Intro Sist Quant

$$\int \frac{d^{3N}p\, d^{3N}q}{h^{3N} N!} e^{-\beta H} \longrightarrow \sum_{\{\text{stati}\}} e^{-\beta E_n}$$

Energia TOTALE sistema a N particelle

① Sistemi non interagenti

$\Downarrow$

$$E = \sum_{i=1}^{N} \epsilon^{(1)}_{i,n_i}$$

stato 1 particella

$E(\{n_i\}) = \sum_{i=1}^{N} \epsilon^{(1)}_{n_i}$ DISTINGUIBILI

$E(\{n_k\}) = \sum_k n_k \epsilon_k$ INDISTING

n_k: # of part in state k

Distinguibili

$$Z = \prod_{i=1}^{N} Z_i^{(1)}$$

cfr classico (gas perfetto)

$$Z = \frac{1}{N!}\left(\prod_i Z_i^{(1)}\right) = \frac{(Z^{(1)})^N}{N!}$$

indist.

$$Z^{(1)} = \int \frac{d^3p\, d^3q}{h^3} e^{-\beta p^2/2m} = \frac{V}{\lambda^3}$$

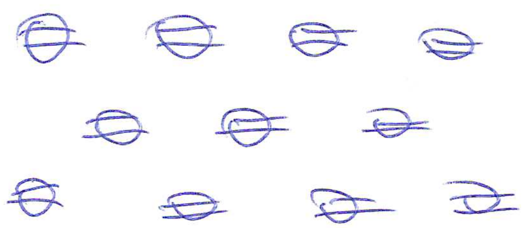
Esempi

- Sistema a 2 livelli

$Z = (Z^{(1)})^N$ sono tutti uguali ma non indistinguibili

es sistema localizzato

non interagenti



livelli non degeneri

$$Z^{(1)} = \sum_{0}^{1}{}_n e^{-\beta E_n} = e^{-\beta E_0} + e^{-\beta E_1}$$

livello degenere

$$Z^{(1)} = \sum_{\text{stati}} e^{-\beta E_n} = g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1}$$

degenerazione del livello

$$Z = \left(e^{-\beta E_0} + e^{-\beta E_1}\right)^N$$

stati microscopici per uno stato macroscopico

Energia interna

$$-\frac{\partial}{\partial \beta} \ln Z = \langle H \rangle$$

oppure valutare direttamente $\langle H \rangle$

$$H = N\langle \epsilon^{(1)} \rangle$$

$$\langle \epsilon^{(1)} \rangle = \frac{e^{-\beta\varepsilon_0}\varepsilon_0 + e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1}}$$

$$\langle \varepsilon^{(1)} \rangle = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}^{(1)} = \langle \hat{H}^{(1)} \rangle$$

infatti

$$\ln \mathcal{Z}^{(1)} = \ln\left(e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1}\right)$$

$$\frac{\partial}{\partial\beta} \ln \mathcal{Z}^{(1)} = \frac{1}{\mathcal{Z}^{(1)}}\left(-\varepsilon_0 e^{-\beta\varepsilon_0} - \varepsilon_1 e^{-\beta\varepsilon_1}\right)$$

$$\langle H^{(1)} \rangle = \frac{\sum_n \langle n|\hat{H}^{(1)}|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

in generale per $\forall$ operatore la media termica

$$\langle \hat{A} \rangle = \frac{\sum_n \langle n|\hat{A}|n\rangle e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}$$

Media termica quantistica

$$\langle H \rangle = \sum_i \langle \hat{H}_i \rangle = N \langle \hat{H}^{(1)} \rangle$$

$$\langle \hat{H}^{(1)} \rangle = \underbrace{\frac{e^{-\beta\varepsilon_0}}{e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1}}}_{n_0} \varepsilon_0 + \underbrace{\frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1}}}_{n_1} \varepsilon_1$$

$$n_0 = \frac{N_0}{N} \quad \begin{array}{l} \#\ \text{stati in } 0 \\ \#\ \text{totale} \end{array}$$

$$U = N n_0 \varepsilon_0 + N n_1 \varepsilon_1$$

in generale per sistemi distinguibili

$$\boxed{n_k = \frac{e^{-\beta\varepsilon_k} g_k}{\sum_k e^{-\beta\varepsilon_k} g_k} \qquad g_k = \text{degenerazione del livello}}$$

interessante per sistemi a 2 livelli e il calore specifico

$$U = N \frac{e^{-\beta\varepsilon_0}\varepsilon_0 + e^{-\beta\varepsilon_1}\varepsilon_1}{e^{-\beta\varepsilon_0} + e^{-\beta\varepsilon_1}}$$

$$\varepsilon_1 - \varepsilon_0 = \Delta > 0$$

$$U = N \left[\frac{\varepsilon_0 + e^{-\beta\Delta}\varepsilon_1}{1 + e^{-\beta\Delta}} \right]$$

