1.1 Van der Waalsova enačba

$$V_m = \frac{V}{n} = \frac{VM}{m} = \frac{M}{\rho}$$

$$pV = nRT$$
$$pV_m = RT$$

razširimo za realni plin

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

Prepiši van der Waalsovo enačbo v brezdimenzijsko obliko

$$P = \frac{p}{p_c} \qquad v = \frac{V}{V_{mc}} \qquad \tau = \frac{T}{T_c}$$

kritični tlak, kritični volumen, kritična temperatura

Iščemo kritično točko

(1) $\left(\frac{\partial p}{\partial V_m}\right)_T = 0 \qquad \left(\frac{\partial^2 p}{\partial V_m^2}\right)_T = 0$

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

$$p = \frac{RT}{V_m - b} - \frac{a}{V_m^2}$$

$$p' = 2\frac{a}{V_m^3} - \frac{RT}{(V_m-b)^2}$$

$$p'' = -6\frac{a}{V_m^4} + 2\frac{RT}{(V_m-b)^3}$$

(3) $\frac{2a}{V_m^3} - \frac{RT}{(V_m-b)^2} = 0$

$$-\frac{6a}{V_m^4} + \frac{2RT}{(V_m-b)^3} = 0$$

$$RT = \frac{2a(V_m-b)^2}{V_m^3}$$

$$-\frac{6a}{V_m^4} + \frac{4a(V_m-b)^2}{(V_m-b)^3 V_m^3} = 0$$

$$\frac{4a}{(V_m-b)V_m^3} - \frac{6a}{V_m^4} = 0$$

$$\frac{2}{V_m - b} - \frac{3}{V_m} = 0$$

$$2V_m = 3V_m - 3b$$

Kritični volumen $\boxed{V_{mc} = 3b}$

(4) $RT = \frac{2a \cdot 4b^2}{27b^3} = \frac{8a}{27b}$

$\boxed{T_c = \frac{8a}{27bR}}$ Kritična temperatura

(5) $p = -\frac{a}{9b^2} + \frac{R \cdot 8a}{27 \cdot b \cdot R \cdot 2 \cdot b}$

$$p = \frac{-3 \cdot a}{3 \cdot 9b^2} + \frac{4a}{27b^2}$$

$\boxed{p_c = \frac{a}{27b^2}}$ Kritični tlak

(6)
$p = P p_c$
$V_m = v V_{mc}$
$T = \tau T_c$

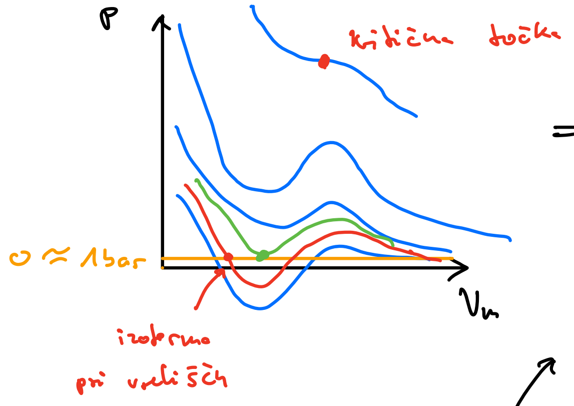
$$\left(p + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

$$\left(P\frac{\cancel{a}}{27\cancel{b^2}} + \frac{\cancel{a}}{v^2 9\cancel{b^2}}\right)(v\,3\cancel{b} - \cancel{b}) = \tau\frac{8\cancel{a}}{27\cancel{b}}$$

$$\left(\frac{P}{27} + \frac{1}{9v^2}\right)(3v - 1) = \frac{8\tau}{27}$$

$$\left(P + \frac{3}{v^2}\right)(3v - 1) = 8\tau$$

1.3 Max temp. pregretja van der Waalsove kapljevine pri majhnem tlaku (1 bar) ≈ 0



$\Rightarrow$ lahko vse pretvorim v brezdimenzijsko

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

$$P = 0$$

$$P = \frac{8T}{3v-1} - \frac{3}{v^2} = 0 \quad \Big/ \cdot \frac{3}{3v-1}$$

Iščem zeleno točko

$$\left(\frac{\partial p}{\partial v}\right)_T = -\frac{3 \cdot 8\,\tau}{(3v-1)^2} + \frac{6}{v^3} = 0$$

$$v = \frac{2}{3}$$

$$\frac{3 \cdot 9}{4} = \frac{8T}{2-1} \Rightarrow \tau = \frac{27}{32} < 1 \checkmark$$

1.9 Prožna gumijasta vrvica (F, x, T)

$$\frac{F}{A} = aT\left(\frac{\ell}{\ell_0} - \left(1 + \sigma\,(T - T_0)\right)\left(\frac{\ell_0}{\ell}\right)^2\right)$$

A ... presek
$a, \ell_0, \sigma, T_0 > 0$ ... konstante

a) temp. koef. dolž. raztezka (α)
b) izotermni prožnostni modul (E_T)

$$d\ell = \ell\,\alpha\,dT + \frac{\ell}{E_T A}\,dF \quad \text{... diferencialna oblika}$$

$$d\ell = \left(\frac{\partial \ell}{\partial T}\right)_F dT + \left(\frac{\partial \ell}{\partial F}\right)_T dF$$

b) $$E_T = \frac{\ell}{A}\left(\frac{\partial F}{\partial \ell}\right)_T \overset{\text{odvajam, pravotno enačbo}}{=} \frac{\ell}{A}\,aAT\left(\frac{1}{\ell_0} + 2\left(1 + \sigma(T - T_0)\right)\frac{\ell_0^2}{\ell^3}\right)$$

$$E_T = aT\left(\frac{\ell}{\ell_0} + 2\left(1 + \sigma(T - T_0)\right)\left(\frac{\ell_0}{\ell}\right)^2\right)$$

a) $$\alpha = \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_F$$

ker sledam pri $F = \text{konst.}$

$$F = F(T, \ell) \Rightarrow dF = \left(\frac{\partial F}{\partial T}\right)_\ell dT + \left(\frac{\partial F}{\partial \ell}\right)_T d\ell = 0$$

$$\left(\frac{\partial F}{\partial T}\right)_\ell dT = -\left(\frac{\partial F}{\partial \ell}\right)_T d\ell$$

$$\alpha = \frac{1}{\ell}\left(\frac{\partial \ell}{\partial T}\right)_F = -\frac{1}{\ell}\,\frac{\left(\frac{\partial F}{\partial T}\right)_\ell}{\left(\frac{\partial F}{\partial \ell}\right)_T} = \frac{1}{T}\,\frac{-\frac{\ell}{\ell_0}+\left(1+\sigma\left(2T-T_0\right)\right)\left(\frac{\ell_0}{\ell}\right)^2}{\frac{\ell}{\ell_0}+2\left(1+\sigma\left(T-T_0\right)\right)\left(\frac{\ell_0}{\ell}\right)^2}$$

$$\left(\frac{\partial F}{\partial T}\right)_\ell = a\left(\frac{\ell}{\ell_0}-\left(1+\sigma\left(T-T_0\right)\right)\left(\frac{\ell_0}{\ell}\right)^2\right)+aT\sigma(-1)\left(\frac{\ell_0}{\ell}\right)^2$$

$$= a\left(\frac{\ell}{\ell_0}-\left(1+\sigma\left(2T-T_0\right)\right)\left(\frac{\ell_0}{\ell}\right)^2\right)$$

Poseben primer: $\sigma = 0$ (popolnoma gibek polimer)

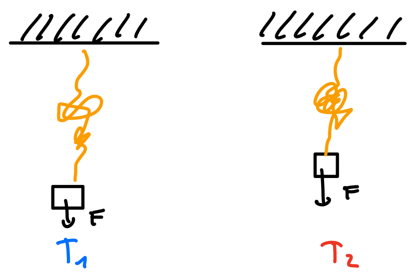
def: $\lambda = \frac{\ell}{\ell_0}$ pri obremenitvi $\lambda > 1$

⋮

$$\alpha = -\underbrace{\frac{1}{T}}_{>0}\,\underbrace{\frac{\lambda^3-1}{\lambda^3+2}}_{>0}$$

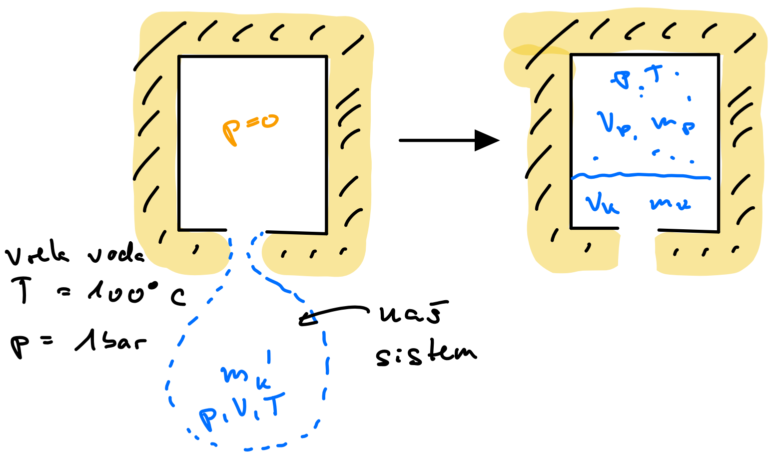
!

$\alpha < 0$ krčenje ko povečamo T



Energijski zakon

2.8 Vdor vrele vode v evakuirano posodo



Iščemo $\frac{m_p}{m_k'} = ?$

$\frac{V_p}{V_k} = ?$

$\frac{1}{\rho_p} = 1{,}673\ \frac{m^3}{kg}$

$\frac{1}{\rho_k} = 1{,}043\ \frac{dm^3}{kg}$

$q_i = 2{,}26\ \frac{MJ}{kg}$

$$\Delta U = W + \cancel{Q}^{\,0}$$

$$m_p\left(q_i - \frac{RT}{M}\right) = pV$$

ker ne rabimo odriniti zraka ko nastane para

$$m_p\left(q_i - \frac{RT}{M}\right) = p\,\frac{m_k'}{\rho_k}$$

$$\frac{m_p}{m_k'} = \frac{p}{\rho_k\left(q_i - \frac{RT}{M}\right)} = 5\cdot 10^{-5}$$

$$\frac{V_p}{V_k} = \frac{m_p\,\rho_k}{\rho_p\,m_k} \approx \frac{m_p}{m_k'}\,\frac{\rho_k}{\rho_p} = 0{,}08$$

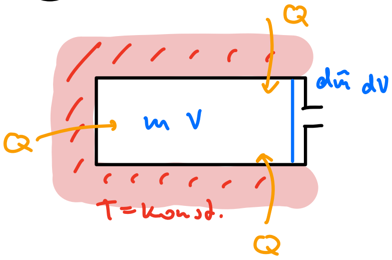
2.5 Plin uide iz termostatirane jeklenke

$T = 20°C$ uide polovica plina ($m \to m/2$)

$V = 5L$

$p' = 10\,bar$ (začetek)

$Q = ?$



$$\Delta U = 0 \quad \text{ker} \quad \Delta T = 0$$

$$d\cancel{U}^{\,0} = dQ + dW$$

Pri idealnem plinu $U(T)$

$$dQ = -dW$$

V vseh ravnovesnih stanjih velja plinska enačba

Plin spuščamo preko majhnih ravnotežnih stanj

$$dQ = p\,dV$$

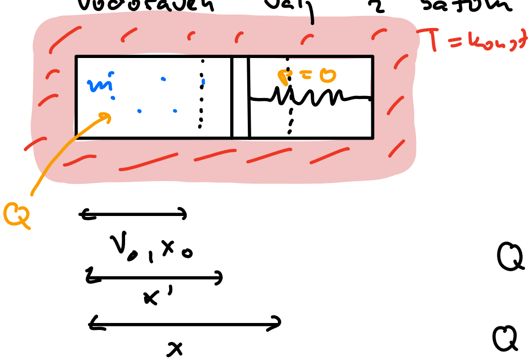
$$Q = \int p\,dV = \int p \frac{d\bar{m}}{\rho}$$

$$Q = \int_{m/2} \frac{mRT}{MV} \frac{d\bar{m}}{m/V} = \int \frac{RT}{M} d\bar{m} \qquad dm = -d\bar{m}$$

$$Q = -\int_{m}^{m/2} \frac{RT}{M} dm$$

$$Q = \frac{RTm}{2M} = \frac{p'V}{2} = 2{,}5\,kJ$$

Kol Vodoraven valj z batom na vzmeti



$T' \to T$

$20°C \to 50°C$

$r = 3\,cm$

$m = 1\,g$

zrak $M = 29$ $c_v = 718$

$k = 10^3\,N/m$

$V_0 = 1\,dm^3$

$Q = ?$

$$Q = \Delta U - W$$

$$Q = m\,c_v(T - T') - \int_{x'}^{x} F\,dx$$

$$Q = m\,c_v(T - T') + \int_{x'}^{x} k(x - x_0)\,dx$$

ker merimo iz ravnovesne lege

$$Q = 23{,}64\,J$$

Delo lahko izračunamo tudi iz prožnostne energije

$$W = -\Delta W_{pr} = -\left(\frac{k(x-x_0)^2}{2} - \frac{k(x'-x_0)^2}{2}\right)$$

$x, x' = ?$

Začetek $\quad p' = k(x' - x_0)/A = \dfrac{mRT'}{M x' A}$

$$x'^2 - x_0 x' - \frac{mRT'}{Mk} = 0$$

$$x'_{1,2} = \frac{1}{2}\left(x_0 \pm \sqrt{x_0^2 + 4\frac{mRT'}{Mk}}\right) \to x' = 0{,}516\,m$$

$$x_{1,2} = \quad (T) \qquad \to x = 0{,}528\,m$$

(T) Delo v magnetnih sistemih (T, H, B) sistem snov in vakuum
(T, H, M) le snov

$$dW_m = \mu_0 H\, d(VB) \qquad B = \mu \mu_0 H$$
$$dW_m = \mu_0 H\, d(VM) \qquad = \mu_0 (H + M) = \mu_0 (\varkappa + 1) H$$

susceptibilnost

$$M = \varkappa H$$

Poseben primer: paramagnet $\quad M(T, H) = \frac{a}{T} H \quad$ (Curiejev zakon)

$$dM = \left(\frac{\partial M}{\partial T}\right)_H dT + \left(\frac{\partial M}{\partial H}\right)_T dH$$

(a) Delo pri magnetenju $(T = \text{konst}, H_1 \to H_2)$

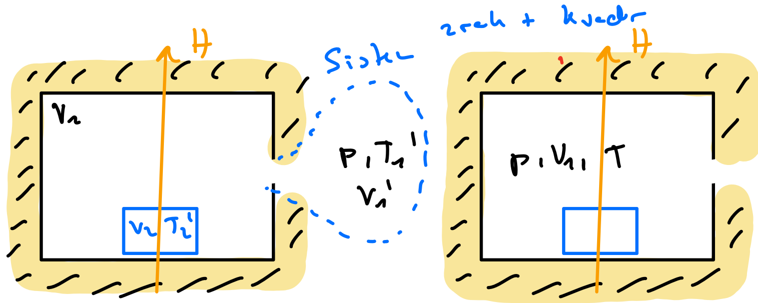
$$\int dW_m = \int_{H_1}^{H_2} \mu_0 V H \frac{a}{T}\, dH \qquad \left(\frac{\partial M}{\partial H}\right)_T = \frac{a}{T} \quad \text{iz Curiejevega zakona}$$

$$W_m = \frac{\mu_0 V a (H_2^2 - H_1^2)}{2T}$$

(b) Delo pri segrevanju $(H = \text{konst}, T_1 \to T_2)$

$$\int dW_m = \int \mu_0 V H\, dM = \mu_0 V H \int_{M_1}^{M_2'} dM = \mu_0 V H (M_2 - M_1)$$
$$= \mu_0 V H a \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

