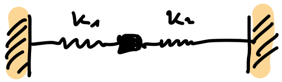
Termodinamika

Enačba stanja

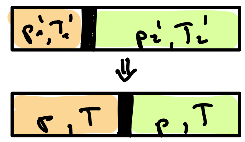
- vedno v ravnovesju
- Kaj je ravnovesje?

Mehanično ravnovesje



Izmenjava dela

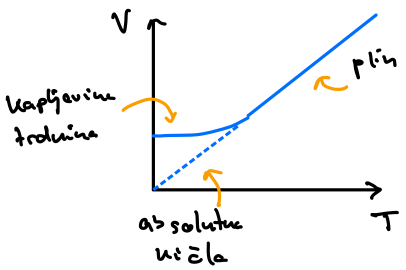
Termodinamično ravnovesje

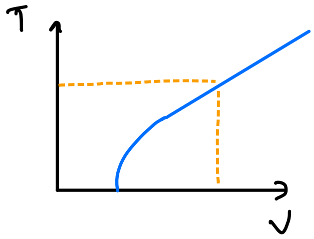


Izmenjava dela in toplote

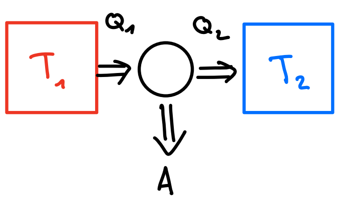
Temperatura

① Operativna definicija: plinski termometer





② Carnotov toplotni stroj



$$\frac{Q_1}{T_1} = \frac{|Q_2|}{T_2} \Longrightarrow \frac{T_2}{T_1} = \frac{|Q_2|}{Q_1}$$

Termodinamične spremenljivke

p, V, T

F, x, T — vzmet

γ, S, T — milnično opno

U, e, T — baterija

$\vec{H}, \vec{p}_m, T$ — magnet

$\hookrightarrow \vec{p}_m = V\vec{M}$

posplošene sile — intenzivne količine: $p = p_1 = p_2$

posplošen odziv — ekstenzivne količine: $V = V_1 + V_2$

v ravnovesju

Delo

$dA = (\text{int kol}) \cdot d(\text{eks. kol.})$

$$dA = -p\,dV = F\,dx = U\,de = \gamma\,dS = H\,d(\mu_0 p_m) = \mu_0 V \vec{H}\,d\vec{M}$$

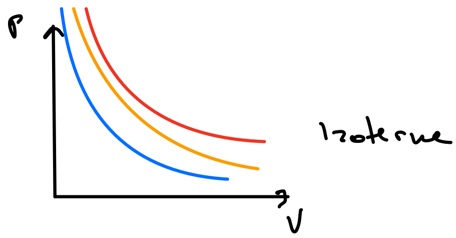
Idealni plin

Boylov zakon: $pV = \text{konst.}$ če je $T = \text{konst.}$

Gay-Lussacov zakon: $\frac{V}{T} = \text{konst.}$ če je $p = \text{konst.}$

$$\left.\begin{aligned} &\frac{pV}{T} = \text{konst.} \\ &\propto m \\ &\propto \frac{m}{M} \end{aligned}\right\} \quad pV = nRT$$

$\uparrow$ Integralna oblika enačbe stanja



Diferencialna oblika enačbe stanja

$$\frac{dV}{V} = \beta\, dT - \chi_T\, dp$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{p=\text{konst}} \qquad \chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{T=\text{konst}}$$

Koef. prost. razteska   Izotermna stisljivost

$$V(p,T) \rightarrow dV = \frac{\partial V}{\partial p} dp + \frac{\partial V}{\partial T} dT$$

Diferencialna oblika enačbe stanja idealnega plina

$$\frac{pV}{T} = \text{konst.}$$

$$d\left(\frac{pV}{T}\right) = d(\text{konst}) = 0$$

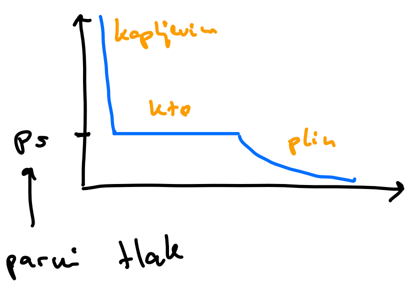
$$\frac{dp\, V}{T} + \frac{p\, dV}{T} - \frac{pV}{T^2} dT = 0 \qquad /: \frac{pV}{T}$$

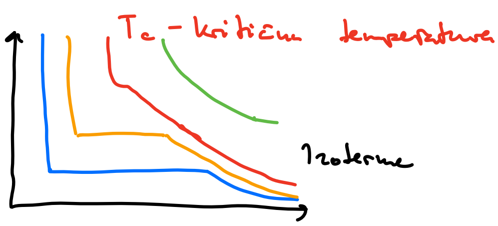
$$\frac{dp}{p} + \frac{dV}{V} - \frac{dT}{T} = 0$$

$$\frac{dV}{V} = \underbrace{\frac{1}{T}}_{\beta} dT - \underbrace{\frac{1}{p}}_{\chi_T} dp$$

za idealni plin

Realni plin



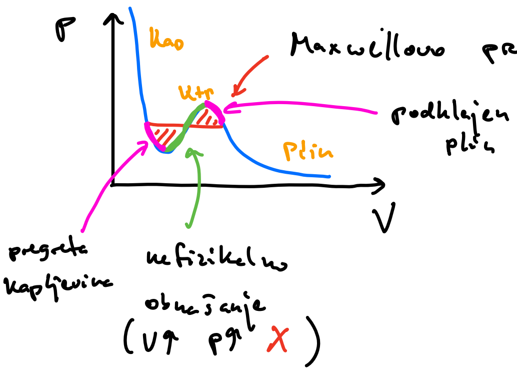


Model: Van der Waalsova enačba

$$\boxed{\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT}$$

V_m = kilomolska prostornina $\qquad V_m = \frac{V}{n} = \frac{VM}{m}$

a ... opisuje privlak med molekulami
b ... opisuje lastno prostornino molekul



Maxwellovo pravilo: če dam vodoravno črto tako, da sta površini enaki, dobim pravo

metastabilno stanje

Magnetni sistemi

Paramagnetni sistemi: Curiejev zakon (visoke temperature)

$$M = \underbrace{\frac{C}{T}}_{\chi} H$$

magnetizacija

Superprevodniki: Meissnerjev pojav $\vec{B} = 0$

$$\vec{B} = \mu_0 (\underbrace{\vec{H} + \vec{M}}_{= 0}) \Rightarrow \vec{M} = -\vec{H}$$

$\chi = -1$ idealni diamagnet

Sevanje črnega telesa

$$p = \frac{4}{3} \frac{\sigma T^4}{c}$$

σ ... Stefanova konst.
c ... hitrost svetlobe

$$dp = \ldots dT + 0 \cdot dV$$

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \rightarrow \chi_T = -\frac{1}{T}\left(\frac{\partial V}{\partial p}\right)_T \rightarrow \infty$$

Energijski zakon

- temeljni zakon
- izkustveno spoznanje
- povezava med zač. in konč. stanjem
- kalorimetrija

$U_1' + U_2' = U_1 + U_2$ $\qquad U = U(T, V)$

$\Delta U = \Delta E = Q + W$ $\qquad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$dU = dQ + dW$$

Pomembno je najprej def. sistem.

Energijski zakon za PVT sistem

- Izohorne spremembe
  - $dV = 0 \Rightarrow dW = 0$
  - $dU = dQ$
  - $dU = mc_V\, dT$
  - $c_V = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_V$

- Izobarne spremembe
  - $dp = 0$
  - $dU = dQ - p\,dV - V\,\cancel{dp}^{\,0}$
  - $\quad = dQ - d(pV)$
  - $dU + d(pV) = dQ$ f. stanja
  - $U + pV = H$ entalpija
  - $dH = dQ$
  - $dH = mc_p\, dT$
  - $c_p = \frac{1}{m}\left(\frac{\partial H}{\partial T}\right)_p$

Zgled

Sprememba U in H pri izparevanju 1 kg vode

$Q = m q_i$ $\qquad p = \text{konst}$

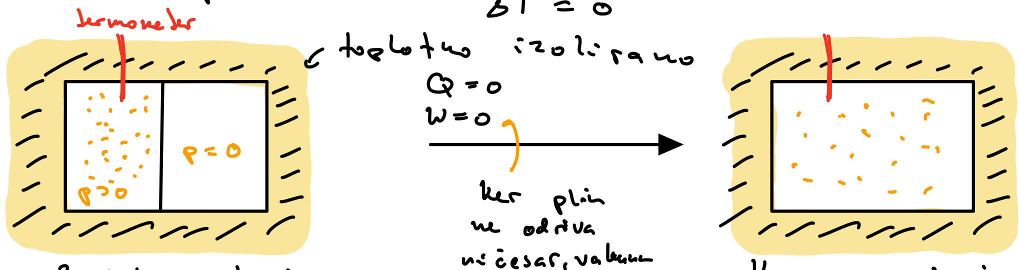
$\Delta U = Q + W = Q - p\Delta V = m q_i - p\,(V_{plin} - \underbrace{V_{tek}}_{\text{zelo majhno v primerjavi}}) = m q_i - p V_{plin}$

$= 2{,}09$ MJ

↳ $\Delta H = \Delta Q$ pri $p = \text{konst}$

$= 2{,}26$ MJ

Hirnov poskus



W ... delo A
U ... notranja en. W_n

$$U' = U$$

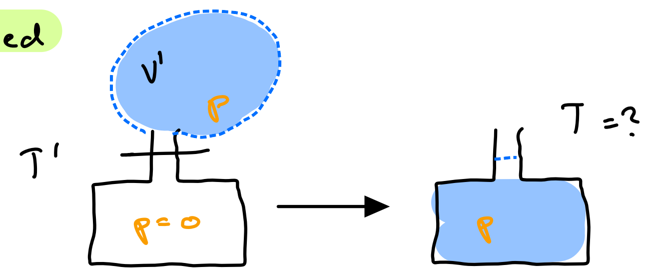
$$\Delta U = Q + W = 0$$

- energijski zakon $\Delta U = 0$
- $U = U(T, V)$
- $\Delta U = \left(\frac{\partial U}{\partial T}\right)_V \overset{=0}{\Delta T} + \overset{=0}{\left(\frac{\partial U}{\partial V}\right)_T} \overset{\neq 0}{\Delta V} = 0$
- eksperimentalno $\Delta T = 0$

Nauk $\left(\frac{\partial U}{\partial V}\right)_T = 0$ Velja za idealni primer

Notranja energija ni odvisna od temperature

Zgled



Sistem: plin, ki konča v posodi

$W = pV'$ ker zunanji plin potisne plin

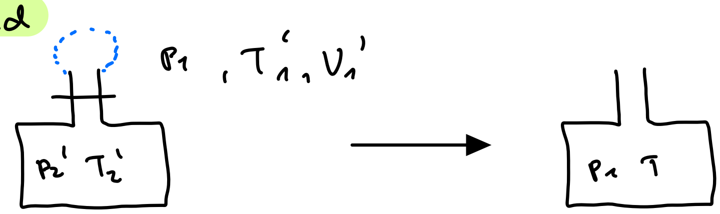
$Q = 0$ hiter proces

$\Delta U = W + Q$

$$mc_v(T - T') = pV' = \frac{mRT'}{M}$$

$$T = T'\left(1 + \frac{R}{c_v M}\right) = \underbrace{\frac{c_p}{c_v}}_{\chi} T'$$

Zgled



Enačba stanja

$$p_1 V_1' = \frac{m_1 R T_1'}{M}$$

$$p_2' V = \frac{m_2 R T_2'}{M}$$

začetno stanje

$$p_1 V = \frac{(m_1 + m_2) R T}{M}$$

končno stanje

Energijski zakon

$$\Delta U = W + Q$$

$$m_1 c_v (T - T_1') + m_2 c_v (T - T_2') = p_1 V_1' + 0$$

$$(m_1 + m_2) T - m_1 T_1' - m_2 T_2' = \frac{p_1 V_1'}{c_v}$$

$$\frac{p_1 V}{R/M} - m_1 T_1' - \frac{p_2' V}{R/M} = \frac{p_1 V_1'}{c_v}$$

$$m_1 = \frac{1}{T_1'}\left(\frac{p_1 V}{R/M} - \frac{p_2' V}{R/M} - \frac{p_1 V_1'}{c_v}\right)$$

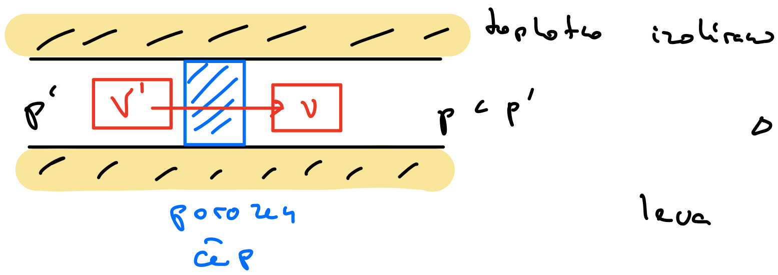
$$T = \frac{p_1 V}{(m_1+m_2)\, R/M} = \frac{p_1 \cancel{V} \,/\, R/M}{\frac{1}{T_1'}\left(\frac{p_1 \cancel{V}}{R/M} - \frac{p_2' \cancel{V}}{R/M} - \frac{p_1 \cancel{V_1'} R}{c_v\, M}\right) + \frac{p_2' \cancel{V}}{T_2'\, R/M}}$$

$$= \frac{T_1'}{1 - \frac{R/M}{c_v} - \frac{p_2'}{p_1} + \frac{T_1'}{T_2'}\frac{p_2'}{p_1}}$$

$$T = \frac{T_1'}{1 - \frac{R/M}{c_v} + \left(\frac{T_1'}{T_2} - 1\right)\frac{p_2'}{p_1}}$$

Nekaj je narobe

Joule - Kelvinov proces



$$\Delta U = W + Q$$

leva $W_L = -p'(0 - V') = p'V'$

desna $W_D = -p(V - 0) = -pV$

$$U - U' = p'V' - pV$$

$$\underbrace{U' + p'V'}_{H'} = \underbrace{U + pV}_{H}$$

entalpija se ohranja pri Joule-Kelvinovem procesu

Entropija

Hirnov poskus

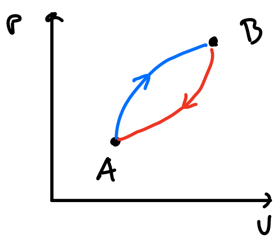
$U' = U$

Obstajati mora neka količina, ki loči začetno stanje od končnega: entropija

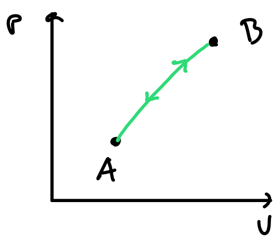
Ireverzibilne spremembe

(ne moremo priti nazaj v zač. stanje preko istih vmesnih stanj)

- trenje
- histereza (stanje odvisno od zgodovine)
- ireverzibilne fazne spremembe (zmrzovanje podhlajene taline)
- ireverzibilne kemijske spremembe (gorenje)
- transportni pojavi (difuzija snovi, toplote)



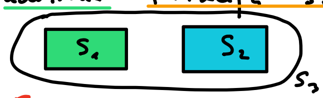
Ireverzibilna sprememba



Reverzibilna sprememba (počasno gretje/hlajenje)

Entropija

- aditivna funkcija stanja

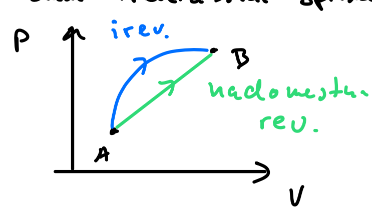


$S_3 = S_1 + S_2$

! entropija je odvisna od stanja, ne od poti do tega stanja

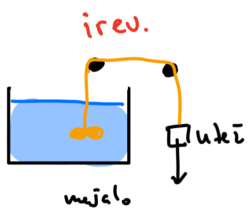
- $dS \geq \frac{dQ}{T}$ Entropijski zakon (irev. $>$, rev. $=$)

- reverzibilna sprememba $dS = \frac{dQ}{T}$
- ireverzibilna sprememba $dS > \frac{dQ}{T}$ (pove le spodnjo mejo)
- nadomestna reverzibilna sprememba, ki jo priredimo dani ireverzibilni spremembi imata skupno začetno in končno stanje



Zgled

Joulovo gretje

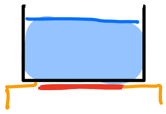


Energijski zakon $\Delta U = \underset{0}{Q} + W$

Entropijski zakon $\Delta S \geq \frac{Q}{T}$, $Q = 0$ $\quad \Delta S > 0$

$\Delta U = m c_v (T - T') = W \Rightarrow T = T' + \frac{W}{m c_v}$

nadomestna rev. $T' \xrightarrow{\text{rev.}} T$



grelec

$$Q = m c_v (T - T')$$
$$\Delta U = \underset{\neq 0}{Q} + \underset{= 0}{W}$$

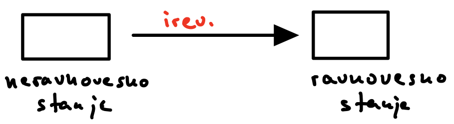
$$\Delta S = \frac{Q}{T} = \frac{m c_v (T - T')}{T} \qquad \text{če je } T \approx T'$$

