(1)

13. 10.

• LHO - klasicky – energia stavu $E = \frac{1}{2} m \omega^2 x^2 + \frac{1}{2}\frac{p^2}{m}$ ← hybnosť lepšie popisuje stav častice ako rýchlosť (viď teoretická mechanika)

$$\sum_i = C \int dx\, dp$$

všetky stavy

$$Z = C \int dx\, dp\, e^{-\beta E} = C \int dx\, dp\, e^{-\beta \frac{1}{2} m \omega^2 x^2 - \frac{1}{2}\beta \frac{p^2}{m}} = C \left[\int dx\, e^{-\frac{1}{2}\beta m \omega^2 x^2} \right] \left[\int dp\, e^{-\frac{1}{2}\frac{\beta}{m} p^2} \right] =$$

$$= C \sqrt{\frac{\pi}{\frac{1}{2}\beta \cancel{m} \omega^2}} \sqrt{\frac{\pi}{\frac{1}{2}\frac{\beta}{\cancel{m}}}} = \boxed{C \frac{2\pi}{\beta \omega}}$$

ako nafixovať konštantu C? → klasický a QM výpočet musí vyjsť v limite $T \to \infty$ $(\beta \to 0)$

$$Z_{QM}(\beta \to 0) = \frac{1}{2\frac{\hbar \omega \beta}{2}} = \frac{1}{\hbar \omega \beta} \Rightarrow \boxed{C = \frac{1}{2\pi\hbar} = \frac{1}{h}}$$

ROZMYSLIEŤ SI, AKO TO BUDE FUNGOVAŤ V 3D

• častice v škatuli (ideálny plyn) – klasicky – už sme počítali v mikrokanonickom rozdelení

od QM $E_{n_1 n_2 n_3} = \frac{\hbar^2 \pi^2}{2 m L^2}(n_1^2 + n_2^2 + n_3^2)$ pre jednu časticu $Z_1 = \sum_{n_1 n_2 n_3} e^{-\beta \epsilon (n_1^2 + n_2^2 + n_3^2)}$

klasicky $Z_1 = \frac{1}{(2\pi\hbar)^3} \boxed{\int d^3x}\, d^3p\, e^{-\beta \frac{p_x^2 + p_y^2 + p_z^2}{2m}} = \frac{1}{(2\pi\hbar)^3} V \int dp\, p^2 4\pi\, e^{-\frac{\beta}{2m} p^2} = \frac{1}{(2\pi\hbar)^3} V \frac{\sqrt{\pi}}{2\left(\frac{\beta}{2m}\right)^{\frac{3}{2}}} =$

$\int d^3x = V$

$$= V \left(\frac{m k T}{2\pi \hbar^2} \right)^{\frac{3}{2}} = \boxed{\frac{V}{\lambda^3}} \Rightarrow \boxed{Z = \frac{1}{N!} Z_1^N}$$

$$\sqrt{\frac{2\pi\hbar^2}{m k T}} = \lambda$$

GIBBSov paradox (v limite $N \to \infty$)

permutácia častíc vedie na rovnaký mikrostav systému, častice sú nerozlíšiteľné

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\log Z = -\frac{\partial}{\partial\beta}\log\frac{1}{N!}\frac{V^N}{\lambda^{3N}} = +3N\frac{\partial}{\partial\beta}\log\lambda = 3N\frac{1}{\lambda}\frac{\partial}{\partial\beta}\lambda = 3N\frac{1}{\lambda}\frac{\partial}{\partial\beta}\sqrt{\frac{2\pi\hbar^2}{m}}\sqrt{\beta} =$$

$$= 3N\frac{1}{\cancel{\sqrt{\frac{2\pi\hbar}{m}}}\sqrt{\beta}}\cancel{\sqrt{\frac{2\pi\hbar}{m}}}\frac{1}{2}\frac{1}{\sqrt{\beta}} = \frac{3}{2}N\frac{1}{\beta} = \boxed{\frac{3}{2}NkT}$$

priamočiaro viac rozmerov, v d rozmeroch $\langle E\rangle = \frac{d}{2}NkT$

• ekvipartičný teorém → na každý kvadratický stupeň voľnosti $\langle \varepsilon\rangle = \frac{1}{2}kT$

• porovnanie $\frac{3p_*^2}{2m} = \langle E\rangle \Rightarrow p_*^2 = mkT$ deBroglie $\lambda = \frac{h}{p}$ → až na konštanty $p_* \leftrightarrow \lambda$

termálna vlnová dĺžka – v dôsledku termálneho pohybu

• entropia $S = \frac{\partial}{\partial T}(kT\log Z) = Nk\left[\log\left(\frac{V}{N\lambda^3}\right) + \frac{5}{2}\right]$ ← Sackur–Tetrode formula

← bez neznámych konštánt

$\hbar$

klasicky vidíme iba rozdiely entropií v nich $\hbar$ vypadne

• dopočítame stavovú rovnicu $p = -\frac{\partial F}{\partial V}\Big|_T = \frac{1}{V}NkT \Rightarrow \boxed{pV = NkT}$

• plyn s interakciou

$$Z=\frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int\underbrace{\left(\prod_{j=1}^{N}d^3x_j\,d^3p_j\right)}_{\text{všetky stavy celého systému }N\text{ častíc}}e^{-\beta E}$$

