Kuchařka ke kanonickému souboru

1, $H(p,q)$ & fázový prostor

2, $Z_c(\beta, V, N) = \int d\Gamma_N \, e^{-\beta H(p,q)}$ $\qquad \frac{1}{N!}$? ... extenzivita F

3, $F(T,V,N) = -\frac{1}{\beta} \log Z_c(\beta, V, N) \Big/_{\beta = \frac{1}{k_B T}}$

4, termodynamika ...

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N} \Big| \ldots$$

4b, $U = \langle H \rangle = -\frac{\partial \log Z_c}{\partial \beta}$ & $\langle (\Delta H)^2 \rangle = \frac{\partial^2 \log Z_c}{\partial \beta^2}$

1, Dvouhladinový systém

$N \gg 1$ nezávislých částic, každá se může nacházet ve

$$|0\rangle \leftrightarrow \epsilon_0 = 0$$
$$|1\rangle \leftrightarrow \epsilon_1 = \epsilon$$

a, $S(T,V,N)$

b, $C(T)$

$Z_c = \sum_{\text{stavy}} e^{-\beta H}$ $\qquad H = \sum_{i=1}^{N} H_1(i)$ $\qquad H_1 = |0\rangle 0 \langle 0| + |1\rangle \epsilon \langle 1|$

stavy $\updownarrow$ $\{n_1, \ldots, n_N\}$ $\qquad n_i \begin{smallmatrix} \nearrow 0 \\ \searrow 1 \end{smallmatrix}$

$$e^{-\beta H} = \prod_i e^{\beta H_1(i)}$$

$$\sum_{\text{stavy}} = \sum_{i=1}^{N} \sum_{j=0}^{1} \qquad \boxed{Z_c = \prod_{i=1}^{N} Z_1 = (Z_1)^N}$$

$$\sum_{i=1}^{2} \sum_{j_i=0}^{1} = e^{-\beta(0+0)} + e^{-\beta(\epsilon+0)} + e^{-\beta(0+\epsilon)} + e^{-\beta(\epsilon+\epsilon)}$$

$$= e^{-\beta 0}\left(e^{-\beta 0} + e^{-\beta\epsilon}\right) + e^{-\beta\epsilon}\left(e^{-\beta 0} + e^{-\beta \epsilon}\right)$$

$$= \underbrace{\left(e^{-\beta 0} + e^{-\beta\epsilon}\right)}_{Z_{i=2}} \underbrace{\left(e^{-\beta 0} + e^{-\beta\epsilon}\right)}_{Z_{i=1}}$$

• *faktorizace partiční funkce*

pro nezávislé skupiny volnosti je $Z_c = \prod_i Z_i$

$$Z_1 = \sum_{\substack{1\text{-částic.} \\ \text{stavy}}} e^{-\beta H} = e^{-\beta 0} + e^{-\beta\epsilon} = 1 + e^{-\beta\epsilon}$$

$$Z_c = (1+e^{-\beta\epsilon})^N \Rightarrow F(\beta, V, N) = -k_B \log Z_c = -N k_B \log(1+e^{-\beta\epsilon})$$

$$U = \langle H \rangle = -\frac{\partial}{\partial\beta}\log Z_c = -N\frac{\partial}{\partial\beta}\log(1+e^{-\beta\epsilon})$$

$0 \cdot p(0) + \epsilon\, p(\epsilon)$

$$= -\frac{N}{1+e^{-\beta\epsilon}} \cdot (-\epsilon e^{-\beta\epsilon}) = N\frac{\epsilon e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}} = N\epsilon\, p(\epsilon)$$

$$\langle 1 | \frac{1}{Z_c} e^{-\beta H} | 1 \rangle = \frac{e^{-\beta\epsilon}}{1+e^{-\beta\epsilon}}$$

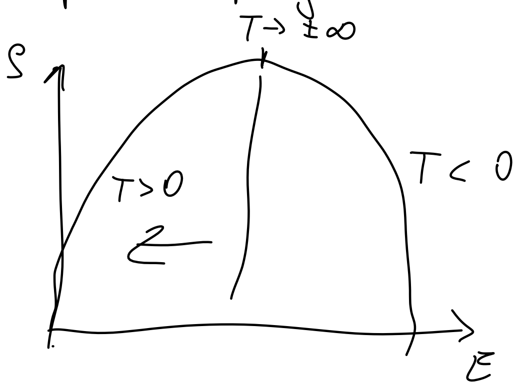
mikro

$$E = \frac{N\epsilon}{1+e^{\epsilon/k_BT}}$$

$C = \frac{\partial U}{\partial T} = \dots$ Schottky

• záporné teploty:

$$\frac{1}{T} = \frac{\partial S}{\partial E}$$



rezervoár ↔ nekonečný systém

$T > 0$!

