Efnamætti og ~~óreiða~~

Höfum skilgreint efnamættið

$$\mu(\tau, V, N) = \left(\frac{\partial F}{\partial N}\right)_{\tau, V}$$

fyrir kerfi í varma og einda-tengslum við geymi.

Leiðum nú út

$$\frac{\mu(U, V, N)}{\tau} = -\left(\frac{\partial \sigma}{\partial N}\right)_{U,V}$$

sambærilegt við

$$\frac{1}{\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N$$

fyrir kerfi í varmatengslum

Óháðar breytur U, V, N

$$\rightarrow d\sigma = \left(\frac{\partial \sigma}{\partial U}\right)_{VN} dU + \left(\frac{\partial \sigma}{\partial V}\right)_{UN} dV + \left(\frac{\partial \sigma}{\partial N}\right)_{UV} dN$$

Gerum ráð fyrir $dV = 0$

Gerum líka ráð fyrir að $d\tau = 0$, merkjum breytingar með því skilyrði sem

$$(\delta\sigma)_\tau, \ (\delta U)_\tau, \text{ and } (\delta N)_\tau$$

þá

$$(\delta\sigma)_\tau = \left(\frac{\partial \sigma}{\partial U}\right)_N (\delta U)_\tau + \left(\frac{\partial \sigma}{\partial N}\right)_U (\delta N)_\tau$$

$$\rightarrow \frac{(\delta\sigma)_\tau}{(\delta N)_\tau} = \left(\frac{\partial \sigma}{\partial U}\right)_N \frac{(\delta U)_\tau}{(\delta N)_\tau} + \left(\frac{\partial \sigma}{\partial N}\right)_U$$

$$\rightarrow \left(\frac{\partial \sigma}{\partial N}\right)_{\tau V} = \overbrace{\left(\frac{\partial \sigma}{\partial U}\right)_{NV}}^{\frac{1}{\tau}} \left(\frac{\partial U}{\partial N}\right)_{\tau V} + \left(\frac{\partial \sigma}{\partial N}\right)_{UV}$$

$$\rightarrow \tau \left(\frac{\partial \sigma}{\partial N}\right)_{\tau V} = \left(\frac{\partial U}{\partial N}\right)_{\tau V} + \tau \left(\frac{\partial \sigma}{\partial N}\right)_{UV}$$

Við höfðum

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau V} = \left(\frac{\partial}{\partial N}\left(U - \tau\sigma\right)\right)_{\tau V}$$

$$= \left(\frac{\partial U}{\partial N}\right)_{\tau V} - \tau \left(\frac{\partial \sigma}{\partial N}\right)_{\tau V}$$

$$\boxed{\mu = -\tau \left(\frac{\partial \sigma}{\partial N}\right)_{UV}}$$

Við höfum fundið μ sem afleiðu af σ eða F

Til viðbótar er

$$\mu(\sigma, V, N) = \left(\frac{\partial U}{\partial N}\right)_{\sigma, V}$$

því má taka saman

	$\sigma(U,V,N)$	$U(\sigma,V,N)$	$F(\tau,V,N)$
τ	$\frac{1}{\tau} = \left(\frac{\partial\sigma}{\partial U}\right)_{VN}$	$\tau = \left(\frac{\partial U}{\partial\sigma}\right)_{VN}$	τ
p	$\frac{p}{\tau} = \left(\frac{\partial\sigma}{\partial V}\right)_{UN}$	$-p = \left(\frac{\partial U}{\partial V}\right)_{\sigma,N}$	$-p = \left(\frac{\partial F}{\partial V}\right)_{\tau N}$
μ	$-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial N}\right)_{UV}$	$\mu = \left(\frac{\partial U}{\partial N}\right)_{\sigma V}$	$\mu = \left(\frac{\partial F}{\partial N}\right)_{\tau V}$

því er hægt að bæta við aljöfnu varmafræðinnar

$$d\sigma = \underbrace{\left(\frac{\partial\sigma}{\partial U}\right)_{VN}}_{\frac{1}{\tau}} dU + \underbrace{\left(\frac{\partial\sigma}{\partial V}\right)_{UN}}_{\frac{p}{\tau}} dV + \underbrace{\left(\frac{\partial\sigma}{\partial N}\right)_{UV}}_{-\frac{\mu}{\tau}} dN$$

Svo hún verði

$$d\sigma = \frac{1}{\tau}\,dU + \frac{p}{\tau}\,dV - \frac{\mu}{\tau}\,dN$$

eða

$$\boxed{dU = \tau\, d\sigma - p\,dV + \mu\, dN}$$

Viljum nú gera það fyrir kerfi í varma- og eindatengslum við geymi

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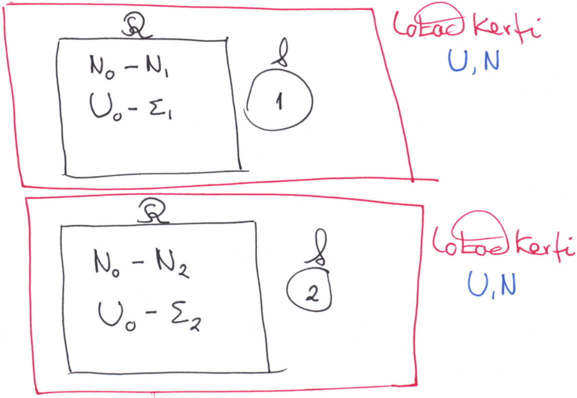
Stuðull Gibbs

Við leiddum út áður stuðul Boltzmanns fyrir líkindi tveggja ástanda

$$\frac{P(\varepsilon_1)}{P(\varepsilon_2)} = \frac{e^{-\varepsilon_1/\tau}}{e^{-\varepsilon_2/\tau}}$$