2.11



Evakuirana, izolirana s paramagnetnim kvadrom

$V_1 = 10\,L \qquad p = 1\,bar$
$V_2 = 0,1\,L \qquad T_1' = 27°C$
$C = 10\,J/K \qquad T_2' = -173°C$
$\varkappa = 1,4 \qquad H = 10^7\,A/m$
$\varkappa = a/T \qquad a = 0,1\,K$
$T = ?$

- $$\Delta U = \underbrace{m_1' c_v (T - T_1')}_{\text{plin}} + \underbrace{C (T - T_2')}_{\text{kvader}}$$

$$W = +p V_1' + \mu_0 V H a \left(\frac{1}{T} - \frac{1}{T_2'}\right)$$

Curijev zakon

$$Q = 0$$

- $$p V_1' = \frac{m_1'}{M} R T_1' \quad \text{(začetek)}$$

$$p V_1 = \frac{m_1'}{M} R T \quad \text{(konec)}$$

⋮
sistem enačb
⋮

Rezultat

$$T = -16,4\,°C$$

Entropijski zakon

3.1 Vroč kos železa vržemo v zmes ledu in vode. Sistem je toplotno izoliran.

$T_0 = 0°C$ $\qquad c_p^v = 4180\ J/kgK$
$m_v = 0{,}8\ kg$ $\qquad c_p^{Fe} = 450\ J/kgK$
$m_L = 0{,}2\ kg$ $\qquad q_t = 336\ kJ/kg$
$m_{Fe} = 1\ kg$ $\qquad$ končno stanje ?
$T_{Fe} = 100°C$ $\qquad \Delta S = ?$

a) Za taljenje celega ledu $\quad Q_L = m_L q_t = 67{,}2\ kJ > Q_{Fe}$

Ohladitev Fe $\quad Q_{Fe} = m_{Fe} c_{Fe} (T_{Fe} - T_0) = 45\ kJ$

$\Downarrow$

Končna temp $T = 0°C$

$$m_L' = \frac{Q_{Fe}}{q_t} = 0{,}134\ kg$$

b) Entropijski zakon

$$dS \geq \frac{dQ}{T} = 0$$

Domislimo se nadomestne rev. spremembe

$$\Delta S = \underbrace{\Delta S_{Fe}}_{\text{sprem. temp.}} + \underbrace{\Delta S_L}_{\text{sprem. faze}} + \underbrace{\Delta S_v}_{=0}$$

0 ker se v vodi nič ne dogaja

ker je oddal Q

$$\Delta S_{Fe} = \int_{T_{Fe}}^{T_0} \frac{m c_p^{Fe} dT}{T} = m c_p^{Fe} \ln \frac{T_0}{T_{Fe}} = -140{,}4\ J/K$$

$$\Delta S_L = \frac{m_L' q_t}{T_0} = 164{,}9\ J/K$$

$$\Delta S = +24{,}5\ J/K$$

3.2 Podhlajeno vodo vcepimo z zrnom ledu. Kolikšen del vode zamrzne?

$T' = -20°C$ $\qquad x = \frac{m'}{m}$
$q_t = 336\ \frac{kJ}{kg}$ $\qquad \Delta s = \frac{\Delta S}{m} = ?$
$c_p^L = 2100\ J/kgK$
$c_p^v = 4200\ J/kgK$

Delamo v kalorimetru. $Q = 0$

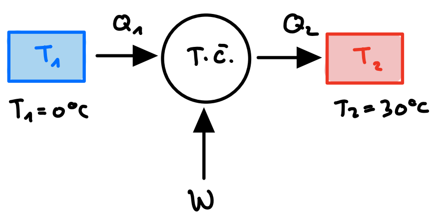
a) $m c_p^v (T - T') = m' q_t$

$$x = \frac{m'}{m} = \frac{c_p^v}{q_t}(T - T') = 0{,}25$$

b) Ireverzibilna sprememba

$$\Delta s = \frac{\Delta S}{m} = \int_{T'}^{T} \frac{c_p^v dT}{T} - \frac{m'}{m}\frac{q_t}{T} = c_p^v \ln\frac{T}{T'} - x\frac{q_t}{T} = 11{,}6\ J/kgK > 0$$

3.4 Toplotna črpalka



$$\frac{W}{Q_2} = ?$$

Energijski zakon $\quad W + Q_1 = Q_2$

Entropijski zakon $\quad 0 \geq \int \frac{dQ}{T} = \frac{Q_1}{T_1} - \frac{Q_2}{T_2}$

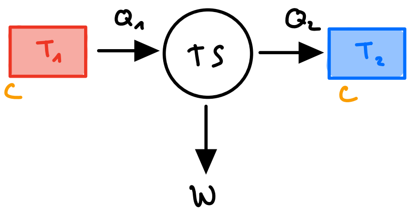
$$\frac{Q_2}{T_2} \geq \frac{Q_1}{T_1} \qquad \frac{Q_2}{T_2} \geq \frac{Q_2 - W}{T_1}$$

$$Q_2\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \geq -\frac{W}{T_1}$$

$$1 - \frac{T_1}{T_2} \leq \frac{W}{Q_2}$$

$$\frac{W}{Q_1} \geq 0{,}099$$

3.6 Idealni toplotni stroj (Carnotov) med končnima toplotnima rezervoarjema

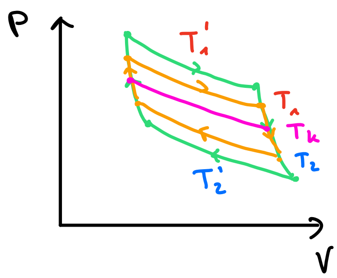


$T_1' = 200°C$
$T_2' = 150°C$
$C = 5\ MJ/K$
$T_k = ?$
$W = ?$

ⓐ En. zakon $\quad dQ_1 = dQ_2 + dW$

Ent. zakon $\quad \Delta S = 0 = \int \frac{dQ_1}{T_1} - \int \frac{dQ_2}{T_2}$

Na rezervoarjih $\quad dQ_1 = -C\,dT_1$
$\quad dQ_2 = C\,dT_2$



Cikli morajo biti zelo kratki, da lahko predpostavimo izoterme.

$$\frac{dQ_2}{T_2} = \frac{dQ_1}{T_1}$$

$$C \int_{T_2'}^{T_k} \frac{dT_2}{T_2} = -C \int_{T_1'}^{T_k} \frac{dT_1}{T_1}$$

$$\ln \frac{T_k}{T_2'} = \ln \frac{T_1'}{T_k}$$

$$T_k = \sqrt{T_1' T_2'} = 447{,}3\,K$$

ⓑ
$$\begin{aligned} W &= Q_1 - Q_2 \\ &= -C(T_k - T_1') - C(T_k - T_2') \\ &= -C(2T_k - T_1' - T_2') \\ &= -7\,MJ \end{aligned}$$

Termodinamski potenciali

1.ep Izpit iz TD 20.3.2009, 3. naloga: Adiabatna reverzibilna demagnetizacija kromovega galuna - paramagnet $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24\,H_2O$

$\mu = 1{,}00029 \quad T' = 20°C \quad \chi = \mu - 1 = 0{,}00029$

Zaradi paramagnetizma velja Curiejev zakon $\chi(T) = \frac{a}{T}$

$\rho = 1830\ \frac{kg}{m^3}$

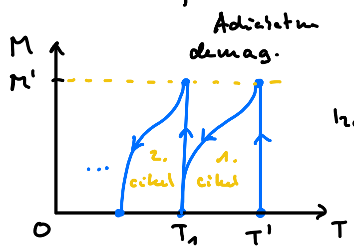
$c_M = 1400\ J/kgK$

$M' = 0 \quad M = 10^5\ A/m \quad$ pri $T =$ konst.

$T_1 = ?$

$T_{meje} = -23°C$

$n = ?$ v koliko korakih pridemo do T meje



Termodinamske spremenljivke: (T, M, H)

Izračun enačbe adiabate

$$dQ = 0 \xRightarrow{REV} dS = 0$$

$$S = S(T,M) \Rightarrow dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_M}_{\frac{m c_M}{T}} dT + \underbrace{\left(\frac{\partial S}{\partial M}\right)_T}_{-V\mu_0 \left(\frac{\partial H}{\partial T}\right)_M} dM = 0$$

ugotovimo

← Maxwellove relacije

H, M, T zvezo dobimo iz enačbe stanja

Maxwellske relacije

① $dU = T\,dS + V\mu_0 H\,dM$

$F = U - TS$
$dF = dU - T\,dS - S\,dT$
$dF = -S\,dT + V\mu_0 H\,dM \Rightarrow$

$F(T,M) \Rightarrow dF = \left(\frac{\partial F}{\partial T}\right)_M dT + \left(\frac{\partial F}{\partial M}\right)_T dM$

②

$G = F - V\mu_0 H M$
$dG = -S\,dT - V\mu_0 M\,dH$

$dG(T,H) = \left(\frac{\partial G}{\partial T}\right)_H dT + \left(\frac{\partial G}{\partial H}\right)_T dH$

Mešani odvod

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

$$\frac{\partial}{\partial M}(-S) = \frac{\partial}{\partial T}(V\mu_0 H)$$

$$\boxed{-\left(\frac{\partial S}{\partial M}\right)_T = V\mu_0 \left(\frac{\partial H}{\partial T}\right)_M}$$

Mešani odvod

$$\frac{\partial^2 G}{\partial H \partial T} = \frac{\partial^2 G}{\partial T \partial H}$$

$$\frac{\partial}{\partial H}(-S) = \frac{\partial}{\partial T}(-V\mu_0 M)$$

$$\boxed{\left(\frac{\partial S}{\partial H}\right)_M = V\mu_0 \left(\frac{\partial M}{\partial T}\right)_H}$$

$$dS = \frac{m c_M}{T} dT - V\mu_0 \underbrace{\left(\frac{\partial H}{\partial T}\right)_M}_{\text{iz enačbe stanja}} = 0$$

$$M(T,H) = \chi(T) H = \frac{a}{T} H$$

$$\Rightarrow H = \frac{TM}{a}$$

$$\left(\frac{\partial H}{\partial T}\right)_M = \frac{M}{a}$$

$$\frac{m c_M}{T} dT - \frac{V\mu_0}{a} M\,dM = 0$$

$$m c_M \ln\frac{T_1}{T'} = \frac{V\mu_0}{2a}(M_0^2 - M'^2)$$

$M_0 = 0$

$$\ln\frac{T_1}{T'} = -\frac{V\mu_0}{2 a m c_M} M'^2$$

$$\chi = \frac{a}{T} \Rightarrow a$$

$$T_1 = T' \underbrace{e^{-\frac{V\mu_0}{2 a m c_M} M'^2}}_{g} = T' e^{-\frac{\mu_0}{2 a \rho c_M} M^2} = \ldots = 284{,}7\,K \Rightarrow \Delta T = -8{,}3\,K$$

po prvem ciklu

Za več ciklov

$g \ldots$ konst

$T_1 = T' g$

$T_n = T' g^n$

$$n = \log_g \frac{T_{mejne}}{T'} = 5{,}4$$

V 6 ciklu dosežemo to mejno temperaturo.

4.9 Jeklena palica

$T = 20\,°C$

$E_T = 2\cdot 10^{11}\ \frac{N}{m^2}$

$E_S = ?$

$\alpha = 10{,}6\cdot 10^{-6}\ K^{-1}$

$c_F \approx c_p = 500\ J/kgK$

$\rho = 7800\ kg/m^3$

TD spremen. (F, l, T)

$$\frac{1}{E_{T}} = \frac{A}{l}\left(\frac{\partial l}{\partial F}\right)_{T}$$

(s pod T: $\frac{1}{E_S} = \frac{A}{l}\left(\frac{\partial l}{\partial F}\right)_S$)

Enačba stanja

$$dl = l\alpha\,dT + \frac{l}{AE_T} dF$$

• Alt. pot

$S = S(F, l)$ (neugodno!)

• $S = S(T, l)$ in $S = S(T, F)$

adiabata

$$dS = \left(\frac{\partial S}{\partial T}\right)_l dT + \underbrace{\left(\frac{\partial S}{\partial l}\right)_T}_{\text{iz Max. relacije}} dl = 0$$

$$dS = \underbrace{\left(\frac{\partial S}{\partial T}\right)_F}_{\text{ne zanima}} dT + \underbrace{\left(\frac{\partial S}{\partial F}\right)_T dF}_{\text{zanima}} = 0$$

Maxwellske relacije

$dU = TdS + Fdl$

$dF = -SdT + Fdl$

$dG = -SdT - l\,dF$

$$-\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial F}{\partial T}\right)_l$$

$$-\left(\frac{\partial S}{\partial F}\right)_T = -\left(\frac{\partial l}{\partial T}\right)_F$$

$$0 = \frac{m c_l}{T} dT - \underbrace{\left(\frac{\partial F}{\partial T}\right)_l}_{\text{iz en. stanja}} dl$$

$$0 = \frac{m c_F}{T} dT + \left(\frac{\partial l}{\partial T}\right)_F dF$$

$$0 = \frac{m c_l}{T} dT - A E_T \alpha\, dl \qquad m c_l \frac{dT}{T} = A E_T \alpha\, dl$$

$$0 = \frac{m c_F}{T} dT + l\alpha\, dF \qquad m c_F \frac{dT}{T} = -l\alpha\, dF$$

$$\frac{c_l}{c_F} = -\frac{AE_T}{l}\left(\frac{dl}{dF}\right)_S$$

$\frac{1}{E_S}$

Izračun $c_F - c_L$ (ne kolokviju)

$$c_F = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_F \qquad S(T, \ell(F,T)) \qquad c_L = \frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_L$$

$$c_F = \underbrace{\frac{T}{m}\left[\left(\frac{\partial S}{\partial T}\right)_\ell\right.}_{c_L} + \left.\left(\frac{\partial S}{\partial \ell}\right)_T \left(\frac{\partial \ell}{\partial T}\right)_F\right]$$

$$c_F - c_L = \frac{T}{m}\left(\frac{\partial S}{\partial \ell}\right)_T\left(\frac{\partial \ell}{\partial T}\right)_F = \frac{T}{m}\left(-\left(\frac{\partial F}{\partial T}\right)_\ell\right)\cdot \ell\lambda = \frac{T}{m} A \alpha^2 E_T \cdot \ell = \frac{T\alpha^2 E_T}{\rho}$$

$$= 0{,}844 \frac{J}{kgK}$$

Uzamemo

$$c_p = c_F(F=0) = 500 \frac{J}{kgK} \Rightarrow c_L = 499{,}156 \frac{J}{kgK} \Rightarrow \frac{c_F}{c_L} = 1{,}0017$$

$$E_S = 2{,}0074\cdot 10^{11} \frac{N}{m^2}$$

Kaj pa $c_F(F) = ?$

$$\left(\frac{\partial c_F}{\partial F}\right)_T = ? = \frac{\partial}{\partial F}\left(\frac{T}{m}\left(\frac{\partial S}{\partial T}\right)_F\right)_T = \frac{T}{m}\frac{\partial}{\partial F}\left(\left(\frac{\partial S}{\partial T}\right)_F\right)_T = \frac{T}{m}\frac{\partial}{\partial T}\left(\left(\frac{\partial S}{\partial F}\right)_T\right)_F$$

$$= \frac{T}{m}\frac{\partial}{\partial T}(\ell\alpha)_F = \frac{T\alpha}{m}\ell\lambda = \frac{T\ell\alpha^2}{m} = \frac{T\alpha^2}{\rho A}$$

$$\Delta c_F = \frac{T\alpha^2}{\rho A}F$$

$$\frac{\Delta c_F}{c_F - c_L} = \frac{T\alpha^2 F \rho}{\rho A T\alpha^2 E_T} = \frac{\overset{\text{majhno}}{F}}{\underset{\text{velik}}{A E_T}} = \text{majhno}$$

Fazni prehodi

5.8 Izparilna toplota tekočine blizu k.T. (CO_2 pri $T = 25\,°C$, $T_c = 31\,°C$, $p_c = 73\,bar$, $V_m = 0{,}096 \frac{m^3}{kmol}$)

$$\left(p + \frac{3}{V^2}\right)(3V-1) = 8T$$

C.C. enačba

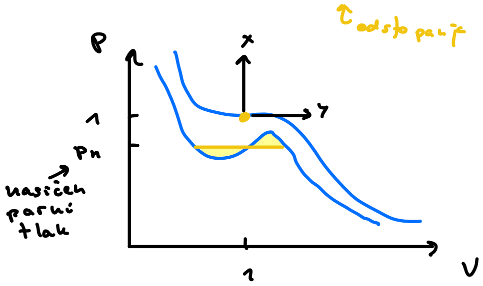
$$\frac{m q_i^{(T)}}{T(V_p^{(T)} - V_k^{(T)})} = \frac{dp_n^{(T)}}{dT}$$

$p = P/p_c \sim 1 + x$ $\qquad 1 \gg x, y, z$

$V = v/v_c \sim 1 + y$

$T = T/T_c \sim 1 + z$

odstopanje



$$P = \frac{8T}{3V-1} - \frac{3}{V^2} = \dots \Rightarrow \underbrace{x = -\frac{3y^3}{2} + 4z - 6yz + 9y^2z - \frac{27}{2}y^3 z + \dots}$$

Poenostavljena Van der Waalsova enačba blizu k.t.