Ideální plyn kanonicky

$$\cdot\ H = \sum_{i=1}^N H_1 = \sum_{i=1}^N \frac{\vec{p}_i^{\,2}}{2m}$$

$$\prod_j e^{-\beta\frac{p_j^2}{2m}}$$

$$Z_c = \int d\tau_N\, e^{-\beta H} = \frac{1}{N!}\int \prod_{i=1}^N \frac{d^3p_i\, d^3q_i}{h^3}\, e^{-\beta\sum_j \frac{p_j^2}{2m}} = \frac{1}{N!}\left(\int \frac{d^3p\, d^3q}{h^3} e^{-\beta\frac{p^2}{2m}}\right)^N$$

$$\Rightarrow Z_c = \frac{1}{N!}(Z_1)^N$$

↑ faktorizace partiční funkce

$$E = \sum_{i=1}^{3N}\frac{p_i^2}{2m} + \sum_{i<j}\phi(q_i, q_j)$$

$$Z_1 = \frac{1}{h^3}\int d^3q\, d^3p\, e^{-\beta\frac{p^2}{2m}} = \frac{V}{h^3}\int d^3p\, e^{-\beta\frac{p^2}{2m}} = \Big/ \text{sfer. współrzędne} \Big/$$

($\int d^3q \to V$, $\quad p^2 = p_x^2 + p_y^2 + p_z^2$)

$$= \frac{4\pi V}{h^3}\int_0^\infty dp\, p^2 e^{-\beta\frac{p^2}{2m}} = \Big/ \; p\sqrt{\frac{\beta}{2m}} = x, \quad dp = dx\sqrt{\frac{2m}{\beta}} \; \Big/$$

$$= \frac{4\pi V}{h^3}\sqrt{\frac{2m}{\beta}}^{\,3}\int_0^\infty dx\, x^2 e^{-x^2}$$

$$Z_1 = \frac{V}{h^3}\underbrace{\left(\int_{-\infty}^{\infty} dp_i\, e^{-\frac{\beta}{2m}p_i^2}\right)^3}_{\sqrt{\frac{2m\pi}{\beta}}} = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2} = V\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}$$

$$Z_c = \frac{1}{N!}(Z_1)^N = \frac{1}{N!}V^N\left(\frac{2\pi m}{h^2\beta}\right)^{\frac{3N}{2}}$$

$(k_BT)^{3/2}$ //

$$\Rightarrow F = -k_BT\log Z_c = -Nk_BT\log\left[V\beta^{-3/2}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right] + \log N!$$

$\log N! = N\log N - N$

$$= -Nk_BT\log\left(T^{3/2}\left(\frac{V}{N}\right)\right)\underbrace{-\frac{3}{2}Nk_B\log\left(\frac{2\pi m k_B}{h^2}\right) - N}_{Nf_0}$$

$$\boxed{F(T,V,N) = -Nk_BT\log\left(T^{3/2}VN^{-1}\right) + NTf_0}$$

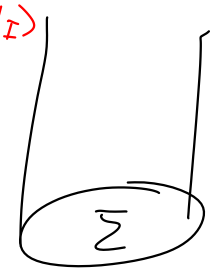
$w(|\vec{v}| = v) \sim e^{-\alpha v^2}$ ($\leftarrow \varepsilon_k$)

C_v: $F(T,V,N)$ wł. f_0 w mikrokanon. formalizmu

- $S_{\mu}(T,V,N)$ vs. $S_c(T,V,N)$

Ideální plyn v grav. poli

$E = \langle H \rangle = U + \langle H_I \rangle$



$$H = \sum_i H_1(i) \qquad H_1 = \frac{p^2}{2m} + \overset{F}{mg}z = \frac{p^2}{2m} + Fz$$

$$= H_0 + H_I$$

$$\Sigma = \int dx\,dy$$

$$Z_c = \frac{1}{N!}\left(Z_1\right)^N \qquad U = \langle H_0 \rangle$$

$$Z_1 = \frac{1}{h^3}\int d^3p\,d^3q\; e^{-\beta H_1} = \Sigma\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\int_0^\infty dz\, e^{-\beta m g z}$$