per $k_BT \gg \Delta$ $\qquad \beta\Delta \ll 1$

$$U = N\,\frac{\varepsilon_0 + \varepsilon_1(1-\beta\Delta)}{1+1-\beta\Delta}$$

$$= N\,\frac{\varepsilon_0+\varepsilon_1}{2}\left[\frac{1-\dfrac{\beta\Delta}{\varepsilon_1+\varepsilon_0}\,\varepsilon_1}{1-\beta\Delta/2}\right]$$

$$= N\,\frac{\varepsilon_0+\varepsilon_1}{2}\left(1-\frac{\beta\Delta}{\varepsilon_1+\varepsilon_0}\,\varepsilon_1\right)\left(1+\frac{\beta\Delta}{2}\right)$$

$$= N\,\frac{\varepsilon_0+\varepsilon_1}{2}\left\{1-\frac{\beta\Delta}{\varepsilon_1+\varepsilon_0}\,\varepsilon_1+\frac{\beta\Delta}{2}\right\}$$

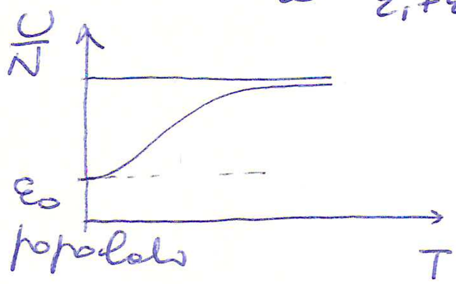
$$\frac{\beta\Delta}{2}\left(1-\frac{2\varepsilon_1}{\varepsilon_1+\varepsilon_0}\right) = \frac{\beta\Delta}{2}\left(\frac{\varepsilon_1+\varepsilon_0-2\varepsilon_1}{\varepsilon_1+\varepsilon_0}\right)$$

$\varepsilon_1 -$

$$= -\frac{\beta\Delta^2}{2}\,\frac{1}{\varepsilon_1+\varepsilon_0}$$

$k_BT \gg \Delta$

$$\boxed{U = N\,\frac{\varepsilon_0+\varepsilon_1}{2} - \frac{\beta\Delta^2}{2(\varepsilon_1+\varepsilon_0)}}$$



$T \to \infty$ 2 livelli egualmente popolati

$$C_V = \frac{\partial U}{\partial T} \sim \frac{1}{T^2}$$

$k_B T \ll \Delta \qquad \beta\Delta \gg 1$

$$U = N \frac{\varepsilon_0 + e^{-\beta\Delta}\varepsilon_1}{1 + e^{-\beta\Delta}} \qquad e^{-\beta\Delta} \to 0$$

$$U \simeq N(\varepsilon_0 + \varepsilon_1 e^{-\beta\Delta})(1 - e^{-\beta\Delta}) \simeq$$

$$\simeq N(\varepsilon_0 - \varepsilon_0 e^{-\beta\Delta} + \varepsilon_1 e^{-\beta\Delta}) + \mathcal{O}(e^{-\beta 2\Delta})$$

$$U \simeq N\varepsilon_0 + N\Delta e^{-\beta\Delta}$$

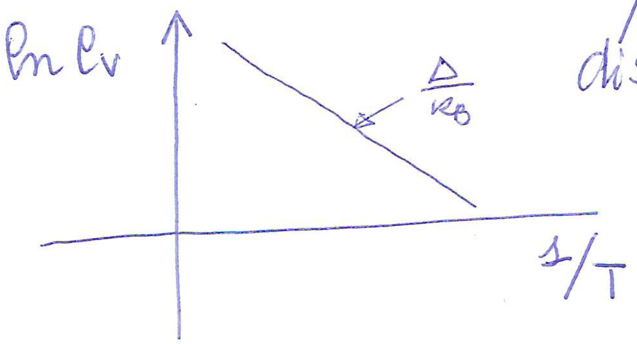
$$\frac{\partial U}{\partial T} = +N\Delta\left(\frac{\partial}{\partial\beta} e^{-\beta\Delta}\right)\left(\frac{\partial\beta}{\partial T}\right) \qquad \beta = \frac{1}{k_B T}$$

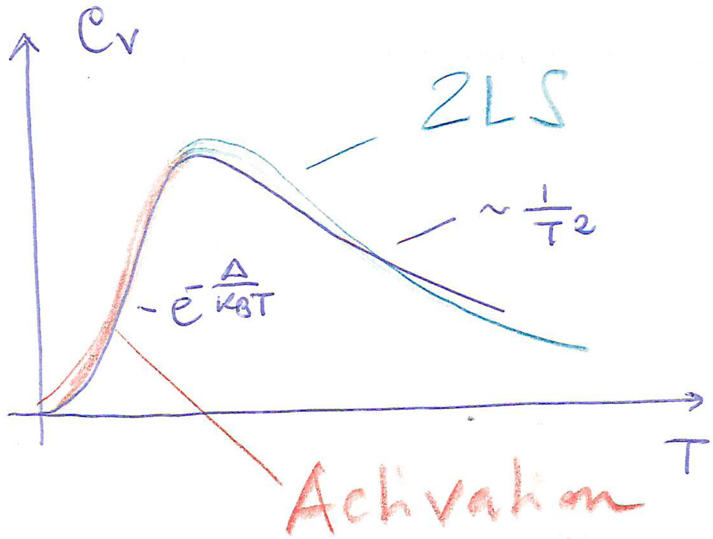
$$+N\Delta(-\Delta e^{-\beta\Delta})\left(-\frac{1}{k_B T^2}\right) \qquad \frac{\partial\beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\boxed{C_V \simeq N \frac{\Delta^2}{k_B T^2} e^{-\frac{\Delta}{k_B T}}}$$