Mehansko ravnotežje $x_p = x_u = x_n$

$$x_n = -\tfrac{3}{2} y_u^3 + 4z - 6zy_u = -\tfrac{3}{2} y_p^3 + 4z - 6zy_p \qquad (1)$$

Kemijsko ravnovesje $\mu_p = \mu_u$

$$\int_u^p p\,dV = p_n (V_u - V_p)$$

$$\int P\,dV = P_n (V_u - V_p)$$

$$\int_{y_u}^{y_p} (1+x)\,dy = (1+x_n)(1+y_p - (1+y_u)) = (1+x_n)(y_p - y_u)$$

$$\int_{y_u}^{y_p} x\,dy = x_n (y_p - y_u)$$

$$\int_{y_u}^{y_p} \left(-\tfrac{3}{2} y^3 + 4z - 6zy\right) dy = -\frac{3y^4}{8} - 4zy - 3zy^2 \Big|_{y_u}^{y_p} = -\tfrac{3}{8}(y_p^4 - y_u^4) - 4z(y_p - y_u) - 3z(y_p^2 - y_u^2)$$

$$\Downarrow$$

$$(2) \qquad x_n = -\tfrac{3}{8}(y_p^2 + y_u^2)(y_p + y_u) + 4z - 3z(y_p + y_u)$$

$$x_n = x_u$$

$$-\tfrac{3}{2} y_u^3 - 6zy_u + \cancel{4z} = -\tfrac{3}{8}(y_p^2 + y_u^2)(y_p + y_u) + \cancel{4z} - 3zy_p - 3zy_u \qquad (3)$$

$$-\tfrac{3}{2} y_p^3 + \cancel{4z} - 6zy_p = -\tfrac{3}{8}(y_p^2 + y_u^2)(y_p + y_u) + \cancel{4z} - 3zy_p - 3zy_u \qquad (4)$$

+

$$-\tfrac{3}{2}(y_u^3 + y_p^3) - \cancel{6z(y_u + y_p)} = -\tfrac{3}{4}(y_p^2 + y_u^2)(y_p + y_u) - \cancel{6z}y_p - \cancel{6z}y_u$$

$$2(y_u^3 + y_p^3) - (y_p^2 + y_u^2)(y_p + y_u) = 0$$

$$(y_p + y_u)(2y_u^2 - 2y_u y_p + 2y_p^2 - y_p^2 - y_u^2) = 0$$

$$(y_p + y_u)(y_u^2 - 2y_u y_p + y_p^2) = 0$$

$$(y_p + y_u)\underbrace{(y_u - y_p)^2}_{\neq 0} = 0$$

ker nismo v kritični točki $\Rightarrow$ $y_p = -y_u$

(4) Vstavim $y_p = -y_u$

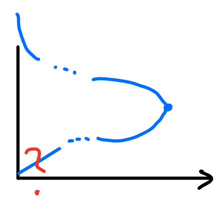
$$-\tfrac{3}{2} y_p^3 - 6zy_p = 0$$

$$y_p^3 + 4zy_p = 0$$

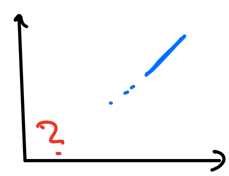
$$y_p^2 + 4z = 0$$

$$y_p = \pm 2\sqrt{-z}$$ → ker smo pod krit. toč. je $z < 0$

$y_p = 2\sqrt{-z}$ $\quad y_u = -2\sqrt{-z}$ $\quad \Rightarrow$ $V_p = 1 + 2\sqrt{1-T}$ $\quad V_u = 1 - 2\sqrt{1-T}$



(2) Vstavim $y_p = -y_u$ $\quad x_n = 4z$ $\quad \rightarrow$ $P_n = 4T - 3$

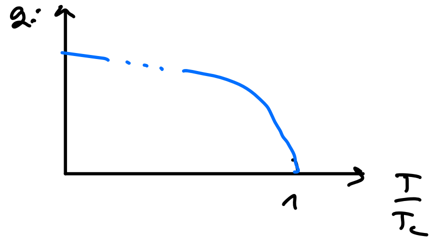


C.C. enačba

$$q_i = \frac{dp_n}{dT}\,\frac{T(v_p - v_k)\cdot \tilde{M}}{m} = q_i = \frac{p_c}{T_c}\frac{dp_n}{dT}\,\frac{T}{M}\,V_m^c\,(v_p - v_k)$$

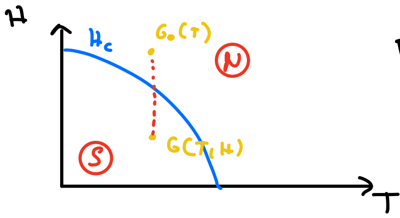
$$= \frac{p_c V_m^c}{M}\,\frac{T}{T_c}\,4\left(1+2\sqrt{1-\frac{T}{T_c}} - (1-2\sqrt{1-T/T_c}\right)$$

$$q_i(T) = 16\,\frac{p_c V_m^c\,T}{M\,T_c}\sqrt{1-\frac{T}{T_c}}$$



S-16 Super prevodnik

$$H_c(T) = H_0\left(1-\left(\frac{T}{T_c}\right)^2\right)$$



Fazni diagram

- Normalna faza N

  $M \doteq 0 \qquad G_N = G_0(T)$

- Superprevodna faza S

  $B = 0 \quad \Rightarrow M = -H$

$\mu_0(H+M) = 0$

enačbi stanja

$$dU = TdS + \mu_0 V H dM$$

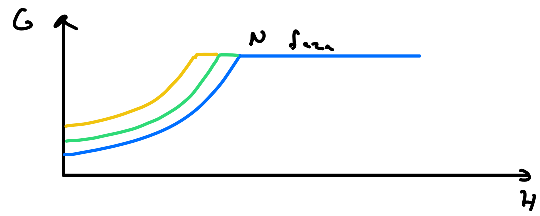
$$dG(T,H) = dG = -\underbrace{S}_{\left(\frac{\partial G}{\partial T}\right)_M}dT - \underbrace{\mu_0 V M}_{\left(\frac{\partial G}{\partial H}\right)_T} dH$$

$$Q_{SN} = T(S_N - S_S)$$

$$= T\left(-\left(\frac{\partial G_N}{\partial T}\right)_H + \left(\frac{\partial G_S}{\partial T}\right)_H\right)$$

$$G_S(T,H) = G_0^N(T) + \int_{H_c}^{H}\left(\frac{\partial G_S}{\partial H}\right)_T dH = G_0(T) - \int_{H_c}^{H}\mu_0 V M dH = G_0(T) + \int_{H_c}^{H}\mu_0 V H dH =$$

$$= G_0(T) + \frac{\mu_0 V}{2}\left(H^2 - H_c^2(T)\right)$$



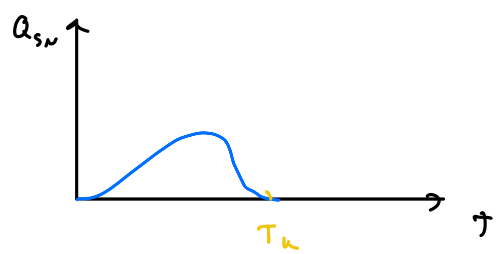
$$Q_{SN} = T\left(-\left(\frac{\partial G_N}{\partial T}\right)_H + \left(\frac{\partial G_S}{\partial T}\right)_H\right)$$

$$= T\left(-\cancel{\frac{dG_0}{dT}} + \cancel{\frac{dG_0}{dT}} - \frac{\mu_0 V}{\cancel{2}}\left(\cancel{2}H_c\frac{dH_c}{dT}\right)\right)$$

$$= -T\mu_0 V H_c \frac{dH_c}{dT}$$

$$= -T\mu_0 V\, H_0\left(1-\left(\frac{T}{T_c}\right)^2\right) H_0\,(-2)\,\frac{T}{T_c^2} =$$

$$Q_{SN} = 2\mu_0 V H_0^2\left(\frac{T}{T_c}\right)^2\left(1-\left(\frac{T}{T_c}\right)^2\right)$$



Alternativno iz C.C. enačbe

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{dp_n}{dT} \rightarrow \left(\frac{\partial S}{\partial m}\right)_T = -\mu_0 V \frac{dH}{dT}$$

$$\frac{\Delta S}{\Delta m} = \frac{m q_{sn}}{T(0-(-H_c))} = -\mu_0 V \frac{dH_c}{dT} \Rightarrow Q_{sN} = -\mu_0 V T H_c \frac{dH_c}{dT}$$

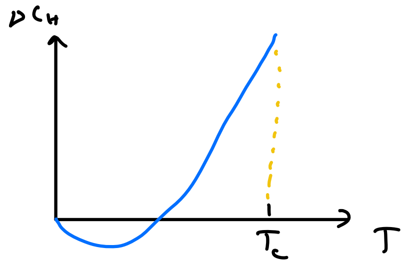
Iščemo še $c_H^S - c_H^N$ pri $H = konst.$

$$c_H^S - c_H^N = \frac{T}{m}\left(\frac{\partial S_s}{\partial T}\right)_H - \frac{T}{m}\left(\frac{\partial S_N}{\partial T}\right)_H = \frac{T}{m}\left(\frac{\partial}{\partial T}(S_s - S_N)\right)_H = \frac{T}{m}\frac{\partial}{\partial T}\left(\frac{-Q_{sN}}{T}\right)_H = \frac{T}{m}\mu_0 V \frac{\partial}{\partial T}\left(H_c \frac{dH_c}{dT}\right)_H$$

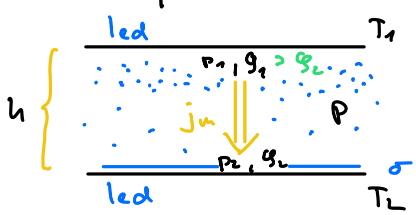
$$= -\frac{T}{m}\left(\frac{\partial}{\partial T}\left(2\mu_0 V \frac{H_0^2}{T}\frac{T^2}{T_c^2}\left(1-\frac{T^2}{T_c^2}\right)\right)\right) =$$

$$= -2\mu_0 \frac{H_0^2 V T}{T_c^2 m}\left(1 - \frac{3T^2}{T_c^2}\right)$$

$$= 2\mu_0 \frac{H_0^2}{\rho T_c}\frac{T}{T_c}\left(\frac{3T^2}{T_c^2} - 1\right)$$



7.6 Destilacija ledu



$p = 1 bar$ $\quad h = 1 cm$

$T_1 = 0°C$ $\quad T_2 = -15°C$

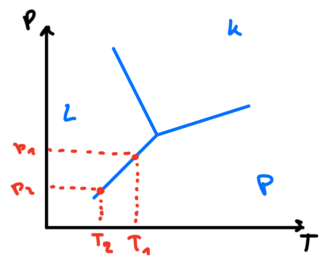
$p_1 = p_n(T_1) = 6 mbar$ $\quad p_2 = p_n(T_2) = h mbar$

$t = 1h$

$D = 0{,}2\ cm^2/s$ $\quad M = 18$

$\rho_L = 916\ kg/m^3$

$\delta = ?$



ker ni ponorov in izvorov snovi

$$j_m = D\frac{d\rho}{dz} = konst \Rightarrow \rho(z) = linearna$$

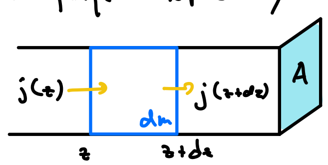
$$= D\frac{\rho_1 - \rho_2}{h}$$

$$= \frac{D}{h}\left(\frac{p_1 M}{RT_1} - \frac{p_2 M}{RT_2}\right) = \frac{DM}{hR}\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right)$$

$$\Rightarrow j_m = \frac{m}{At} = \frac{\rho A \delta}{At} = \frac{\rho_L \delta}{t}$$

$$\delta = \frac{t D M}{\rho_L h R}\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) = \dots = 11 \mu m$$

Prevajanje toplote; primer z izvori/ponori: $q\ [\frac{W}{m^3}]$ prostorninska gostota >0 izvora, <0 ponora



$$(j(z+dz) - j(z))A\,dt = q A\,dz\,dt - dm\,c_p\,dT$$

$$\frac{dj}{dz} A\,dz\,dt = q A\,dz\,dt - \rho A\,dz\,c_p\,dT$$

Transportna enačba

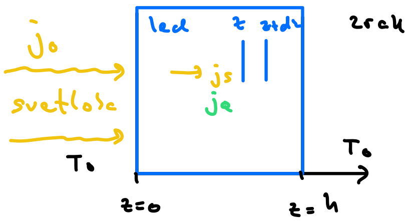
$$\boxed{j = -\lambda \frac{dT}{dz}}$$

$$\boxed{\frac{dj}{dz} = q - \rho c_p \frac{dT}{dt}}$$ Kontinuitetna enačba

$$-\lambda\frac{d^2T}{dz^2} = q - \rho c_p \frac{dT}{dt}$$

$$\boxed{\frac{d^2T}{dz^2} = -\frac{q}{\lambda} + \frac{\rho c_p}{\lambda}\frac{dT}{dt}}$$ Difuzijska enačba za izvore in ponore.

