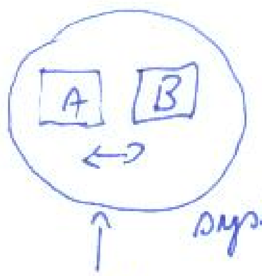
ENTROPIA v mikrokanonickom rozdelení

$$S(E) = k \log \Omega(E)$$

↳ počet mikrostavov s energiou E (fixovaná)



S_A, S_B

$\Omega_A \quad \Omega_B$

$N_A \quad N_B$

celková energia $E = E_A + E_B$

$N = N_A + N_B$

$$\Omega(E) = \sum_{E_\alpha}{}' \Omega_A(E_\alpha)\,\Omega_B(E - E_\alpha) \;\stackrel{\cdot}{=}$$

↓ dominovaná $E_{\alpha max}$ – maximalizuje súčin

$$\stackrel{\cdot}{=} \sum_{E_\alpha}{}' e^{\frac{1}{k}\left[S_A(E_\alpha) + S_B(E - E_\alpha)\right]}$$

$$s(E_\alpha) = N s(\varepsilon) = N\left[s(\varepsilon_{max}) + s'(\varepsilon_{max})(\varepsilon - \varepsilon_{max}) + \frac{1}{2} s''(\varepsilon_{max})(\varepsilon - \varepsilon_{max})^2\right]$$

($s'(\varepsilon_{max}) = 0$)

$$\varepsilon = \frac{E_\alpha}{N}$$

$$= \sum_{\varepsilon}{}' e^{\frac{N}{k}\left[s(\varepsilon_{max}) + \frac{1}{2} s''(\varepsilon - \varepsilon_{max})^2\right]} = e^{\frac{1}{k} s(E_{\alpha max})} \sum_{\varepsilon}{}' e^{\frac{N}{k}\frac{1}{2} s''(\varepsilon - \varepsilon_{max})^2}$$

$N\, d\varepsilon = \Delta E$

$$N \int d\varepsilon\, e^{+\frac{N}{k}\frac{1}{2} s''(\varepsilon_{max})(\varepsilon - \varepsilon_{max})^2}$$

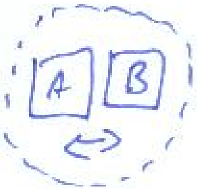
$s''(\varepsilon_{max}) < 0$

$\sim \sqrt{N}$

$$\stackrel{\cdot}{=} e^{\frac{1}{k} s(E_{\alpha max})} \sqrt{N}\, C$$

$$\log \Omega(E) = \frac{1}{k} s(E_{\alpha max}) + \frac{1}{2}\log N$$

$\frac{1}{k} s(E_{\alpha max}) \sim 10^{23}$, $\frac{1}{2}\log N \sim 23$



- energia sa prerozdelí medzi A a B tak, aby celkový počet mikrostavov bol maximálny $\Leftrightarrow$ maximalizuje celková entropia $(N \to \infty)$ (čísla N vs. $\log N$)

- systém A+B je v makrostave (rovnovážnom) ktorému zodpovedá najviac mikrostavov

- maximalizujeme $\Omega_A(E_\alpha)\Omega_B(E-E_\alpha) \Leftrightarrow S_A(E_\alpha)+S_B(E-E_\alpha)$

$$\left.\frac{\partial S_A}{\partial x}\right|_{x=E_\alpha} - \left.\frac{\partial S_B}{\partial x}\right|_{x=E-E_\alpha} = 0 \quad \text{podmienka pre } E_\alpha$$

$$\underbrace{\left.\frac{\partial S_A}{\partial x}\right|_{x=E_\alpha}}_{\text{iba } A} = \underbrace{\left.\frac{\partial S_B}{\partial x}\right|_{x=E-E_\alpha}}_{\text{iba } B} = \frac{1}{T}$$

- preto $\frac{\partial S}{\partial E}$ musí súvisieť s teplotou !!!

$$\frac{\partial S}{\partial E} = f(T) \rightarrow \text{klesajúca fcia teploty}$$

$S_{AB} = S_A(E_A) + S_B(E_B)$

$$0 < \delta S_{AB} = \frac{\partial S_A}{\partial E_A}\delta E_A + \frac{\partial S_B}{\partial E_B}\delta E_B = \delta E_A \underbrace{\left(\frac{\partial S_A}{\partial E_A} - \frac{\partial S_B}{\partial E_B}\right)}_{<0}$$

$\delta E_B = -\delta E_A$ $\left.\begin{matrix}\delta E_A < 0 \\ \delta E_B > 0\end{matrix}\right\}$ energia δE_A prešla z E_A do E_B, zodpovedajúca zmena entropie A+B je δS_{AB}

A | B · dovolím meniť aj objem

$\delta V_A \geq 0$

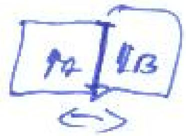
$\delta V_B \leq 0$

$\delta V_A = -\delta V_B$

$$0 < \delta S_{AB} = \frac{\partial S_A}{\partial V_A}\delta V_A + \frac{\partial S_B}{\partial V_B}\delta V_B = \delta V_A \left(\frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}\right)$$

↳ súvisí s tlakom

$$\boxed{\frac{\partial S}{\partial V} = \frac{p}{T}}$$



- tepelná kapacita

$$C = \frac{\partial E}{\partial T} \Rightarrow \partial E = C \cdot \partial T$$

