v_x^2}{2}} dv_x = 1 \ , \quad 1 = C\sqrt{\frac{2\pi}{k'}} \ , \quad C = \sqrt{\frac{k'}{2\pi}} \ , \quad f(v_x) = \sqrt{\frac{k'}{2\pi}} e^{-\frac{k' v_x^2}{2}}$$

$$\because g = f(v_x) f(v_y) f(v_z) = \left(\frac{k}{2\pi}\right)^{\frac{3}{2}} e^{-\frac{k' v_x^2}{2}} e^{-\frac{k' v_y^2}{2}} e^{-\frac{k' v_z^2}{2}}$$

$$\langle E \rangle = \frac{3m\langle v^2 \rangle}{2} = \frac{3m}{2}\left(\frac{k'}{2\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{k' v_x^2}{2}} dv_x \int_{-\infty}^{\infty} e^{-\frac{k' v_y^2}{2}} dv_y \int_{-\infty}^{\infty} e^{-\frac{k' v_z^2}{2}} dv_z$$

$$= \frac{3m}{2}\left(\frac{k'}{2\pi}\right)^{\frac{3}{2}} \frac{2\pi}{k'} \int_{-\infty}^{\infty} v_x^2 e^{-\frac{k' v_x^2}{2}} dv_x$$

$$= \frac{3m\sqrt{k'}}{2\sqrt{2\pi}} \frac{\sqrt{2\pi}}{k'^{\frac{3}{2}}} = \frac{3m}{2k'}$$

$$\langle E \rangle = \frac{3kT}{2} = \frac{3m}{2k'} \ , \quad k' = \frac{m}{kT}$$

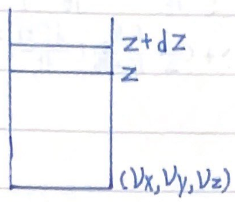
$$\Rightarrow f(v_x) = \sqrt{\frac{m}{2\pi kT}} e^{-\frac{m v_x^2}{2kT}}$$

$$\Rightarrow g_v = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}}$$

$$g_v dv = g_v \Delta v_x \Delta v_y \Delta v_z = 4\pi v^2 g_v dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} dv$$

Boltzmann Distribution



$\rho(z)dz\, f(\nu_x)d\nu_x\, f(\nu_y)d\nu_y\, f(\nu_z)d\nu_z$

the probability when the molecule at $z \to z+dz$ $\nu_x \to \nu_x + d\nu_x$ $\nu_y \to \nu_y + d\nu_y$ $\nu_z \to \nu_z + d\nu_z$

$$\Rightarrow \rho(0) e^{-\frac{mgz}{kT}} \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{m\nu^2}{2kT}} dz\, d\nu_x d\nu_y d\nu_z \propto e^{-\frac{\epsilon_p+\epsilon_k}{kT}} = e^{-\frac{E}{kT}}$$

where $\epsilon_p = mgz$ $\epsilon_k = \frac{1}{2}m\nu^2$ $E = \epsilon_p + \epsilon_k$

Heat Capacities

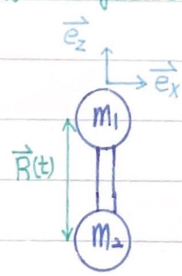
monatomic gas

$$\epsilon_k = \frac{1}{2}m(\nu_x)^2 + \frac{1}{2}m\nu_y^2 + \frac{1}{2}m\nu_z^2$$
$$= \langle \tfrac{1}{2}m\nu_x^2 \rangle + \langle \tfrac{1}{2}m\nu_y^2 \rangle + \langle \tfrac{1}{2}m\nu_z^2 \rangle$$
$$= \frac{3}{2}kT$$

$K_{tr} = \frac{3}{2}nRdT$, $dQ = nC_v dT$, $nC_v dT = \frac{3}{2}nRdT$ C_v molar heat capacities at constant volume

$\Rightarrow C_v = \frac{3}{2}R$

diatomic gas (dumbbell shape)