7.2 Obsijana plast ledu



$h = 1\,m$
$T_0 = -10\,°C$
$j_0 = 100\,\frac{W}{m^2}$
$\mu = 2\,m^{-1}$
$\lambda = 2{,}2\,\frac{W}{mK}$

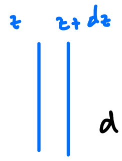
$T(z) = ?$
$T_{max} = ?$

$$\frac{d^2T}{dz^2} = -\frac{q}{\lambda} + \frac{\rho c_p}{\lambda}\underbrace{\frac{dT}{dt}}_{=0}$$

ker $dT = 0$ pri začetnih pogojih

$$\frac{d^2T}{dz^2} = -\frac{q(z)}{\lambda}$$

$$j_s + j_a = konst$$
$$dj_s + dj_a = 0$$
$$dj_a = -dj_s = q\,dz$$



$dj_s = -\mu j_s\,dz$

Iz kontinuitetne enačbe

$$\frac{dj}{dz} = q$$

$$q = -\frac{dj_s}{dz} = \mu j_s \qquad q = \mu j_s$$

$$\Downarrow$$

$$\int_{j_0}^{j_s} \frac{dj_s}{j_s} = -\mu\int_0^z dz$$

$$j_s(z) = j_0 e^{-\mu z}$$

$$\frac{d^2T}{dz^2} = -\frac{\mu}{\lambda} j_0 e^{-\mu z}$$

$$\int d^2T = -\frac{\mu j_0}{\lambda}\int e^{-\mu z}\,dz^2$$

$$dT = -\frac{\mu j_0}{\lambda} e^{-\mu z}\left(\frac{1}{-\mu}\right) + A \quad dz$$

$$T = -\frac{j_0}{\mu\lambda} e^{-\mu z} + Az + B$$

Iz robnih pogojev
$T(0) = T_0 = T(h)$

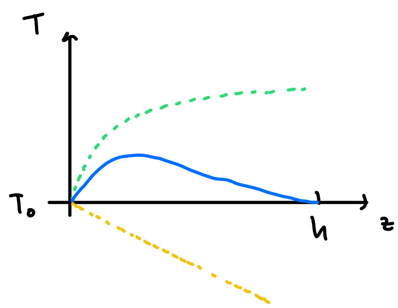
$$T(0) = -\frac{j_0}{\mu\lambda} + B = T_0 \qquad B = T_0 + \frac{j_0}{\mu\lambda}$$

$$T(h) = -\frac{j_0}{\mu\lambda} e^{-\mu h} + Ah + T_0 + \frac{j_0}{\mu\lambda} = T_0$$

$$A = \frac{j_0}{\mu\lambda h}\left(e^{-\mu h} - 1\right)$$

$$T(z) = -\frac{j_0}{\mu\lambda} e^{-\mu z} + \frac{j_0}{\mu\lambda h}\left(e^{-\mu h} - 1\right)z + \frac{j_0}{\mu\lambda} + T_0$$

$$T(z) = T_0 + \frac{j_0}{\mu\lambda}\left(1 - e^{-\mu z} + \frac{z}{h}\left(e^{-\mu h} - 1\right)\right)$$



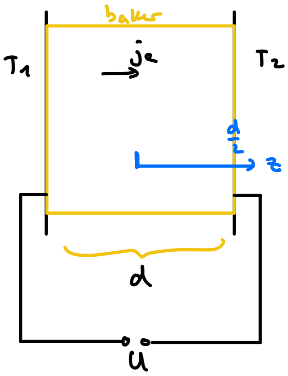
$$T_{max} \quad \frac{dT}{dz} = 0 = \frac{j_0}{\lambda} e^{-\mu z} + \frac{j_0}{\lambda\mu h}\left(e^{-\mu h} - 1\right) = 0$$

$$e^{-\mu z} = \frac{1}{\mu h}\left(1 - e^{-\mu h}\right) \Rightarrow$$

$$z = -\frac{1}{\mu}\ln\left(\frac{1}{\mu h}\left(1 - e^{-\mu h}\right)\right) = 0{,}419\,m \Rightarrow T_{max}$$

$T_{max} = -5{,}3\,°C$

Izpit iz STD 17. 9. 2013 2. naloga



$d = 1\,m$

$\varrho = 1{,}68 \cdot 10^{-8}\ \Omega m$

$\lambda = 400\ W/mK$

$j_e = 2 \cdot 10^{6}\ A/m^2$

$T_1 = 20°C$

$T_2 = 80°C$

$T(0) = ?$

$T_{max} = ?$

$$dP = dU\,dI = j_e\,dA\,\varrho\,\frac{dz}{dA}\,j_e\,dA$$

$$dP = j_e^2\,\varrho\,dV$$

$$q = \frac{dP}{dV} = j_e^2\varrho = 67{,}2\ \frac{kW}{m^3}$$

$$\frac{d^2T}{dz^2} = -\frac{q}{\lambda}$$

Zakaj stacionarne oblike

ker se j ne spreminja s časom.

$$dT = -\frac{q}{\lambda}z + A \quad dz$$

$$T(z) = -\frac{q}{2\lambda}z^2 + Az + B$$

Robni pogoji $T(\frac{d}{2}) = T_2$ $\quad T(-\frac{d}{2}) = T_1$

$$\left.\begin{aligned} T_1 &= -\frac{q}{\lambda}\frac{d^2}{8} - A\frac{d}{2} + B \\ T_2 &= -\frac{q}{\lambda}\frac{d^2}{8} + A\frac{d}{2} + B \end{aligned}\right] -$$

$$T_2 - T_1 = Ad \qquad A = \frac{T_2 - T_1}{d}$$

$$T_1 + T_2 = -\frac{q d^2}{4\lambda} + 2B \qquad B = \frac{T_1 + T_2}{2} + \frac{q d^2}{8\lambda}$$

$$T(z) = -\frac{q}{2\lambda}z^2 + \frac{T_2 - T_1}{d}z + \frac{T_1 + T_2}{2} + \frac{q d^2}{8\lambda}$$

$$T(0) = 71°C$$

Statistična termodinamika

npr. enoatomni plin

N atomov, $\underbrace{\vec{r}_i, \ \vec{p}_i}_{6N \text{ dim. prostor}}$ (fazni prostor, Γ)

$$\int_\Gamma \rho \, d\Gamma = 1$$

Stacionarne razmere: $\rho = \rho(E)$ ravnovesno stanje

npr. sistem v termostatu $T = \text{konst}$ (kanonični ansambel)

$$\rho \propto e^{-\beta E} \qquad \beta = \frac{1}{k_B T}$$

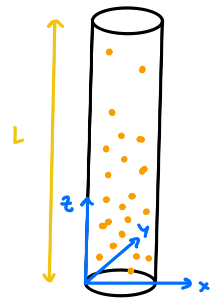
$$\underset{\uparrow}{Z} = c \int_\Gamma e^{-\beta E} d\Gamma = \underset{\uparrow}{e^{-\beta F}}$$

fazna vsota/integral — prosta energija

$$\langle E \rangle = \frac{d\beta F}{d\beta} \quad \dots \text{notranja energija } (u)$$

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \dots = -\frac{d^2 \beta F}{d\beta^2}$$

1.1 Idealni enoatomni plin v visokem valju. Specifična toplota $c_v = ?$ Pri dani temperaturi T.



$$c_v = \frac{1}{N}\frac{d\langle E \rangle}{dT}$$

$$E = \sum_{i=1}^{n} \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m} + m g z_i$$

$$d\Gamma = \prod_{i=1}^{n} dp_{ix}\, dp_{iy}\, dp_{iz}\, dx_i\, dy_i\, dz_i$$

$$e^{-\beta F} = c \int_\Gamma e^{-\frac{\beta}{2m}\sum_{i=1}^{n}(p_{ix}^2 + p_{iy}^2 + p_{iz}^2) - \beta m g \sum_{i=1}^{n} z_i} d\Gamma$$

$$e^{-\beta F} = c \prod_{i=1}^{n} \int e^{-\beta/2m (p_{ix}^2 + p_{iy}^2 + p_{iz}^2) - \beta m g z_i} dp_{ix}\, dp_{iy}\, dp_{iz}\, dx_i\, dy_i\, dz_i$$

ker ni interakcij med delci (idealni plin) lahko ločimo integrale.

problem pri visokih v (pretvorba na rel. p)

$$e^{-\beta F} = c\left(\left(\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp\right)^3 \int_0^L e^{-\beta m g z} dz \int_A dx\, dy\right)^n$$

Gaussov integral

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

$$e^{-\beta F} = c A^n \left(\frac{\pi 2m}{\beta}\right)^{3n/2} \left(\frac{1}{-\beta m g} e^{-\beta m g z}\Big|_0^L\right)^n$$

$$e^{-\beta F} = c A^n \left(\frac{2\pi m}{\beta}\right)^{\frac{3n}{2}} \left(\frac{1}{-\beta m g}\right)^n \left(e^{-\beta m g L} - 1\right)^n$$

$$e^{-\beta F} = c' \beta^{-\frac{3n}{2}} \beta^{-n} \left(1 - e^{-\beta m g L}\right)^N$$

$$-\beta F = -\frac{3n}{2}\ln\beta - n\ln\beta + n\ln\left(1 - e^{-\beta m g L}\right) + \ln c'$$

$$\beta F = \frac{5n}{2}\ln\beta - n\ln\left(1 - e^{-\beta m g L}\right) - \ln c'$$

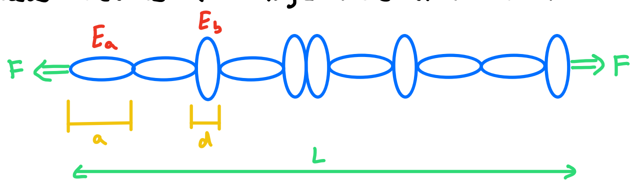
$$\langle E \rangle = \frac{d\beta F}{d\beta} = \frac{5n}{2}\frac{1}{\beta} - n\frac{(-mgL)(-e^{-\beta m g L})}{1 - e^{-\beta m g L}} = \frac{5n}{2\beta} - \frac{nmgL}{e^{\beta m g L} - 1}$$

Limitni primeri:

① $\beta m g L \gg 1$ $\quad T \to 0$ $\quad \langle E \rangle = \frac{5N}{2}k_B T - \frac{nmgL}{e^{\beta m g L}} = \frac{5N}{2}k_B T \Rightarrow c_v = \frac{dE}{dT} = \frac{5}{2}N k_B$

Ekviparticijski izrek ② $\beta m g L \ll 1$ $\quad T \to \infty$ $\quad \langle E \rangle = \frac{5N}{2}k_B T - \frac{nmgL}{\underbrace{1 + \beta m g L + \dots}_{\text{Taylor}} - 1} = \frac{5}{2}N k_B T - N k_B T = \frac{3}{2}N k_B T \Rightarrow c_v = \frac{3}{2}k_B N$

2.9 Volneno vlakno (= veriga molekul keratina). Podatki: a, d, E_a, E_d, n



$\langle E \rangle = ?$

$\langle \ell(T) \rangle = ?$

$E = n_a E_a + n_d E_d \qquad n_a + n_d = n$

$L = n_a a + n_d d$

ⓐ

$$Z_n = \sum_{\text{po kombinacijah}} e^{-\beta E(N_a, N_d)} = \sum_{\text{po kombinacijah}} e^{-\beta(n_a E_a + n_d E_d)}$$

npr. $n = 3$ št. kombinacij 2^3

	N_a			N_a	
000	3	1	011	1	3
001	2	3	101	1	
010	2		110	1	
100	2		111	0	1

Binomsko

$$Z_n = \sum_{n_a=0}^{n} \binom{n}{n_a} e^{-\beta(N_a E_a + (N-N_a)E_d)}$$

$$Z_n = \sum_{n_a=0}^{n} \binom{n}{n_a} \left(e^{-\beta E_a}\right)^{N_a} \left(e^{-\beta E_d}\right)^{N-N_a}$$

Binomska vrsta

$$\sum_{N_a=0}^{N} \binom{N}{N_a} x^{N_a} y^{N-N_a} = (x+y)^N$$

$$e^{-\beta F} = Z_n = \left(e^{-\beta E_a} + e^{-\beta E_d}\right)^n = Z_1^{\,n}$$

monomeri neodvisni

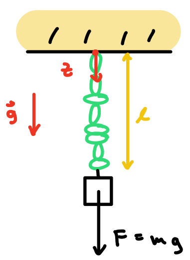
$$\beta F = -n \ln\left(e^{-\beta E_a} + e^{-\beta E_d}\right)$$

$$\langle E \rangle = \frac{d\beta F}{d\beta} = \cancel{-}\, n \frac{\cancel{-}E_a e^{-\beta E_a} \cancel{+} E_d e^{-\beta E_d}}{e^{-\beta E_a} + e^{-\beta E_d}}$$

$$\langle E \rangle = n \frac{E_a e^{-\beta E_a} + E_d e^{-\beta E_d}}{e^{-\beta E_a} + e^{-\beta E_d}} = \langle N_a \rangle E_a + \langle N_d \rangle E_d$$

ⓑ

$$\langle L \rangle = \langle N_a \rangle a + \langle N_d \rangle d = N \frac{a e^{-\beta E_a} + d e^{-\beta E_d}}{e^{-\beta E_a} + e^{-\beta E_d}}$$



ⓒ Obremenitev verige s silo F

Utež je še del sistema in dobimo še gravitacijsko energijo

$$E(n_a, n_d) = E_a n_a + E_d n_d - \overset{F}{mg}\, L$$

$$= E_a n_a + E_d n_d - F(N_a \cdot a + N_d \cdot d)$$

$$= N_a(E_a - Fa) + N_d(E_d - Fd)$$

Povsod $E_a \to E_a - Fa \qquad E_d \to E_d - Fd$

$$\langle \ell \rangle(T, F) = N \frac{a e^{-\beta(E_a - Fa)} + d e^{-\beta(E_d - Fd)}}{e^{-\beta(E_a - Fa)} + e^{-\beta(E_d - Fd)}}$$

Enačba stanja

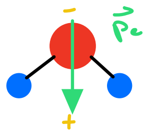
Enačba stanja

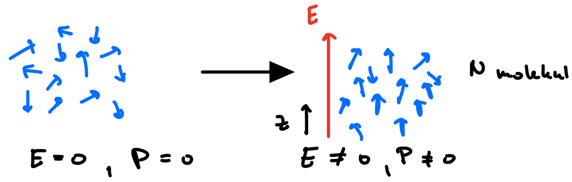
2.1 Dielektrična polarizacija nasičene vodne pare pri $T = 100°C$ (kot idealni plin)

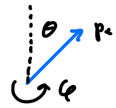
$\chi = ?$

$p_e = 6{,}1 \cdot 10^{-30}\ \mathrm{As\,m}$

↳ el. dipolni moment vodne pare







$$P = \varepsilon_0 \chi E$$

$$P = \frac{\text{el. dipolni moment}}{V} \Longrightarrow P = \frac{N \langle (p_e)_z \rangle}{V} = \frac{N}{V} p_e \langle \cos\theta \rangle$$

Energija

$$\langle \xi \rangle = \langle -\vec{p}_e \cdot \vec{E} \rangle = -p_e E \langle \cos\theta \rangle$$

def. povprečja $\quad \langle A \rangle = \dfrac{\int_\Gamma \rho A \, d\Gamma}{\int_\Gamma \rho \, d\Gamma}$

Alt. pot od fazn. vsot

$$\langle \cos\theta \rangle = \frac{c \int_\Gamma \cos\theta \, e^{-\beta \overset{-p_e E \cos\theta}{\xi}} \, d\Gamma}{c \int_\Gamma e^{-\beta \xi} \, d\Gamma} \qquad \frac{\int \dots dx\,dy\,dz \int dp_x\,dp_y\,dp_z}{\int \dots dx\,dy\,dz \int dp_x\,dp_y\,dp_z}$$

kar $\cos\theta$ ni odvisen od $\vec{r}$ in $\vec{p}$ se to pokrajša

prehod na sferične koord.

$$d\Gamma = d\Omega = \sin\theta \, d\theta \, d\varphi$$

↳ prostorski kot

$$= \frac{\int_0^\pi \cos\theta \, e^{\overbrace{\beta p_e E \cos\theta}^{\alpha}} \sin\theta \, d\theta \cancel{\int_0^{2\pi} d\varphi}}{\int_0^\pi e^{\beta p_e E \cos\theta} \sin\theta \, d\theta \cancel{\int_0^{2\pi} d\varphi}}$$

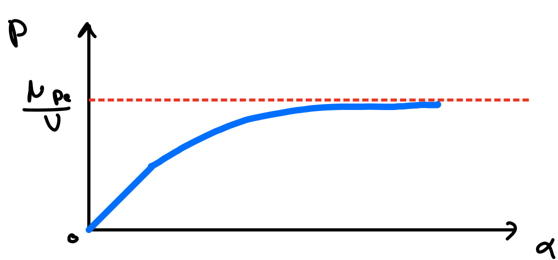
$$= \frac{\int_0^\pi \cos\theta \, e^{\alpha \overbrace{\cos\theta}^{u}} \overbrace{\sin\theta \, d\theta}^{-du}}{\int_0^\pi e^{\alpha\cos\theta} \sin\theta \, d\theta} \qquad u = \cos\theta$$

$$= \frac{\int_1^{-1} u e^{\alpha u} du}{\int_1^{-1} e^{\alpha u} du} \overset{\text{per partes}}{=} \frac{u \cancel{\frac{1}{\alpha}} e^{\alpha u}\Big|_{-1}^{1} - \int_{-1}^{1} \cancel{\frac{1}{\alpha}} e^{\alpha u} du}{\cancel{\frac{1}{\alpha}} e^{\alpha u}\Big|_{-1}^{1}} =$$

$$= \frac{e^{\alpha} + e^{-\alpha} - \frac{1}{\alpha} e^{\alpha u}\Big|_{-1}^{1}}{e^{\alpha} - e^{-\alpha}} = \frac{e^{\alpha} + e^{-\alpha} - \frac{1}{\alpha}(e^{\alpha} - e^{-\alpha})}{e^{\alpha} - e^{-\alpha}} =$$

$$= \frac{2\,\mathrm{ch}\,\alpha - \frac{2}{\alpha}\mathrm{sh}\,\alpha}{2\,\mathrm{sh}\,\alpha} = \coth\alpha - \frac{1}{\alpha} = \mathcal{L}(\alpha)$$ Langvierova funkcija

$$P = \frac{N}{V} p_e \left(\coth\alpha - \frac{1}{\alpha} \right)$$



- $\alpha \to \infty \qquad P \to 1$
- $P = \frac{N p_e}{V} \left(\frac{1}{\alpha} + \frac{\alpha}{3} + \dots - \frac{1}{\alpha} \right) = \frac{N p_e \alpha}{3V}$ (Taylor)

$$\frac{N p_e}{3V} \beta p_e E = \varepsilon_0 \chi E \Rightarrow \chi = \frac{N p_e^2}{3 V k_B T \varepsilon_0} \propto \frac{1}{T}$$ Curiejev zakon.

