

$$E_{n,l} = \hbar\omega \left(n + \frac{1}{2}\right) + \frac{\hbar^2}{2I} l(l+1) + \alpha l(l+1) \left(n + \frac{1}{2}\right)$$

Bibrazirva

Braketa

akoplavandua

$$E_{bb}(n)$$

$$E_{br}(l)$$

$$E_{b-b}(l,n)$$

$$\left[ \hbar\omega \right]_{\text{III}}$$

$$\left[ \frac{\hbar^2}{2I} \right]_{\text{III}}$$

$$\left[ \alpha \right]_{\text{III}} \frac{1}{k_B}$$

$$\Theta_{bb}$$

$$\Theta_{br}$$

$$\Theta_{bb}$$

$$> T \gg \gg$$

$$\Theta_{bb} > T \gg \gg \Theta_{br} \gg \gg \Theta_{bb}$$

$$\langle E \rangle \equiv U \leftarrow F_{\text{trk lmfu}}$$

$$F = -(k_B T) \ln [Z_N(T, V)]$$

$$Z_N(T, V) = \frac{1}{N!} [Z_1(T, V)]^N$$

$$Z_1(T, V) = \prod_j Z_1^j(T, V) \quad j < \begin{matrix} \text{translatsionu} \\ \text{brazetarak} \end{matrix}$$

$$\begin{aligned} Z_N(T, V) &= \frac{1}{N!} [Z_1^{\text{trm}}(T, V) \cdot Z_1^{\text{brm}}(T, V)]^N \\ &= \frac{1}{N!} [Z_1^{\text{trm}}(T, V)]^N \cdot [Z_1^{\text{br}}(T, V)]^N \end{aligned}$$

$$Z_N(T, V) = \frac{V}{\lambda_T^3} \cdot [Z_1^{\text{br}}(T, V)]^N$$

$$Z_1^{\text{brm}}(T, V) =$$

$$Z_1(T, V) = \sum_{\text{aggen}} e^{-\frac{\epsilon}{k_B T}} \quad \text{partikula bakamaven energi-standatiks belovak}$$

$$Z_1(T, V) = \sum_{\text{aggen}} e^{-\frac{1}{k_B T} [E_{b1b} + E_{b1r} + E_{bb}]} \rightarrow (n, l)$$

$$Z_1^{bar}(T, V) = \sum_{n=0}^{\infty} \sum_{l=0}^{\infty} (2l+1) e^{-\frac{l(l+1)\Theta_{br}}{T}} e^{-\frac{(n+\frac{1}{2})\Theta_{b1b}}{T}} e^{-\frac{l(l+1)(n+\frac{1}{2})\Theta_{bb}}{T}}$$



$$\sum_{l=0}^{\infty} (2l+1) e^{-\frac{l(l+1)\Theta_{br}}{T}} e^{-\frac{l(l+1)(n+\frac{1}{2})\Theta_{bb}}{T}}$$

+ hyperbolic  
Baldwin's eqn

$$\left[ \dots \right]$$

$$\sum_{l=0}^{\infty} (2l+1) e^{-\frac{l(l+1)}{T} [\Theta_{br} + (n+\frac{1}{2})\Theta_{bb}]}$$

$$= \frac{T}{[\Theta_{br} + (n+\frac{1}{2})\Theta_{bb}]}$$

$$Z_1^{bar}(T, V) = \sum_{n=0}^{\infty} \frac{T}{[\Theta_{br} + (n+\frac{1}{2})\Theta_{bb}]} \cdot e^{-\frac{(n+\frac{1}{2})\Theta_{b1b}}{T}}$$

$$\left. \begin{aligned} \frac{1}{\Theta_{br} + (n+\frac{1}{2})\Theta_{bb}} &= \frac{1}{\Theta_{br}} \frac{1}{[1 + (n+\frac{1}{2})\frac{\Theta_{bb}}{\Theta_{br}}]} \\ \frac{1}{1+x} &\approx 1-x \quad x \rightarrow 0 \end{aligned} \right\} \frac{1}{\Theta_{br}} \left[ 1 - (n+\frac{1}{2})\frac{\Theta_{bb}}{\Theta_{br}} \right]$$

$$Z_1^{bar}(T, V) = \sum_{n=0}^{\infty} \frac{1}{\Theta_{br}} e^{-\frac{(n+\frac{1}{2})\Theta_{b1b}}{T}} - \frac{T}{\Theta_{br}} \sum_{n=0}^{\infty} (n+\frac{1}{2}) \frac{\Theta_{bb}}{\Theta_{br}} e^{-\frac{(n+\frac{1}{2})\Theta_{b1b}}{T}}$$

$$- \sum_{n=0}^{\infty} \frac{T}{\theta_{bir}} \left(n + \frac{1}{2}\right) \frac{\theta_{bb}}{\theta_{bir}} e^{-\left(n + \frac{1}{2}\right) \frac{\theta_{bib}}{T}}$$