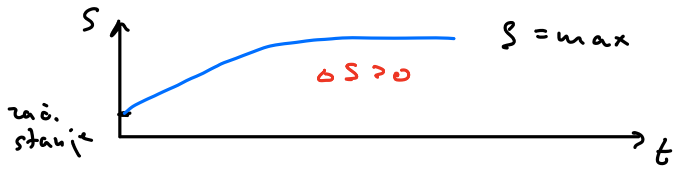
$$\Delta S = \int \frac{m c_v \, dT}{T} = m c_v \ln \frac{T}{T'} \qquad T \neq T'$$

Posledice entropijskega zakona

① Toplotno izoliran sistem $Q = 0$ $\quad \Delta S > 0$ (Hirnov poskus, vesolje)

② Vzpostavitev termodinamičnega ravnovesja

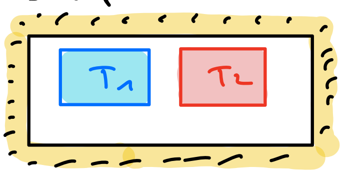




$S = max$ Pri toplotno izoliranem sistemu

entropija kot termodinamični potencial: ekstrem (maksimum določa rav. stanje)

③ Prenos toplote



telesi izolirani od okolice

$$\Delta S \geq 0$$
$$\Delta S_1 + \Delta S_2 \geq 0$$
$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} \geq 0 \qquad Q_1 = -Q_2$$
$$\frac{Q_1}{T_1} - \frac{Q_1}{T_2} \geq 0$$
$$Q_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geq 0$$

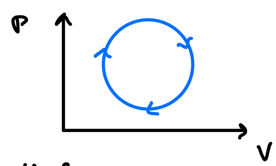
- $Q_1 > 0$ $\Downarrow$ $T_1 < T_2$ prvo telo prejme toploto
- $Q_1 < 0$ $\Downarrow$ $T_1 > T_2$ prvo telo odda toploto

Toplota prehaja iz toplejšega na hladnejše telo

④ Krožna sprememba

končno in začetno stanje sta enaki, zato

$$\left.\begin{aligned} \Delta U &= 0 \\ \Delta S &= 0 \end{aligned}\right\} \text{ zato ker sta } U, S \text{ funkciji stanja}$$



$$\Delta S = 0 \geq \frac{Q}{T} \geq \oint \frac{dQ}{T} \Longrightarrow \oint \frac{dQ}{T} \leq 0$$

⑤ Izotermna krožna sprememba

$T = \text{konst}$

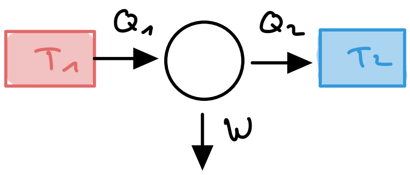
$\oint \frac{dQ}{T} = \frac{1}{T}\oint dQ \le 0 \quad / \cdot T$

$\oint Q \le 0$ Sistem toploto odda

$\Delta U = Q + W = 0$

$<0 \quad >0 \quad \Rightarrow W \ge 0$ Sistem vedno dobi delo

⑥ Carnotov toplotni stroj



Krožna sprememba: $\Delta S = 0$

$0 = \Delta S \ge \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = \frac{Q_1}{T_1} - \frac{|Q_2|}{T_2}$

$\frac{Q_1}{T_1} - \frac{|Q_2|}{T_2} \le 0$

$\frac{T_2}{T_1} \le \frac{|Q_2|}{Q_1}$

(Stirlingov toplotni stroj ima enak izkoristek kot Carnotov)

Izkoristek

$\eta = \frac{|W|}{Q_1} = 1 - \frac{|Q_2|}{Q_1} \le 1 - \frac{T_2}{T_1}$

$=$ pri carnotovem stroju

Entropija idealnega plina

$dU = dQ + dW = dQ - pdV$

$dS = \frac{dQ}{T}$

$dU = TdS - pdV$

$dS = \frac{dU}{T} + \frac{pdV}{T} \leftarrow$ Za idealni plin $dU = mc_v dT$, $\quad \frac{pV}{T} = \frac{mR}{M}$

$dS = mc_v \frac{dT}{T} + m\frac{R}{M}\frac{dV}{V}$

$(T', V') \longrightarrow (T, V)$

$\Delta S = mc_v \ln T/T' + m\frac{R}{M}\ln V/V'$

$S(T,V) = S(T',V') + mc_v \ln T/T' + m\frac{R}{M}\ln V/V'$

Hirnov poskus

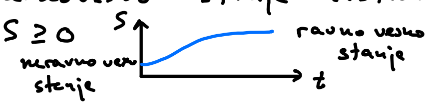
$T = T' \quad V > V'$

$S(T,V) = S(T',V') + \frac{mR}{M}\ln\frac{V}{V'} > S(T',V')$

Termodinamični potenciali

so količine, katerih ekstrem določa ravnovesno stanje sistema

- entropija : toplotno izoliran sistem : $\Delta S \geq 0$



- termostat : toplotni rezervoar

T termostat — Izmenjava toplote

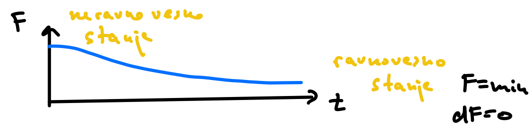
- prosta energija
  $F = U - TS$
- totalni dif F
  $dF = dU - TdS - SdT$
  $dU = dQ + dW$

$dF = dQ + dW - TdS - SdT$
$dS \geq \frac{dQ}{T}$ $\quad dQ \leq TdS$

$dF \leq TdS + dW - TdS - SdT$

$\boxed{dF \leq dW - SdT}$
rev. sprem.

- Termostat $\quad dT = 0$
  vzpostavljanje ravnovesja ne troje dela $dW = 0$
  $dF \leq 0$



- „prosta energija" : $\quad dT = 0$
  $dF \leq dW$
  $\Rightarrow$ F predstavlja zalogo energije, ki jo sistem lahko odda pri T=konst.

- Zgled 1 : Izparevanje vode pri 100°C
  $\Delta U = m(q_i - \frac{RT}{M})$
  $\Delta H = m q_i$
  $\Delta F = \Delta(U - TS) = \Delta U - T\Delta S - S\Delta T = m\left(q_i - \frac{RT}{M}\right) - T\frac{m q_i}{T} = -m\frac{RT}{M} = -0{,}17\ \mathrm{MJ}$ za 1kg

- Zgled 2 : F idealnega plina
  $U = m c_v T$
  $S = m c_v \ln\frac{T}{T'} + m\frac{R}{M}\ln\frac{V}{V'}$
  referenčno stanje

  $F = U - TS = m c_v T - m c_v T \ln\frac{T}{T'} - m\frac{R}{M}T\ln\frac{V}{V'}$
  $= m c_v T\left(1 - \ln\frac{T}{T'}\right) - m\frac{R}{M}T\ln\frac{V}{V'}$

Legendrova transformacija

Notranja energija $\quad dU = dQ + dW \quad$ za PVT sistem
$= TdS - pdV \quad$ rev. sprem.
$\Rightarrow U = U(S,V)$

Entalpija $\quad H = U + pV$
$dH = dU + pdV + Vdp \quad$ za PVT sistem
$= TdS - pdV + pdV + Vdp \quad$ rev. sprem.
$dH = TdS + Vdp$
$\Rightarrow H = H(S,p)$

Prosta energija $F = U - TS$

$dF = dU - TdS - SdT$

$dF = TdS - pdV - TdS - SdT$

$dF = -SdT - pdV$

$\Rightarrow F = F(T, V)$

za PVT sistem

rev. sprem.

Prosta entalpija $G = F + pV$

$dG = dF + pdV + Vdp$

$dG = -SdT - pdV + pdV + Vdp$

$dG = -SdT + Vdp$

$\Rightarrow G = G(T, p)$

$G = H - TS$

$dG = dH - dTS$

$dG = TdS + Vdp - TdS - SdT$

$dG = -SdT + Vdp$

$\Rightarrow G = G(T, p)$

Primer: Magnetni sistem

- $dU = TdS + \underbrace{V\mu_0 \mathcal{H}\, dM}_{\text{delo}}$

- $H = U - V\mu_0 \mathcal{H} M$

  $dH = dU - V\mu_0 \mathcal{H} dM - V\mu_0 M d\mathcal{H}$

  $dH = TdS - V\mu_0 M d\mathcal{H}$

- $F = U - TS$

  $\vdots$

  $dF = -SdT + V\mu_0 \mathcal{H} dM$

- $G = F - V\mu_0 \mathcal{H} M$

  $\vdots$

  $dG = -SdT - V\mu_0 M d\mathcal{H}$

Maxwellovi relaciji

F: $dF = -SdT - pdV$

$$\frac{\partial^2 F}{\partial T \partial V} = \frac{\partial^2 F}{\partial V \partial T}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial}{\partial T}(-p)$$

$$\parallel$$

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = \frac{\partial}{\partial V}(-S)$$

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$

1. Maxwellova relacija

dobimo iz enačbe stanja

$$\frac{dV}{V} = \beta dT - \chi_T dp$$

$dV = 0$

$$\frac{dp}{dT} = \frac{\beta}{\chi_T}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{\chi_T}}$$

G: $dG = -SdT + Vdp$

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p\, dT}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)_T = \frac{\partial}{\partial T} V$$

$$\parallel$$

$$\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right)_p = \frac{\partial}{\partial p}(-S)$$

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T}$$

2. Maxwellova relacija

$$\boxed{\left(\frac{\partial S}{\partial p}\right)_T = -\beta V}$$

Totalna diferenciala entropije

- $S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$dS = \frac{m c_v}{T} dT + \frac{\beta}{\chi_T} dV \quad (1)$$

$$dS = dQ/T = \frac{m c_v dT}{T}$$

$$\left(\frac{dS}{dT}\right)_V = \frac{m c_v}{T}$$

- $S = S(T, p)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$dS = \frac{m c_p}{T} dT - \beta V dp \quad (2)$$

- $S = S(p, V)$

$$dS = \left(\frac{\partial S}{\partial p}\right)_V dp + \left(\frac{\partial S}{\partial V}\right)_p dV$$

$$\frac{c_p}{c_v} (1) - (2)$$

$$(\kappa - 1)\, dS = \kappa \frac{\beta}{\chi_T} dV + \beta V dp$$

$$dS = \frac{\beta}{\kappa - 1}\left(\frac{\kappa}{\chi_T} dV + V dp\right) \quad (3)$$

- Enačba adiabate $dS = 0$

Iz (3) $\quad \frac{\kappa}{\chi_T} dV = - V dp$

$$\chi_S = \frac{\chi_T}{\kappa} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_S$$

adiabatna stisljivost

Zgled Termostat, Hg, $p \dots 0 \to 1000\,\text{bar}$, $m_{Hg} = 1\,\text{kg}$

$\Delta U = ?$

$$\Delta U = \overset{\neq 0}{Q} + W$$

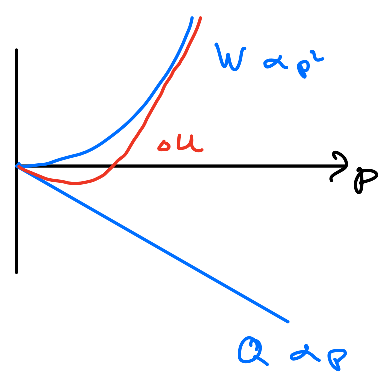
ker je Hg tek. in nestisljiva $V \neq V(p)$

$$Q = T\Delta S = T\int_0^p \left(\frac{\partial S}{\partial p}\right)_T dp = T\int_0^p -\beta V dp = -\beta V T p = -399\,\text{J}$$

$$W = -\int_0^p p\,dV = -\int_0^p p(-V\chi_T)\,dp \doteq V\chi_T \frac{p^2}{2} = 14\,\text{J}$$

iz enačbe stanja v dif. obliki

$$\Delta U = -385\,\text{J} < 0$$



Razlika specifičnih toplot

• Za idealen plin $c_p - c_v = \frac{R}{M}$; $U = m c_v T$; $H = m c_p T$

$$= U + pV = U + \frac{mR}{M}T$$
$$= m c_v T + \frac{mRT}{M}$$
$$\Rightarrow c_p - c_v = \frac{R}{M}$$

• Splošno

$$Q = T\Delta S = m c_v \Delta T \Rightarrow c_v = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_V \qquad c_p = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_p$$

$$S = S(T, V(p,T))$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \Big[\underbrace{\left(\frac{\partial V}{\partial T}\right)_p}_{\beta V} dT + \underbrace{\left(\frac{\partial V}{\partial p}\right)_T}_{-V\chi_T} dp \Big]$$

pri $p = \text{konst}$

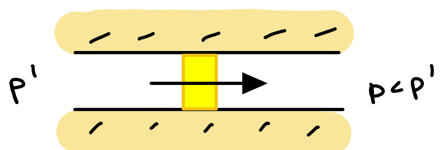
$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p dT \qquad /:dT$$

$$\left(\frac{dS}{dT}\right)_p = \left(\frac{dS}{dT}\right)_V + \frac{\beta}{\chi_T}\beta V \qquad /\cdot\frac{T}{m}$$

$$c_p = c_v + \frac{\beta^2 V T}{m\chi_T}$$

$$\boxed{c_p - c_v = \frac{T\beta^2}{\rho\chi_T}}$$

Joule-Kelvinov pojav



$$\left(\frac{\partial T}{\partial p}\right)_H = ?$$

$$dH = 0$$
$$TdS + Vdp = 0 \qquad dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$0 = T\left(\frac{m c_p}{T} dT - \beta V dp\right) + V dp$$

$$m c_p dT - V(\beta T - 1) dp = 0$$
$$\vdots$$

$$\boxed{\left(\frac{\partial T}{\partial p}\right)_H = \frac{\beta T - 1}{\rho c_p}}$$ Joule-Kelvinov koeficient

Za idealen plin $\left(\frac{\partial T}{\partial p}\right)_H = 0$

$\beta = \frac{1}{T}$

Fazni prehodi

- trdno, kapljevinasto, plinasto, plazma
- stanja se razlikujejo po: gostota (kapljevina ↔ plin), [tekoča voda ↔ para]
  simetrija (trdnina ↔ kapljevina), [led ↔ tekoča voda]
  električne, magnetne ali druge snovne lastnosti [superprevodnik ↔ normalne kovine]
- Primera

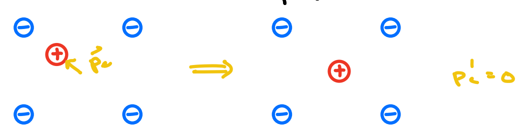
Voda

Feroelektrik - paraelektrik

električna polarizacija

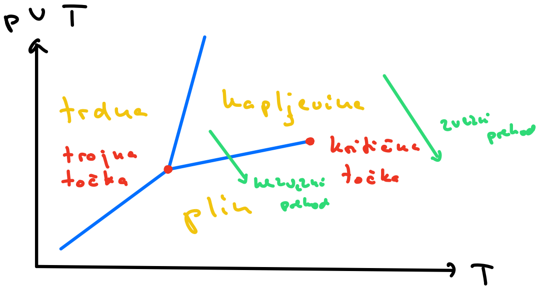
se pojavi sama od sebe

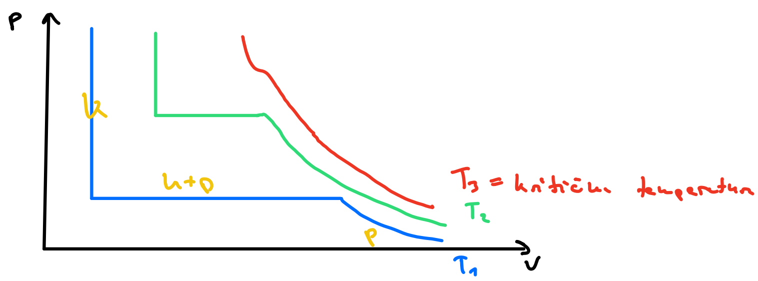
se pojavi ob prisotnosti zun. E



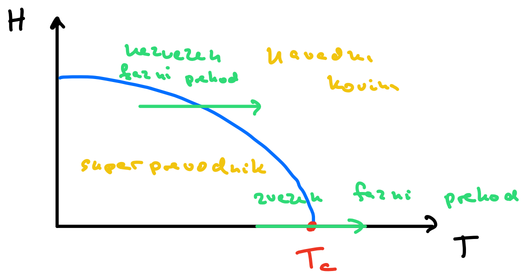
Fazni diagram

- T; $\underbrace{p, H, E, \ldots}_{\text{posplošene zunanje sile}}$
- p ∪ T



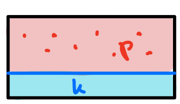


- Superprevodnik - normalne kovine



Ravnovesje faz

- kapljevina - plin



$T_k = T_p$ ker sta v stiku

$p_k = p_p$ ker gladina miruje

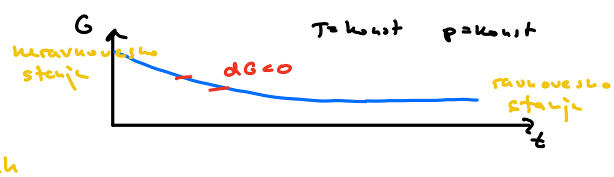
$\underset{\text{kemijski potencial}}{\mu_k} = \mu_p$ snov se ne seli iz ene faze v drugo (kot ravnotežna konst.)

