Mecânica estatística clássica:

Limite clássico ⇒ dois conceitos quânticos fundamentais: h e indistinguibilidade

$$\mathrm{Tr} \xrightarrow[\text{limite clássico}]{} \frac{1}{N!\,h^{3N}} \int d^{3N}q \, d^{3N}p$$ expressão semi-clássica

$$d^{3N}q \, d^{3N}p \equiv \prod_i d^3r_i \, d^3p_i$$

$$\hat{A} \to A(q,p) \qquad (q,p) \to (\vec{r}_1 \ldots \vec{r}_N, \vec{p}_1 \ldots \vec{p}_N)$$

$$\Rightarrow A = \frac{1}{Z} \mathrm{Tr}\left[\hat{A} e^{-\beta \hat{H}}\right] \to \frac{\int d^3q \, d^3p \, A(q,p) \, e^{-\beta H(q,p)}}{\int d^3q \, d^3p \, e^{-\beta H(q,p)}}$$

independente de h e $N!$

Distribuição de Maxwell:

$$H(q,p) = H_K(p) + H_U(q) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} U(|\vec{r}_i - \vec{r}_j|)$$

$$\Rightarrow \rho(q,p) = \frac{e^{-\beta H(q,p)}}{Z} \quad \text{e} \quad Z = Z_K Z_U$$ (note que p_i e q_j comutam)

$$Z_U = \frac{1}{V^N} \int d^{3N}q \, e^{-\beta H_U}$$

$$Z_K = \frac{V^N}{N!} \int \frac{d^{3N}p}{h^{3N}} e^{-\beta H_K(p)} = \frac{1}{N!} \left(\frac{V}{\lambda_T^3}\right)^N$$

$$\lambda_T = \frac{h}{\sqrt{2\pi m k T}}$$

Gás ideal $U=0 \Rightarrow Z_U = 1$.

Consideremos $g(\vec{p}_i)$

$$\Rightarrow \langle g(\vec{p}_i)\rangle = \left\{ \int d^{3N}p\, d^{3N}q\; e^{-\beta H_K} \right\}^{-1} \int d^{3N}q\, d^{3N}p\; g(\vec{p}_i)\, e^{-\beta H_K}$$

$$= \left\{ \int d^3 p_i\; g(\vec{p}_i)\, e^{-\beta p_i^2/2m} \right\} \left\{ \int d^3 p_i\, e^{-\beta p_i^2/2m} \right\}^{-1}$$

$$= \frac{1}{(2\pi m k T)^{3/2}} \int d^3 p\; e^{-\frac{p^2}{2mkT}}\, g(\vec{p}) = \int d^3 p\; g(\vec{p})\, \bar{\varphi}(\vec{p})$$

$$\bar{\varphi}(\vec{p}) \equiv \frac{1}{(2\pi m k T)^{3/2}}\, e^{-\frac{p^2}{2mkT}} = \frac{1}{m^3}\left(\frac{m}{2\pi k T}\right)^{3/2} e^{-\frac{mv^2}{2kT}} \equiv \frac{1}{m^3}\varphi(\vec{v})$$

$$\Rightarrow \bar{\varphi}(\vec{p})\, d^3 p = \varphi(v)\, d^3 v$$

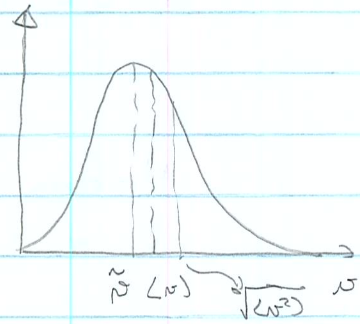
Se $g(\vec{p}) = p^2 \Rightarrow \langle p_\alpha^2 \rangle = mkT$ e $\langle v_\alpha^2 \rangle = \dfrac{kT}{m}$

$$\Rightarrow \left\langle \sum_\alpha p_\alpha^2 \right\rangle = 3mkTN \Rightarrow \sum_\alpha \frac{\langle p_\alpha^2 \rangle}{2m} = \frac{3}{2} kTN$$

