5. VJEŽBE STATISTIČKA
3.4.2019.

TERMODINAMIČKI POTENCIJALI

ENTALPIJA $H = U + pV$

sustavu je zadan pritisak

HELMHOLTZOVA SLOBODNA ENERGIJA $F = U - TS$

sustavu su zadani volumen temperatura $F(V,T)$

GIBBSOVA SLOBODNA ENERGIJA $G = U - TS + pV$

kontroliramo temperaturu i pritisak $G(p,T)$

Termodinamički potencijal → veličina koja je u ravnotežnom stanju ekstremalna

→ mješovita derivacija daje generaliziranu silu.

$$dU = TdS - pdV + \mu dN$$

$$dH = dU + pdV + Vdp = TdS - \cancel{pdV} + \mu dN + \cancel{pdV} + Vdp$$

$$dH = TdS + Vdp + \mu dN$$

$$dF = dU - TdS - SdT = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} + SdT$$

$$dF = SdT - pdV + \mu dN$$

$$dG = dU - TdS - SdT + pdV + Vdp = \cancel{TdS} - \cancel{pdV} + \mu dN - \cancel{TdS} - SdT + \cancel{pdV} + Vdp$$

$$dG = Vdp - SdT + \mu dN$$

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \qquad T = \left(\frac{\partial H}{\partial S}\right)_{p,N} \qquad S = \left(\frac{\partial F}{\partial T}\right)_{V,N} \qquad V = \left(\frac{\partial G}{\partial p}\right)_{T,N}$$

$$-p = \left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad V = \left(\frac{\partial H}{\partial p}\right)_{S,N} \qquad -p = \left(\frac{\partial F}{\partial V}\right)_{T,N} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_{p,N}$$

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{T,V} \qquad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,p} \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} \qquad \mu = \left(\frac{\partial G}{\partial N}\right)_{p,T}$$

MAXWELLOVE RELACIJE

$$\frac{\partial U}{\partial S} = T \qquad \left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial^2 U}{\partial S \partial V}$$

= ovo mora biti jednako

$$\frac{\partial U}{\partial V} = -p \qquad -\left(\frac{\partial p}{\partial S}\right)_V = \frac{\partial^2 U}{\partial V \partial S}$$

$$\rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V = \frac{\partial^2 U}{\partial V \partial S}$$

Analogno možemo dobiti i ostale Maxwellove relacije iz drugih termodin. potencijala.

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p = \frac{\partial^2 H}{\partial S \partial p}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial T \partial V}$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p = \frac{\partial^2 G}{\partial T \partial p}$$

① Zadan je Gibbsov potencijal.

$$G(p,T) = aT^2 \ln \frac{bp^3}{T} \qquad a, b = \text{const.}$$

Odredite:

① jednadžbu stanja ② $S(p,T)$?

③ $F(V,T)$?

$$dG = dU - d(TS) + d(pV) = \cancel{TdS} - \cancel{pdV} - \cancel{TdS} - SdT + \cancel{pdV} + Vdp$$

$$\boxed{dG = Vdp - SdT}$$

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

$$V = \frac{aT^2}{p\cancel{^3}} \cdot 3\cancel{p^2} \longrightarrow \boxed{V = \frac{3aT^2}{p}} \text{ jedb. stanja}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -\left\{ 2aT \ln \frac{bp^3}{T} - \frac{aT^{\cancel{2}}}{\cancel{T}} \right\}$$

2) $$\boxed{S = aT\left(1 - 2\ln \frac{bp^3}{T}\right)}$$

3) $$F = G - pV = aT^2 \ln \frac{bp^3(V,T)}{T} - p(V,T) \cdot V$$

$$= aT^2 \ln\left(\frac{b}{T} \cdot \left(\frac{aT^2}{V}\right)^3\right) - \left(\frac{3aT^2}{V}\right) \cdot V$$

$$F(V,T) = aT^2 \left(\ln\left(\frac{T^5}{V^3} b(3a)^3\right) - 3 \right)$$

(2) Zadana je $S(U,V,N) = a(UVN)^{1/3}$

$F, G, H, U = ?$ Termodinamički potencijali (ovo smo jednom prije radili)