$m_p + m_k = $ konst.

$d(m_p + m_k) = 0 \rightarrow dm_p = -dm_k$

- kemijski potencial $\mu_i = \left(\frac{\partial G}{\partial m_i}\right)_{T, m_j}$

$G = G(T, p, m) \Rightarrow dG = -SdT + Vdp + \underset{\text{po fazah}}{\sum_i} \mu_i dm_i$



$T = \text{konst} \qquad p = \text{konst}$

$$dG = \sum_i \mu_i dm_i \Rightarrow \qquad dG = \mu_k \, dm_k + \mu_p \, dm_p \leq 0$$

$$dG = (\mu_k - \mu_p) \, dm_k \leq 0$$

- $\mu_k > \mu_p \Rightarrow dm_k < 0$ (kap → plin)
- $\mu_k < \mu_p \Rightarrow dm_k > 0$ (plin → kap)

Zvezni in nezvezni fazni prehodi

Gostota proste entalpije $g = G/m$

$$dg = -\frac{S}{m} dT + \frac{dp}{\rho}$$

Opazujemo prehod pri $p = \text{konst}$

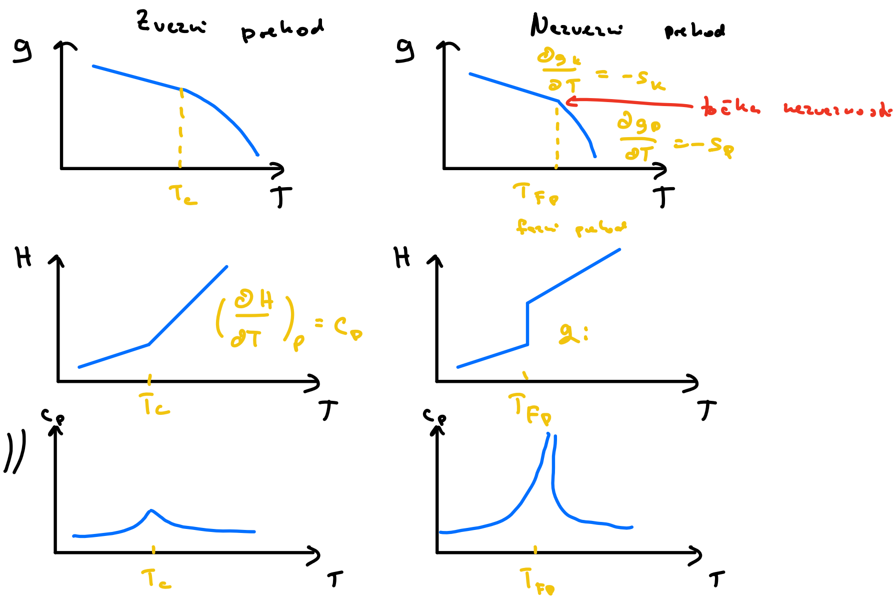
$$dg = -s \, dT$$

$$\Delta S = Q/T = \frac{m q_i}{T}$$

$$\Delta s = \frac{q_i}{T}$$

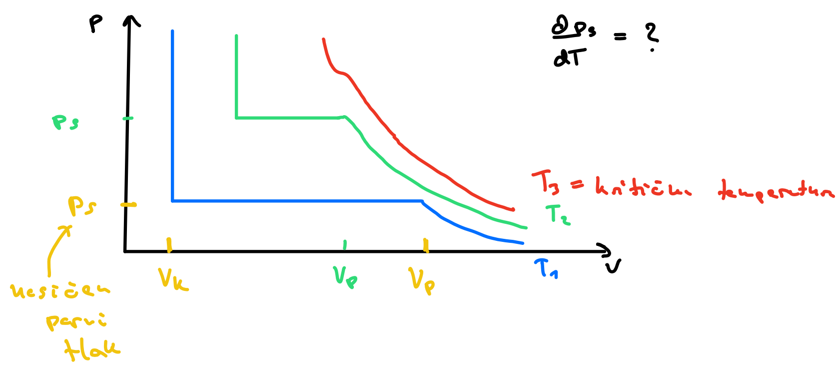
$$q_i = T_{fp} (s_p - s_k) = T_{fp}\left(-\left(\frac{\partial g_p}{\partial T}\right)_p - \left(-\left(\frac{\partial g_k}{\partial T}\right)_p\right)\right)$$

latentna toplota



Clausius - Clapeyronova enačba

$$\frac{dp_s}{dT} = ?$$



$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \text{1. Maxwellova relacija}$$

$$\Downarrow \qquad \Downarrow$$

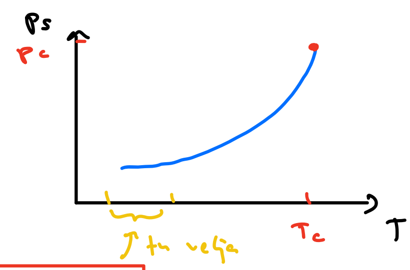
$$\frac{\Delta S}{\Delta V} = \frac{dp_s}{dT}$$

$$\boxed{\frac{dp_s}{dT} = \frac{m q_i}{T(V_p - V_k)}}$$

Predpostavimo q_i ne spreminja z T

Če je $T \ll T_c$ pri fiksni masi $\Rightarrow V_k \ll V_p$

Plinasto fazo lahko obravnavamo kot idealni plin



$$\frac{dp_s}{dT} = \frac{m q_i}{T V_p} = \frac{m q_i M p_s}{T m R T} = \frac{M q_i p_s}{T^2 R}$$

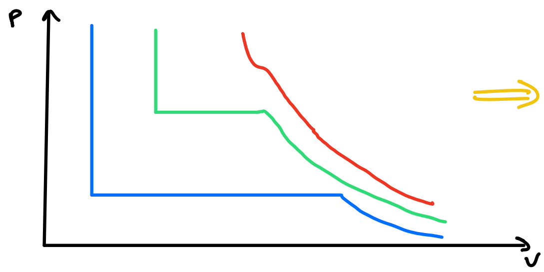
$$\frac{dp_s}{p_s} = \frac{M q_i}{R} \frac{dT}{T^2} \quad \Big/ \int_{\text{referenčno stanje}}^{\text{željeno stanje}}$$

Za idealni plin

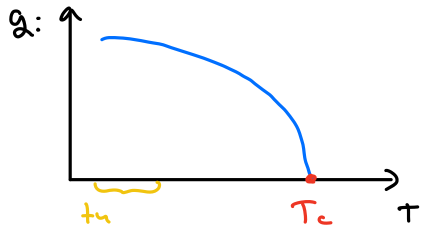
$$\boxed{\ln \frac{p_s}{p_s'} = -\frac{M q_i}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)}$$

$$p_s(T) = p_s(T') \exp\left(-\frac{M q_i}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right)$$

Izparilna toplota



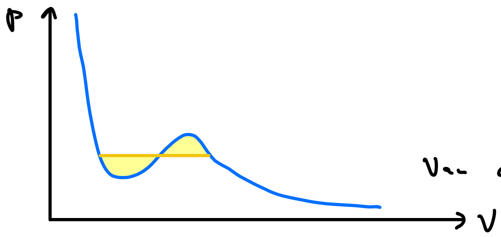
$\Longrightarrow$



$q_i \neq q_i(T)$

in velja Claus-Clap.

Maxwellovo pravilo



Van der Waalsova izoterma

Pogoji:

$T_k = T_p$

$p_k = p_p$

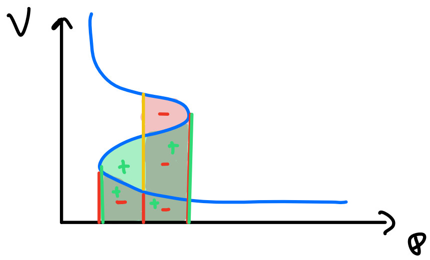
$\mu_k = \mu_p \Rightarrow G_k = G_p$

$$G_p = G_k + \int_k^p dG$$

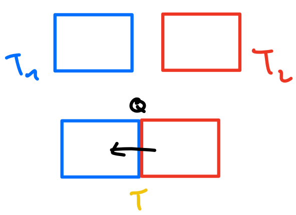
$dG = 0$, $dG = -SdT + Vdp$

Maxwellovo pravilo

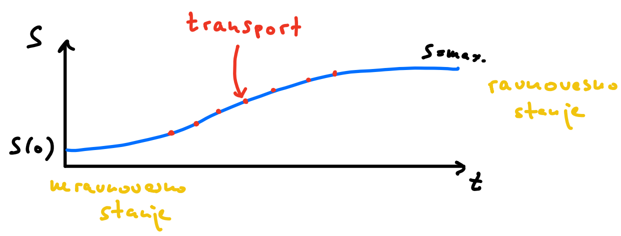
$$\int_k^p V\,dp = 0$$



Transportni pojavi

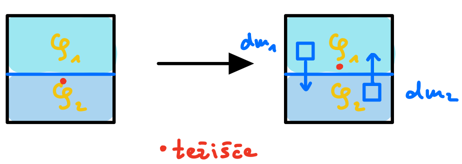


toplotni tok



- transport snovi / difuzija
- transport toplote
- ohranitveni zakon (ohranitev mase ali energije) — protokol izpeljave
- fenomenološki opis toka

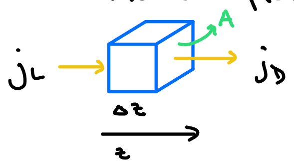
Transport snovi



V splošnem se težišče premika.

- Idealiziran primer $\rho_1 = \rho_2 \Rightarrow$ ni premika težišča

- kontrolna prostornina



- spremembe mase v kontrolni prostornini

$$\frac{dm}{dt} = -Aj_D + Aj_L = -A(j_D - j_L)$$

$$m_1 = \rho_1 V = \rho_1 S \Delta z$$

$$A \Delta z \frac{\partial \rho_1}{\partial t} = -A(j_D - j_L)$$

$$\frac{\partial \rho_1}{\partial t} = -\frac{j_D - j_L}{\Delta z} = -\frac{\partial j_z}{\partial z}$$

gradient

$$\Rightarrow \frac{\partial \rho_1}{\partial t} = -\underbrace{\left(\frac{\partial j_x}{\partial x} + \frac{\partial j_y}{\partial y} + \frac{\partial j_z}{\partial z}\right)}_{\text{divergenca}} = -\nabla \cdot \vec{j}_1$$

$$\boxed{\frac{\partial \rho_1}{\partial t} = -\nabla \cdot \vec{j}_1}$$ kontinuitetna enačba

- Od česa je odvisna gostota snovnega toka?
  - (i) $\vec{j}$ odvisen od razlike gostot snovi ; od gradienta gostote
  - (ii) $\vec{j}$ je linearna funkcija $\nabla \rho$
  - (iii) $\vec{j}$ kaže v nasprotni smeri $\nabla \rho$
  - (iv) $\boxed{\vec{j}_1 = -D \nabla \cdot \rho_1}$ Fickov zakon

    ↳ difuzijska konstanta

- Fickov zakon vstavimo v kontinuitetno enačbo

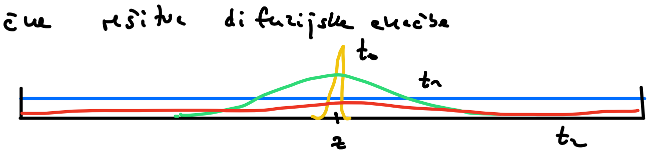
$$\frac{\partial \rho_1}{\partial t} = -\nabla \cdot (-D \nabla \rho_1)$$

$$\boxed{\frac{\partial \rho_1}{\partial t} = D \nabla^2 \cdot \rho_1}$$ Difuzijska enačba $$\frac{\partial \rho_1}{\partial t} = D\left(\frac{\partial^2 \rho_1}{\partial x^2} + \frac{\partial^2 \rho_1}{\partial y^2} + \frac{\partial^2 \rho_1}{\partial z^2}\right)$$

- Parabolična parcialna diferencialna enačba
- D ... m^2/s
- plini $D \sim 10^{-4}\ m^2/s$

  kapljevine $D \sim 10^{-9}\ m^2/s$
- Tipične rešitve difuzijske enačbe

• 1D

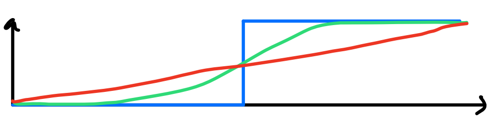


$$\rho_1(z, t=0) \propto \delta(z)$$

↑ delta funkcija

$$x_1(z,t) = \frac{m_1}{\rho A \sqrt{4\pi D t}} \exp\left(-\frac{z^2}{4Dt}\right)$$ Gaussova funkcija

• Začetna porazdelitev: Heavisidova funkcija

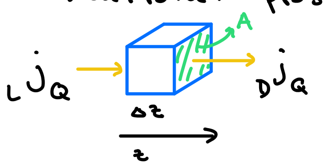


$$x_1(z,t) = \frac{x_0}{2}\left(1 + \mathrm{erf}\left(\frac{z}{\sqrt{4Dt}}\right)\right)$$

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt$$

Transport toplote

- kontrolna prostornina



- $P = -A(_D j_Q - _L j_Q) = -A\,\Delta j_Q$

$$\left.\begin{aligned} &P = -A(_D j_Q - _L j_Q) = -A\,\Delta j_Q \\ &\frac{\partial Q}{\partial t} = \frac{\partial H}{\partial t} = m c_p \frac{\partial T}{\partial t} = \rho A \Delta z\, c_p \frac{\partial T}{\partial t} \end{aligned}\right\} \quad \frac{\partial T}{\partial t} = -\frac{1}{\rho c_p}\frac{\Delta j_Q}{\Delta z}$$

$$\boxed{\frac{\partial T}{\partial t} = -\frac{1}{\rho c_p}\nabla\cdot\vec{j}_Q}$$

- zveza med $\vec{j}_Q$ in ∇T

$$\boxed{\vec{j}_Q = -\lambda\,\nabla T}$$

- Difuzijska enačba za toploto

$$\boxed{\frac{\partial T}{\partial t} = \underbrace{\frac{\lambda}{\rho c_p}}_{D}\nabla^2 T}$$

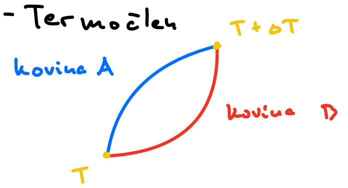
- λ : 40 - 400 W/mK (kovine)
  ~1 W/mK (izolator)
  ~0,01 W/mK (plin)

Križni transportni pojavi

$\nabla \rho_1 \to \vec{j}_1$, $\nabla T \to \vec{j}_Q$ direktni transportni pojav

$\nabla T \longrightarrow \vec{j}_1 \longrightarrow I$ (el. tok) križni transportni pojav

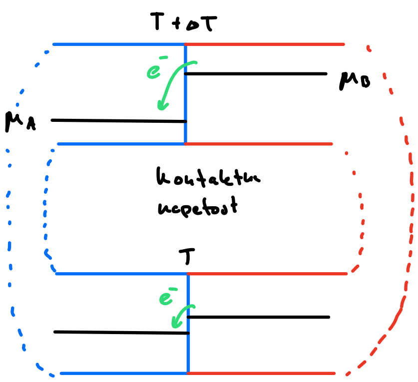
- Termočlen



$\Delta T \longrightarrow U \to I$

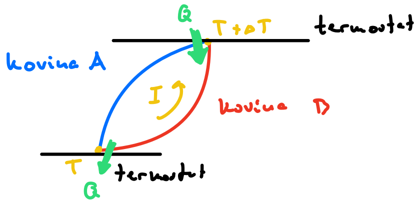
$U = a\,\Delta T$

↳ termoelektrični koeficient (~ $10\ \frac{\mu V}{K}$ kovine)