2.12
2.13

Neidealni plin

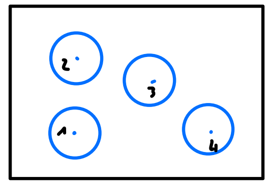
TD: $dF = -S\,dT - p\,dV$

$$p = -\left(\frac{\partial F}{\partial V}\right)_\beta \quad \text{... enačba stanja}$$

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

$$E = \underbrace{\sum_{j=1}^{n} \frac{p_j^2}{2m}}_{W_{kin}} + \underbrace{\sum_{i<j}\sum \phi(r_{ij})}_{\text{Interakcije}} \qquad r_{ij} = |\vec r_i - \vec r_j|$$

$$e^{-\beta F} = c \underbrace{\int e^{-\beta \sum \frac{p_i^2}{2m}}\, d^{3N}p}_{\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}} \underbrace{\int e^{-\beta \sum_{i<j} \phi(r_{ij})}\, d^{3N}r}_{f(V)}$$



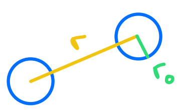
$$\dots = \ln f(V) = N \ln V - B_2 \frac{N^2}{V}$$

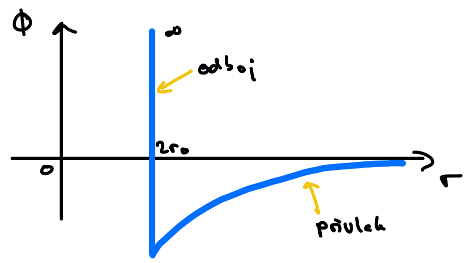
2. virialni koeficient $\quad B_2 = \frac{1}{2}\int_0^\infty \left(1 - e^{-\beta\phi(r)}\right) 4\pi r^2\, dr$

$$p = \frac{N}{V} k_B T \left(1 + B_2 \frac{N}{V}\right)$$

→ Plin trdnih kroglic s privlačno interakcijo (enačba stanja, notranja energija)

$$\phi(r) = \begin{cases} \infty \ ; & r < 2r_0 \\ -\phi_0 \left(\frac{r_0}{r}\right)^s ; & r \geq 2r_0 \end{cases}$$





$$1 - e^{-\beta\phi(r)} = \begin{cases} 1 \ ; & r < 2r_0 \\ 1 - e^{\beta\phi_0 \left(\frac{r_0}{r}\right)^s} ; & r \geq 2r_0 \end{cases}$$

↓ ker je težko izračunati integral, iščemo visoko temp. približek $\beta\phi_0 \ll 1$

$$1 - \left(1 + \beta\phi_0 \left(\frac{r_0}{r}\right)^s + \dots\right) = -\beta\phi_0 \left(\frac{r_0}{r}\right)^s$$

$$B_2 = \frac{1}{2}\int_0^{2r_0} 1\, 4\pi r^2\, dr + \frac{1}{2}\int_{2r_0}^{\infty} -\beta\phi_0 \left(\frac{r_0}{r}\right)^s 4\pi r^2\, dr$$

$$= \frac{1}{2} 4\pi \frac{(2r_0)^3}{3} - \frac{1}{2}\beta\phi_0 4\pi r_0^s \int_{2r_0}^{\infty} r^{-s+2}\, dr$$

$$= \frac{16\pi r_0^3}{3} - \beta \underbrace{2\pi \phi_0 r_0^s \frac{1}{(3-s)}\left(0 - (2r_0)^{3-s}\right)}_{\alpha > 0} \qquad \text{če } s > 3$$

npr. Van der Waalsove sile $s = 6$

def $V_0 = \frac{4}{3}\pi r_0^3$

$$B_2 = 4V_0 - \alpha\beta \qquad \alpha > 0$$

tlak

$$p = \frac{N}{V} k_B T \left(1 + \frac{N}{V}\left(4v_0 - \beta\alpha\right)\right)$$

$$p = \frac{N}{V} k_B T \left(1 + \frac{N}{V} 4V_0\right) - \frac{N^2}{V^2}\alpha$$

$$p + \frac{N^2}{V^2}\alpha = \frac{N}{V} k_B T \left(1 + \frac{N}{V} 4V_0\right)$$

$$\frac{p + \frac{N^2}{V^2}\alpha}{1 + \frac{N}{V}4V_0} = \frac{N}{V} k_B T \qquad\qquad \frac{1}{1+\varepsilon} = 1 - \varepsilon + \dots$$

$$\left(p + \frac{N^2}{V^2}\alpha\right)\left(1 - \frac{N}{V}4V_0\right) = \frac{N}{V} k_B T$$

$$\Big(p + \underbrace{\overbrace{\frac{N^2}{V^2}\alpha}^{a}}_{\text{privlak}}\Big)\Big(V - \underbrace{\overbrace{4NV_0}^{b}}_{\text{odboj}}\Big) = N k_B T$$

notranja energija

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

$$-\beta F = \ln C' - \frac{3N}{2}\ln\beta + \underbrace{\ln f(V)}_{=\, N\ln V - B_2\frac{N^2}{V} \,=\, N\ln V - (4V_0 - \beta\alpha)\frac{N^2}{V}}$$

$$\langle E\rangle = \frac{\partial \beta F}{\partial\beta} = \frac{3N}{2}\frac{1}{\beta} + \frac{N^2}{V}(-\alpha)$$

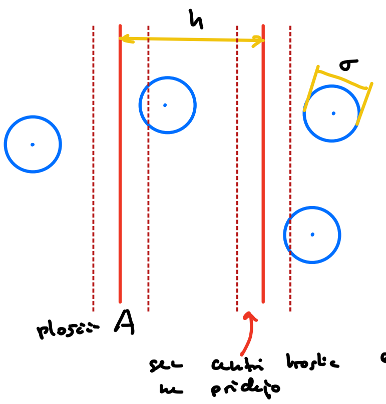
$$= \underbrace{\frac{3N}{2}k_B T}_{\text{kinetični prispevek}} - \underbrace{\frac{N^2}{V}\alpha}_{\text{interakcija}} = \underbrace{u(T,V)}_{\text{notranja energija}} \quad \text{neidealni plin}$$

Entropija

3.2 Deplecijska sila med ploščama v suspenziji trdnih kroglic

redke suspenzije, idealni sistem

$\sigma = 100\,nm$ (premer), $A = 1\,mm^2$, $\frac{N}{V} = 10^{18}\,\frac{1}{m^3}$, $T = 20°C$, $\mathcal{F} = ?$



Termodinamične spr.: $T, \mathcal{F}, h$

Prosta energija

$$dF = -S\,dT + \mathcal{F}\,dh$$

$$\mathcal{F} = \left(\frac{\partial F}{\partial h}\right)_T$$

N kroglic

$$e^{-\beta F} = C\left(\int_{V_r} dV \int d^3p\, e^{-\beta\frac{p^2}{2m}}\right)^N = C\, V_r^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

V_r ... razpoložljivi volumen

$V - 2A\sigma$; $h > \sigma$

$V - A(\sigma + h)$; $h < \sigma$

Zanima nas $F(h)$

$$-\beta F = \ln\tilde{C} + N\ln V_r(h)$$

$$F(h) = -\frac{\ln\tilde{C}}{\beta} - \frac{N}{\beta}\ln V_r(h) = F_0(T) - Nk_B T\ln V_r(h)$$

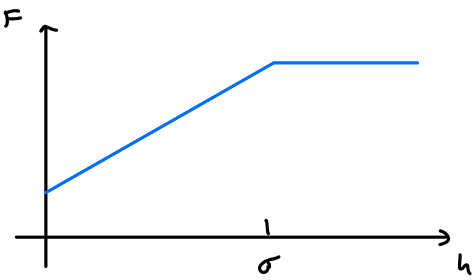
Sila se pojavi le pri $h < \sigma$, saj je le tam $V_r(h)$

$$F(h) = F_0 - N k_B T \ln (V - A(\sigma + h)) = F_0 - N k_B T \ln \left(V\left(1 - \frac{A}{V}(\sigma+h)\right)\right)$$

$$= F_0 - N k_B T \ln V - N k_B T \ln \left(1 - \frac{A}{V}(\sigma+h)\right)$$

$\ln(1+\varepsilon) = \varepsilon$

$$= F_0 - N k_B T \ln V + N k_B T \frac{A}{V}(\sigma + h)$$



$$\mathcal{F} = \left(\frac{\partial F}{\partial h}\right)_T = N k_B T \frac{A}{V} = \dots = k \cdot 10^{-9}\ \mathrm{N}$$

Deplecijska sila

T Entropija v stat. fiziki

- $S = \frac{\bar{E} - F}{T} = k_B \beta (\bar{E} - F) = -k_B \langle \ln \frac{\rho}{C} \rangle = S_0 - k_B \int \rho \ln \rho \, d\Gamma$

  če je kanonični ansambel $\rho = C e^{-\beta(E-F)}$

  Gibbsova definicija entropije

  enakovredni v termodinamični limiti $N \to \infty$

- $S(E) = S_0 + k_B \ln(\Delta\Gamma(E))$ Boltzmannova definicija entropije

3.8 Dvonivojski sistem (N delcev) (npr. spin $\frac{1}{2}$ v mag. polju)

↑↑↓↑↓↓↓↑↓↓↑ (neodvisni)

ε —— $N_2 = N - N_1$

0 —— N_1

$$E = N_2 \varepsilon = (N - N_1)\varepsilon$$

$$S_{N_2}(E) = k_B \ln \Delta\Gamma_{N_2}(E) \qquad \Delta\Gamma(E) = \binom{N}{N_2}$$

$$= k_B \ln \frac{N!}{N_2!\,(N-N_2)!}$$

$$= k_B \left(\ln N! - \ln N_2! - \ln (N-N_2)!\right)$$

Stirlingova formula
$\ln N! = N \ln N - N$
dobro za $N \to \infty$

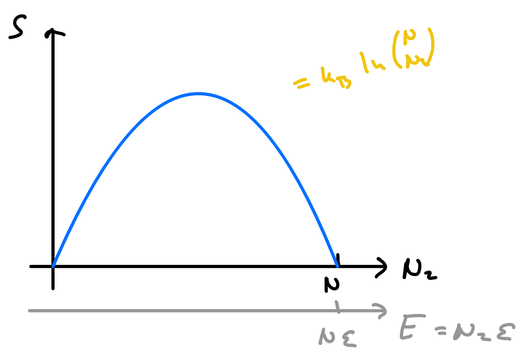
$$= k_B \left(N \ln N - N - N_2 \ln N_2 + N_2 - N_1 \ln N_1 + N_1\right)$$

$$= k_B \left(N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2}\right)$$

$$= -k_B N \left(\frac{N_1}{N} \ln \frac{N_1}{N} + \frac{N_2}{N} \ln \frac{N_2}{N}\right)$$

$$= -k_B N \sum_{i=1}^{2} \frac{N_i}{N} \ln \frac{N_i}{N}$$

$$= -k_B N \sum_{i=1}^{2} p_i \ln p_i$$



če sistem ne opravlja dela

$$dS = \frac{dQ}{T} = \frac{dE}{T} \Rightarrow \frac{\partial S}{\partial E} = \frac{1}{T}$$

TD definicija temperature

$-S$ ... merilo o količini informacij o sistemu (Shannon

za $N_2 > \frac{N}{2} \Rightarrow T < 0$?! neravnovesna stanja
temp. pa je def. v ravn. stanju

Določitev ravnovesnega N_2 pri dani T.

a) preko fazne vsote
b) minimizacije F

$$F(N_2) = E(N_2) - T\,S(N_2)$$
$$= \varepsilon N_2 - T\,k_B\left(N\ln N - N_2\ln N_2 - (N-N_2)\ln(N-N_2)\right)$$

Ravnovesje $F = \min$

$$\frac{dF}{dN_2} = \varepsilon - k_B T\left(0 - \ln N_2 - \frac{N_2}{N_2} - (-1)\ln(N-N_2) - \cancel{(N-N_2)}\frac{(-1)}{\cancel{(N-N_2)}}\right)$$

$$= \varepsilon - k_B T \ln\frac{N-N_2}{N_2} = 0$$

$$\frac{\varepsilon}{k_B T} = \ln\frac{N}{N_2} - 1$$

$$\frac{N}{N_2} = 1 + e^{\varepsilon\beta}$$

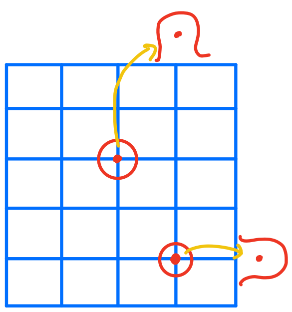
$$p_2 = \frac{N_2}{N} = \frac{1}{1+e^{\beta\varepsilon}} = \frac{e^{-\beta\varepsilon}}{e^{-\beta\varepsilon}+1} \Rightarrow \frac{N_1}{N_2} = \frac{1}{e^{-\beta\varepsilon}+1} = p_1$$

$$\Rightarrow p_i \propto e^{-\beta E_i}$$ izpeljali smo kanonično porazdelitev

limitna primera

$T \to 0$	$N_2 \to 0$	$N_1 \to N$	$F = \min \Rightarrow E = \min$	"red"
$T \to \infty$	$N_2 = N_1 = \frac{N}{2}$		$F = \min \Rightarrow S = \max$	"nered"

3.7 Schottky-jevi defekti v kristalu



N atomov
n lukenj
$N+n$ ... možnih mest

$$\frac{N}{V} = 5{,}02\cdot 10^{28}\ \frac{1}{m^3}$$
$\varepsilon = 2{,}6\ eV$ ... energija defekta
$T = 700\ °C$

$$E(n) = \varepsilon n$$

$$S(n) = k_B \ln \Delta\Gamma(n) = k_B \ln\binom{N+n}{N} = k_B \ln\frac{(N+n)!}{N!\,n!}$$

$$= \dots =$$

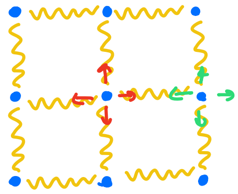
$$F(n) = E(n) - T S(n)$$

$$\frac{dF}{dn} = 0 \quad\rightarrow\quad \frac{n}{N} = \frac{1}{e^{\beta\varepsilon}-1}$$

$$\Rightarrow \frac{n}{V} = 7{,}1\cdot 10^{5}\ \frac{1}{m^3} \ll \frac{N}{V}$$

Kvantna statistična fizika

4.2 Einsteinov model trdnine pri visoki T obnašanje, $c_V = ?$. Sistem neskopljenih harmoničnih oscilatorjev. Baker, $M = 64 \frac{kg}{kmol}$, $\omega_E = 4\cdot 10^{13}$ Hz. Relativno odstopanje c_V od visoke T limite?