$|\vec{R}(t)|^2 = \text{constant}$ $\vec{R}(t)\frac{d\vec{R}(t)}{dt} = 0$ $\frac{d\vec{R}(t)}{dt} = \vec{\omega} \times \vec{R}(t)$

$$\epsilon_k = \frac{1}{2}(m_1+m_2)(\nu_{cm\text{-}x}^2 + \nu_{cm\text{-}y}^2 + \nu_{cm\text{-}z}^2) + \frac{1}{2}\frac{m_1m_2}{m_1+m_2}\frac{d\vec{R}(t)}{dt}\frac{d\vec{R}(t)}{dt}$$
$$= \langle \tfrac{1}{2}(m_1+m_2)(\nu_{cm\text{-}x}^2 + \nu_{cm\text{-}y}^2 + \nu_{cm\text{-}z}^2) \rangle + \frac{1}{2}\frac{m_1m_2}{m_1+m_2}[\vec{\omega}\times\vec{R}(t)]\cdot[\vec{\omega}\times\vec{R}(t)]$$
$$= \frac{3}{2}kT \qquad + \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2$$
$$= \frac{3}{2}kT \qquad + \langle \tfrac{1}{2}I_x\omega_x^2 + \tfrac{1}{2}I_y\omega_y^2 \rangle$$
$$= \frac{3}{2}kT + kT = \frac{5}{2}kT$$

$e^{-\frac{\epsilon}{kT}}$, $\langle \epsilon_k \rangle = \frac{5}{2}kT$

$\Rightarrow C_v = \frac{5}{2}kT$

$$\epsilon_k = \frac{1}{2}(m_1+m_2)(v_{cm \cdot x}^2 + v_{cm \cdot y}^2 + v_{cm \cdot z}^2) + \frac{1}{2}\frac{m_1 m_2}{m_1+m_2}\left[\frac{d\vec{R}(t)}{dt}\cdot\frac{d\vec{R}(t)}{dt}\right]$$

$$= \langle \frac{1}{2}(m_1+m_2)(\vec{v}_{cm}\cdot\vec{v}_{cm})\rangle + \langle \frac{1}{2}I_x\omega_x^2\rangle + \langle \frac{1}{2}I_y\omega_y^2\rangle + \langle \frac{1}{2}\frac{m_1 m_2}{m_1+m_2}\left(\frac{d\delta(t)}{dt}\right)^2\rangle$$

$$= \frac{3}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT$$

$$= \frac{7}{2}kT$$

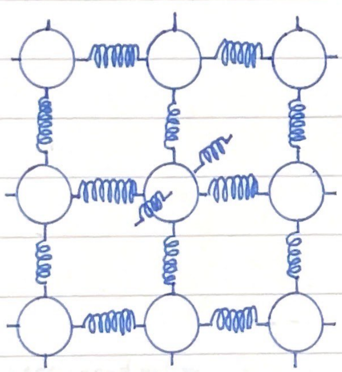
$$\epsilon_p = \frac{k}{2}[\delta(t)]^2 \quad \overline{\epsilon_p} = \frac{1}{2}kT$$

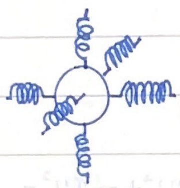
$$\langle \frac{1}{2}\frac{m_1 m_2}{m_1+m_2}\left(\frac{d\delta(t)}{dt}\right)^2\rangle + \langle \frac{k}{2}[\delta(t)]^2\rangle = \frac{1}{2}kT + \frac{1}{2}kT$$

$$\overline{\epsilon_k} + \overline{\epsilon_p} = \frac{7}{2}kT$$

$$\Rightarrow C_V = \frac{7}{2}R$$

solid : Dulong-Petit law



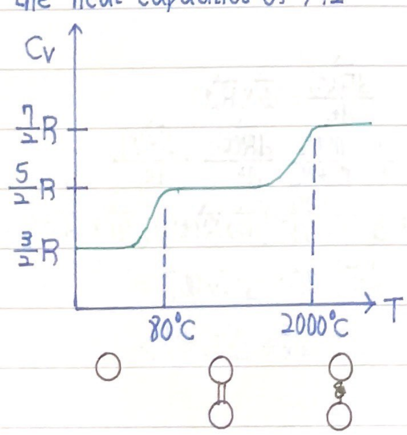


N_A metal ion have $3N_A$ strings

$3N_A kT = 3RT$

$C_V = 3R$

the heat capacities of H_2



the C_V of diamond