Ker kontaktni napetosti nista enaki teče tok

Peltierov pojav



$$P = \Pi I$$

↳ Peltierov koeficient

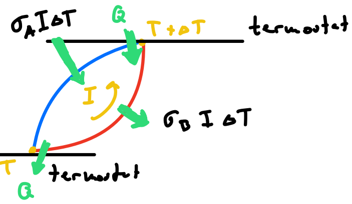
termočlen kot Carnotov toplotni stroj

$$\eta = \frac{W}{Q} = \frac{UIt}{Pt} = \frac{\alpha \Delta T\, I}{\Pi I}$$

$$= 1 - \frac{T}{T+\Delta T} \doteq \frac{\Delta T}{T}$$

$$\boxed{\Pi = \alpha T}$$

Splošna obravnava



$$\Pi(T+\Delta T)I - \Pi(T)I + \sigma_A I \Delta T - \sigma_B I \Delta T - \underbrace{(R_A + R_B) I^2}_{\text{Joulova toplota}} = 0$$

$$UI = \alpha \Delta T I$$

$$\Pi(T) + \frac{d\Pi}{dT}\Delta T - \Pi(T) + (\sigma_A - \sigma_B)\Delta T - \alpha \Delta T = 0$$

$$\frac{d\Pi}{dT} + \sigma_A - \sigma_B - \alpha = 0$$

$$\boxed{\frac{d\Pi}{dT} = \sigma_B - \sigma_A + \alpha}$$

Statistična fizika

- termodinamika: makroskopske opazljivke (p, V, T), izkustveni zakoni ⇒ fenomenološki opis snovi
- statistična fizika: mikroskopske interakcije, mikroskopska struktura snovi ⇒ makroskopske lastnosti
- Maxwell: kinetična teorija plinov
- Boltzmann, Gibbs
- „delci" + interakcija ⇒ enačbe gibanja (reševanje ni mogoče, ni praktično in ni potrebno)
- statistični opis sisteme: statistični ansambel
    - Nabor stanj sisteme
    - Nabor verjetnosti za zasedenost stanj

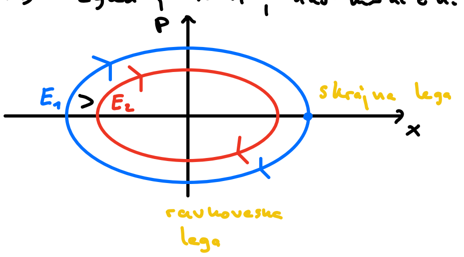
Fazni prostor (prostor stanj)

- N atomov: $3N$ komponent + $3N$ komponent gibalne količine

$$\{q_1, q_2, \dots q_{3N}\} \quad \{p_1, p_2, \dots p_{3N}\}$$

- točke v faznem prostoru ... stanje

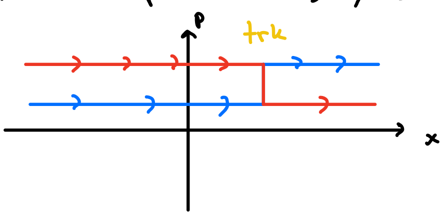
  časovni razvoj sisteme ... tir
- 1D zgled, $N=1$, harmonični oscilator



tir ... elipsa

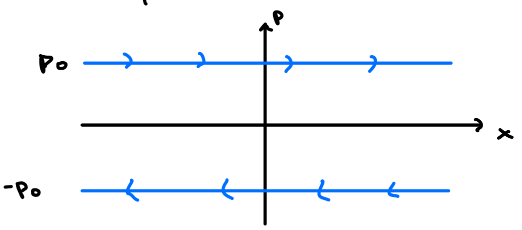
$E = \text{konst}$

- Idealni plin v 1D, dva delca



Skupna energija se ohranja. Zamenjate se identiteti delcev, ker pa nas ne zanima. Pomembna je verjetnost za zasedenost stanj.

- Mirujoč idealni plin ($\bar{v} = 0$)



$$E_1 = \frac{p_0^2}{2m}$$

$$E_2 = \frac{(-p_0)^2}{2m} = E_1$$

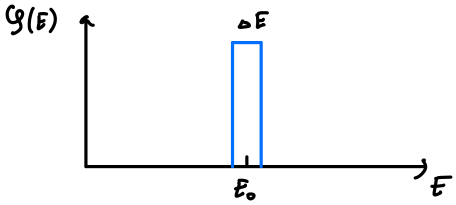
- Verjetnost za zasedenost stanj v odvisnosti od energije

$$\rho(q_i, p_i) \Rightarrow \rho(E(q_i, p_i))$$

Kanonična porazdelitev

- $\rho \stackrel{?}{=} \rho(E)$ kolikšna je verjetnost, da je sistem v določenem stanju $/d\Gamma$
- povprečne vrednosti opazljivk $\bar{Y} = \int_\Gamma \rho(E)\, Y\, d\Gamma$ ← po faznem prostoru $d\Gamma = g(E)\, dE$ ↑ gostota stanj

- mikrokanonična porazdelitev

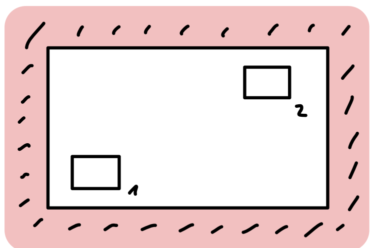


$$\rho(E) = \begin{cases} \frac{\Delta E}{g(E_0)}, & E_0 - \frac{\Delta E}{2} < E < E_0 + \frac{\Delta E}{2} \\ 0, & \text{sicer} \end{cases}$$

$$1 = \int \rho(E)\, g(E)\, dE = \frac{1}{g(E_0)\Delta E}\, g(E_0)\, \Delta E = 1$$

Velja za sistem s fiksno energijo

- Termostat



Podsisteme sta šibko sklopljena

$$E_{1+2} = E_1 + E_2$$
$$\rho_{1+2}(E_{1+2}) = \rho_1(E_1)\, \rho_2(E_2)$$

$$\ln \rho_{1+2}(E_{1+2}) = \ln \rho_1(E_1) + \ln \rho_2(E_2) \qquad \frac{\partial}{\partial E_1}\ \frac{\partial}{\partial E_2}$$

$$\left.\begin{aligned} \frac{1}{\rho_{1+2}} \frac{\partial \rho_{1+2}}{\partial E_{1+2}} \underbrace{\frac{\partial E_{1+2}}{\partial E_1}}_{1} &= \frac{1}{\rho_1} \frac{d\rho_1}{dE_1} \\ \frac{1}{\rho_{1+2}} \frac{d\rho_{1+2}}{dE_{1+2}} \underbrace{\frac{\partial E_{1+2}}{\partial E_2}}_{1} &= \frac{1}{\rho_2} \frac{d\rho_2}{dE_2} \end{aligned}\right\} \frac{1}{\rho}\frac{d\rho}{dE} = \text{konst.} = -\beta$$

$$\frac{d\rho}{\rho} = -\beta\, dE$$
$$\ln \rho = -\beta E + \text{konst}'$$
$$\boxed{\rho \propto \exp(-\beta E)} \qquad \boxed{\beta = \frac{1}{k_B T}} \qquad k_B = 1{,}38 \cdot 10^{23}\ \frac{J}{K}$$

fazna vsota (statistična vsota, fazni integral, particijska funkcija)
je integral verjetnostne gostote ρ po faznem prostoru

$$e^{-\beta F} = c \int e^{-\beta E}\, d\Gamma \qquad /: e^{-\beta F}$$

↑ normirna konstanta

$$1 = c \int e^{-\beta(E-F)}\, d\Gamma \qquad \int \rho(E)\, d\Gamma = 1$$
$$\Rightarrow \rho(E) = c\, e^{-\beta(E-F)}$$

Povprečna energija

- povprečje na splošno
$$\bar{Y} = c \int e^{-\beta(E-F)}\, d\Gamma$$

- $Y = E$

$$\bar{E} = c \int e^{-\beta(E-F)} E\, d\Gamma = e^{\beta F} c \int e^{-\beta E} E\, d\Gamma$$

$$= \frac{c \int e^{-\beta E} E\, d\Gamma}{e^{-\beta F}} = \frac{c \int e^{-\beta E} E\, d\Gamma}{c \int e^{-\beta E}\, d\Gamma} \quad ①$$

- $\boxed{\bar{E} = \frac{d(\beta F)}{d\beta}}$ $\qquad e^{-\beta F} = c \int e^{-\beta E}\, d\Gamma \qquad \beta F = -\ln\left(c \int e^{-\beta E}\, d\Gamma\right)$

$$\frac{d\,\beta F}{d\beta} = \cancel{-}\, \frac{c \int (\cancel{-}E) e^{-\beta E}\, d\Gamma}{c \int e^{-\beta E}\, d\Gamma} \quad ② = ①$$

Povprečna energija enoatomnega idealnega plina

- $E_i = \sum_i \frac{\vec{p}_i^{\,2}}{2m}$
- fazni integral $\quad e^{-\beta F} = C \int \exp\left(-\frac{\beta}{2m}\left(p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 + \dots\right)\right) \underbrace{dx_1\, dy_1\, dz_1}_{V}\, \underbrace{dx_2 \dots}_{V}\, dp_{1x}\, dp_{1y} \dots$

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

$$= C V^N \underbrace{\int_{-\infty}^{\infty} \exp\left(-\beta \frac{p_{1x}^2}{2m}\right) dp_{1x}}_{\text{Gaussov integral}} \int_{-\infty}^{\infty} \exp\left(-\beta \frac{p_{1y}^2}{2m}\right) dp_{1y} \dots$$

$$= C V^N \sqrt{\frac{2\pi m}{\beta}} \cdot \sqrt{\frac{2\pi m}{\beta}} \dots = \boxed{C V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}}$$

$$\beta F = -\ln\left(C V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}\right) = -\ln C - \ln V^N - \ln\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$
$$= -\ln C - N \ln V - \frac{3N}{2} \ln 2\pi m + \frac{3N}{2} \ln \beta$$

$$\bar{E} = \frac{d\beta F}{d\beta} = \frac{3N}{2\beta} = \boxed{\frac{3N}{2} k_B T}$$

Iz termodinamike $U = U(T)$

Ekviparticijski izrek

- povprečna energija vsake komponente, neodvisne in kvadratične prostostne stopnje sistema enaka $k_B T / 2$.

$q \in (-\infty, \infty)$ $\quad E \neq q_1 q_2$ $\quad E = a q^2$ prostostna stopnja

- $E(\dots q_1, q_2) = \dots + a_1 q_1^2 + a_2 q_2^2$

$$e^{-\beta F} = C \int \exp\left(-\beta\left(\dots + a_1 q_1^2 + a_2 q_2^2\right)\right) d\dots\, dq_1\, dq_2$$
$$= C \int_{-\infty}^{\infty} \exp(-\beta a_1 q_1^2)\, dq_1 \int_{-\infty}^{\infty} \exp(-\beta a_2 q_2^2)\, dq_2 \dots$$
$$= C \sqrt{\frac{\pi}{\beta a_1}} \cdot \sqrt{\frac{\pi}{\beta a_2}} \cdot \dots$$

$$\beta F = -\ln C - \frac{1}{2} \ln \frac{\pi}{a_1} + \frac{1}{2} \ln \beta - \frac{1}{2} \ln \frac{\pi}{a_2} + \frac{1}{2} \ln \beta \dots$$

$$\bar{E} = \frac{d\beta F}{d\beta} = \underbrace{\frac{1}{2}\beta^{-1}}_{a_1 q_1^2} + \underbrace{\frac{1}{2}\beta^{-1}}_{= \frac{k_B T}{2}} + \dots = \frac{3N}{2\beta}$$

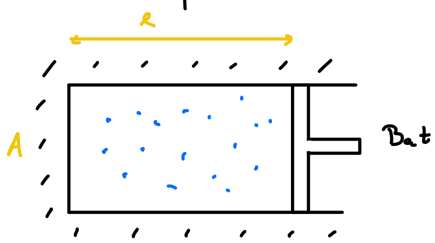
Fluktuacije energije

$$\sigma_E^2 = \overline{(E - \bar{E})^2} = \overline{E^2 - 2E\bar{E} + \bar{E}^2} = \overline{E^2} - 2\bar{E}\bar{E} + \bar{E}^2 = \overline{E^2} - \bar{E}^2$$

$$\sigma_E^2 = -\frac{d^2 \beta F}{d\beta^2} = -\frac{d}{d\beta} \frac{d\beta F}{d\beta} = -\frac{d}{d\beta} \bar{E} = -\frac{dT}{d\beta} \frac{d}{dT} \bar{E} = k_B T^2 \frac{d\bar{E}}{dT} = k_B T^2 \underbrace{C_v}_{\text{toplotna kapaciteta } \propto N}$$

$$\sigma_E^2 \propto N$$
$$\sigma_E \propto \sqrt{N}$$
$$\frac{\sigma_E}{\bar{E}} \propto \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \xrightarrow[N \to \infty]{\text{termodinamična lim}} 0$$

Enačba stanja



$$e^{-\beta F} = c\int e^{-\beta E}$$

$$\langle E\rangle = \frac{d\beta F}{d\beta} \qquad \beta = \frac{1}{k_B T}$$

$$\langle E\rangle = \frac{3}{2} N k_B T$$

$$C_v = \frac{3}{2} N k_B = \frac{3}{2}\frac{m}{M} N_A k_B$$

$$c_v = \frac{C_v}{m} = \frac{3}{2}\frac{R}{M}$$

Idealni plin

$$c_p = c_v + \frac{R}{M} = \frac{5}{2}\frac{R}{M}$$

$$\chi = 5/3$$

$$u_i(x_i, L) = \begin{cases} 0, & x_i < L \\ \infty, & x_i > L \end{cases}$$

$$= u_i(x_i - L)$$

Energija

$$E = E_{kin} +$$

$$= \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \underbrace{\sum_i u_i(x_i - L)}_{u}$$

Sila bata na plin

ker $W_k \neq W_k(L)$ zato $\frac{\partial W_k}{\partial L} = 0$

$$F_x = \sum_i F_{xi} = -\sum \frac{\partial u_i}{\partial x_i} = -\sum_i \frac{\partial u_i}{\partial(-L)} = \frac{\partial}{\partial L}\sum_i u_i = \frac{\partial u}{\partial L} = \frac{\partial E}{\partial L}$$

Tlak plina

$$p = -\frac{\langle F_x\rangle}{A} = -\frac{1}{A}\left\langle\frac{\partial E}{\partial L}\right\rangle = -\left\langle\frac{\partial E}{\partial V}\right\rangle$$

Fazni integral

$$e^{-\beta F} = c\int e^{-\beta E}\, d\Gamma \qquad /: e^{-\beta F}$$

$$1 = \underline{c}\int \underbrace{e^{-\beta(E-F)}}_{g(E)}\, d\Gamma \qquad /\frac{\partial}{\partial V}$$

$$0 = c\int\left(-\frac{\partial E}{\partial V}\right)e^{-\beta(E-F)}\, d\Gamma + c\int \frac{\partial F}{\partial V}\, e^{-\beta(E-F)}\, d\Gamma$$

$$0 = -\int \frac{\partial E}{\partial V}\, g(E)\, d\Gamma + \frac{\partial F}{\partial V}\underbrace{c\int e^{-\beta(E-F)}\, d\Gamma}_{1}$$

$$0 = -\left\langle\frac{\partial E}{\partial V}\right\rangle + \frac{\partial F}{\partial V}$$

$$\left\langle\frac{\partial E}{\partial V}\right\rangle = \frac{\partial F}{\partial V}$$

$$\boxed{p = -\left(\frac{\partial F}{\partial V}\right)_\beta}$$

Enačba stanja idealnega plina

$$E = W_k = \frac{p_{1x}^2}{2m} + \frac{p_{1y}^2}{2m} + \frac{p_{1z}^2}{2m} + \dots$$

$$e^{-\beta F} = c\int e^{-\beta\sum_i \frac{1}{2m}(p_{ix}^2 + p_{iy}^2 + p_{iz}^2)}\underbrace{\prod_{i=1}^{N} dx_i\, dy_i\, dz_i}_{V^N}\, dp_{ix}\, dp_{iy}\, dp_{iz}$$

$$= cV^N\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

$$F = -\frac{1}{\beta}\left(\ln C + N\ln V + \frac{3N}{2}\ln\frac{2\pi m}{\beta}\right)$$

$$p = -\frac{\partial F}{\partial V} = \frac{1}{\beta} N \frac{1}{V}$$

$$pV = N k_B T$$

$$pV = \frac{m}{M} N_A k_B T$$

$$pV = \frac{m}{M} R T$$

Virialna enačba stanja
↳ sile med delci

Idealni plin $p = \frac{N}{\beta V} = \frac{\varrho}{\beta}$

virialni koeficienti

$$\frac{\beta p}{\varrho} = 1 + \sum_{2}^{\infty} B_i \varrho^{i-1}$$

Idealni plin — Odstopanje od idealnega zaradi sil med delci

Energija realnega plina

$$E = E_{kin} + \sum_{i<j} \phi_{ij}$$

↳ parski potencial med delcema i in j
$\phi_{ij} = \phi(|\vec{r}_i - \vec{r}_j|)$