Podsjetnik na formule: $S = \frac{3U}{T} \quad U = pV \quad p^2 V = mT^3$

$$U(V,T) = \sqrt{mVT^3} \quad , \quad S(V,T) = 3\sqrt{mVT}$$

I. $U(S,V,N) = ?$

$$\boxed{U = \frac{S^3}{a^3 VN}} = U(S,V,N)$$

$$\underline{dU = TdS - pdV}$$

II. $F = U - TS = F(T,V) = U(T,V) - TS(T,V)$

$$= U - 3U = -2U(T,V) \longrightarrow \boxed{F = -2\sqrt{mT^3 V}}$$

$$dF = dU - d(TS) = \underline{-SdT - pdV}$$

III. $G = \underbrace{U - TS}_{F} + pV = G(p,T)$

$$= -2U + U = -U(p,T) = -pV(p,T)$$

$$= -p \cdot \frac{mT^3}{p^2} \longrightarrow \boxed{G(p,T) = -\frac{mT^3}{p}}$$

$$\underline{dG = Vdp - SdT}$$

IV $H(S,p) = G + TS = U - \cancel{TS} + pV + \cancel{TS}$

$= U + pV = 2pV$

$H(S,p) = 2p \cdot V(S,p)$

$S = 3\sqrt{UVT} \; \Big|^2$

$Vp^2 = UT^3$

$\frac{S^2}{9UV} = T$

$V = \frac{UT^3}{p^2} \longrightarrow \frac{U}{p^2}\left(\frac{S^2}{9UV}\right)^3 = V$

$\frac{U}{p^2} \frac{S^6}{9^3 U^3 V^3} = V \longrightarrow \boxed{V^4 = \frac{1}{p^2} \frac{S^6}{9^3 U^2}}$

$V = \frac{S^{3/2}}{\sqrt{pU\,27}}$

$H(S,p) = 2\sqrt{\frac{pS^3}{27U}}$

$dH = TdS + Vdp$

ANSAMBL - zamišljeni sistemi među kojima uzimamo nasumični uzorak su članovi ansambla

Rekli smo zadnji put da za kanonski ansambl:

$$P_r \sim e^{-\beta E_r}$$

i

$$\boxed{\bar{y} = \frac{\sum_r y_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}}$$ srednja vrijednost nečeg mjerenog

$$Z = \sum_r e^{-\beta E_r}$$, Particijska funkcija

KANONSKI ANSAMBL - u statističkoj fizici je statistički ansambl koji reprezentira skup mogućih stanja sistema koja se nalaze u termodinamičkoj ravnoteži s okolinom

Statistički ansambl koji predstavlja moguća stanja sistema u termalnoj ravnoteži s toplinskim spremnikom

→ Sistem može izmjenjivati energiju s toplinskim spremnikom, tako da će se pojedina stanja razlikovati međusobno u energiji.

$$P = \frac{1}{Z} e^{-E/kT}$$ Vjerojatnost realizacije nekog posebnog mikrostanja sistema

PRIMJENA KANONSKOG ANSAMBLA

- Koristimo ga za male ili velike sustave koji su u kontaktu s termostatom pod pretpostavkom da je termostat velik.

- Koristimo ga za sustave s konstantnim brojem čestica! Za sisteme s varijabilnim brojem čestica → velekanonski ansambl.

③ Zadana je particijska funkcija $Z = 2\cosh(\beta\varepsilon)$

1) Koliko ukupno energetskih nivoa imamo i koji su to?
2) Srednja energija čestice na niskim temp $\bar{E}(T \to 0) = ?$
3) Srednja energija čestice na visokim temp $\bar{E}(T \to \infty) = ?$

1) $Z = 2\cosh(\beta\varepsilon)$

$$= 2\,\frac{e^{\beta\varepsilon} + e^{-\beta\varepsilon}}{2} = e^{\beta\varepsilon} + e^{-\beta\varepsilon}$$

$Z = \sum_r e^{-\beta\varepsilon_r} \longrightarrow$ Dakle imamo 2 člana reda $\rightarrow$ 2 energetska nivoa

NIVOI: $-\varepsilon, +\varepsilon$

2)

$$\bar{\varepsilon} = \frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum_i e^{-\beta\varepsilon_i}} = \frac{-\varepsilon e^{\beta\varepsilon} + \varepsilon e^{-\beta\varepsilon}}{e^{+\beta\varepsilon} + e^{-\beta\varepsilon}} = \varepsilon\,\frac{e^{-\beta\varepsilon} - e^{\beta\varepsilon}}{e^{-\beta\varepsilon} + e^{\beta\varepsilon}}$$

$T \to 0 : \beta \to \infty$

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

$$\varepsilon\,\frac{-e^{\beta\varepsilon}}{e^{\beta\varepsilon}} = \boxed{-\varepsilon}. \qquad \bar{\varepsilon} = -\varepsilon$$