↑ definícia tepelnej kapacity

↓

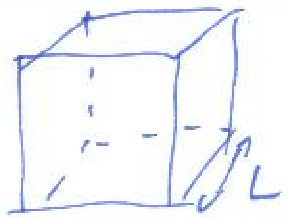
Ako sa dobre meria

$$\frac{1}{T} = \frac{\partial S}{\partial E} \quad / \cdot \frac{\partial}{\partial E}$$

$$-\frac{1}{T^2}\frac{\partial T}{\partial E} = \boxed{\frac{\partial^2 S}{\partial E^2} = -\frac{1}{T^2 C}} \Rightarrow \boxed{C > 0}$$

ENTROPIA PRE PLYN NEINTERAGUJÚCICH ČASTÍC

• QM :



$V = L^3$

jednočasticové stavy majú energiu

$$\varepsilon_{n_1 n_2 n_3} = \frac{\pi^2 \hbar^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right)$$

N častíc
E celková energia } $\Omega(E)$ i jednoduchšie $\varphi(\varepsilon)$ – # stavov jednej častice s energiou ε alebo menšou

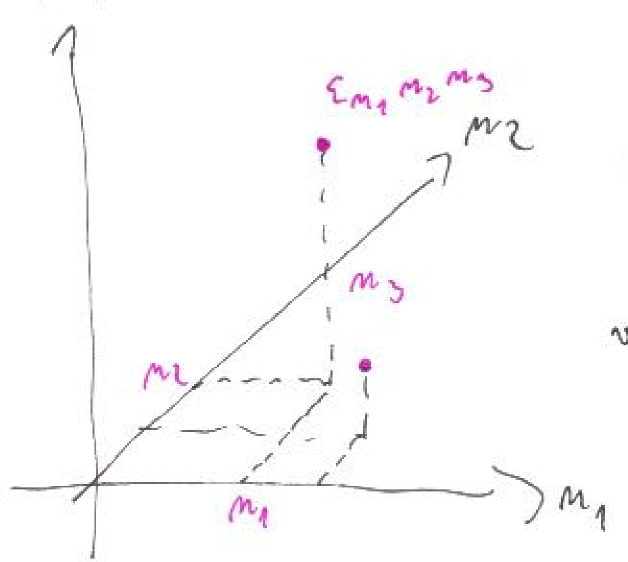
$$\Omega(E) = \frac{1}{N!}\left(\varphi'(\bar{\varepsilon}) \cdot \delta\bar{\varepsilon}\right)^N$$

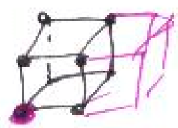
N → neinteragujúce častice.

$$\bar{\varepsilon} = \frac{E}{N}$$

$N!$ – GIBBS ↓ nerozlíšiteľné častice (permutácie častíc nedávajú nové stavy)

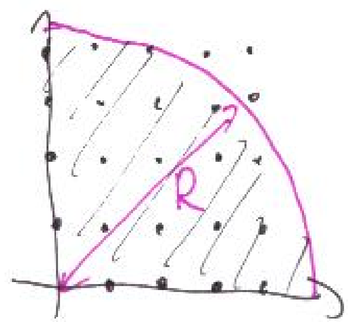
$\varphi'(\bar{\varepsilon}) \cdot \delta\bar{\varepsilon}$ – # stavov v intervale $(\bar{\varepsilon}, \bar{\varepsilon} + \delta\bar{\varepsilon})$ jednočasticových stavov





← jednotkový objem

v 2D



$$R = \sqrt{\frac{2mL^2\varepsilon}{\pi^2\hbar^2}}$$

iba kladné hodnoty n_1, n_2, n_3

$$V = \frac{1}{8}\frac{4}{3}\pi R^3 \Rightarrow \varphi(\varepsilon) = \frac{1}{6}\pi\left(\frac{2mL^2}{\pi^2\hbar^2}\right)^{3/2}\varepsilon^{3/2}$$

5/10/20 (5)

z toho $\Omega(E) = \frac{1}{N!}\left(K^{\frac{3}{2}}\right)^N \left[\frac{3}{2}\left(\frac{E}{N}\right)^{\frac{1}{2}}\right]^N (\delta E)^N = \frac{1}{N!} K^{\frac{3N}{2}} V^N \left(\frac{E}{N}\right)^{N/2} (\delta \Sigma)^N$

$\left[(L^2)^{\frac{3}{2}}\right]^N = (L^3)^N = V^N$

$S(E) = k \log \Omega(E) = k\left[-\log N! + \frac{3N}{2}\log K + N\log V + \frac{N}{2}\log\frac{E}{N} + N\log\delta\Sigma\right]$

STIRLING: $N - N\log N$

$\delta\Sigma = \alpha\frac{E}{N}$ ← konštanta

$= k\left[\frac{N}{2}\log\frac{E}{N} + N\log\frac{E}{N} + N\log\alpha + N\log\frac{V}{N} + kN + \frac{3N}{2}\log K\right] =$

$S(E) = k\,\frac{3}{2}N\log\frac{E}{N} + kN\log\frac{V}{N} + N\cdot A$

v rozdieloch entropie A vypadne (g v derivácii)

$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{3}{2}Nk\,\frac{1}{\frac{E}{N}}\frac{1}{N} \Rightarrow E = \frac{3}{2}NkT$

$\frac{p}{T} = \frac{\partial S}{\partial V} = Nk\,\frac{1}{\frac{V}{N}}\frac{1}{N} \Rightarrow pV = NkT$

chcem aby $N \to 2N$, $V \to 2V$ } $S \to 2S$

to platí vďaka $1/N!$ v definícii $\Omega(E)$