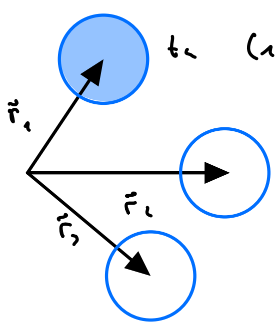
Fazni integral

$$e^{-\beta F} = c \underbrace{\int \exp\left(-\beta \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}\right) \prod_{i=1}^{N} d\vec{p}_i}_{\text{Integral po GK}} \underbrace{\int \exp\left(-\beta \sum_{i<j} \phi_{ij}\right) \prod_{i=1}^{N} d\vec{r}_i}_{\text{Konfiguracijski integral } Q_N}$$

$$= \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

$$Q_N = \int \exp(-\beta\phi_{12}) \exp(-\beta\phi_{13}) \dots \exp(-\beta\phi_{23}) \dots \; d\vec{r}_1 \, d\vec{r}_2 \dots d\vec{r}_N$$

$$= \int \left(1-(1-e^{-\beta\phi_{12}})\right)\left(1-(1-e^{-\beta\phi_{13}})\right) \dots \; d\vec{r}_1 \, d\vec{r}_2 \dots d\vec{r}_N =$$



tu $\left(1-(1-e^{-\beta\phi_{12}})\right) \neq 1$

$$\doteq \int \left(1 - (1-e^{-\beta\phi_{12}}) - (1-e^{-\beta\phi_{13}}) - \dots - (1-e^{-\beta\phi_{23}}) - \dots\right) d\vec{r}_1 \, d\vec{r}_2 \dots d\vec{r}_N$$

Če je plin dovolj redek se okolice ne prekrivajo

$$= V^N - V^{N-2}\int \left(1-e^{-\beta\phi_{12}}\right) d\vec{r}_1\, d\vec{r}_2 - V^{N-2}\int \left(1-e^{-\beta\phi_{13}}\right) d\vec{r}_1\, d\vec{r}_3 - \dots$$

$\phi_{12} = \phi(|\vec{r}_1 - \vec{r}_2|)$

$\vec{r}_{12} = \vec{r}_1 - \vec{r}_2$

$$= V^N - V^{N-1}\underbrace{\int \left(1-e^{-\beta\phi_{12}}\right) d\vec{r}_{12}}_{2B_2} - V^{N-1}\int \left(1-e^{-\beta\phi_{13}}\right) d\vec{r}_{13}$$

... drugi virialni koeficient

Število parov $\frac{n(n-1)}{2}$

$$= V^N - V^{N-1}\, 2B_2\, \frac{N(N-1)}{2}$$

pri $N \gg 1$

$$\doteq V^N - V^{N-1} B_2 N^2$$

$$e^{-\beta F} \approx C\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} \left(V^N - V^{N-1} B_2 N^2\right)$$

$$= C\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} V^N \left(1 - \frac{B_2 N^2}{V}\right)$$

$$F = -\frac{1}{\beta}\left(\ln C + \frac{3N}{2}\ln\frac{2\pi m}{\beta} + N\ln V + \ln\left(1 - \frac{B_2 N^2}{V}\right)\right)$$

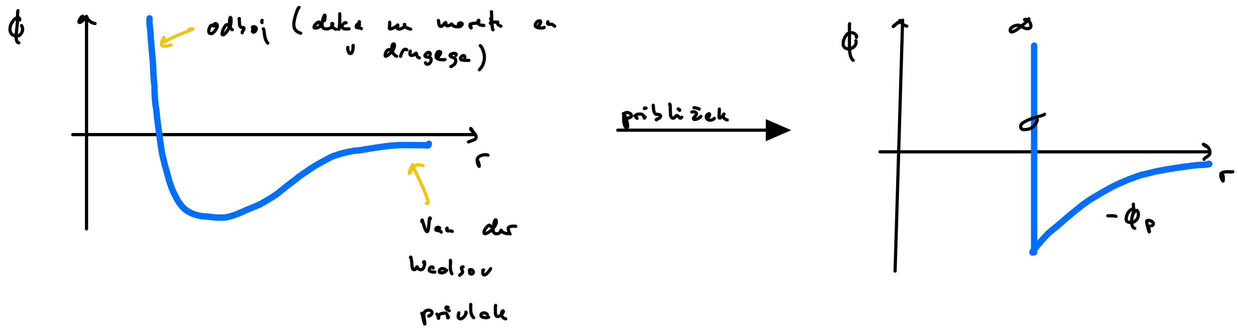
Taylor

$$F = -\frac{1}{\beta}\left(\dots + \dots + N\ln V - \frac{N^2 B_2}{V}\right)$$

$$p = -\frac{\partial F}{\partial V} = \frac{1}{\beta}\left(\frac{N}{V} - \frac{N^2 B_2}{V^2}\right)$$

$$\frac{\beta p}{\rho} = 1 + B_2 \rho$$

Drugi virialni koeficient



$$B_2 = \frac{1}{2}\int \left(1 - e^{-\beta\phi}\right) d\vec{r} = \frac{1}{2}\int \left(1 - e^{-\beta\phi}\right) 4\pi r^2\, dr$$

$$= 2\pi \int_0^\sigma 1\, r^2\, dr - 2\pi\int_\sigma^\infty \left(1 - \left(1 - \beta\phi_p\right)\right) r^2\, dr$$

$$= 2\pi\frac{\sigma^3}{3} - 2\pi\int_\sigma^\infty \beta\,\phi_p\, r^2\, dr$$

samo nova sprem.

$$\alpha = 2\pi\int_\sigma^\infty \phi_p\, r^2\, dr$$

$$= 2\pi\frac{\sigma^3}{3} - \beta\,\alpha$$

$$p = \frac{N}{\beta V} + \frac{1}{\beta}\frac{N^2}{V^2} B_2$$
$$= \frac{N}{\beta V} + \frac{1}{\beta}\frac{N^2}{V^2}\left(2\pi \frac{\sigma^3}{3} - \beta \alpha\right)$$
$$= \frac{N}{\beta V} + \frac{1}{\beta}\frac{N^2}{V^2}\frac{2\pi}{3}\sigma^3 - \frac{N^2}{V^2}\alpha$$
$$= \frac{N k_B T}{V} + \frac{N^2 k_B T}{V^2}\frac{2\pi}{3}\sigma^3 - \frac{N^2 \alpha}{V^2}$$

Van der Waals

$$RT = \left(p + \frac{a}{V_m^2}\right)(V_m - b)$$
$$p + \frac{a}{V_m^2} = \frac{RT}{V_m - b} = \frac{RT}{V_m(1 - b/V_m)}$$
$$\doteq \frac{RT}{V_m}\left(1 + \frac{b}{V_m}\right) = \frac{RT}{V_m} + \frac{RTb}{V_m^2}$$
$$p = \frac{RT}{V_m} + \frac{RTb}{V_m^2} - \frac{a}{V_m^2}$$

Entropija

$$\bar{E} = \frac{d\beta F}{d\beta} = \left(\frac{\partial \beta F}{\partial \beta}\right)_V$$
$$p = -\left(\frac{\partial F}{\partial V}\right)_\beta = -\left(\frac{\partial \beta F}{\partial \beta V}\right)_\beta$$

$$d\beta F = \bar{E}\, d\beta - p\, d\beta V = \bar{E}\, d\beta - p\beta\, dV \quad (1)$$

$$\beta = \frac{1}{k_B T}$$
$\bar{E}$ ... U

Spomnimo sa

$$dU = dQ - pdV \rightarrow d\bar{E} = dQ - pdV \quad /\cdot\beta$$
$$\beta d\bar{E} = \beta dQ - p\beta\, dV \quad (2)$$

(1) − (2):

$$d\beta F - \beta d\bar{E} = \bar{E}\, d\beta - \beta dQ$$
$$d\beta F + \beta dQ = \bar{E}\, d\beta + \beta d\bar{E}$$
$$-\beta dQ = d\beta F - d\beta \bar{E}$$
$$-\beta dQ = d(\beta(F - \bar{E}))$$
$$-\beta dQ = d(\beta(\overline{F - E})) \qquad \beta = \frac{1}{k_B T}$$

$$dS = \frac{dQ}{T} = k_B\, d\,\frac{\overline{E - F}}{k_B T} = d\,\frac{\bar{E} - F}{T}$$

$$\boxed{S = \frac{\bar{E} - F}{T}} \Rightarrow \boxed{F = \bar{E} - TS} \quad \text{prosta energija}$$

$$S = k_B\, \beta(\overline{E - F})$$

- Kanonična porazdelitev $\rho(E) = C e^{-\beta(E - F)}$
  $$\beta(E - F) = -\ln \frac{\rho}{C}$$
- Računanje povprečja $\bar{Y} = \int Y \rho\, d\Gamma$
- Entropija

$$\boxed{S = -k_B \int \rho \ln \frac{\rho}{C}\, d\Gamma} \quad \text{Gibbsova formula za entropijo}$$

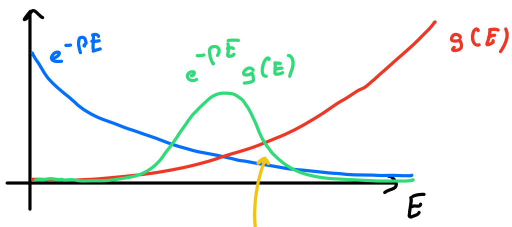
Boltzmanova formula

- kanonična vs. mikrokanonična porazdelitev

$$1 = \int \rho \, d\Gamma = c \int e^{-\beta(E-F)} d\Gamma = c \int e^{-\beta(E-F)} g(E)\, dE = c e^{\beta F} \int e^{-\beta E} g(E)\, dE$$

↳ $d\Gamma = g(E)\, dE$

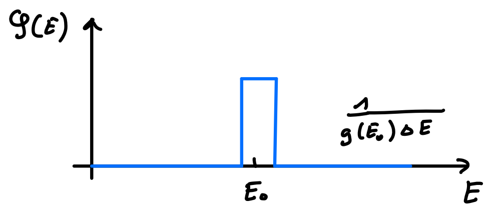
↳ Gostota stanj $\frac{d\Gamma}{dE}$



lahko dobro aproksimiramo z gaussovko ali pa s škatlo (mikrokanonična porazdelitev)

- mikrokanonična porazdelitev

$$\rho(E) = \begin{cases} \frac{1}{g(E_0)\Delta E} \; ; & E_0 - \frac{\Delta E}{2} < E < E_0 + \frac{\Delta E}{2} \\ 0 \; ; & \text{sicer} \end{cases}$$



v Gibbsovo formulo

$$1 = \int \rho \, d\Gamma = \int \rho \, g(E)\, dE$$

$$S = -k_B \int \rho \ln \frac{\rho}{c} \, d\Gamma$$

$$= -k_B \int_{E_0 - \frac{\Delta E}{2}}^{E_0 + \frac{\Delta E}{2}} \frac{1}{g(E_0)\Delta E} \ln \frac{1}{g(E_0)\Delta E\, c} \, g(E_0)\, dE$$

$$= -k_B \frac{1}{g(E_0)\Delta E} \ln \frac{1}{g(E_0)\Delta E\, c} \, g(E_0)\, \Delta E$$

$$= k_B \ln g(E_0)\Delta E\, c$$

$\boxed{S = k_B \ln (c\, \Delta\Gamma)}$ Boltzmanova formula za entropijo

$$S(E) = k_B \ln \left(c\, \Delta\Gamma(E)\right)$$

↳ število stanj pri določeni energiji oz. velikost faznega prostora pri določeni energiji

Entropija idealnega plina

$$e^{-\beta F} = c V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

$$F = -k_B T \ln c V^N - k_B T \frac{3N}{2} \ln (2\pi m k_B T)$$
$$= -k_B T \ln c - N k_B T \ln V - \frac{3N}{2} k_B T \ln (2\pi m k_B T)$$

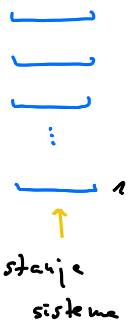
$$\bar{E} = \frac{3}{2} N k_B T$$

$$S = \frac{\bar{E} - F}{T} = \frac{3}{2} N k_B + k_B \ln c + N k_B \ln V + \frac{3N}{2} k_B \ln (2\pi m k_B T) = \underbrace{N k_B}_{\frac{\tilde{m}}{M} \underbrace{N_A k_B}_{R}} \ln V + \underbrace{\frac{3N k_B}{2}}_{} \ln T + \text{konst.} =$$

$N = \frac{\tilde{m}}{\mu} N_A \quad C_v = \frac{3}{2} k_B N$

$$= \tilde{m} \frac{R}{\mu} \ln V + \tilde{m}\, c_v \ln T + \text{konst.}$$

Od Boltzmannove formule k Gibbsovi



j ; N_j število delcev v stanju j

stanje sistema = $\{N_1, N_2, \dots N_j, \dots\}$

Diskretna stanja sistema

$$S = k_B \ln(c\,\Delta\Gamma)$$

c lahko izpustimo ker so stanja diskretna

$\underbrace{\text{Multinomski simbol}}$ (posplošitev binomskega simbola)

$$\Delta\Gamma = \frac{N!}{N_1!\,N_2!\,N_3!\dots(N-N_1-N_2-N_3-\dots)!} \qquad N = N_1 + N_2 + \dots$$

Stirlingova formula $\ln N! \doteq N\ln N - N$

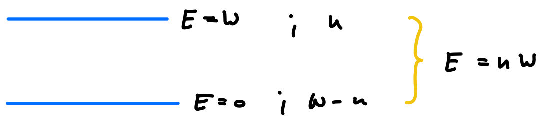
$$S = k_B(\ln N! - \ln N_1! - \ln N_2! - \dots)$$
$$= k_B(N\ln N \cancel{-N} - N_1\ln N_1 \cancel{+N_1} - N_2 \ln N_2 \cancel{+N_2} - \dots)$$
$$= k_B((N_1+N_2+N_3+\dots)\ln N - N_1\ln N_1 - N_2\ln N_2 - \dots)$$
$$= -Nk_B\left(\frac{N_1}{N}\ln\frac{N_1}{N} + \frac{N_2}{N}\ln\frac{N_2}{N} + \dots\right)$$

$p_i = \frac{N_i}{N}$ ... verjetnost da smo v stanju i

$$= -Nk_B\sum_{j=1}^{k} p_j \ln p_j$$

$\Leftarrow$ ekvivalentno Gibbsovi formuli

Dvonivojski sistem

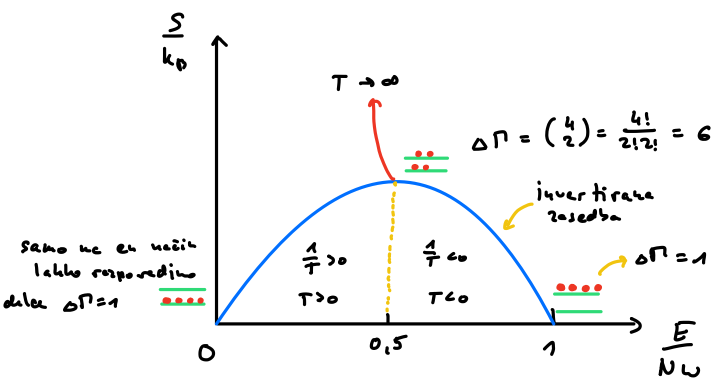


N število vseh delcev
n število delcev v zgornjem stanju

$$S = k_B \ln \Delta\Gamma(E)$$

$\uparrow$ določen z binomskim simbolom

$$= k_B \ln\frac{N!}{n!\,(N-n)!}$$
$$= k_B \ln\frac{N!}{\left(\frac{E}{w}\right)!\,\left(N-\frac{E}{w}\right)!}$$



$$\Delta\Gamma = \binom{4}{2} = \frac{4!}{2!\,2!} = 6$$

$\ln 1 = 0$

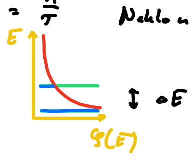
Dvonivojski sistem: O delu ni mogoče govoriti, ker sistem nima fizične dimenzije $dW = 0$

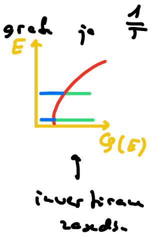
- Energijski zakon
  $dE = dQ = T\,dS$

$$\frac{dE}{dS} = T \qquad \frac{dS}{dE} = \frac{1}{T}$$

Naklon grafa je $\frac{1}{T}$

- $\rho(E) \propto e^{-\beta E}$





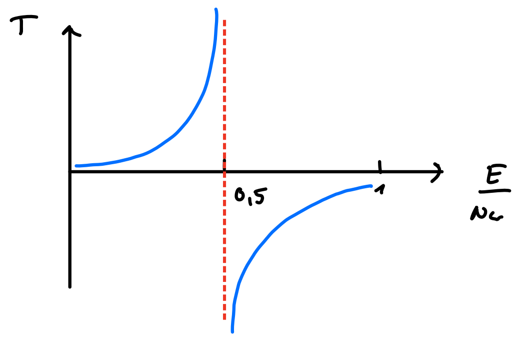
ker ni višjih stanj lahko kljub e^{+x} normiramo.