← celková energia N častíc

$$E=\sum_j\frac{(\vec{p}_j)^2}{2m}+\text{interakcie}$$

↓ párové interakcie

závisia iba od veľkosti vzdialenosti častíc (z rotačnej sym.)

párové interakcie

rotačná symetria

$$E=\sum_{j=1}^{N}\frac{(\vec{p}_j)^2}{2m}+\underbrace{\sum_{i=1}^{N}\sum_{j=1}^{i-1}}_{\sum_{i,j;\,j<i}}U(\vec{x}_i,\vec{x}_j)=\sum_{j=1}^{N}\frac{(\vec{p}_j)^2}{2m}+\sum_{i=1}^{N}\sum_{j=1}^{i-1}U(|\vec{x}_i-\vec{x}_j|)$$

ako predtým

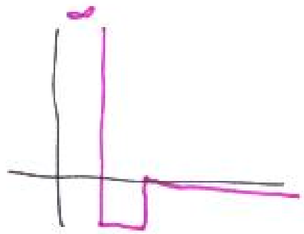
$$Z=\frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}}\int\left(\prod_{j=1}^{N}d^3x_j\,\boxed{d^3p_j\right)e^{-\beta\sum_{j=1}^{N}\frac{(\vec{p}_j)^2}{2m}}}\,e^{-\beta\sum_{j<i}U(|\vec{x}_i-\vec{x}_j|)}=\frac{1}{N!}\left[Z_{1,\text{ideál}}\right]^N\frac{1}{V^N}\int\prod_j d^3x_j\,e^{-\beta\sum_{j<i}U}$$

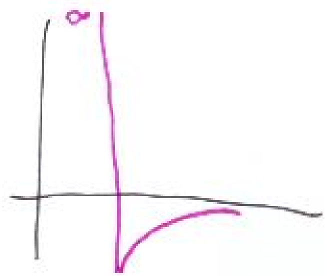
ako vyzerá realistický potenciál U?

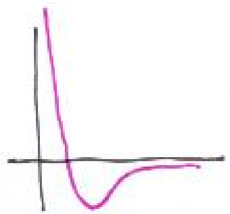
↳ veľké vzdialenosti → takmer nič

↳ na malých vzdialenostiach → slabé priťahovanie

↳ na veľmi malých vzdialenostiach → veľmi silné odpudzovanie







$$U=4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right]$$

• čo potrebujeme?

$$\beta \cdot U \ll 1$$

$$\int \Big(\prod_j d^3x_j\Big) e^{-\beta \sum_{j<i} U(|\vec{x}_i - \vec{x}_j|)} = (\beta \to 0) = \int \Big(\prod_j d^3x_j\Big)\Big(1 - \beta \sum_{j<i} U(|\vec{x}_i - \vec{x}_j|)\Big) =$$

počet dvojíc · integrále pre jednu dvojicu · zmena súradníc do ŤS

$$= V^N - \frac{N(N-1)}{2} \int d^3x_1 d^3x_2 \, \beta U(|\vec{x}_1 - \vec{x}_2|) \int \Big(\prod_{j=3}^{N} d^3x_j\Big) = V^N - V^{N-2}\frac{N(N-1)}{2}\beta \underbrace{\int d^3R}_{V} \int d^3r \, U(\vec{r}) =$$

pre veľké N

$$= V^N\Big[1 + \frac{N^2}{V}\beta\underbrace{\Big(-\frac{1}{2}\int dr\, U(r)\Big)}_{\text{označenie „a"}}\Big] = V^N\Big[1 + \frac{N^2}{VkT}a\Big]$$

výsledok $\quad Z = \dfrac{1}{N!}\big[Z_{1,\text{ideál}}\big]^N \Big\{1 + \dfrac{N^2}{VkT}a\Big\}$

stavová rovnica

$$p = -\frac{\partial F}{\partial V}\Big|_T = -\frac{\partial}{\partial V}\Big(-\frac{1}{\beta}\log Z\Big)\Big|_\beta = +\frac{1}{\beta}\frac{\partial}{\partial V}\log Z = +\frac{1}{\beta}\Big[N\frac{\partial}{\partial V}\log Z_{1,\text{ideál}} + \frac{\partial}{\partial V}\underbrace{\log\Big(1 + \frac{N^2}{VkT}a\Big)}_{\approx \frac{N^2}{VkT}a}\Big] =$$

$$= \frac{1}{\beta}\frac{N}{V} + \cancel{\frac{1}{\beta}}\frac{N^2 a}{\cancel{kT}}\Big(-\frac{1}{V^2}\Big) \Rightarrow \boxed{p = \frac{kTN}{V} - \frac{N^2 a}{V^2}}$$

inak $\boxed{\frac{pV}{NRT} = 1 - a\frac{1}{RT}\frac{N}{V}}$

oprava úmerná hustote plynu

vo všeobecnosti

$$\frac{pV}{NRT} = 1 + \#\frac{N}{V} + \#\frac{N^2}{V^2} + \#\frac{N^3}{V} + \dots$$

ak
• sa povie $V \to V - bN$

$$\boxed{\left(p + \frac{aN^2}{V^2}\right)(V - bN) = NRT}$$