3) $T \to \infty \quad \beta \to 0$ Razvijamo u red

$$\bar{\varepsilon} = \varepsilon\,\frac{\cancel{1} - \beta\varepsilon + \cancel{\frac{(\beta\varepsilon)^2}{2}} - \cancel{1} - \beta\varepsilon - \cancel{\frac{(\beta\varepsilon)^2}{2}}}{1 - \cancel{\beta\varepsilon} + \left(\frac{\beta\varepsilon}{2}\right)^2 + 1 + \cancel{\beta\varepsilon} + \left(\frac{\beta\varepsilon}{2}\right)^2} = \varepsilon\,\frac{-\cancel{2}\beta\varepsilon}{\cancel{2} + \underbrace{(\beta\varepsilon)^2}_{0}}$$

$$= \underline{-\beta\varepsilon^2}$$

4 $Z = 4\cosh^2(\beta\varepsilon)$

1) Energetski nivoi?

2) $\bar{\varepsilon}$ $(T\to 0)$?

3) $\bar{\varepsilon}$ $(T\to\infty)$?

1) $$Z = 4\cosh^2(\beta\varepsilon)$$

$$= 4\left(\frac{e^{\beta\varepsilon}+e^{-\beta\varepsilon}}{2}\right)^2 = \cancel{4}\,\frac{e^{2\beta\varepsilon}+2e^{\beta\varepsilon-\beta\varepsilon}+e^{-2\beta\varepsilon}}{\cancel{4}}$$

$$Z = e^{2\beta\varepsilon} + 2e^0 + e^{-2\beta\varepsilon}$$

Imamo 4 energetska nivoa!

$$-2\varepsilon,\underbrace{0,0}_{\text{degenerirani}},2\varepsilon$$

2) $$\bar{\varepsilon} = \frac{\sum_i \varepsilon_i e^{-\beta\varepsilon_i}}{\sum e^{-\beta\varepsilon_i}} = -2\varepsilon\,\frac{e^{\beta 2\varepsilon}-e^{-\beta 2\varepsilon}}{e^{-\beta 2\varepsilon}+e^{\beta 2\varepsilon}} = 2\varepsilon\,\frac{e^{-\beta 2\varepsilon}-e^{\beta 2\varepsilon}}{e^{-\beta 2\varepsilon}+e^{\beta 2\varepsilon}}$$

$T\to 0$

$\beta\to\infty$ $$2\varepsilon\,\frac{\cancel{e^{-\beta 2\varepsilon}}^{\to 0}-e^{\beta 2\varepsilon}}{\cancel{e^{-\beta 2\varepsilon}}^{0}+e^{\beta 2\varepsilon}} = \underline{-2\varepsilon = \bar{\varepsilon}}$$

3) $T\to\infty$ Taylor

$\beta\to 0$

$$\beta 2\varepsilon \equiv x \to 0$$

$$2\varepsilon\,\frac{e^{-\beta 2\varepsilon}-e^{\beta 2\varepsilon}}{e^{-\beta 2\varepsilon}+2+e^{\beta 2\varepsilon}} = 2\varepsilon\,\frac{\cancel{1}-x+\cancel{\frac{x^2}{2}}-\cancel{1}-x-\cancel{\frac{x^2}{2}}}{1-\cancel{x}+\frac{x^2}{2}+1+\cancel{x}+\frac{x^2}{2}+2} = 2\varepsilon\,\frac{-2x}{2+\cancel{x^2}_{\to 0}+2}$$

$$= 2\varepsilon\,\frac{-2x}{4} = -\varepsilon x$$

$$= \varepsilon(-x) = \varepsilon(-\beta 2\varepsilon) = \underline{-2\beta\varepsilon^2}$$

⑤ Zadana je particijska funkcija

$$Z = 2\cosh(\beta\varepsilon) + 4\cosh^2(\beta\varepsilon)$$

1) Koliko ukupno energetskih nivoa imamo i koji su to?