Distribuição $\phi(v)$

$$\phi(v)\, dv = \int d\Omega\, v^2\, \varphi(\vec{v})\, dv$$

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



$$\tilde{v} = \sqrt{\frac{2kT}{m}} \qquad \langle v \rangle = \sqrt{\frac{8kT}{\pi m}} = 1.13\,\tilde{v}$$

$$\text{e} \quad \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} = 1.22\,\tilde{v}$$

Teorema de equipartição.

$$H = \sum_{i,j=1}^{\nu} x_i a_{ij} x_j + \tilde{H} \qquad x_i = q_i, p_i$$

M graus de liberdade e ν coordenadas quadráticas
$\Rightarrow \nu \leq 2M$ e $2M - \nu$ contribuições não
quadráticas para H (todas em $\tilde{H}$)

$$\Rightarrow \left\langle \sum_{i,j=1}^{\nu} x_i a_{ij} x_j \right\rangle = \sum_{i,j=1}^{\nu} a_{ij} \langle x_i x_j \rangle$$

Cálculo de $\langle x_i x_j \rangle$

$$I_n \equiv \int_0^{\infty} dx\, x^n e^{-\frac{Ax^2}{2}} = \frac{2^{(n-1)/2}\,\Gamma((n+1)/2)}{A^{(n+1)/2}}$$

$$\Gamma(p) = (p-1)! \quad \text{pois} \quad \Gamma(x+1) = \int_0^{\infty} e^{-t} t^x dt = x\Gamma(x)$$

$$f(u) \equiv N \int_{-\infty}^{\infty} dx\, e^{-\frac{1}{2}Ax^2} e^{ux} \quad ; \ N \text{ tq } f(0) = 1$$

$$x = x' - u/A \quad \Rightarrow f(u) = N e^{u^2/2A} \int_{-\infty}^{\infty} dx' e^{-\frac{A}{2}x'^2}$$

$$= e^{u^2/2A}$$

$$\Rightarrow \langle x^2 \rangle = \left.\frac{d^2 f}{du^2}\right|_{u=0} = \frac{1}{A} \quad ; \quad \langle x^4 \rangle = \left.\frac{d^4 f}{du^4}\right|_{u=0} = \frac{3}{A^2}$$

N-dim.

$$\sum_{ij} x_i A_{ij} x_j = x^T A x \quad ; \quad \sum x_i u_i = x^T u.$$

$$f(u) = N \int \prod_i dx_i\, e^{-\frac{1}{2} x^T A x} e^{u^T x} \quad ; \ N \text{ tq } f(0) = 1$$

$$x = x' - A^{-1} u$$

$$f(u) = e^{\frac{u^T A^{-1} u}{2}} \mathcal{N} \int \prod_i dx'_i \, e^{-\frac{1}{2} x'^T A x'} = e^{\frac{u^T A^{-1} u}{2}}$$

$$\Rightarrow \langle x_i x_j \rangle = \left. \frac{\partial^2 f}{\partial u_i \partial u_j} \right|_{u=0} = (A^{-1})_{ij}$$

$$\langle x_i x_j x_k x_l \rangle = \left. \frac{\partial^4 f}{\partial u_i \partial u_j \partial u_k \partial u_l} \right|_{u=0} = \langle x_i x_j \rangle \langle x_k x_l \rangle + \langle x_i x_k \rangle \langle x_j x_l \rangle + \langle x_i x_l \rangle \langle x_j x_k \rangle .$$

$$\mathcal{N} = \frac{(\det A)^{1/2}}{(2\pi)^{N/2}}$$

$$H = \sum_{i,j} a_{ij} x_i x_j \Rightarrow A_{ij} = 2\beta a_{ij} \quad \text{em} \quad e^{-\beta H}$$

$$\langle x_i x_j \rangle = \frac{kT}{2} (a^{-1})_{ij}$$

$$\Rightarrow \langle H_\nu \rangle = \sum_{ij} a_{ij} (a^{-1})_{ji} \frac{kT}{2} = \nu \frac{kT}{2}$$