1D HO $\quad E_n = \hbar\omega\left(n+\frac{1}{2}\right) \qquad n = 0, 1, 2, \dots$

1D:
$$e^{-\beta F} = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} = e^{-\beta\hbar\omega/2}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n} =$$
$$= e^{-\beta\hbar\omega/2}\,\frac{1}{1-e^{-\beta\hbar\omega}} = \frac{1}{e^{\beta\hbar\omega/2}-e^{-\beta\hbar\omega/2}} = \frac{1}{2\,\mathrm{sh}(\beta\hbar\omega/2)}$$

3D: N atomov. Privzamemo da so x, y, z neodvisni

$$e^{-\beta F} = \left(\frac{1}{2\,\mathrm{sh}\,\beta\hbar\omega/2}\right)^{3N} \qquad 3N \text{ prostorskih stopenj}$$

$$-\beta F = -3N\ln\left(2\,\mathrm{sh}\,\frac{\beta\hbar\omega}{2}\right) \qquad \frac{\beta\hbar\omega}{2} = x$$

$$\langle E\rangle = \frac{d\beta F}{d\beta} = 3N\,\frac{1}{\mathrm{sh}\frac{\beta\hbar\omega}{2}}\,\mathrm{ch}\frac{\beta\hbar\omega}{2}\,\frac{\hbar\omega}{2} = \frac{3N}{2}\hbar\omega\,\mathrm{cth}\frac{\beta\hbar\omega}{2}$$

$$\frac{1}{2}\mathrm{cth}\,x = \frac{1}{2}\,\frac{e^{x}+e^{-x}}{e^{x}-e^{-x}} = \frac{1}{2}\left(1+\frac{2e^{-x}}{e^{x}-e^{-x}}\right) =$$
$$= \frac{1}{2}\left(1+\frac{2}{e^{2x}-1}\right) = \frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}$$
$$\frac{1}{e^{\beta\hbar\omega}-1} = \bar{n}$$

povprečno število kvantov nihanja

$$\langle E\rangle = \frac{3N}{2}\hbar\omega\,\mathrm{cth}\frac{\hbar\omega}{2k_BT} \qquad \text{def. } T_E = \frac{\hbar\omega}{k_B} = \dots = 304{,}6\,K$$
$$= \frac{3N}{2}\hbar\omega\,\mathrm{cth}\frac{T_E}{2T}$$

$$c_V = \frac{d\bar{E}}{dT} = \frac{3N}{2}\hbar\omega\left(-\frac{1}{\mathrm{sh}^2\frac{T_E}{2T}}\right)\left(-\frac{T_E}{2T^2}\right)\frac{k_B}{k_B}$$
$$= 3Nk_B\,\frac{\left(\frac{T_E}{2T}\right)^2}{\mathrm{sh}^2\left(\frac{T_E}{2T}\right)} = 3Nk_B\,\frac{x^2}{\mathrm{sh}^2 x} \qquad \text{Visoko T limita } x\to 0$$

v limiti
$$\overset{\text{Taylor}}{=} 3Nk_B\,\frac{x^2}{\left(x+\frac{x^3}{6}\right)^2} = 3Nk_B\,\frac{1}{\left(1+\frac{x^2}{6}\right)^2} \overset{\text{Taylor}}{=} 3Nk_B\left(1+2\frac{x^2}{6}+\dots\right)$$
$$= 3Nk_B\left(1-\frac{1}{3}\left(\frac{T_E}{2T}\right)^2+\dots\right) = 3Nk_B\left(1-\frac{1}{12}\left(\frac{T_E}{T}\right)^2\dots\right)$$

Visoko temp limita $\quad c_V = 3Nk_B \qquad$ Ekviparticijski izrek

Dulong - Petitova limita
$$c_v = \frac{C_V}{m} = \frac{3Nk_B N_A}{MN} = 3\frac{R}{M}$$

Nizko temp. limita $\quad x\to\infty$

$$c_V = 3Nk_B\,\frac{x^2}{\mathrm{sh}^2 x} = 3Nk_B\left(x\,\frac{2}{e^{x}+e^{-x}}\right)^2$$

Izpit 19.2.2010, 3. naloga : Ravninski rotator $E(j) = k_B T_r j^2$ $\quad j = 0, 1, 2, \ldots$

ni degenerirano $\quad$ 2x degenerirano

$T_r = 150\,K$ $\quad g_j = \begin{cases} 1 & j=0 \\ 2 & \text{sicer} \end{cases}$

ⓐ $T' = 25K \rightarrow T = 30\,K$ $\quad \Delta S = ?$

ⓑ $T' = 1500\,K \rightarrow T = 1505\,K$ $\quad \Delta S = ?$

$$S = \frac{\langle E \rangle - F}{T} \quad \text{ali: } S = -\frac{dF}{dT}$$

$$e^{-\beta F} = \sum_{j=0}^{\infty} g_j e^{-\beta k_B T_r j^2}$$

ⓐ Nizko T limita $(T \ll T_r)$:

$$e^{-\beta F} = \underset{j=0}{1} + \underset{\substack{j=1 \\ = 0{,}017}}{2e^{-\beta k_B T_r}} + \underset{\substack{j=2 \\ = 4\cdot 10^{-9}}}{2e^{-\beta k_B T_r 4}} + \ldots$$

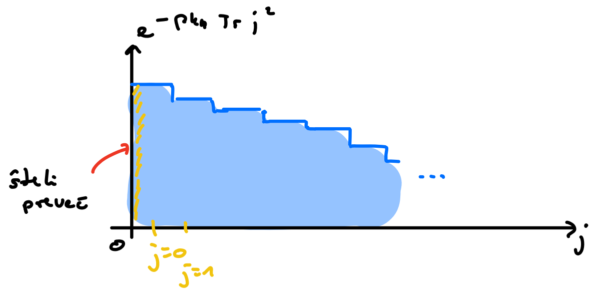
$$-\beta F = \ln(1 + 2e^{-\beta k_B T_r}) \overset{\text{Taylor}}{=} 2e^{-\beta k_B T_r}$$

$$\langle E \rangle = \frac{d\beta F}{d\beta} = -2e^{-\beta k_B T_r}(-k_B T_r)$$

$$S = \frac{1}{T}(\langle E \rangle - F) = \frac{1}{T}\left(2k_B T_r e^{-\beta k_B T_r} - \left(-\frac{1}{\beta} 2e^{-\beta k_B T_r}\right)\right)$$

$$S(T) = \frac{2k_B}{T} e^{-\beta k_B T_r}(T + T_r) = 2k_B e^{-\beta k_B T_r}\left(1 + \frac{T_r}{T}\right)$$

$$\Delta S = S(30) - S(25) = \ldots = 4\cdot 10^{-6}\,\frac{eV}{K}$$



ⓑ Visoka T limita $(T \gg T_r)$:

$$e^{-\beta F} = \sum_{j=0}^{\infty} 2e^{-\beta k_B T_r j^2} - 1$$

$$= 2\left(1 \cdot \frac{1}{2} + \int_0^{\infty} e^{-\beta k_B T_r j^2}\, dj\right) - 1$$

$$= 2\int_0^{\infty} e^{-\beta k_B T_r j^2}\, dj = 2 \cdot \frac{1}{2}\sqrt{\frac{\pi}{\beta k_B T_r}} = \sqrt{\pi}\sqrt{\frac{T}{T_r}}$$

$$-\beta F = -\frac{1}{2}\ln\left(\frac{\beta k_B T_r}{\pi}\right) = -\frac{1}{2}\ln\beta - \frac{1}{2}\ln\frac{k_B T_r}{\pi}$$

$$\langle E \rangle = \frac{1}{2\beta} = \frac{1}{2}k_B T \quad \ldots \text{ ekviparticija za 1 prostostno stopnjo}$$

$$S = \frac{\langle E \rangle - F}{T} = \frac{1}{T}\left(\frac{1}{2}k_B T - \frac{1}{2}k_B T \ln\beta - \frac{1}{2}k_B T \ln\frac{k_B T_r}{\pi}\right)$$

$$S = \frac{k_B}{2}\left(1 + \ln k_B T - \ln\frac{k_B T_r}{\pi}\right)$$

$$\Delta S = \frac{k_B}{2}\left(-\ln k_B T_2 + \ln k_B T_1\right) = \frac{k_B}{2}\ln\frac{T_1}{T_2}$$

Alternativa $\quad C = \frac{d\langle E \rangle}{dT} = \frac{k_B}{2}$

$$\Delta S = \int \frac{dQ}{T} = \int_{T_1}^{T_2} \frac{C\,dT}{T} = C\ln\frac{T_2}{T_1} = \frac{k_B}{2}\ln^{T}$$

4.10 Specifična toplota "magnetna" $Gd_2(SO_4)_3 \cdot 8H_2O$ pri $B=2T$ in $T=4K$ (40K) =? . Nosilci magnetizma so Gd ioni s spinom $j = 7/2$; $g=2$; $M = 746\,\frac{kg}{kmol}$; $\rho = 3010\,\frac{kg}{m^3}$

$$E = -\vec{p}_m \cdot \vec{B} = -p_{mz} B = -g \mu_B m_j B$$

Bohrov magneton $\mu_B = 9{,}27\cdot 10^{-24}\,Am^2$

$$m_j \in [-j, j] = [-\tfrac{7}{2}, -\tfrac{5}{2}, \dots, \tfrac{5}{2}, \tfrac{7}{2}]$$

$$z_1 = \sum_{m_j=-j}^{j} e^{-\beta E(m_j)} = \sum_{m_j=j}^{j} e^{\overbrace{\beta g \mu_B B}^{\alpha} m_j} = \sum_{m_j=j}^{j} e^{\alpha m_j} \overset{\mu = m_j + j}{=} \sum_{\mu=0}^{2j} (e^{\alpha})^{\mu - j} =$$

$$= e^{-\alpha j} \sum_{0}^{2j} (e^{\alpha})^{\mu} \overset{geo.}{=} e^{-\alpha j}\, \frac{e^{\alpha(2j+1)} - 1}{e^{\alpha} - 1} = \frac{e^{\alpha(j+1)} - e^{-\alpha j}}{e^{\alpha} - 1} = \frac{e^{\frac{\alpha}{2}}}{e^{\alpha/2}}\, \frac{e^{\alpha(j+\frac{1}{2})} - e^{-\alpha(j+\frac{1}{2})}}{e^{\alpha/2} - e^{-\alpha/2}}$$

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

$$-\beta F = \ln \operatorname{sh} \alpha(j+\tfrac{1}{2}) - \ln \operatorname{sh} \alpha/2$$

$$\langle E \rangle = \left(\frac{\partial \beta F}{\partial \beta}\right)_{H,B} = \frac{\partial \beta F}{\partial \alpha}\, \frac{\partial \alpha}{\partial \beta} = g \mu_B B \left(-\frac{\operatorname{ch} \alpha(j+1/2)}{\operatorname{sh} \alpha(j+\frac{1}{2})} (j + 1/2) + \frac{\operatorname{ch} \alpha/2}{2 \operatorname{sh} \alpha/2} \right) =$$

$$= -g \mu_B B \left((j+\tfrac{1}{2}) \coth \alpha(j+\tfrac{1}{2}) - \tfrac{1}{2} \coth \tfrac{\alpha}{2} \right) = -\langle p_m \rangle B$$

mimogrede $M = \frac{N}{V} \langle p_z \rangle \overset{\uparrow}{=} \dots \propto \alpha \propto \frac{1}{T} \dots$ Curiejev zakon

visoko T lim. $(\beta \to 0, \alpha \to 0) \Rightarrow \coth x \doteq \frac{1}{x} + \frac{x}{3}$

$$c_H = \frac{d\langle E \rangle}{dT} = \frac{d\langle E \rangle}{d\alpha}\, \frac{d\alpha}{dT} = + g \mu_B B \left((j+\tfrac{1}{2}) \left(-\frac{(j+\frac{1}{2})}{\operatorname{sh}^2 \alpha(j+1/2)}\right) + \frac{1}{2}\, \frac{\frac{1}{2}}{\operatorname{sh}^2 \frac{\alpha}{2}} \right) \frac{-g\mu_B B}{k_B T^2}$$

$$= \alpha^2 k_B \left(-\frac{(j+\frac{1}{2})^2}{\operatorname{sh}^2 \alpha(j+\frac{1}{2})} + \frac{1}{4 \operatorname{sh}^2 \alpha/2} \right)$$

Pri $T = 40K$, $B = 2T$ $\Rightarrow$ $c = 0{,}0235\, k_B$

2 Gd na molekulo

$$c_H = \frac{C}{m} N = \frac{1}{m} \frac{m}{M} N_A c = \frac{N_A}{M} c\, 2 = 0{,}52 \,\frac{J}{kg\,K}$$

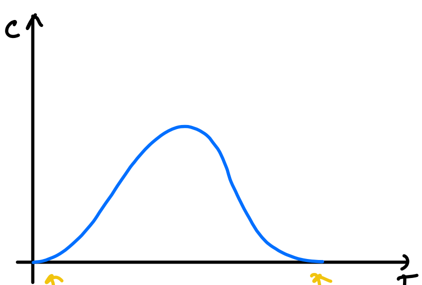
- visoko T lim. $\alpha \to 0$, $T \to \infty$ $\operatorname{sh} x \sim x$

$$c = k_B \alpha^2 \left(\frac{1}{4 (\frac{\alpha}{2})^2} - \frac{(j+\frac{1}{2})^2}{\alpha^2 (1 + \frac{1}{2})^2} \right) = 0$$

- nizko T lim.

$\alpha \to \infty$, $T \to 0$ $\operatorname{sh} x = \frac{1}{2} e^{\frac{\alpha}{2}}$

$$c = k_B \alpha^2 \left(\frac{1}{4}\, \frac{1}{\underbrace{\left(\frac{e^{\alpha/2}}{2}\right)^2}_{0}} - \frac{(j+\frac{1}{2})^2}{\underbrace{(\dots)}_{0}} \right) = 0$$

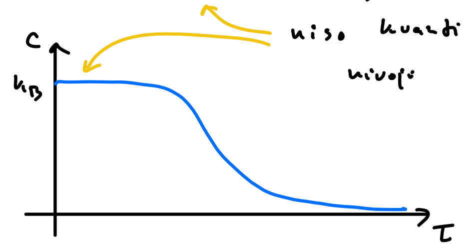


vsi nivoji so enako zasedeni

kvantizacija

Primerjava: el. dipoli (naloga 2.2)

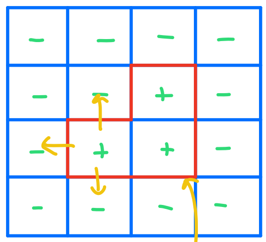
niso kvantizirani nivoji



3.9 Razišči stabilnost feromagneta v 2D (1D), uporabi Isingov model

$$H = -J \sum_{\langle i,j \rangle} s_i s_j \quad ; \quad s_i = \pm \frac{1}{2} \quad ; \quad J > 0 \text{ izmenjalni integral}$$

↳ najbližje sosede



domenske stena

Soseda: ↑↑, ↓↓ $E_p = -\frac{J}{4}$
↑↓, ↓↑ $E_p = +\frac{J}{4}$ $\Big\}$ $\Delta E = \frac{J}{2}$

$E(L) = L \Delta E = \frac{LJ}{2}$ — L: dolžina stene

$F(L) = E(L) - T S(L)$

$S(L) = k_B \ln \Delta\Gamma(L) \approx k_B \ln 3^L$ ← krepko precenili

$F(L) = \frac{LJ}{2} - T k_B L \ln 3 = \left(\frac{J}{2} - k_B T \ln 3\right) L$

Ko so vsi − ali + je $F(0) = 0$
Kdaj je še stabilno stanje

$F(L) < 0 \qquad \left(\frac{J}{2} - k_B T \ln 3\right) L < 0$

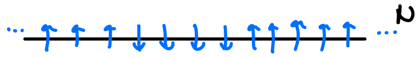
$T > \frac{J}{2 k_B \ln 3}$ tvorba otokov ugodna, feromagnetna faza ni stabilna.

