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$$Z = \sum_i \exp(-\beta E_i) = \sum_E \Omega(E)\exp(-\beta E), \quad S = k_B \ln \Omega$$

$$\exp(a+b) = e^a e^b = e^a e^{\ln \tilde{b}} = \tilde{b}\, e^a$$

$$Z = \sum_E \exp(-\beta E + \ln \Omega) = \sum_E \exp\left(-\beta E + \frac{S}{k_B}\right), \quad \beta = \frac{1}{k_B T}$$

$$Z = \sum_E \exp\left(-\beta\left(E - \frac{S}{k_B \beta}\right)\right) \Rightarrow \boxed{Z = \sum_E \exp(-\beta(E - ST))}$$

$$Z \simeq \exp\left(-\beta \min\{E - ST\}\right)$$

F - energia livre de Helmholtz

$$\boxed{Z = \exp(-\beta F)}$$

$$\ln Z = -\beta F \Rightarrow F = -\frac{1}{\beta}\ln Z, \quad f = \frac{F}{N}$$

$$f(T, v) = -\frac{1}{\beta} \lim_{\substack{V, N \to \infty \\ \frac{V}{N} = v}} \frac{1}{N} \ln Z$$

Sólido de Einstein: $\mathcal{H} = \hbar\omega \sum_{i=1}^{N} \left(\frac{1}{2} + n_i\right)$

$$Z = \sum_{\{n_i\}} \exp(-\beta\mathcal{H}), \quad Z = Z_1^N$$

- Válido para sistemas sem interação.

$\to$ f. de partição de uma partícula

$$Z_1 = \sum_{n=0}^{\infty} \exp\left(-\beta\hbar\omega\left(\frac{1}{2}+n\right)\right)$$

$$Z_1 = \sum_{n=0}^{\infty} \exp\left(-\frac{\beta\hbar\omega}{2}\right)\exp(-\beta\hbar\omega n) = \exp\left(-\frac{\beta\hbar\omega}{2}\right)\underbrace{\sum_{n=0}^{\infty} \exp(-\beta\hbar\omega n)}$$

$$\to = e^0 + e^{-\beta\hbar\omega\cdot 1} + e^{-\beta\hbar\omega\cdot 2} + \dots = \frac{1 - \cancel{\exp(-\beta\hbar\omega\infty)}}{1-\exp(-\beta\hbar\omega)} \quad \to 0$$

$$Z = \Bigg[\underbrace{\frac{\exp(-\beta\hbar\omega/2)}{1-\exp(-\beta\hbar\omega)}}_{Z_1}\Bigg]^N, \quad \ln Z = N\ln Z_1$$

$$f(T,v) = -\frac{1}{\beta}\lim_{N,V\to\infty}\frac{1}{\cancel{N}}\cancel{N}\ln Z_1$$

$$f(T,v) = -\frac{1}{\beta}\left[\ln\left(\exp\left(-\frac{\beta\hbar\omega}{2}\right)\right) - \ln\left(1-\exp(-\beta\hbar\omega)\right)\right]$$

$$f(T,v) = -\frac{1}{\beta}\left[-\frac{\beta\hbar\omega}{2} - \ln\left(1 - \exp\left(-\hbar\omega\beta\right)\right)\right]$$

$$f(T,v) = \frac{1}{2}\hbar\omega + k_B T \ln\left[1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)\right]$$

$$df(T,v) = -s\,dT - p\,dv$$

$$-s = \frac{\partial f}{\partial T}$$