$$\Rightarrow H = \sum_{i=1}^{N} \frac{p_i^2}{2m} \rightarrow \langle H \rangle = \frac{3}{2} N kT$$

$$H = \frac{p^2}{2m} + \frac{1}{2} k x^2 \rightarrow \langle H \rangle = kT$$

$\Rightarrow$ ν coordenadas harmônicas $\langle H \rangle = \nu kT \Rightarrow \frac{\partial E}{\partial T} = C_v = \nu k$

Como $\langle (\Delta H)^2 \rangle = \frac{\partial^2 \ln Z}{\partial \beta^2} = kT^2 C_v = -\frac{\partial E}{\partial \beta}$

Temos, neste caso, $\langle (\Delta H)^2 \rangle = \langle H^2 \rangle - \langle H \rangle^2 = \langle H^2 \rangle - \frac{\nu^2 k^2 T^2}{4}$

$$H^2 = \sum_{ijkl} a_{ij} x_i x_j a_{kl} x_k x_l$$

$$\langle H^2 \rangle = \sum_{ijkl} a_{ij} a_{kl} \langle x_i x_j x_k x_l \rangle = \frac{k^2 T^2}{4} \left\{ \sum_{ijkl} (a_{ij} a_{kl} a^{-1}_{ij} a^{-1}_{kl} + a_{ij} a_{kl} a^{-1}_{ik} a^{-1}_{jl} + a_{ij} a_{kl} a^{-1}_{il} a^{-1}_{jk}) \right\} = \frac{\nu^2 k^2 T^2}{4} + \frac{2\nu k^2 T^2}{4}$$

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$$\Rightarrow \langle H^2 \rangle - \langle H \rangle^2 = \frac{1}{2} \nu k^2 T^2$$

Mas $\langle (\Delta H)^2 \rangle = kT^2 C_V \Rightarrow \boxed{C_V = \frac{1}{2} \nu k}$

Calor específico do gás diatômico.
N moléculas idênticas.

m_1 o——o m_2 $\quad \tilde{L}_{rot} = \frac{1}{2} I \dot{\theta}^2 + \frac{1}{2} I \sin^2\theta \, \dot{\varphi}^2$

$$\tilde{H}_{rot} = \frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I \sin^2\theta}$$

onde $p_\theta = \frac{\partial \tilde{L}_{rot}}{\partial \dot{\theta}} = I\dot{\theta}$ e $p_\varphi = \frac{\partial \tilde{L}_{rot}}{\partial \dot{\varphi}} = I \sin^2\theta \, \dot{\varphi}$

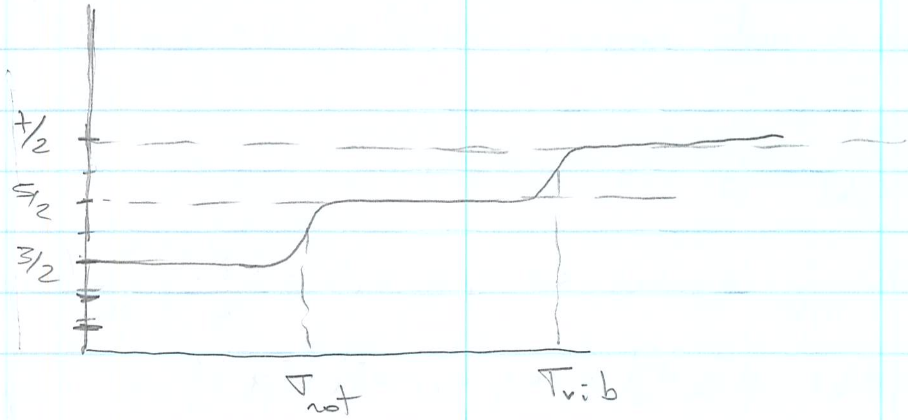
$\Rightarrow \nu = 2$

massa reduzida: $\mu \equiv \frac{m_1 m_2}{m_1 + m_2}$

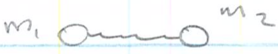
$\Rightarrow \tilde{H}_{vib} = \frac{p^2}{2\mu} + \frac{1}{2} \mu \omega_{vib}^2 q^2 \Rightarrow \nu = 2$