$T_c = \frac{J}{2 k_B \ln 3} \doteq 0{,}455 \frac{J}{k_B}$

$T < \frac{J}{2 k_B \ln 3}$ tvorba otokov ni ugodna, feromagnet je stabilen

kritična temperatura
(fazni prehod)

1D feromagnet



N spinov

$E = 2\frac{J}{2} = J$

$S = k_B \ln \Delta\Gamma = k_B \ln \frac{(N-1)(N-2)}{2} = k_B \ln \binom{N-1}{2} \approx$

$\approx k_B \ln \frac{N^2}{2} \approx k_B \ln N^2$

$F \doteq J + 2 k_B \ln N \, T \xrightarrow[\text{TD lim}]{N \to \infty} -\infty$

Feromagnetna faza v 1D ni stabilna

Velekanonični porazdelitev

$$e^{-\beta\Omega} = \sum_{N=0}^{\infty} \underbrace{\sum_{i}}_{\text{po vseh stanjih}} e^{-\beta E_i + \beta\mu N}$$

kemijski potencial

$$\langle E \rangle = \left(\frac{\partial \beta\Omega}{\partial \beta}\right)_{\beta\mu, V} \qquad \sigma_E^2 = -\left(\frac{\partial^2 \beta\Omega}{\partial \beta^2}\right)_{\beta\mu, V}$$

$$\langle N \rangle = -\left(\frac{\partial \beta\Omega}{\partial \beta\mu}\right)_{\beta V} \quad \text{in} \quad \sigma_N^2 = -\left(\frac{\partial^2 \beta\Omega}{\partial \beta\mu^2}\right)_{\beta, V}$$

Če pVT sistem:

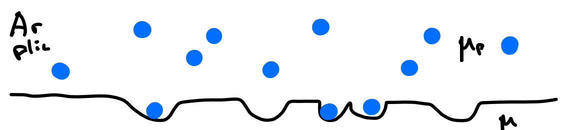
$$\Omega = F - G = -pV \qquad \text{Če pVT} \qquad p = -\left(\frac{\partial \beta\Omega}{\partial \beta V}\right)_{\beta, \beta\mu}$$

Za enoatomni nedegeneriran idealen plin

$$\mu = k_B T \ln \frac{P}{J T^{5/2}}$$

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

5.20 Adsorpcija atomov Ar na steni posode ($p = 1\,\text{bar}$, $T = 20°C$, $E = -w$, $w = 1\,\text{meV}$)



N_0 adsorpcijskih mest

$m = 39{,}9\ \frac{\text{kg}}{\text{kmol}}$, E vezavna energija, $j = 0$ vrtilna količina

$\frac{\langle N \rangle}{N_0} = ?$

$$e^{-\beta\Omega} = \underset{\substack{N=0 \\ \text{vsa mesta prazna}}}{1} + N_0 e^{-\beta(-w) + \beta\mu\cdot 1} + \binom{N_0}{2} e^{-\beta(-2w - 2\mu)} + \ldots =$$

$\binom{N_0}{0}$, $\binom{N_0}{1}$ – na koliko mest lahko damo en delec

$$= \sum_{N=0}^{N_0} \binom{N_0}{N} e^{\beta(w+\mu)N}\, 1^{N_0 - N} \overset{\text{Binomska vrsta}}{=} \Big(\underbrace{e^{\beta(w+\mu)} + 1}_{\text{fermionska vsota ene lokacije}}\Big)^{N_0}$$

(polno adsorpcijsko mesto: $e^{\beta(w+\mu)}$; prazno: 1)

$$\langle N \rangle = -\frac{\partial \beta\Omega}{\partial \beta\mu} = \qquad -\beta\Omega = N_0 \ln\left(1 + e^{\beta(w+\mu)}\right)$$

$$= N_0 \frac{1}{e^{-\beta(w+\mu)} + 1} \qquad \mu \text{ še ne poznamo}$$

V ravnovesju je $\mu_p = \mu$

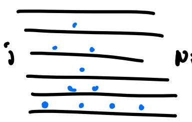
$$\mu_p = k_B T \ln \frac{P}{J T^{5/2}}$$

$$J = \frac{k_B^{5/2} (2j+1)(2\pi m)^{3/2}}{h^3} = 6{,}6 \cdot 10^5 \ \frac{\text{Pa}}{\text{K}^{5/2}}$$

$$e^{\beta\mu_p} = \frac{P}{J T^{5/2}} =$$

$$\frac{\langle N \rangle}{N_0} = \frac{1}{e^{-\beta(w+\mu)} + 1} = \frac{1}{1 + e^{-\beta w} \frac{J T^{5/2}}{P}} = \ldots = 1{,}07 \cdot 10^{-7}$$

Bose-Einsteinova statistika



enodelčna stanja

$$\beta\Omega = \sum_j \ln\left(1-e^{\beta(\mu-E_j)}\right)$$

$$\langle N\rangle = -\frac{\partial\beta\Omega}{\partial\beta\mu} = +\sum_i \frac{e^{\beta\mu-\beta E_i}}{1-e^{\beta(\mu-E_j)}} = \sum_j \underbrace{\frac{1}{e^{\beta(E_j-\mu)}-1}}_{\langle N_j\rangle}$$

5.6 Tlak sevanja črnega telesa pri 300 K? Entropija v $V=1\,cm^3$, $\langle E\rangle=?$, $j=?$
(fotonski plin)

foton ima spin $S=1$ → bozon

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

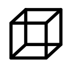
k velikost val. vektorja

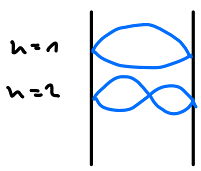
$$E_j = \hbar\omega_j = h\nu = \hbar c k_j$$

$$\beta\Omega = -\beta pV = \sum_j \ln\left(1-e^{\beta(\mu-E_j)}\right)$$

Za fotone $\mu=0$
ker se ne ohranjajo (njihovo število)

Stoječi valovi v škatli



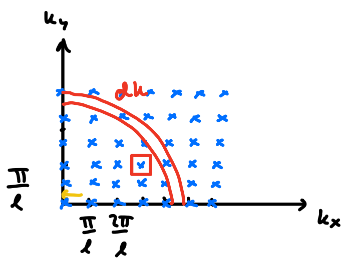


$\frac{\lambda}{2} = l$

$\lambda = l$

$\frac{n\lambda}{2} = l \qquad \lambda_n = \frac{2l}{n} = \frac{2\pi}{k_n}$

$k_n = \frac{n\pi}{l}$



Volumen sferične lupinje

$$\sum_j 1 \to \int \frac{4\pi k^2\,dk}{\left(\frac{\pi}{l}\right)^3\cdot 8}\cdot 2 = \dots = l^3\int\frac{k^2\,dk}{\pi^2}$$

volumen enega stanja

le 1. oktant rabimo

2 polarizaciji

Alternativna pot
Bohr-Sommerfeldovo pravilo:

polarizacija

$$\frac{d\Gamma}{h^3} = \frac{d^3p\,d^3r}{h^3} = \frac{\hbar^3 d^3k\,d^3r}{h^3} = \frac{V}{(2\pi)^3}\,2\cdot 4\pi k^2\,dk = \frac{V k^2\,dk}{\pi^2}$$

$$-\beta pV = V\int_0^\infty \ln\left(1-e^{-\beta\hbar ck}\right)\frac{k^2\,dk}{\pi^2}$$

(dovolj velika škatla)

$\beta\hbar ck = u \qquad dk = \frac{du}{\beta\hbar c} \qquad k = \frac{u}{\beta\hbar c}$

$\ln(1-x) = -\left(x + \frac{x^2}{2} + \frac{x^3}{3} + \dots\right)$

$$= \frac{V}{(\beta\hbar c)^3\pi^2}\int_0^\infty \ln\left(1-\underbrace{e^{-u}}_{<1}\right)u^2\,du = \frac{V}{(\beta\hbar c)^3\pi^2}\int_0^\infty\sum_{n=1}^\infty\frac{e^{-un}}{n}u^2\,du =$$

$$= \frac{V}{(\beta\hbar c)^3\pi^2}\sum_{n=1}^\infty\frac{1}{n^4}\int_0^\infty e^{-un}(un)^2\,d(un) = \frac{V}{(\beta\hbar c)^3\pi^2}\sum_{n=1}^\infty\frac{1}{n^4}\,2! = \frac{2V}{(\beta\hbar c)^3\pi^2}\zeta(4) = \frac{V\pi^2}{45(\beta\hbar c)^3}$$

Riemanova zeta funkcija $\zeta(z) = \sum_{n=1}^{\infty} \frac{1}{n^z}$

$\zeta(1) = \infty$
$\zeta(2) = \frac{\pi^2}{6}$
$\zeta(3) = 1{,}202\ldots$
$\zeta(4) = \frac{\pi^4}{90}$
$\zeta(5) = 1{,}037\ldots$

$$-\beta p \cancel{V} = \frac{\cancel{V}\,\pi^2}{45(\beta\hbar c)^3}$$

$$p = \frac{1}{\beta^4(\hbar c)^3}\frac{\pi^2}{45} = \frac{k_B^4 T^4 \pi^2}{(\hbar c)^3\, 45}$$

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

def. $\sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} = 5{,}67\cdot 10^{-8}\,\frac{W}{m^2K^4}$

Štefanova konstanta

$p \propto T^4$

$p \neq p(V)$ $\qquad \chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \to \infty$

Entropija

$dF = -S\,dT - p\,dV + \cancel{\mu\, dN} \to 0$ $\quad (\mu = 0)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{4}{3}\frac{\sigma}{c}V\frac{d}{dT}T^4 = \frac{16}{3}\frac{\sigma}{c}VT^3 = 2{,}7\cdot 10^{-14}\ \frac{J}{K}$$

$$\mathcal{g} = F - \underset{\mu N}{G} = -pV$$

$F = -pV$

Adiabata $VT^3 = \text{konst.}$

Energija $F = U - TS$

$$U = F + TS = -pV + TS = -\frac{4}{3}\frac{\sigma T^4}{c}V + T\frac{16}{3}V\frac{\sigma}{c}T^3 = 4V\frac{\sigma}{c}T^4 = uV$$

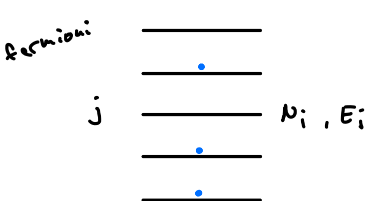
Gostota energijskega toka

$$j = \frac{u\cdot c}{4} = 4\frac{\sigma T^4}{c}\cdot\frac{c}{4} = \sigma T^4$$

neusmerjen tok

Fermi-Diracova statistika

Primer: degeneriran plin e^- • kovini

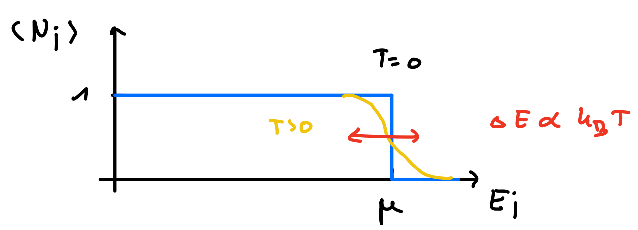


… velepotencial

$$-\beta\,\mathcal{g} = \sum_j \ln\left(1 + e^{\beta(\mu - E_j)}\right)$$

$$\langle N\rangle = -\left(\frac{\partial \beta \mathcal{g}}{\partial \beta\mu}\right)_\beta = \sum_j \frac{e^{\beta(\mu-E_j)}}{1+e^{\beta(\mu-E_j)}} = \sum_j \underbrace{\frac{1}{e^{\beta(E_j-\mu)}+1}}_{\langle N_j\rangle}$$

$f(E_j)$ fermijevo zasedbeno število



5.8 Elektronski plin v kovini (Ag)

$\mu(T=0) = ?$ $\quad p(T=0) = ?$ $\quad \chi_T(T=0) = ?$

$\rho = 10500\ \mathrm{kg/m^3}$ $\quad$ 1 prevodniški e^-/atom $\quad M = 107{,}9$

$$E_j = \frac{p_j^2}{2m}$$ ... kin. en. (ostalih ne upoštevamo) ; Ne^-

ⓐ $N = \sum_j \langle N_j \rangle$ $\qquad$ D: spremljajoče relacije

Bohr-Sommerfeld

$p = \sqrt{2mE}$

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

$$\sum_j 1 \to \underset{\uparrow}{2} \int \frac{d^3p\, d^3q}{h^3} = 2V \int \frac{d^3p}{h^3} = \frac{2V}{h^3}\int 4\pi p^2 dp = \frac{2V}{h^3}\,4\pi \int 2mE\,\sqrt{2m}\,\frac{1}{2\sqrt{E}}\,dE =$$

2 spina ↑↓

Energija ni odvisna od kraja

na sferične koordinate ker nas zanima le velikost p in ne $\vec{p}$.

kvanta velikost faznega prostora

cel fazni prostor

$$= \int \underbrace{\frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\sqrt{E}}_{\substack{\text{gostota stanj} \\ g(E)}}\, dE \qquad \Rightarrow \qquad \sum_j 1 \to \int g(E)\,dE$$

$$N = \int_0^\infty f(E)\,g(E)\,dE \overset{T=0}{=} \int_0^{\mu_0} 1\; g(E)\,dE = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\mu_0} E^{1/2}\,dE =$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{2}{3}E^{3/2}\Big|_0^{\mu_0} = \frac{V}{3\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{3/2}$$

$$\boxed{\mu_0 = \left(\frac{3N\pi^2}{V}\right)^{2/3}\frac{\hbar^2}{2m_{e^-}} = \left(\frac{3\pi^2 \rho N_A}{M}\cdot z\right)^{2/3}\frac{\hbar^2}{2m_{e^-}}} = \ldots = 5{,}5\,\mathrm{eV}$$

ⓑ PVT sistem

$$\mathcal{G} = -pV$$

$$-\beta\mathcal{G} = \beta pV = \sum_j \ln\left(1 + e^{\beta(\mu - E_j)}\right) = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty \ln\left(1+e^{\beta(\mu-E)}\right)\sqrt{E}\,dE \overset{\text{per partes}}{=} \ldots$$

... $u = \ln\left(1+e^{\beta(\mu-E)}\right)$ $\qquad dv = \sqrt{E}\,dE$

$$du = \frac{-\beta e^{\beta(\mu-E)}}{1+e^{\beta(\mu-E)}}\,dE \qquad v = \frac{2}{3}E^{3/2}$$

$$du = \frac{-\beta}{e^{\beta(E-\mu)}+1}\,dE$$

$$\ldots = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\left[\overset{=0}{\frac{2}{3}E^{3/2}\ln\left(1+e^{\beta(\mu-E)}\right)\Big|_0^\infty} - \int_0^\infty \frac{2}{3}E^{3/2}\frac{-\beta\,dE}{1+e^{\beta(E-\mu)}}\right] =$$

↳ spodnja meja : 0

↳ zgornja meja : $0\cdot\infty$

$$\text{L'Hop}\quad \frac{\ln\left(1+e^{\beta(\mu-E)}\right)}{E^{-3/2}} \overset{\text{L'Hop}}{=} \frac{-\beta e^{\beta(\mu-E)}}{\left(1+e^{\beta(\mu-E)}\right)E^{-5/2}\left(-\frac{3}{2}\right)} = \frac{\frac{2}{3}\beta E^{5/2}}{e^{\beta(E-\mu)}+1} = 0$$

→ exp hitreje narašča

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta\,\frac{2}{3}\int_0^\infty E^{3/2}\underbrace{\frac{1}{1+e^{\beta(E-\mu)}}}_{f(E)=1}dE \underset{T=0}{=} \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta\,\frac{2}{3}\int_0^{\mu_0}E^{3/2}\,dE =$$

$$= \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\beta\,\frac{2}{3}\,\frac{2}{5}\,\mu_0^{5/2} = \frac{2V\beta}{15}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{5/2} = \beta p V$$

$$p = \frac{2}{15\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\mu_0^{5/2} = \ldots = \frac{2}{5}\frac{N}{V}\mu_0 = \ldots = 2{,}05\cdot 10^{10}\ \mathrm{Pa}$$