δ í einu staumta ástandi

fjöldi ástanda í heildarkerfinu

$$g(\mathcal{R}+\delta) = g(\mathcal{R}) \times 1$$

líkindin fyrir ástandi (N, Σ_s)

$$P(N,\Sigma_s) \propto g(N_0-N, U_0-\Sigma_s)$$

$$\rightarrow \frac{P(N_1,\Sigma_1)}{P(N_2,\Sigma_2)} = \frac{g(N_0-N_1, U_0-\Sigma_1)}{g(N_0-N_2, U_0-\Sigma_2)}$$

Notum grunnjöfnuna

$$\sigma = \ln g$$

$$\rightarrow g\,\exp(\sigma)$$

til að fá

$$\frac{P(N_1,\Sigma_1)}{P(N_2,\Sigma_2)} = \frac{\exp\{\sigma(N_0-N_1, U_0-\Sigma_1)\}}{\exp\{\sigma(N_0-N_2, U_0-\Sigma_2)\}}$$

$$= \exp\left\{\sigma(N_0-N_1, U_0-\Sigma_1) - \sigma(N_0-N_2, U_0-\Sigma_2)\right\}$$

$$= e^{\Delta\sigma}$$

Liðum

$$\sigma(N_0-N, U_0-\Sigma) = \sigma(N_0,U_0) - N\underbrace{\left(\frac{\partial\sigma}{\partial N_0}\right)_{U_0}}_{-\frac{\mu}{\tau}} - \Sigma\underbrace{\left(\frac{\partial\sigma}{\partial U_0}\right)_{N_0}}_{\frac{1}{\tau}} + \cdots$$

$$\rightarrow \Delta\sigma = \frac{(N_1 - N_2)\mu}{\tau} - \frac{(\Sigma_1 - \Sigma_2)}{\tau}$$

$$\rightarrow \boxed{\frac{P(N_1, \Sigma_1)}{P(N_2, \Sigma_2)} = \exp\left\{ \frac{(N_1 - N_2)}{\tau}\mu - \frac{(\Sigma_1 - \Sigma_2)}{\tau} \right\}}$$

stuðull Gibbs (stóra kórdreifingin)

Skilgreinum stóru kórsummuna

$$\mathcal{Z}(\mu, \tau) = \sum_{N=0}^{\infty} \sum_{s(N)} \exp\left\{ (N\mu - \Sigma_{s(N)}) \frac{1}{\tau} \right\}$$

$\Sigma_{s(N)}$: orka N-einda ástands kerfisins

byrjum með tóma kerfið $N=0$ í summunni

líkindi þess að finna kerfið í ástandi (N_1, Σ_1) er

$$\boxed{P(N_1, \Sigma_1) = \frac{\exp\left\{\frac{(N_1\mu - \Sigma_1)}{\tau}\right\}}{\mathcal{Z}}}$$

Meðaltal mælistærðar eða breytu X er

$$\langle X \rangle = \sum_{N=0}^{\infty} \sum_{s} X(N,s) P(N, \Sigma_s)$$

Fjöldi einda er

$$\langle N \rangle = \frac{\sum_{N=0}^{\infty} \sum_{s} N \exp\left\{\frac{(N\mu - \Sigma_s)}{\tau}\right\}}{\mathcal{Z}} = \frac{\tau}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu} = \tau \frac{\partial \ln \mathcal{Z}}{\partial \mu}$$

Oft er skilgreind „algilda virkni" (alvirkni)
(absolute activity)

$$\boxed{\lambda = e^{\frac{\mu}{\tau}}}$$

og påverður

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{s} \lambda^N e^{-\frac{\varepsilon_s}{\tau}}$$

og

$$\langle N \rangle = \lambda \frac{\partial}{\partial \lambda} \ln \mathcal{Z}$$

Miðal orkan

$$U = \langle \varepsilon \rangle = \sum_{Ns} \varepsilon_s e^{\beta(N\mu - \varepsilon_s)}$$

p.s. $\beta = \frac{1}{\tau} = \frac{1}{k_B T}$

athugum tí

$$\langle N\mu - \varepsilon \rangle = \langle N \rangle \mu - U$$

$$= \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \mathcal{Z}$$

$$\rightarrow U = \left\{ \frac{\mu}{\beta} \frac{\partial}{\partial \mu} - \frac{\partial}{\partial \beta} \right\} \ln \mathcal{Z}$$

Dæmi

Íbótar atóm í hálfleiðara, rafgjafi (donor)

þrjú ástönd

getur leiðni rafeindir til kristallsins, allar aðrar, en bundnar
→ leiðnin er mjög τ-háð.

númer	lýsing	N	ε
1	Engin rafeind	0	0 ← valinn núllp.
2	Bundin rafeind spuni ↑	1	$-\Delta\varepsilon$
3	Bundin rafeind spuni ↓	1	$-\Delta\varepsilon$

Getur ekki bundið fleiri en eina rafeind

$$\mathcal{Z} = 1 + 2e^{\frac{\mu + \Delta\Sigma}{\tau}}$$

<u>líkindi jónunar</u>

$$P_I = P(0,0) = \frac{1}{\mathcal{Z}} = \frac{1}{1 + 2e^{\frac{\mu+\Delta\Sigma}{\tau}}} \qquad \lim_{\tau \to 0} P_I = 0$$

ef $\mu + \Delta\Sigma > 0$

<u>líkindi þess að rafgjafinn sé ójónaður</u>

$$P_0 = P(1\uparrow, -\Delta\Sigma) + P(1\downarrow, -\Delta\Sigma) = 1 - P(0,0)$$

samkvæmt skilgreiningu á líkindum