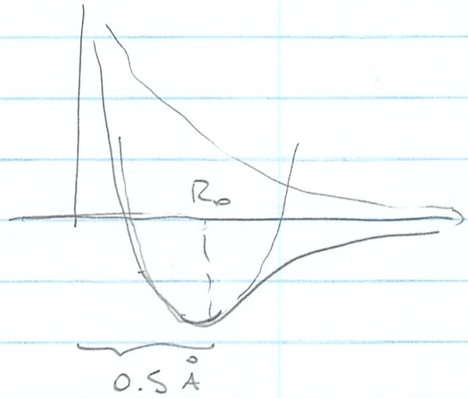
$$\left.\begin{array}{ll} \Rightarrow E_{tr} = \frac{3}{2} NkT & \Rightarrow C_V^{(tr)} = \frac{3}{2} Nk \\ E_{rot} = NkT & C_V^{(rot)} = Nk \\ E_{vib} = NkT & C_V^{(vib)} = Nk \end{array}\right\} \Rightarrow C_V = \frac{7}{2} Nk.$$

mas



Osciladores quânticos e rotores.





$E_0 \sim 13.6 \text{ eV} \simeq Ry.$

$I \sim \mu a_0^2$ $\quad\quad$ $U(R) \sim U(R_0) + \frac{1}{2} k (R - R_0)^2$

$$K = \left.\frac{d^2 U}{dR^2}\right|_{R=R_0} \simeq \frac{Ry}{a_0^2}$$

$$\bar{E}_{vib} = \hbar \omega_{vib} = \hbar \sqrt{\frac{K}{\mu}} \simeq \frac{1}{\sqrt{\alpha}} \sqrt{\frac{m_e}{m_p}} \, Ry$$

$$\Rightarrow T_{vib} \sim \frac{\bar{E}_{vib}}{k} \sim \frac{1}{\sqrt{\alpha}} \times 3700 \text{ K} \; ; \quad \mu = \frac{m_1 m_2}{m_1 + m_2} = \alpha m_p.$$

$$\bar{E}_{rot} = \frac{\hbar^2}{2I} \simeq \frac{1}{\alpha} \frac{m_e}{m_p} Ry \quad\quad T_{rot} \sim \frac{\bar{E}_{rot}}{k} \simeq \frac{1}{\alpha} \times 85 \text{ K}$$

$T \gg T_{vib}, T_{rot}$ $\Rightarrow$ todos os níveis estão excitados e há muitos estados acessíveis $\Rightarrow$ aprox. clássica e Teo. equipartição.

Se $T < T_{vib}$ $\Rightarrow$ grau de liberdade vibracional é congelado

Função de partição da molécula.

$$Z_N = \frac{1}{N!} \left[\zeta(\beta) \, \xi_{vib} \, \zeta_{rot} \right]^N \quad\quad \zeta(\beta) = \frac{V}{\lambda_T^3}$$

$$\epsilon_n^{(vib)} = -\mu_0 + \left(n + \frac{1}{2}\right)\hbar\omega_{vib}$$

$$\mu_0 = -E_0 \sim 1\,Ry$$

i) $$\zeta_{vib} = \sum_{n=0}^{\infty} e^{-\beta\epsilon_n^{(vib)}} = \frac{e^{\beta\mu_0}\, e^{-\beta\frac{\hbar\omega_{vib}}{2}}}{1 - e^{-\beta\hbar\omega_{vib}}}$$

$$\Rightarrow \epsilon_{vib} = \langle \epsilon_n^{(vib)} \rangle = -\frac{\partial \ln \zeta_{vib}}{\partial \beta} = -\mu_0 + \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_{vib}} - 1}\right)\hbar\omega_{vib}$$