• S: Stirlingova formula

$$S = k_B\left(N\ln N - \frac{E}{w}\ln\frac{E}{w} - \left(N-\frac{E}{w}\right)\ln\left(N-\frac{E}{w}\right)\right)$$
$$= -Nk_B\left(\frac{E}{Nw}\ln\frac{E}{Nw} + \left(1-\frac{E}{Nw}\right)\ln\left(1-\frac{E}{Nw}\right)\right)$$

$$\frac{dS}{dE} = -Nk_B\left(\frac{1}{Nw}\ln\frac{E}{Nw} + \frac{1}{Nw} - \frac{1}{Nw}\ln\left(1-\frac{E}{Nw}\right) + \left(1-\frac{E}{Nw}\right)\frac{1}{1-\frac{E}{Nw}}\left(-\frac{1}{Nw}\right)\right)$$
$$= -Nk_B\left(\frac{1}{Nw}\ln\frac{E/Nw}{1-E/Nw}\right)$$
$$= \frac{k_B}{w}\ln\left(\frac{Nw}{E}-1\right)$$

$$T = \frac{w}{k_B}\left(\ln\left(\frac{Nw}{E}-1\right)\right)^{-1}$$



Kvantna statistična fizika

• večdelčna funkcija stanja $\psi(\vec r_1, \vec r_2, \dots, t)$
• Schrödingerjeva enačba $i\hbar\frac{\partial\psi}{\partial t} = \hat H\psi$
• Delci neodvisni: ψ faktoriziramo = produkt enodelčnih funkcij stanja $\psi_\alpha(\vec r_1)\psi_\beta(\vec r_2)\dots$
• Delci nerazločljivi: zamenljivi delci
• Bozoni: delci s celim spinom (He)
• Fermioni: delci s polcelim spinom (e^-, p^+)
  ↳ Paulijevo izključitveno načelo (dva delca ne moreta biti v istem stanju (mestu))
• 2 delca

simetrična → $\psi_S(\vec r_1, \vec r_2) = \frac{1}{\sqrt 2}\left(\psi_\alpha(\vec r_1)\psi_\beta(\vec r_2) + \psi_\beta(\vec r_1)\psi_\alpha(\vec r_2)\right)$ Bozoni

antisimetrična → $\psi_{AS}(\vec r_1, \vec r_2) = \frac{1}{\sqrt 2}\left(\psi_\alpha(\vec r_1)\psi_\beta(\vec r_2) - \psi_\beta(\vec r_1)\psi_\alpha(\vec r_2)\right)$ Fermioni (dva delca v istem stanju $\Rightarrow \psi_{AS} = 0$)

• Za 1 pravilno simetrizirano večdelčno funkcijo stanja potrebujemo več enodelčnih funkcij stanja. Koliko? Enako je število permutacij vseh stanj ($n!$)
• $n = 3$ bozoni fermioni

$$\psi(\vec r_1, \vec r_2, \vec r_3) = \frac{1}{\sqrt 6}\Big(\psi_\alpha(\vec r_1)\psi_\beta(\vec r_2)\psi_\gamma(\vec r_3) \pm \psi_\alpha(\vec r_1)\psi_\gamma(\vec r_2)\psi_\beta(\vec r_3) + \psi_\beta(\vec r_1)\psi_\gamma(\vec r_2)\psi_\alpha(\vec r_3)$$
$$\pm \psi_\beta(\vec r_1)\psi_\alpha(\vec r_2)\psi_\gamma(\vec r_3) + \psi_\gamma(\vec r_1)\psi_\alpha(\vec r_2)\psi_\beta(\vec r_3) \pm \psi_\gamma(\vec r_1)\psi_\beta(\vec r_2)\psi_\alpha(\vec r_3)\Big)$$

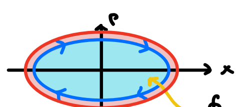
• $e^{-\beta F} = C\int e^{-\beta E}\,d\Gamma$
• fazni prostor = prostor stanj. Stanja so kvantizirana → kvantiziran fazni prostor
• $e^{-\beta F} = C\int e^{-\beta E}d\Gamma = \int e^{-\beta E}\,C\,d\Gamma$

simetričnost $C = \frac{(2j+1)^N}{N!\,h^{3N}}$ spin, (volumen) kvant faznega prostora

• Bohr-Sommerfeldovo načelo: Za vsako vezano stanje $\oint p\,dq = nh$ po koordinati (ali) GK

po 1 orbiti v faznem prostoru $n = 0, 1, 2, \dots$

Primer 1D HO

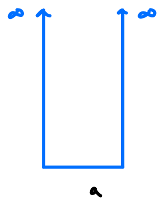


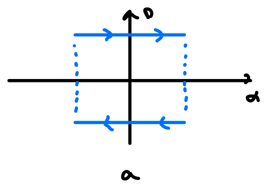
$\oint p\,dx$ = ploščina znotraj elipse $= nh$

kolobar ima ploščino h

• kvant faznega prostora $= h$
• 3D, N delcev ... h^{3N}
• $C = \frac{(2j+1)^N}{N!\,h^{3N}}$

• Zgled: 1D delec v ∞ pot jami:



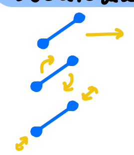


$$\oint p\,dx = 2pa = 2\sqrt{2mE_n}\,a = nh$$

$$E_n = \frac{n^2h^2}{8ma^2}$$

? Marjka

Dvoatomni plin



translacija

rotacija

vibracija

$$E = E_{kin} + E_{rot} + E_{vib}$$

$$e^{-\beta F} = \sum_{tr}\sum_{rot}\sum_{vib} e^{-\beta E_{tr}} e^{-\beta E_{rot}} e^{-\beta E_{vib}} = \sum_{tr} e^{-\beta E_{tr}} \sum_{rot} e^{-\beta E_{rot}} \sum_{vib} e^{-\beta E_{vib}} = e^{-\beta F_{tr}} e^{-\beta F_{rot}} e^{-\beta F_{vib}}$$

$$\bar{E} = \bar{E}_{tr} + \bar{E}_{rot} + \bar{E}_{vib}$$

$$C = \frac{d\bar{E}}{dT} = C_{tr} + C_{rot} + C_{vib}$$

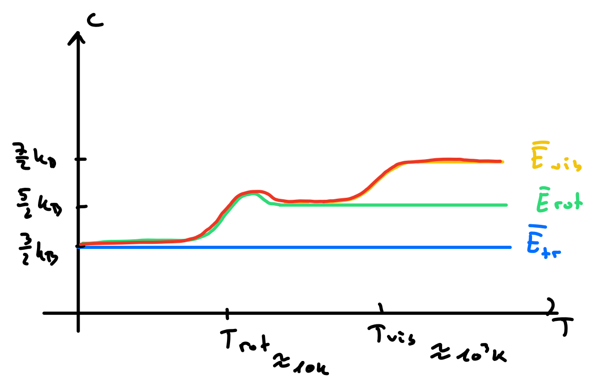
Translacija

→ klasična obravnava

$$e^{-\beta F_{tr}} = C\,V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

$$\bar{E}_{tr} = \frac{3}{2} N k_B T$$

$$C = \frac{3}{2} N k_B$$



Rotacije

• spekter $E_j = \frac{j(j+1)\hbar^2}{2I}$ — vrtilna količina $j = 1, 2, \dots$; I: vztrajnostni moment molekule; degeneracija $2j+1$

• fazna vsota
$$e^{-\beta F_{rot}} = \sum_{\text{po vseh stanjih}} \exp\left(-\beta\frac{j(j+1)\hbar^2}{2I}\right) = \sum_{j=0}^{\infty}(2j+1)\,e^{-\beta\frac{j(j+1)\hbar^2}{2I}}$$

po vseh stanjih → po vseh j, po vseh j_z

• nizkotemperaturna limita $k_B T \ll \frac{\hbar^2}{2I}$, $T \ll \frac{\hbar^2}{2Ik_B} \overset{\text{def.}}{=} T_{rot}$ $\qquad \beta_{rot} = \frac{1}{k_B T_{rot}}$

$$e^{-\beta F} = \underset{j=0}{1} + \underset{j=1}{3e^{-\beta\frac{2\hbar^2}{2I}}} + \dots = 1 + 3e^{-2\frac{\beta}{\beta_{rot}}}$$

$$\beta F_{rot} = -\ln\left(1 + 3e^{-2\frac{\beta}{\beta_{rot}}}\right) \doteq -3e^{-2\beta/\beta_{rot}}$$

$$\bar{E}_{rot} = 6\frac{1}{\beta_{rot}}e^{-2\beta/\beta_{rot}} = 6k_BT_{rot}\,e^{-2\frac{T_{rot}}{T}}$$

$$C = \frac{d\bar{E}_{rot}}{dT} = 12k_B\left(\frac{T_{rot}}{T}\right)^2 e^{-2T_{rot}/T}$$

• visokotemperaturna limita $k_B T \gg \frac{\hbar^2}{2I}$ $\qquad T \gg T_{rot}$

$$e^{-\beta F_{rot}} \doteq \int_0^\infty e^{-\overbrace{j(j+1)\beta/\beta_{rot}}^{u}}(2j+1)\,dj = \frac{\beta_{rot}}{\beta}\int_0^\infty e^{-u}\,du = \frac{\beta_{rot}}{\beta}$$

$$\beta F_{rot} = -\ln\frac{\beta_{rot}}{\beta} = \ln\beta - \ln\beta_{rot}$$

$$\bar{E}_{rot} = \frac{1}{\beta} = k_B T$$

Vibracije

1D HO $\quad E_n = (n + 1/2)\hbar\omega \quad n = 0, 1, 2, \dots\infty$

$$e^{-\beta F_{vib}} = \sum_{n=0} e^{-\beta(n+1/2)\hbar\omega} = e^{-\beta\hbar\omega/2}\sum_{n=0} e^{-n\beta\hbar\omega} \overset{\text{geometrijska vsota}}{=} e^{-\beta\hbar\omega/2}\frac{1}{1-e^{-\beta\hbar\omega}}$$

$$\beta F_{vib} = \beta\frac{\hbar\omega}{2} + \ln\left(1 - e^{-\beta\hbar\omega}\right) \qquad \bar{E}_{vib} = \frac{\hbar\omega}{2} + \frac{\hbar\omega\,e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} = \hbar\omega\left(\frac{1}{2} + \underbrace{\frac{1}{e^{\beta\hbar\omega}-1}}_{\bar{n}}\right)$$

$$C_{vib} = k_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \to \text{limita}$$

Paramagnetizem

- Snov je paramagnetna, če se v njej pojavi magnetizacija ko je v zun. mag. polju $M \propto H$, $\vec{M} \parallel \vec{H}$
- Magnetna susceptibilnost $M = \chi H$ $\quad 0 < \chi \ll 1$
- Atomi neodvisni, bistvena sklopitev z zunanjim mag. poljem

$\vec{p}_m$ $\quad$ $\vec{p}_m$ $\quad$ $\vec{B}$

- Energija $E = -\vec{p}_m \cdot \vec{B} = -p_{mz} B$
  - $\hookrightarrow p_{mz}$ kvantiziran

$p_{mz} = \gamma \hbar j_z \qquad \gamma \ldots$ giromagnetno razmerje (g) $\qquad j_z \ldots$ vrtilna količina na z-osi

$\hookrightarrow \gamma = e_0/m_e \qquad j_z = -j, -j+1, \ldots, j-1, j \quad (2j+1)$ vrednosti

- $M \propto \overline{p_{mz}} = -\dfrac{\bar{E}}{B}$

- $$e^{-\beta F} = \sum_{j_z=-j}^{j} e^{+\beta \overbrace{\gamma\hbar B}^{\alpha} j_z} = \sum_{j_z=-j}^{j} e^{\alpha j_z} = e^{\alpha j} \sum_{j_z=-2j}^{0} e^{\alpha j_z} = e^{\alpha j}\left(1 + e^{-\alpha} + e^{-2\alpha} + \ldots + e^{-2j\alpha}\right) =$$

$$= e^{\alpha j} \frac{1-e^{-(2j+1)\alpha}}{1-e^{-\alpha}} = \frac{e^{\alpha(j+\frac{1}{2})}}{e^{\alpha\frac{1}{2}}} \frac{1-e^{-(2j+1)\alpha}}{1-e^{-\alpha}} = \frac{e^{\alpha(j+\frac{1}{2})} - e^{-\alpha(j+\frac{1}{2})}}{e^{\alpha/2} - e^{-\alpha/2}} = \frac{\operatorname{sh} \alpha(j+\frac{1}{2})}{\operatorname{sh} \alpha/2}$$

$$\beta F = -\ln \operatorname{sh} \alpha(j+\tfrac{1}{2}) + \ln \operatorname{sh} \alpha/2 = \qquad \frac{d}{d\beta} = \frac{d}{d\alpha}\frac{d\alpha}{d\beta} = \frac{d}{d\alpha}\gamma\hbar B$$

$$\bar{E} = -\gamma\hbar B\left(\frac{\operatorname{ch} \alpha(j+\frac{1}{2}) \cdot (j+\frac{1}{2})}{\operatorname{sh} \alpha(j+\frac{1}{2})} - \frac{\operatorname{ch} \alpha/2 \cdot \frac{1}{2}}{\operatorname{sh} \alpha/2}\right) = -\gamma\hbar B\left((j+\tfrac{1}{2}) \coth(\alpha(j+\tfrac{1}{2})) - \tfrac{1}{2}\coth \alpha/2\right)$$

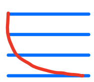
$$\overline{p_{mz}} = -\frac{\bar{E}}{B} = \gamma\hbar\left((j+\tfrac{1}{2})\coth(\alpha(j+\tfrac{1}{2})) - \tfrac{1}{2}\coth \alpha/2\right)$$

- Nizko- in visokotemperaturna limita:

$-3/2$, $-1/2$, $1/2$, $3/2$ $\qquad E = -\gamma\hbar B j_z \qquad$ Ekvidistančna stanja

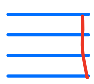
$\Delta E = \gamma\hbar B$ $\quad$ značilna energija

- Nizke T: $k_B T \ll \gamma\hbar B$



zasedenost stanj

- Visoke T: $k_B T \gg \gamma\hbar B$



- Curiejev zakon

$k_B T \gg \gamma\hbar B \Rightarrow \beta\gamma\hbar B \ll 1 \Rightarrow$ razvijemo $\coth x = \frac{1}{x} + \frac{x}{3} + \ldots$

$$\overline{p_{mz}} = \gamma\hbar\left(\cancel{(j+\tfrac{1}{2})}\frac{1}{\cancel{(j+1/2)}\alpha} + (j+\tfrac{1}{2})\tfrac{1}{3}(j+\tfrac{1}{2})\alpha - \cancel{\tfrac{1}{2}\tfrac{1}{\alpha/2}} - \tfrac{1}{2}\tfrac{1}{3}\tfrac{\alpha}{2}\right) = \gamma\hbar\frac{\alpha}{3}\left((j+\tfrac{1}{2})^2 - \tfrac{1}{4}\right) =$$

$$= \gamma\hbar\frac{\alpha}{3} j(j+1) = \frac{1}{3}(\gamma\hbar)^2 j(j+1)\frac{B}{k_B T} \Big\} \; M \propto \frac{H}{T}$$

$M = \dfrac{N\,\overline{p_{mz}}}{V}$ $\qquad$ Curiejev zakon

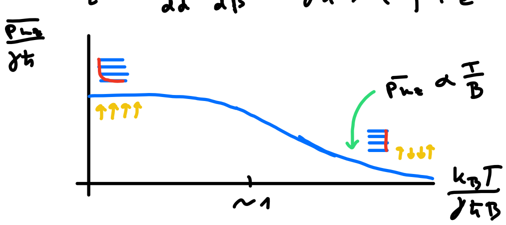
- Nizko temp. limita

Vzamemo le prvi 2 stanji ker sta najbolj zasedeni

$$e^{-\beta F} \doteq \underbrace{e^{+\alpha j}}_{j_z = j} + \underbrace{e^{+\alpha(j-1)}}_{j_z = j-1} = e^{\alpha j}(1 + e^{-\alpha})$$

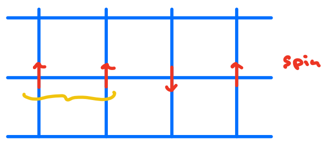
$$\beta F = -\alpha j - \ln(1 + e^{-\alpha}) \doteq -\alpha j - e^{-\alpha}$$

$$\bar{E} = \frac{d\beta F}{d\alpha}\frac{d\alpha}{d\beta} = \gamma\hbar B(-j + e^{-\alpha}) = \underbrace{-\gamma\hbar B j}_{\text{energija osnovnega stanja}} + \underbrace{\gamma\hbar B}_{\Delta E \text{ za osnovno in prvo stanje}} \underbrace{e^{-\alpha}}$$ verjetnost, da je stanje zasedeno