(c)

$$\chi_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \;; \qquad p \propto V^{-5/3} \qquad p = \frac{A}{V^{5/3}}$$

$$= -\frac{1}{V}\,\frac{dV\,V^{8/3}}{A(-5/3)\,dV} \qquad\qquad dp = A\left(-\frac{5}{3}\right)\frac{dV}{V^{8/3}}$$

$$= \frac{V^{5/3}}{A}\,\frac{3}{5} = \frac{3}{5}\,\frac{1}{p} = \ldots = 2{,}9\cdot 10^{-11}\ \mathrm{Pa}^{-1}$$

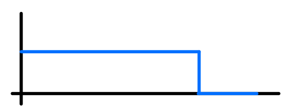
Primerjava $\frac{1}{E_Y} = 1{,}21\cdot 10^{-11}\ \mathrm{Pa}^{-1}$

Nizko temp. limita:

bel pritlikavec $(T = 10^5\,\mathrm{K})$

$k_B T \sim 8{,}6\,\mathrm{eV}$

$\mu \sim 1\,\mathrm{MeV}$



nevtronske zvezde (nevtronski plin)

5.1 Trdna snov: valovanje z disperzijsko relacijo $\omega(k) = ak^n$;

k valovni vektor

Nizko (in visoko) T obnašanje spec. toplote:

$n=1$; fononi (mrežno nihanje v kristalu): $\omega \propto k$, $\omega = \overset{a}{\overset{\shortparallel}{c}}k$

$n=2$; magnoni (spinski valovi) $\uparrow\uparrow\uparrow\downarrow\uparrow\uparrow$: $\omega \propto k^2$

bozoni, nevidezni delci, njihovo št. se ne ohranja, $\mu = 0$

$$\langle E\rangle = \sum_j \underbrace{\hbar\omega_j}_{E_j}\underbrace{\langle N_j\rangle}_{\text{Bose Ein. porazd.}} = \sum_j \hbar\omega_j\,\frac{1}{e^{\beta E_j}-1} = \sum \frac{\hbar\omega_j}{e^{\beta\hbar\omega_j}-1}$$

$$\sum_j \to \underbrace{p}_{\text{št. polarizacij}}\int\frac{d\Gamma}{h^3} = p\int\frac{d^3r\,d^3p}{h^3} = p\,\frac{V}{h^3}\int\hbar^3 d^3k = \frac{pV}{(2\pi)^3}\int 4\pi k^2\,dk$$

$$\omega = ak^n \Rightarrow k = \left(\frac{\omega}{a}\right)^{\frac{1}{n}} \qquad dk = \left(\frac{1}{a}\right)^{\frac{1}{n}}\frac{1}{n}\,\omega^{\frac{1}{n}-1}\,d\omega$$

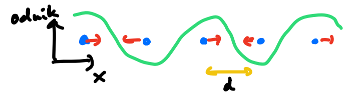
$$\sum_j \to \frac{pV\,4\pi}{(2\pi)^3}\int\left(\frac{\omega}{a}\right)^{\frac{2}{n}}\frac{1}{a^{1/n}}\,\frac{1}{n}\,\omega^{\frac{1}{n}-1}\,d\omega = \frac{pV}{n2\pi^2}\int\frac{\omega^{3/n}}{a^{3/n}}\,\frac{d\omega}{\omega}$$

$$\langle E\rangle = \sum \frac{\beta\hbar\omega_i}{e^{\beta\hbar\omega_i}-1} = \frac{pV}{2\pi^2 n}\int \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\left(\frac{\omega}{a}\right)^{3/n}\frac{d\omega}{\omega} = \frac{pV\hbar}{2\pi^2 n\, a^{3/n}}\int_{\omega_{min}}^{\omega_{max}} \frac{\omega^{3/n}}{e^{\beta\hbar\omega}-1}\,d\omega = \dots$$

Min

Vzamemo neskončno velike posode $\omega_{min}\to 0$

Max



Bolj gosto ne moremo iti.

$$u = \beta\hbar\omega$$
$$du = \beta\hbar\, d\omega$$

$$\dots = \frac{pV\hbar}{2\pi^2 n\, a^{3/n}}\,\frac{1}{(\beta\hbar)^{3/n+1}}\int_0^{u_{max}} \frac{u^{3/n}}{e^u-1}\,du$$

- Nizko T limita; $\beta\to\infty$, $u_{max}\to\infty$, $\omega_{max}\to\infty$

$$\boxed{\langle E\rangle = \frac{pV\hbar}{2\pi^2 n\, a^{3/n}}\,\frac{1}{(\beta\hbar)^{3/n+1}}\int_0^{\infty} \frac{u^{3/n}}{e^u-1}\,du}$$

Zvok: $n=1$; $a=c$; $p=3$

$$\langle E\rangle = \frac{3V}{2\pi^2 c^3}\,\frac{\hbar\,1}{(\beta\hbar)^4}\underbrace{\int_0^\infty \frac{u^3}{e^u-1}\,du}_{I} = \frac{3V}{2\pi^2 c^3}\,\frac{\hbar\,1}{(\beta\hbar)^4}\,\frac{\pi^4}{15} = \frac{\pi^2 V k_B^4 T^4}{10(\hbar c)^3}$$

$$I = \int_0^\infty \frac{u^3 e^{-u}}{1-\underbrace{e^{-u}}_{<1}}\,du = \int_0^\infty u^3 e^{-u}\sum_{j=0}^\infty e^{-ju}\,du = \int_0^\infty u^3 \sum_{j=1}^\infty e^{-ju}\,du = \sum_{j=1}^\infty \int_0^\infty u^3 e^{-ju}\,du =$$

$$= \sum_{j=1}^\infty \frac{1}{j^4}\,3! = 6\sum_{j=1}^\infty \frac{1}{j^4} = 6\,\zeta(4) = 6\cdot\frac{\pi^4}{90} = \frac{\pi^4}{15}$$

$$C = \frac{d\langle E\rangle}{dT} = \frac{2\pi^2 V k_B^4}{5(\hbar c)^3}\,T^3 \propto T^3$$

- Visoko T limita; fononi (zvok)

$$\langle E\rangle = \frac{3V}{2\pi^2 c^3}\,\frac{\hbar\,1}{(\beta\hbar)^4}\int_0^{u_{max}} \underbrace{\frac{u^3}{e^u-1}}\,du = \dots \qquad u_{max} = \beta\hbar\omega_{max} \ll 1$$

$$e^u \approx 1+u+O(u^2)+\dots$$

$$\int \frac{u^3}{1+u-1}\,du = \int u^2\,du = \frac{u_{max}^3}{3}$$

Določitev u_{max}: $\omega_{MAX} = \omega_D$

Debye: N atomov

$3N$ prostostnih stopenj

$$3N = \sum_j 1 = pV\int \frac{4\pi p^2\,dp}{h^3} = \frac{pV\,4\pi\hbar^3}{(2\pi)^3\hbar^3}\int k^2\,dk =$$

$$\overset{p=3}{=} \frac{3V\,4\pi}{8\pi^3 c^3}\int_0^{\omega_{MAX}} \omega^2\,d\omega = \frac{3V}{2\pi^2 c^3}\,\frac{\omega_{max}^3}{3}$$

$$\omega_{MAX}^3 = \frac{6N\pi^2 c^3}{V}$$

$$\dots = \frac{3V\hbar}{2\pi^2 c^3}\,\frac{k_B^4 T^4}{\hbar^4}\,\frac{1}{3}(\beta\hbar)^3\,\frac{6N\pi^2 c^3}{V} = 3Nk_BT \qquad C = \frac{d\bar{E}}{dT} = 3Nk_B$$

Kinetična teorija plinov

↳ projekcija Maxwellove porazdelitve na hitrosti podprostor:

$$3D:\ dw = \frac{dN}{N} = \left(\frac{\beta m_1}{2\pi}\right)^{3/2} e^{-\beta \frac{m_1 v^2}{2}}\, d^3v = w(v)\, d^3v \qquad m_1 = \frac{M}{N_A}$$

d^3v: $dv_x\, dv_y\, dv_z$, $v^2\, dv\, d\Omega$

$$\int w(v)\, dv = 1$$

$$1D:\ dw = \frac{dN}{N} = \left(\frac{\beta m_1}{2\pi}\right)^{1/2} e^{-\beta \frac{m_1 v_x^2}{2}}\, dv_x = w(v_x)\, dv_x$$

$$\int w(v_x)\, dv_x = 1$$

Povprečna hitrost $\langle v_x \rangle = 0$

velikost $\langle v \rangle = \int v\, w(v)\, d^3v = \sqrt{\frac{8 k_B T}{\pi m_1}}$

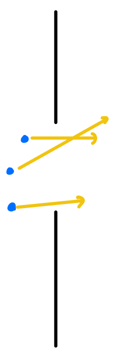
$n = \frac{p}{k_B T}$

povprečna prosta pot $\langle l_p \rangle = \frac{k_B T}{\pi (2r)^2 p \sqrt{2}}$

6.3 Termični nevtroni v sredici jedrskega reaktorja

$j = 4 \cdot 10^{16} \frac{\text{nevtronov}}{m^2 s}$ $\qquad n = ?$ $\qquad p = ?$

Pomeni da jih lahko obravnavamo kot idealni plin pri $T = 300K$



Iz predavanj

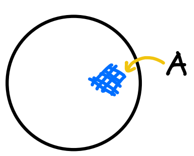
$j = \frac{1}{4} n \langle v \rangle$ $\qquad \langle v \rangle = \sqrt{\frac{8 k_B T}{\pi m_1}} \doteq 2515\ m/s$

$\Rightarrow n = \ldots = 6{,}4 \cdot 10^{13}\ /m^3$

$$p = n k_B T = \ldots =$$

6.4 Okrogla bučka z vodno paro, ki ji ohladimo del stene, molekule primrznejo na A

$V = 10\ dm^3$
$T = 20°C$ – konst.
$p' = 10$ mbar
$t = 1\ s$
$p = 10^{-3} p'$
$A = ?$



$$p(t) = n(t)\, k_B T$$

To lahko gledamo kot prehajanje plina skozi luknjo

$$j = \frac{1}{4} n \langle v \rangle$$

$dN = -j\, A\, dt$; $n = \frac{N}{V}$

$V dn = -j\, A\, dt$
$= -\frac{1}{4} n A \langle v \rangle\, dt$

⋮

$$\int_{\substack{n' \\ \parallel \\ n(t=0)}}^{n(t)} \frac{dn}{n} = -\frac{A\langle v\rangle}{4V}\int_0^t dt$$

$$\ln\frac{n(t)}{n'} = -\frac{A\langle v\rangle t}{4V}$$

$$\ln\frac{p(t)}{p'} = -\frac{A\langle v\rangle t}{4V} \Longrightarrow A = -\frac{4V\ln p(t)/p'}{\langle v\rangle t} = \dots = 4{,}7\ cm^2$$

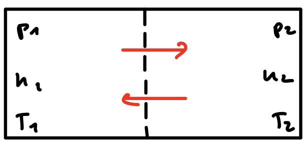
$$p(t) = p' e^{-\frac{A\langle v\rangle t}{4V}}$$

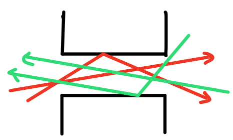
6.8 Posoda s porozno steno; v njej O_2 ; $T_1 = 27°C$ $T_2 = 30°C$ konst.

redek plin

(a) $p_1 = 10\ Pa$ $p_2 = ?$ $\Delta p = ?$

Premer por $\ll \langle l_p\rangle$





Ker je v ravnovesju

$$j_{1\to 2} = j_{2\to 1}$$

$$\frac{1}{4} n_1 \langle v_1\rangle = \frac{1}{4} n_2 \langle v_2\rangle$$

$$\frac{p_1}{k_B T_1}\sqrt{\frac{8k_B T_1}{\pi m_1}} = \frac{p_2}{k_B T_2}\sqrt{\frac{8k_B T_2}{\pi m_1}}$$

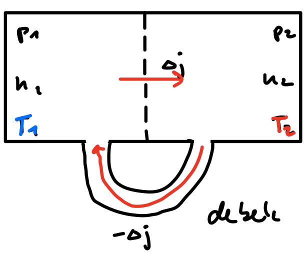
$$\frac{p_1}{\sqrt{T_1}} = \frac{p_2}{\sqrt{T_2}}$$

$$p_2 = p_1\sqrt{\frac{T_2}{T_1}} = 10{,}05\ Pa$$

$\Delta T \to \Delta p$

$\Delta p = 0{,}05\ Pa$ termomehanični pojav

(b)



debela cev $\Rightarrow$ $p_1 = p_2 = p$

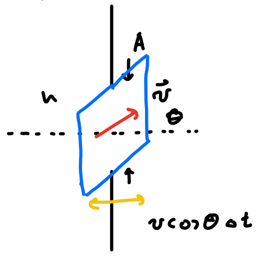
$$\Delta j = j_{1\to 2} - j_{2\to 1} = ?$$

$$= \frac{1}{4} n_1\langle v_1\rangle - \frac{1}{4} n_2\langle v_2\rangle$$

$$= \frac{p}{4k_B T_1}\sqrt{\frac{8k_B T_1}{\pi m_1}} - \frac{p}{4k_B T_2}\sqrt{\frac{8k_B T_2}{\pi m_1}} =$$

$$= \frac{p\sqrt{2}}{2\sqrt{k_B \pi m_1}}\left(\frac{1}{\sqrt{T_1}} - \frac{1}{\sqrt{T_2}}\right) = \dots = 1{,}37\cdot 10^{21}\ /m^2 s$$

Energijski tok skozi okvir (redek plin) $\sqrt{A} \ll l_1$



$$E = j_Q A\, dt = \int_{v,\Omega} n A v \cos\theta\, dt\ \frac{1}{2} m_1 v^2\, w(v,\theta)\, d^3v$$

$$j_Q = n m \frac{1}{2} \int v^3\, w(v,\theta) \cos\theta\, d^3v$$

$$= \frac{n m_1}{2} \int v^3 \cos\theta \left(\frac{\beta m_1}{2\pi}\right)^{3/2} e^{-\beta \frac{m_1 v^2}{2}}\, v^2 dv\, 2\pi\, d\cos\theta$$

$u = \frac{\beta m_1}{2} v^2$

$du = \beta m_1 v\, dv$

$$= \frac{n m_1}{2} \left(\frac{\beta m_1}{2\pi}\right)^{3/2} 2\pi \int_0^\infty v^5 e^{-\beta \frac{m_1 v^2}{2}} dv \int_0^1 \cos\theta\, d\cos = $$

$$= \frac{n m_1}{2} \left(\frac{\beta m_1}{2\pi}\right)^{3/2} 2\pi \frac{1}{\beta m_1} \left(\frac{2}{\beta m_1}\right)^2 \int_0^\infty u^2 e^{-u} du \int_0^1 z\, dz =$$

$$= \frac{n m_1}{\cancel{2}} \left(\frac{\beta m_1}{2\pi}\right)^{3/2} 2\pi \frac{1}{\beta m_1} \left(\frac{\cancel{2}}{\beta m_1}\right)^2 \frac{1}{\cancel{2}} \underbrace{\int_0^\infty u^2 e^{-u} du}_{\Gamma(3) = 2!}$$

$$= n m_1 \left(\frac{\beta m_1}{2\pi}\right)^{3/2} 2\pi \frac{1}{(\beta m_1)^3}\, 2$$

$$= \frac{n m_1\, 2}{(\beta m_1)^{3/2} \sqrt{2\pi}} = \frac{\sqrt{2}\, n}{\sqrt{\pi} \sqrt{m_1}\, (\beta)^{3/2}} = \frac{n}{\beta} \sqrt{\frac{2}{\pi m_1 \beta}} = \frac{n k_B T}{2} \sqrt{\frac{8 k_B T}{\pi m_1}}$$

$$j_Q = \frac{1}{2} n k_B T \langle v \rangle$$