$$\Rightarrow \langle n \rangle = \frac{1}{e^{\beta\hbar\omega_{vib}} - 1}$$

$$C_v = \frac{\partial E}{\partial T} = -k\beta^2 \frac{\partial E}{\partial \beta} = +k\beta^2 \hbar\omega_{vib} \frac{\hbar\omega_{vib}\, e^{\beta\hbar\omega_{vib}}}{(e^{\beta\hbar\omega_{vib}} - 1)^2}$$

$$= k\frac{(\hbar\omega_{vib})^2}{(kT)^2} \frac{e^{\beta\hbar\omega_{vib}}}{(e^{\beta\hbar\omega_{vib}} - 1)^2} = k\left(\frac{T_{vib}}{T}\right)^2 \frac{e^{T_{vib}/T}}{(e^{T_{vib}/T} - 1)^2}$$

$$\approx \begin{cases} k\,(T_{vib}/T)^2\, e^{-T_{vib}/T} \to 0 & \text{se } T \ll T_{vib} \\ k & \text{se } T \gg T_{vib} \end{cases}$$

$$T_{vib} \equiv \frac{\hbar\omega_{vib}}{k}$$

ii) $\zeta_{rot} = ?$

$$J^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle.$$

$$j = 0, \ldots \infty \qquad m = \underbrace{-j, -j+1, \ldots, j-1, j}_{2j+1}$$

$$\epsilon_{jm}^{(rot)} = j(j+1)\frac{\hbar^2}{2I} = j(j+1)\,k\,T_{rot}$$

$$\zeta_{rot} = \sum_{j=0}^{\infty} \sum_{-j}^{j} e^{-\beta \epsilon_{jm}^{(rot)}} = \sum_{j=0}^{\infty} (2j+1)\, e^{-j(j+1)\frac{T_{rot}}{T}}$$

$$T >> T_{rot} \Rightarrow \frac{T_{rot}}{T} \sim \epsilon \to 0$$

$$\Rightarrow \zeta_{rot} = \frac{1}{\epsilon} \sum_j \Delta j \sqrt{\epsilon}\, (2j\sqrt{\epsilon} + \sqrt{\epsilon})\, e^{-(j\sqrt{\epsilon})^2 - (j\sqrt{\epsilon})\sqrt{\epsilon}}$$

$$\simeq \frac{1}{\epsilon} \int_0^{\infty} dx\, 2x\, e^{-x^2} = \frac{T}{T_{rot}} \int_0^{\infty} -d(e^{-x^2}) = \frac{T}{T_{rot}}$$

$$\Rightarrow \epsilon_{rot} = -\frac{\partial}{\partial \beta} \ln \zeta_{rot} = kT \quad \text{e} \quad C_v = \frac{\partial \epsilon_{rot}}{\partial T} = k.$$

$$T << T_{rot} \Rightarrow \zeta_{rot} \approx 1 + 3e^{-2T_{rot}/T} + 5e^{-6T_{rot}/T} + \dots$$

$$\frac{T_{rot}}{T} \to \infty \Rightarrow \zeta_{rot} \approx 1 + \delta \quad \text{onde} \quad \delta = 3e^{-2T_{rot}/T}\left[1 + \frac{5}{3} e^{-4T_{rot}} \right.$$

$$\Rightarrow \ln \zeta_{rot} \approx \delta = 3e^{-2T_{rot}/T} = 3e^{-2kT_{rot}\beta}$$

$$\epsilon_{rot} = -\frac{\partial}{\partial \beta} \ln \zeta_{rot} = 6kT_{rot}\, e^{-2T_{rot}/T}$$

$$C_v = -k\beta^2 \frac{\partial E}{\partial \beta} = +\frac{12}{kT^2} (kT_{rot})^2\, e^{-2T_{rot}/T}$$

$$= k\, 12 \left(\frac{T_{rot}}{T}\right)^2 e^{-2T_{rot}/T} \to 0.$$