Arrhenius activation

discrete levels





generalizzazione per degenerazione g_0 e $g_1 \neq 1$

$\Longrightarrow$

Oscillatori Armonici distinti & indipendenti (d=1)

$$H^{(1)} = \hbar\omega\left(a^\dagger a + \frac{1}{2}\right) \qquad \epsilon_n^{(1)} = \hbar\omega\left(n + \frac{1}{2}\right)$$

$$Z^{(1)} = \sum_0^\infty {}_n\, e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)}$$

$$\langle \hat{H}^{(1)} \rangle = \frac{\sum_n \langle n | H^{(1)} | n \rangle e^{-\beta \epsilon_n}}{\sum_n e^{-\beta \epsilon_n}}$$

$$\langle \hat{H}^{(1)} \rangle = -\frac{\partial}{\partial\beta} \ln Z^{(1)}$$

$$\ln Z^{(1)} = \ln\left(\sum_0^\infty {}_n\, e^{-\beta\hbar\omega n}\right) e^{-\beta\frac{\hbar\omega}{2}}$$

$$= -\beta\frac{\hbar\omega}{2} + \ln \sum_0^\infty {}_n\, e^{-\beta\hbar\omega n}$$

$$= -\beta\frac{\hbar\omega}{2} + \ln \frac{1}{1 - e^{-\beta\hbar\omega}}$$

$$-\frac{\partial}{\partial\beta}\ln Z^{(1)} = \frac{\hbar\omega}{2} + \hbar\omega\,\frac{\cancel{\beta}\,e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$-\ln(1-e^{-\beta\hbar\omega}) = \frac{1}{1-e^{-\beta\hbar\omega}}\,\hbar\omega\, e^{-\beta\hbar\omega}$$

Il numero medio di occupazione dello stato k è

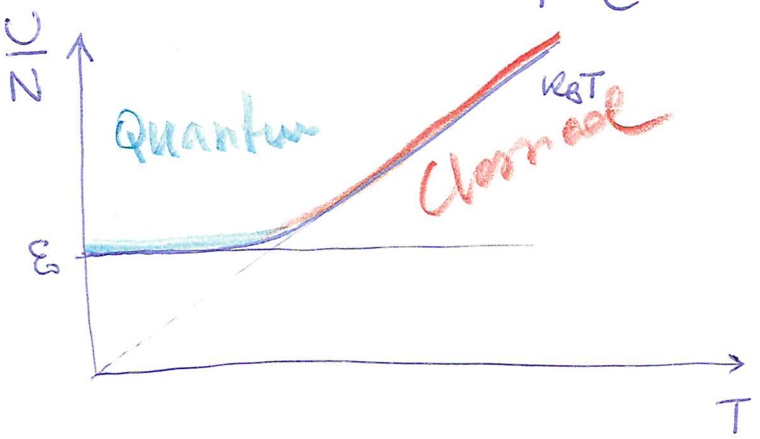
$$\langle n_k\rangle = \frac{e^{-\beta\hbar\omega k}}{\sum_{n=0}^{\infty} e^{-\beta\hbar\omega n}} = (1-e^{-\beta\hbar\omega})\,e^{-\beta\hbar\omega k}$$

$$\langle H^{(1)}\rangle = \underbrace{\frac{\hbar\omega}{2}}_{\varepsilon_0} + \hbar\omega\,\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$U = N\varepsilon_0 + N\hbar\omega\,\frac{e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$\beta\hbar\omega \gg 1 \quad U \to N\varepsilon_0$

$\beta\hbar\omega \ll 1 \quad U \to N\varepsilon_0 + N\cancel{\hbar\omega}\,\frac{1}{\beta\cancel{\hbar\omega}}$



Equipartizione a $d = 1$

$$H^{(1)} = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

$$\frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

$U = Nk_BT \qquad C_V = Nk_B$

$$C_V = \left(\frac{\partial U}{\partial T}\right)$$

$\boxed{\beta\hbar\omega \gg 1}$ Quantum

$$U = N\varepsilon_0 + N\hbar\omega\, e^{-\beta\hbar\omega}\left(1 + e^{-\beta\hbar\omega}\right) \simeq N\varepsilon_0 + N\hbar\omega\, e^{-\beta\hbar\omega}$$

attivazione

$$C_V \simeq \frac{N(\hbar\omega)^2}{k_B T^2}\, e^{-\beta\hbar\omega}$$

$\boxed{\beta\hbar\omega \gg 1}$

$$U \simeq N k_B T \qquad C_V \simeq N k_B$$