Isingov model

- prehod iz paramagnetnega stanja v feromagnetno



Interakcija le med najbližjimi sosedi

$$H = -J \sum_{ij} \vec{S}_i \cdot \vec{S}_j \Rightarrow -J \sum_{ij} S_{iz} S_{jz}$$

izmenjalni integral — sosedi — spin

- Približek povprečnega polja

$$H = -\sum_i \gamma\hbar \, S_{iz} \bar{B}_i$$

↳ lokalno polje

z ... koordinacijsko število = št. sosedov

$$B_i = J \sum_{j \text{ sosedi od } i} \frac{S_j}{\gamma\hbar} \rightarrow \bar{B}_i = \frac{zJ\bar{S}_j}{\gamma\hbar} = \frac{zJ}{\gamma\hbar}\frac{\bar{p}_j}{\gamma\hbar}$$

- $S_i = \pm\frac{1}{2} \Rightarrow p_B$ ... Bohrov magneton $= \frac{\gamma\hbar}{2}$

$$\bar{B}_i = \frac{zJ\bar{p}_{zj}}{4p_B^2}$$

- fazna vsota za $S = \pm 1/2$, imamo samo 2 člena

$$e^{-\beta F} = e^{\alpha/2} + e^{-\alpha/2}$$

$$\vdots$$

$$\bar{p}_z = p_B \tanh \beta p_B B$$

$$B \propto \bar{p}_z$$

$$\frac{\bar{p}_z}{p_B} = \tanh \frac{\beta p_B zJ \bar{p}_z}{4p_B^2} = \tanh \frac{zJ}{4k_BT}\frac{\bar{p}_z}{p_B}$$

$$\Rightarrow \mu = \tanh \frac{\mu}{\tau} \qquad \mu = \frac{\bar{p}_z}{p}, \quad \tau = \frac{zJ}{4k_BT}$$

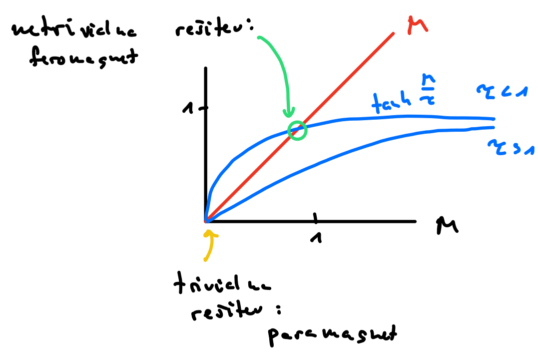
Ta enačba ni analitično rešljiva

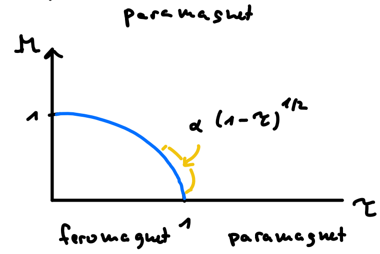
- Pri $\tau \ll 1$ $\quad \left(x \ll 1: \tanh x = x - \frac{x^3}{3}\right)$

$$\mu \doteq \frac{\mu}{\tau} - \frac{1}{3}\left(\frac{\mu}{\tau}\right)^3$$

$$\mu = \pm\sqrt{3\tau^2(1-\tau)} \; ; \; \tau < 1$$

$\propto (1-\tau)^{1/2} \Rightarrow \beta = 1/2$ kritični eksponent za urejevalni parameter





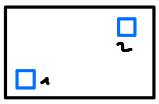
Velekanonična porazdelitev

- mikrokanonična porazdelitev: $E = \text{konst}$, $N = \text{konst}$
- kanonična porazdelitev: $E \neq \text{konst}$, $N = \text{konst}$
- velekanonična porazdelitev: $E \neq \text{konst}$, $N \neq \text{konst}$
- verjetnostna gostota: $\rho(E) \rightarrow \rho(E,N)$

$$\sum_j \rho_j = 1 \rightarrow \sum_{N=0}^{\infty} \underbrace{\sum_j \rho_{Nj}}_{\frac{(2j+1)^N}{N!\,h^{3N}} \int \rho_N \, d\Gamma_N} = 1$$

$$= c_N$$

- odvisnost $\rho(E,N)$ od N?



$$N_{1+2} = N_1 + N_2$$

$$\rho_{1+2}(N_{1+2}) = \rho_1(N_1)\,\rho_2(N_2) \quad \text{šibko sklopljeni} \quad \Big|\ \ln,\ \frac{\partial}{\partial N_1},\ \frac{\partial}{\partial N_2}$$

$$\frac{1}{\rho_{1+2}} \frac{\partial \rho_{1+2}}{\partial N_{1+2}} \underbrace{\frac{\partial N_{1+2}}{\partial N_1}}_{=1} = \frac{1}{\rho_1}\frac{d\rho_1}{dN_1}$$

$$\frac{1}{\rho_{1+2}} \frac{\partial \rho_{1+2}}{\partial N_{1+2}} \underbrace{\frac{\partial N_{1+2}}{\partial N_2}}_{=1} = \frac{1}{\rho_2}\frac{d\rho_2}{dN_2}$$

$$\frac{1}{\rho_1}\frac{d\rho_1}{dN_1} = \frac{1}{\rho_2}\frac{d\rho_2}{dN_2} = \beta\mu$$

$$f(N_1) = g(N_2) = \text{konst.}$$

$$\frac{1}{\rho}\frac{d\rho}{dN} = \beta\mu \Rightarrow \frac{d\rho}{\rho} = \beta\mu\, dN \Rightarrow \ln\rho = \beta\mu N \Rightarrow \rho(N) \propto e^{\beta\mu N}$$

kemijski potencial

$$\boxed{\rho(E,N) \propto \exp(\beta\mu N - \beta E)}$$ do normirne konstante

- fazna vsota

$$e^{-\beta\Omega} = \sum_{N=0}^{\infty} \sum_j \exp(\beta\mu N - \beta E)$$

velepotencial

po vseh stanjih

po številih delcev v sistemu

- $\bar{E} = \left(\frac{d\beta\Omega}{d\beta}\right)_{\beta\mu, V}$

$$\bar{N} = -\left(\frac{\partial \beta\Omega}{\partial \beta\mu}\right)_{\beta, V}$$

$$\beta\Omega = -\ln \sum_{N=0}^{\infty} \sum_j \exp(\beta\mu N - \beta E)$$

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{\beta, \beta\mu}$$

$$\bar{N} = -\left(-\frac{\sum_{N=0}^{\infty} \sum_j N \exp(\beta\mu N - \beta E)}{\sum_{N=0}^{\infty} \sum_j \exp(\beta\mu N - \beta E)}\right)$$

- $d\beta\Omega = \bar{E}\, d\beta - \bar{N}\, d\beta\mu - p\beta\, dV$

$$d\beta F = \bar{E}\, d\beta \qquad - p\beta\, dV \quad (\text{glej entropijo})$$

$$d\beta\Omega = d\beta F - \bar{N}\, d\beta\mu$$

$$\Rightarrow \beta\Omega = \beta F - \bar{N}\beta\mu$$

$$\Omega = F - \bar{N}\mu$$

kemijski potencial prosta entalpija na delec

$$= F - G = -pV \quad (\text{ker } G = F + pV)$$

$$\boxed{\Omega = -pV}$$

- μ za klasični enoatomni plin

Taylor $e^x = \sum \frac{x^n}{n!}$

$$e^{-\beta\Omega} = \sum_{N=0}^{\infty} c_N \int \varphi_N \, d\Gamma_N = \sum_{N=0}^{\infty} \frac{(2j+1)^N}{N!\, h^{3N}} V^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} e^{\beta\mu N} = \exp\left(\frac{2j+1}{h^3} V \left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} e^{\beta\mu}\right)$$

vpostavimo $e^{\beta\mu N - \beta E}$ ↳ že izračunali

$$e^{\beta\mu} = \frac{h^3}{(2j+1)\left(\frac{2\pi m}{\beta}\right)^{3/2} V} (-\beta\Omega) \quad -pV$$

$$= \underbrace{\frac{h^3}{(2j+1)(2\pi m)^{3/2} k_B^{5/2}}}_{\frac{1}{J}} \frac{p}{T^{5/2}}$$

J je kemijska konstanta

- Enačba stanja

$$p = -\left(\frac{\partial \Omega}{\partial V}\right)_{\beta, \beta\mu} = -\frac{\partial \beta\Omega}{\partial \beta V} \quad \text{ali}$$

$$\bar{N} = -\frac{\partial \beta\Omega}{\partial \beta\mu} = + \frac{(2j+1)\left(\frac{2\pi m}{\beta}\right)^{3/2} V}{h^3} e^{\beta\mu} = -\beta\Omega \qquad \beta\Omega = -\frac{(2j+1)\left(\frac{2\pi m}{\beta}\right)^{3/2} V}{h^3} e^{\beta\mu}$$

$$= -\beta\Omega = -\beta(-pV$$

$$\bar{N} = \beta p V$$

$$pV = k_B \bar{N} T$$

Velekanonična fazna vsota

$$e^{-\beta\Omega} = \sum_{N=0}^{\infty} \sum_{\substack{\{N_i\} \\ \sum_j N_j = N}} \exp(\beta\mu N - \beta E(\{N_i\}))$$

$N = \sum_j N_j$, $E = N_j E_j$

stanja: N_1, N_2, N_3, N_4

$$= \sum_{\{N_j\}} \exp\left(\beta\mu \sum_j N_j - \beta \sum_j N_j E_j\right) = \sum_{\{N_j\}} \prod_j \underbrace{\exp(\beta\mu N_j - \beta N_j E_j)}_{\exp a_j N_j} = \qquad a_j = \beta\mu - \beta E_j$$

$$= e^{a_1 \cdot 0} e^{a_2 0} e^{a_3 0} \dots + \quad \text{nobenega delca}$$

$$e^{a_1 \cdot 1} e^{a_2 0} e^{a_3 0} \dots + \quad \text{en delec v 1. stanju}$$

$$e^{a_1 0} e^{a_2 1} e^{a_3 0} \dots + \quad \text{en delec v 2. stanju}$$

$$\vdots$$

$$e^{a_1 2} e^{a_2 0} e^{a_3 0} + \quad \text{dva delca v 1. stanju}$$

$$e^{a_1 1} e^{a_2 1} e^{a_3 0} + \quad \text{en delec v 1. in en v 2. stanju}$$

$$+ \dots$$

$$= (e^{a_1 0} + e^{a_1 1} + e^{a_1 2} + \dots)(e^{a_2 0} + e^{a_2 1} + \dots) \dots =$$

$$= \underline{\prod_j \sum_{N_j} e^{\beta\mu N_j - \beta E_j N_j}}$$

po vseh možnih delcih v stanju j

- Fermioni (Paulijevo izključitveno načelo $N_j = 0$ ali 1)

$$e^{-\beta\Omega} = \prod_j \left(e^{\beta\mu 0 - \beta E_j 0} + e^{\beta\mu - \beta E_j} \right) = \prod_j \left(1 + e^{\beta\mu - \beta E_j}\right)$$

$$\beta\Omega = -\ln \prod_j \left(1 + \exp \beta\mu - \beta E_j\right) = -\sum_j \ln\left(1 + \exp \beta\mu - \beta E_j\right)$$

$$\bar{N} = -\left(\frac{\partial \beta\Omega}{\partial \beta\mu}\right) = \sum_j \frac{(\mu - E_j)\exp(\beta\mu - \beta E_j)}{1 + \exp(\beta\mu - \beta E_j)} = \sum_j \underbrace{\frac{\mu - E_j}{\exp(\beta E_j - \beta\mu) + 1}}_{\bar{N}_{FD}}$$

Povprečno zasedbeno število $\bar{N}_{FD}$ Fermi Diracova porazdelitev

- Bozoni (ni Paulijevega načela, $N_j = 0, 1, 2, \ldots$)

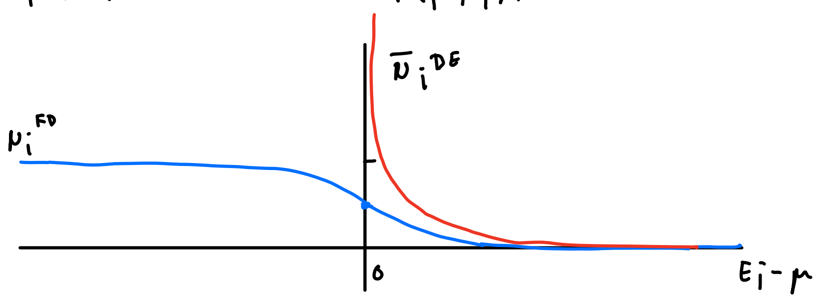
$$e^{-\beta\Omega} = \prod_j \sum_{N_j=0}^{\infty} \exp\left(\beta(\mu - E_j)N_j\right) \overset{\text{geo. vrsta}}{=} \prod_j \frac{1}{1 - \exp(\beta(\mu - E_j))}$$

$$\beta\Omega = \sum_j \ln\left(1 - \exp(\beta(\mu - E_j))\right)$$

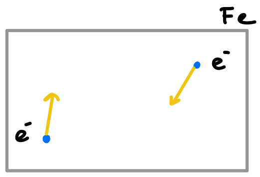
$$\bar{N} = -\frac{\partial \beta\Omega}{\partial \beta\mu} = -\sum_j \frac{-\exp(\beta(\mu - E_j))}{1 - \exp(\beta(\mu - E_j))} = \sum_j \underbrace{\frac{1}{\exp(\beta E_j - \beta\mu) - 1}}_{\bar{N}_{BE}}$$

Bose Einsteinova porazdelitev

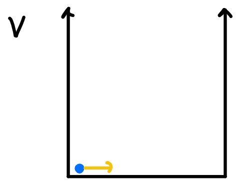
$$\bar{N}_j^{FD} = \frac{\mu - E_j}{\exp(\beta E_j - \beta\mu) + 1} \qquad \bar{N}_j^{BE} = \frac{1}{\exp(\beta E_j - \beta\mu) - 1}$$



Plin prostih elektronov v kovini (kaj je kemijski potencial μ)



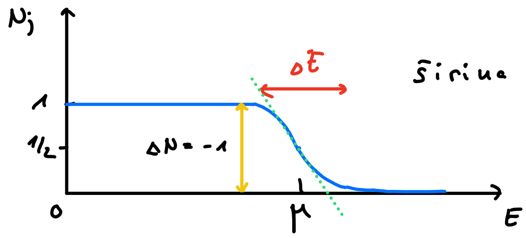
$\longrightarrow$ kovino lahko obravnavamo kot ∞ pot. jamo za e^-.



$$E = E_{kin} = \frac{p^2}{2m}$$

$$\bar{N}_j = \frac{1}{\exp(\beta(E_j-\mu))+1}$$

zasedbeno število



širina stopnice

$$\bar{N} = \int_0^\infty \bar{N}(E)\, g(E)\, dE$$

skupno št e^-

št e^- pri določeni E (zasedbeno število)

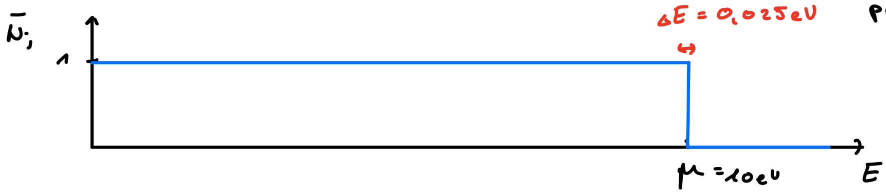
$$\left.\frac{dN_i}{dE}\right|_{E=\mu} = \left.\frac{-\beta \exp(\beta(E-\mu))}{(\exp(\beta(E-\mu))+1)^2}\right|_{E=\mu} = -\frac{\beta}{4}$$

$$\frac{\delta N_i}{\delta E} = -\frac{\beta}{4} \quad \Rightarrow \quad \delta E = \frac{4}{\beta} = 4 k_B T$$

Širina stopnice je sorazmerna s termično energijo $k_B T$ (oz. s temp.)