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(1)

$$- \frac{T}{\theta_{bir}} \frac{\theta_{bb}}{\theta_{bir}} \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) e^{-\left(n + \frac{1}{2}\right) \frac{\theta_{bib}}{T}}$$

$$\sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \frac{\hbar\omega}{\hbar\omega} e^{-\left(n + \frac{1}{2}\right) \frac{\theta_{bib}}{T}}$$

$$- \frac{T}{\theta_{bir}} \frac{\theta_{bb}}{\theta_{bir}} \frac{1}{\hbar\omega} \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar\omega e^{-\left(n + \frac{1}{2}\right) \frac{\theta_{bib}}{T}}$$

$$\left[ \frac{Z_{bib}}{Z_{mb}} \right]$$

$$- \frac{T}{\theta_{bir}} \frac{\theta_{bb}}{\theta_{bir}} \frac{1}{\hbar\omega} Z_{bib} \underbrace{\left[ \frac{1}{Z_{bib}} \sum_{n=0}^{\infty} \left(n + \frac{1}{2}\right) \hbar\omega e^{-\left(n + \frac{1}{2}\right) \frac{\theta_{bib}}{T}} \right]}_{\bar{\epsilon}_{bib}}$$

$$\frac{1}{k_B \frac{\hbar\omega}{k_B}}$$

$$\frac{1}{k_B \theta_{bib}}$$

$$- \frac{T}{\theta_{bir}} \frac{\theta_{bb}}{\theta_{bir}} \frac{Z_{bib}}{k_B \theta_{bib}} \cdot \bar{\epsilon}_{bib}$$

$$\frac{T}{\theta_{bir}} Z_{bib} - \left( \frac{T}{\theta_{bir}} \frac{\theta_{bb}}{\theta_{bir}} \frac{Z_{bib}}{k_B \theta_{bib}} \right) \cdot \bar{\epsilon}_{bib}$$

$$\frac{T}{\theta_{bir}} Z_{mb} \left[ 1 - \frac{\theta_{bb}}{\theta_{bir}} \frac{1}{k_B \theta_{bib}} \bar{\epsilon}_{mb} \right]$$

(2)

$$Z_1(T, V) \approx \frac{V}{\lambda_T^3} \cdot \left[ \frac{T}{\Theta_{\text{bir}}} \cdot Z_{\text{bib}} \left\{ 1 - \frac{\Theta_{\text{bb}}}{\Theta_{\text{bir}} \Theta_{\text{bib}}} \cdot \frac{\bar{E}_{\text{bib}}}{k_B} \right\} \right]$$

$$Z_N(T, V) = \frac{1}{N!} \left[ \frac{V}{\lambda_T^3} \left[ \frac{T}{\Theta_{\text{bir}}} \cdot Z_{\text{bib}} \left\{ 1 - \frac{\Theta_{\text{bb}}}{\Theta_{\text{bir}} \Theta_{\text{bib}}} \cdot \frac{\bar{E}_{\text{bib}}}{k_B} \right\} \right] \right]^N$$

$$\left( F = -k_B T \ln Z_N(T, V) \right) \text{ borne}$$

$$F = -(k_B T) N \ln \left[ \underbrace{\frac{T}{\Theta_{\text{bir}}}}_1 \underbrace{Z_{\text{bib}}}_2 \underbrace{\left\{ 1 - \frac{\Theta_{\text{bb}}}{\Theta_{\text{bir}} \Theta_{\text{bib}}} \cdot \frac{\bar{E}_{\text{bib}}}{k_B} \right\}}_3 \right]$$

$$F^1 = -(k_B T) N \ln \left( \frac{T}{\Theta_{\text{bir}}} \right)$$

—————> berakutak

$$F^2 = -(k_B T) N \ln (Z_{\text{bib}})$$

—————> vibratirak

$$F^3 = -(k_B T) N \ln \left\{ 1 - \frac{\Theta_{\text{bb}}}{\Theta_{\text{bir}} \Theta_{\text{bib}}} \cdot \frac{\bar{E}_{\text{bib}}}{k_B} \right\}$$

$$\ln (1 - x) \approx -x$$

$$x \ll 1$$

$$+ (k_B T) N \left( \frac{\Theta_{\text{bb}}}{\Theta_{\text{bir}} \Theta_{\text{bib}}} \cdot \frac{\bar{E}_{\text{bib}}}{k_B} \right)$$