$\left(\sqrt{2\pi m k_B T} = \lambda_T \;\dots\right.$ termální vlnová délka $\left.\right)$

$$= \Sigma\left(\frac{2\pi m}{h^2\beta}\right)^{3/2}\frac{e^{-\beta m g z}}{\beta m g}\Bigg|_\infty^0 = \underset{\sim N}{\Sigma}\left(\frac{2\pi m}{h^2}\right)^{3/2}\beta^{-5/2}\frac{1}{mg} = Z_1$$

$N\log N - N$

$$\Rightarrow F = -\frac{1}{\beta}\log Z_c = -\frac{N}{\beta}\log Z_1 + \frac{1}{\beta}\log N!$$

$$F = -\frac{N}{\beta}\log\left(\frac{\Sigma}{N}\beta^{-5/2}\right) - \frac{N}{\beta}\log\left[\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{1}{mg}\right] - \beta N$$

$$F(T,\Sigma,N) = -Nk_BT\log\left(T^{5/2}\frac{\Sigma}{N}\right) - Nk_BT\log\left[\frac{k_B^{5/2}}{mg}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right] - k_BTN$$

$$w = \frac{1}{Z_c}\,e^{-\beta H_0 - \beta m g z}$$

$$G(T,\Sigma,\overset{F}{mg},N)$$

$$Z_c = \int d\Gamma_N\; e^{-\beta H_0 - \beta m g z}$$

↓

Legendre v TD potenciálu

$$S(U,V,N) \to S\left[\frac{1}{T}\right]\left(\frac{1}{T}, V, N\right) \qquad \text{pro } H = H_0 = \frac{p^2}{2m}$$

$V \downarrow x, y, z$

$$\searrow\; S\left[\frac{1}{T}, \frac{F_z}{T}\right]\left(\frac{1}{T}, \frac{F_z}{T}, y, x, N\right)$$

$$\langle z \rangle = \int dz\, z\, w = -\frac{1}{\beta m}\frac{\partial}{\partial g}\log Z_1$$

Tepelná kapacita

$$C_{\Sigma,N} = T\left(\frac{\partial S}{\partial T}\right)_{\Sigma,N} = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_{\Sigma,N}$$

$$F(T,\Sigma,N) = -Nk_BT\log\left(T^{5/2}\frac{\Sigma}{N}\right) - Nk_BT\log\left[\frac{k_B^{5/2}}{mg}\left(\frac{2\pi m}{h^2}\right)^{3/2}\right] - k_BTN$$

$$F \simeq -Nk_BT\log T^{5/2} \qquad \frac{\partial^2}{\partial T^2} = 0$$

$$\frac{\partial F}{\partial T} = -Nk_B\log T^{5/2} - \frac{5}{2}Nk_B\frac{T}{T} \qquad E = \langle H\rangle = \frac{5}{2}Nk_BT$$

$$\frac{\partial^2 F}{\partial T^2} = -\frac{5}{2}Nk_B\frac{1}{T} \Rightarrow C_\Sigma = \frac{5}{2}Nk_B = \frac{3}{2}Nk_B + \frac{2}{2}Nk_B$$

(kin. energie) (grav. pole)

C_V vs. C_p # kvadratických st. volnosti! $T\nearrow$ $\langle z\rangle\nearrow$

$$C_V = \frac{f}{2}k_B$$

$\langle z\rangle$:

$$\Sigma\left(\frac{2\pi m}{h^2}\right)^{3/2}\beta^{-5/2}\frac{1}{mg} = Z_1$$

$$\langle z\rangle = \int dz\, z\, w = -\frac{1}{\beta m}\frac{\partial}{\partial g}\log Z_1$$

$$\log Z_1 = -\log g + \log\left(\Sigma\left(\frac{2\pi m}{h^2}\right)^{3/2}\beta^{-5/2}\frac{1}{m}\right)$$

$$\Rightarrow -\frac{1}{\beta m}\frac{\partial}{\partial g}\log Z_1 = \frac{1}{\beta m g} \Rightarrow \langle z\rangle = \frac{k_BT}{mg}$$

$\nearrow$ s T roste lineárně

$$U = \langle H_0\rangle = \langle H\rangle - Nmg\langle z\rangle = -\frac{\partial\log Z_c}{\partial\beta} - Nk_BT$$

$$H = H_0 + mgz$$

$$\frac{\partial\log Z_c}{\partial\beta} \downarrow \frac{5}{2}Nk_BT$$