2) Srednja energija čestice na niskim temperaturama $\bar{E}(T\to 0) = ?$

3) Srednja energija čestice na visokim temperaturama $\bar{E}(T\to\infty) = ?$

1) $Z = 2\cosh(\beta\varepsilon) + 4\cosh^2(\beta\varepsilon)$

$$= \cancel{2}\,\frac{e^{\beta\varepsilon}+e^{-\beta\varepsilon}}{\cancel{2}} + \cancel{4}\,\frac{(e^{\beta\varepsilon}+e^{-\beta\varepsilon})^2}{\cancel{4}} = e^{\beta\varepsilon}+e^{-\beta\varepsilon}+e^{2\beta\varepsilon}+2e^{\overset{0}{\beta\varepsilon-\beta\varepsilon}}+e^{-2\beta\varepsilon}$$

Energetski nivoi: $-2\varepsilon, -\varepsilon, \underbrace{0, 0}_{\text{degenerirani}}, \varepsilon, 2\varepsilon$

Imamo ukupno 6 en. nivoa

2) $$\bar{\varepsilon} = \frac{\sum_r \varepsilon_r e^{-\beta\varepsilon_r}}{\sum_r e^{-\beta\varepsilon_r}} = \frac{-2\varepsilon e^{+2\beta\varepsilon} - \varepsilon e^{\beta\varepsilon} + 0 + 0 + \varepsilon e^{-\beta\varepsilon} + 2\varepsilon e^{-2\beta\varepsilon}}{e^{2\beta\varepsilon}+e^{\beta\varepsilon}+1+1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$$

$$= \frac{\varepsilon(-2e^{2\beta\varepsilon} - e^{\beta\varepsilon} + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})}{2+e^{2\beta\varepsilon}+e^{\beta\varepsilon}+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}}$$

$T\to 0\ ;\ \beta\to\infty$

$$= \frac{\varepsilon(-2e^{\beta\varepsilon} - e^{\beta\varepsilon} + \cancel{e^{-\beta\varepsilon}}^{\to 0} + \cancel{2e^{-2\beta\varepsilon}}^{\to 0})}{2+e^{2\beta\varepsilon}+e^{\beta\varepsilon}+\underset{\downarrow 0}{e^{-\beta\varepsilon}}+\underset{\downarrow 0}{e^{-2\beta\varepsilon}}} = \varepsilon\,\frac{-2e^{2\beta\varepsilon} - e^{\beta\varepsilon}}{2+e^{2\beta\varepsilon}+e^{\beta\varepsilon}} =$$

$$\lim_{x\to\infty}\frac{-2e^{2x}-e^{x}}{2+e^{2x}+e^{x}}\ \begin{matrix} /:e^{2x} \\ /:e^{2x}\end{matrix} = \lim_{x\to\infty}\frac{-2-\cancel{e^{-x}}^{\to 0}}{\underset{\downarrow 0}{\frac{2}{e^{2x}}}+1+\underset{\searrow 0}{e^{-x}}} = -2$$

$$\underline{\bar{E} = -2\varepsilon}$$

3) $\bar{E}(T\to\infty) \quad \beta \to 0$

$$\bar{E} = \varepsilon\,\frac{\left(-2e^{2\beta\varepsilon} - e^{\beta\varepsilon} + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}\right)}{2 + e^{2\beta\varepsilon} + e^{\beta\varepsilon} + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}$$ Sad razvijamo ovo u red

$$= \varepsilon\,\frac{\overbrace{-2 - 2(2\beta\varepsilon)}^{-4\beta\varepsilon} - 2\frac{(2\beta\varepsilon)^2}{2} \overbrace{-1 - (\beta\varepsilon)}^{-\beta\varepsilon} - \frac{(\beta\varepsilon)^2}{2} \overbrace{+1 - (\beta\varepsilon)}^{-\beta\varepsilon} + \frac{(\beta\varepsilon)^2}{2} \overbrace{+2 + 2(-2\beta\varepsilon)}^{-4\beta\varepsilon} + 2\frac{(-2\beta\varepsilon)^2}{2}}{2 + 1 + 2\beta\varepsilon + \frac{(2\beta\varepsilon)^2}{2} + 1 + \beta\varepsilon + \frac{(\beta\varepsilon)^2}{2} + 1 - \beta\varepsilon + \frac{(\beta\varepsilon)^2}{2} + 1 - 2\beta\varepsilon + \frac{(2\beta\varepsilon)^2}{2}}$$

$$= \varepsilon\,\frac{-10\ \beta\varepsilon}{6 + 4(\beta\varepsilon)^2 + (\beta\varepsilon)^2} = \varepsilon\,\frac{-10\ \beta\varepsilon}{6 + 5(\beta\varepsilon)^2}$$ $\to 0$

$$= \varepsilon\,\frac{-\overset{5}{\cancel{10}}\beta\varepsilon}{\cancel{6}\,3} = -\frac{5}{3}\beta\varepsilon^2$$