μ v kovinah tipično nekaj eV (5eV, 10eV)

$\delta E = 0{,}025\,\mathrm{eV}$ pri $T = 300\,\mathrm{K}$ $\quad k_B T = 0{,}025\,\mathrm{eV}$



Skoraj Heavisidova porazdelitev

$$\bar{N} = \int_0^\infty \frac{1}{\exp(\beta(E-\mu))+1}\, g(E)\, dE \doteq \int_0^\mu g(E)\, dE$$

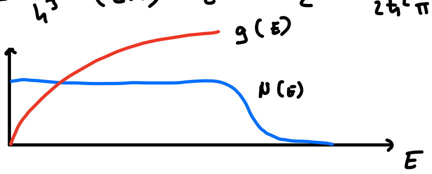
Gostota stanj $\quad g(E)\, dE = d\Gamma = 2\,\frac{d^3r\, d^3p}{h^3} \rightarrow 2V\,\frac{4\pi p^2}{h^3}\, dp = \ldots$

v vsakem stanju sta dva spina

$$E = \frac{p^2}{2m}$$

$$dp = \frac{1}{2}\sqrt{\frac{2m}{E}}\, dE$$

$$\ldots = \frac{8\pi V}{h^3}(2m)^{3/2} E^{1/2}\, \frac{dE}{2} = \frac{V}{2\hbar^2\pi^2}(2m)^{3/2}\sqrt{E}\, dE$$



$$\bar N = \int_0^\mu g(E)\,dE = \frac{V}{\pi^2\hbar^3}(2m)^{3/2}\,\frac{1}{2}\int_0^\mu \sqrt{E}\,dE = \frac{V}{3\pi^2\hbar^3}(2m)^{3/2}\mu^{3/2}$$

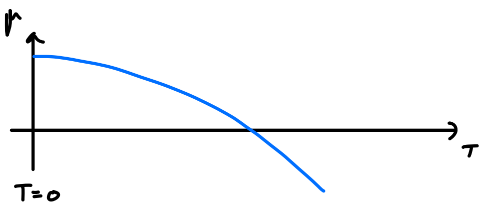
$$\boxed{\mu = \frac{\hbar^2}{2m}\left(\frac{3\pi^2\bar N}{V}\right)^{2/3}}$$

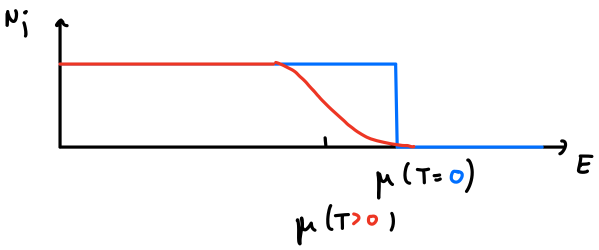
$\bar N$ ... povprečno število valenčnih e^-

za $T = 0\,K$, dober približek tudi za višje T.

valenca

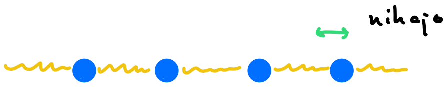
$$\frac{\bar N}{V} = \frac{m}{M}N_A\, z\,\frac{1}{V} = \frac{z\,\rho\, N_A}{M}$$





Specifična toplota trdnin

- 1D model



- Einsteinov model: sistem neodvisnih harmoničnih oscilatorjev
- Fazna vsota za HO 1D

$$e^{-\beta F} = \sum_0^\infty \exp\left(-\beta\hbar\omega\left(n+\tfrac{1}{2}\right)\right) = e^{-\beta\hbar\omega/2}\sum_0^\infty e^{-\beta\hbar\omega n} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}$$

$$\bar E = \frac{d\beta F}{d\beta} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$$

$$C = \frac{d\bar E}{dT} = \frac{d\bar E}{d\beta}\frac{d\beta}{dT} = -\frac{1}{k_BT^2}\hbar\omega(-1)\frac{\hbar\omega\, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} = \qquad \frac{d\beta}{dT} = -\frac{1}{k_BT^2}$$

$$C = k_B(\hbar\omega\beta)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

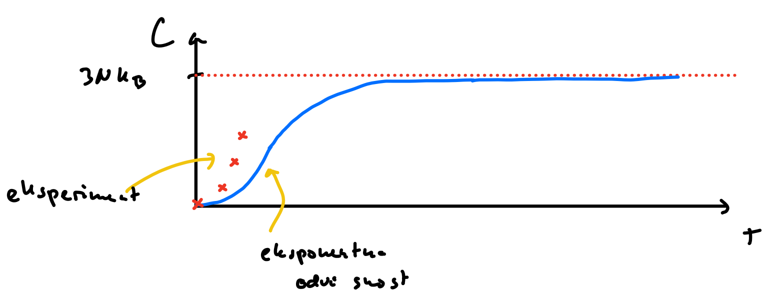
Nizko temp. limit

$$C = k_B\left(\frac{\hbar\omega}{k_BT}\right)^2 e^{-\frac{\hbar\omega}{k_BT}}$$

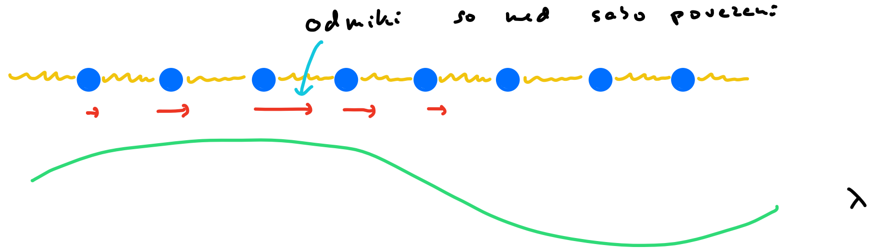
Visokotemperaturna limit

$$C = k_B$$

} za 1 HO
N delcev ima 3N prost. stopenj.



Debyev model

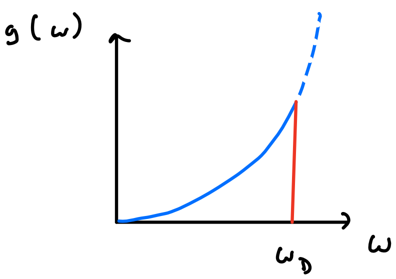


$$\omega = ck = c\frac{2\pi}{\lambda} \qquad p = \frac{\hbar\omega}{c} \qquad dp = \frac{\hbar\, d\omega}{c}$$

$$\bar E = \int_0^\infty \underbrace{\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)}_{\text{povp. energije HO s frekvenco } \omega} \underbrace{g(\omega)}_{\text{gostota stanj}}\, d\omega$$

$$d\Gamma = \underset{\text{3 polarizacije zvoka v trdnini}}{3}\,\frac{d^3r\, d^3p}{h^3} = 3\,\frac{V\, 4\pi p^2\, dp}{h^3} = \dots$$

$$\dots = 3\,\frac{V\, 4\pi\hbar^3\omega^2\, d\omega}{h^3 c^3} = \frac{3V}{2\pi^2 c^3}\,\omega^2\, d\omega$$



(λ ne more biti manjši od razdalje med delci)

Debyeva frekvenca

$$3N = \int_0^{\omega_D} g(\omega)\, d\omega = \frac{3V}{2\pi^2 c^3}\int_0^{\omega_D}\omega^2\, d\omega \Rightarrow$$

$$\omega_D = \sqrt[3]{\frac{6\pi^2 N}{V}}\; c$$

Povprečna energija

$$\bar E = \int_0^{\omega_D}\hbar\omega\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}\right)\frac{3V}{2\pi^2c^3}\,\omega^2\, d\omega$$

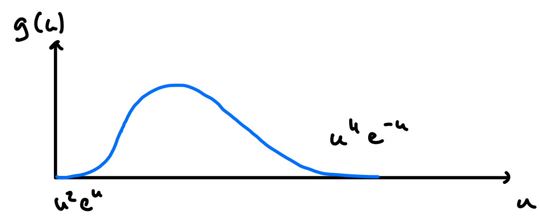
Toplotna kapaciteta $\qquad u = \beta\hbar\omega$

$$C = \frac{d\bar E}{dT} = \frac{d\beta}{dT}\frac{d\bar E}{d\beta} = -\frac{1}{k_B T^2}\int_0^{\omega_D}\hbar\omega\,(-1)\,\frac{\hbar\omega\, e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,\frac{3V}{2\pi^2c^3}\,\omega^2\, d\omega =$$

$$= \frac{3V}{2\pi^2c^3}\,k_B\left(\frac{k_BT}{\hbar}\right)^3\int_0^{\beta\hbar\omega_D}\frac{u^4e^u}{(e^u-1)^2}\, du$$

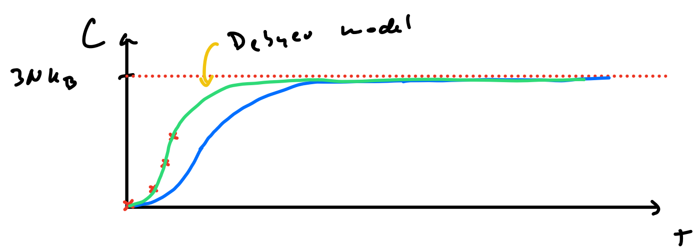
Kaj se dogaja ko $T\to 0$

$$g(\omega) = \frac{u^4e^u}{(e^u-1)^2}$$



Pri $T\to 0$ $\quad \int_0^{\omega_D}\frac{u^4e^u}{(e^u-1)^2}\, du$ ni odvisen od T

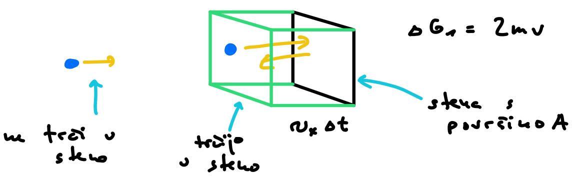
$\Rightarrow$ $\underline{C \propto T^3}$



Kinetična teorija plinov

- šibke interakcije, enostaven opis
- $\rho = \rho(v)$

Tlak idealnega plina



$\Delta G_1 = 2mv$

$$F_x = \frac{\Delta G}{\Delta t} = \frac{\Delta N}{\Delta t}\Delta G_1$$

$$\Delta N = A\, v_x\, \Delta t\, n\, \rho(v_x)$$

številska gostota $\frac{N}{V}$

$$dF_x = A\, v_x\, n\, \rho(v_x)\, 2m\, v_x\, dv_x$$

$$p = \frac{1}{A}\int dF_x = 2mn \int_0^\infty \rho(v_x)\, v_x^2\, dv_x =$$

soda

zanimajo nas le molekule ki se gibljejo iz leve proti desni.

$$p = mn \int_{-\infty}^{\infty} \rho(v_x)\, v_x^2\, dv_x = 2n \int_{-\infty}^{\infty} \rho(v_x)\, \frac{m v_x^2}{2}\, dv_x =$$

$$= 2n \langle E_{kin} \rangle = 2n\, \tfrac{1}{2} k_B T = n k_B T$$

$$= \frac{N}{V} k_B T = \frac{m}{MV} N_A k_B T = \frac{mRT}{MV}$$

Porazdelitvene funkcije

$$\rho(\vec{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-mv^2/2k_B T\right)$$

Povprečna velikost hitrosti

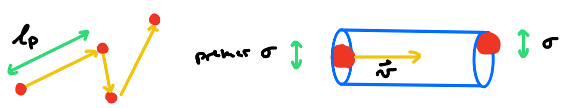
$$\langle v \rangle = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty e^{-\frac{mv^2}{k_B T}}\, v\, 4\pi v^2\, dv$$

$$\boxed{\langle v \rangle = \sqrt{\frac{8 k_B T}{\pi m}}}$$

masa ene molekule

$\langle v \rangle_{zrak} = 450\, m/s$

Povprečna prosta pot



Prostornina valja $\quad \pi \sigma^2 l_p = V$

Št. mol. v valju $\quad N = n \cdot V$

def. $\quad N = 1$

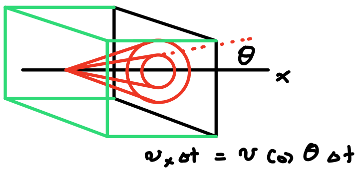
$$1 = n \pi \sigma^2 l_p$$

$$\boxed{l_p = \frac{1}{\pi \sigma^2 n} \quad \left(\text{pravilno izraz } \frac{1}{\sqrt{2}\pi\sigma^2 n}\right)}$$

$l_{p\,zrak} \sim 100\,nm \leftrightarrow \sigma \sim 0{,}1\,nm$

Gostota snovnega toka

•Predpostavimo: vse mol. imajo enako hitrost



• Prostornina kvadra $A v_x \Delta t = A v \cos\theta \, \Delta t$

• Št. mol. ki gredo $d(\Delta N) = A v \cos\theta \, \Delta t \, n \frac{d\Omega}{4\pi}$ skozi okvir v času Δt

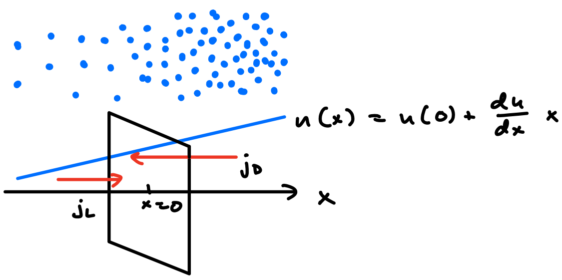
• Gostota snovnega toka $j = \frac{1}{A}\frac{\Delta N}{\Delta t}$

$$j = n \frac{1}{4\pi} v \int_0^{\pi/2} \cos\theta \, d\Omega = \frac{nv}{4\pi}\int_0^{\pi/2} \cos\theta \, (-2\pi) \, d(\cos\theta)$$

$$j = -\frac{nv}{2}\int_0^{\pi/2} \cos\theta \, d(\cos\theta) = \frac{nv}{4}$$

$$\boxed{j = \frac{n\langle v\rangle}{4}}$$

Difuzija



Neto gostota snovnega toka

$$j_x = j_L - j_D = \frac{n_L\langle v\rangle}{4} - \frac{n_D\langle v\rangle}{4}$$

$n(x=-l_p)$ $n(x=l_p)$

Samo še molekule lahko difundirajo

$$j_x = \frac{\langle v\rangle}{4}\left(n(x=-l_p) - n(x=l_p)\right) =$$

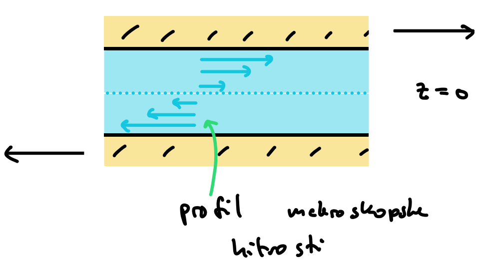
$$= \frac{\langle v\rangle}{4}\left(n(0) + \frac{dn}{dx}(-l_p) - \left(n(0) + \frac{dn}{dx} l_p\right)\right) =$$

$$= -\underbrace{\frac{l_p\langle v\rangle}{2}}\frac{dn}{dx} \quad \leftrightarrow \quad \vec{j} = -D\nabla n$$

D ... difuzijska konstanta.

Točen rezultat $D = 0{,}6 \, l_p \langle v\rangle$

Viskoznost



$$F_x = \frac{\Delta G}{\Delta t} = \frac{m u_2 A j \Delta t - m u_1 A j \Delta t}{\Delta t}$$

$u = \frac{du}{dz} z$ Hitrost $\uparrow b$

$$F_x = mAj\left(\frac{du}{dz}(l_p) - \frac{du}{dz}(-l_p)\right)$$

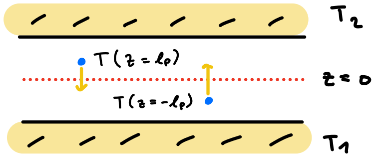
$$= mA\frac{n\langle v\rangle}{4} 2 l_p \frac{du}{dz}$$

$$\frac{F_x}{A} = \frac{mn\langle v\rangle l_p}{2}\frac{du}{dz}$$

$$\frac{F_x}{A} = \underbrace{\frac{\rho\langle \vec{v}\rangle l_p}{2}}_{\eta}\frac{du}{dz}$$

η ... viskoznost

Toplotna prevodnost



$\frac{dT}{dz}$ temp. gradient

$$T(z) = T(0) + \frac{dT}{dz} z$$

Toplotni tok

$$P = \frac{\Delta E_{kin}}{\Delta t} = -\frac{1}{\Delta t}\left(jA\frac{3}{2}k_B T(z=l_p) - jA\frac{3}{2}k_B T(z=-l_p)\right)\Delta t$$

$$P = -\frac{n\langle v\rangle}{4} A \frac{3}{2} k_B \, 2 l_p \frac{dT}{dz}$$

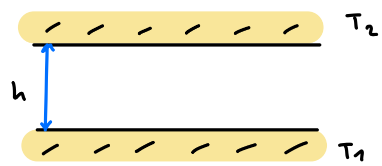
Gostota toplotnega toka

$$j_Q = \frac{P}{A} = -\underbrace{\frac{3 n \langle v\rangle l_p k_B}{4}}_{\lambda} \frac{dT}{dz} \quad \longleftrightarrow \quad j_Q = -\lambda \nabla T$$

Prevajanje toplote v razredčenem plinu

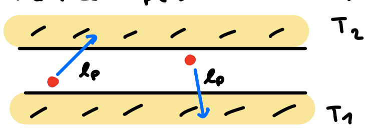
$$j_Q = -\lambda \frac{dT}{dz}$$

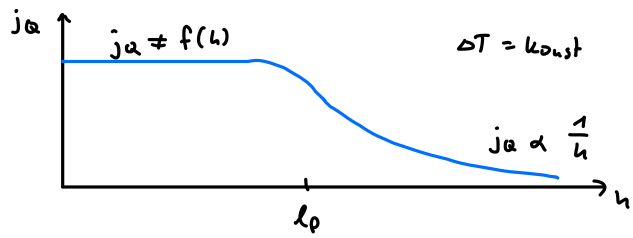
$$= -\lambda \frac{\Delta T}{h}$$



$$\Rightarrow \frac{dT}{dz} = \frac{\Delta T}{h}$$

Tanka plast : $h < l_p$





$j_Q \propto \Delta T$: ni odvisna od h