TEORIA DELLA RISPOSTA LINEARE

Caso statico

Hamiltoniana : $H + \Delta H$ $\quad \Delta H = -\phi A \quad A(\{\vec{r}_i\}) \rightarrow$ osservabile $\quad \phi = \phi(\vec{r})$

Regime risposta lineare : $\Delta H \ll k_B T$

$\langle \dots \rangle_p \rightarrow e^{-\beta(H+\Delta H)}$

$\langle \dots \rangle \rightarrow e^{-\beta H} \qquad Z = Tr[e^{-\beta H}]$

$$\langle A \rangle_p = \frac{Tr[e^{-\beta(H+\Delta H)} A]}{Tr[e^{-\beta(H+\Delta H)}]} = \frac{Tr[e^{-\beta H}(1-\beta\Delta H) A]}{Tr[e^{-\beta H}(1-\beta\Delta H)]} + O[(\beta\Delta H)^2]$$

$$= \frac{Tr[e^{-\beta H}(1-\beta\Delta H) A]}{Z} \cdot \left(1 + \frac{Tr[e^{-\beta H}\beta\Delta H]}{Z}\right)$$

$$= (\langle A \rangle - \beta\langle \Delta H A \rangle) \cdot (1 + \beta\langle \Delta H \rangle) \simeq \langle A \rangle - \beta\langle \Delta H A \rangle + \beta\langle \Delta H \rangle\langle A \rangle$$

$$= \langle A \rangle - \beta(\langle \Delta H A \rangle - \langle \Delta H \rangle\langle A \rangle) = \langle A \rangle - \beta\langle \underbrace{(A - \langle A \rangle)(\Delta H - \langle \Delta H \rangle)}_{\langle \delta A \, \delta \Delta H \rangle} \rangle$$

↳ covarianza ΔH e A

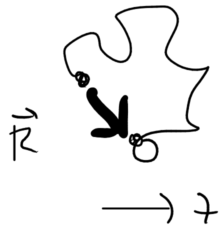
$$\Delta H = -\phi A \qquad \phi = \text{cost}$$

$$\underset{\substack{\uparrow \\ \text{risposta} \\ \text{lineare}}}{\delta\langle A\rangle} \equiv \langle A\rangle_p - \langle A\rangle = +\phi\beta\langle (A-\langle A\rangle)^2\rangle = \underset{\substack{\uparrow \\ \text{fluttuazioni} \\ \text{equilibrio}}}{\phi\beta\langle\delta A^2\rangle}$$

<u>Funzione di risposta</u>:

$$\chi \equiv \frac{\delta\langle A\rangle}{\phi} = \beta\langle\delta A^2\rangle$$

Esempio: catena polimerica ideale N+1 monomeri, distanza legame A



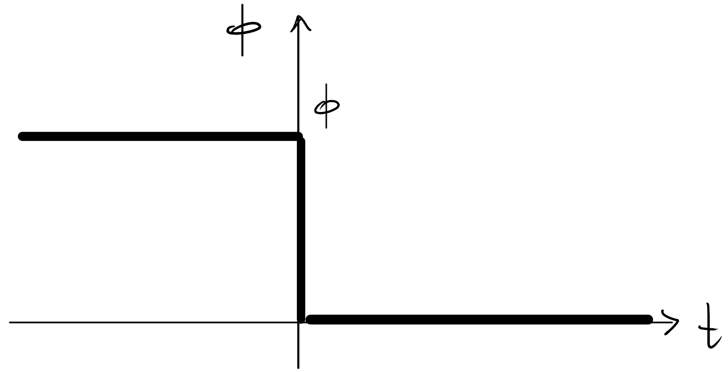
$$\vec{R} = \vec{r}_{N+1} - \vec{r}_1 \qquad \langle\vec{R}\rangle = \vec{0} \qquad \langle|\vec{R}|^2\rangle = a^2N \qquad \langle R_z^2\rangle = \frac{1}{3}a^2N$$

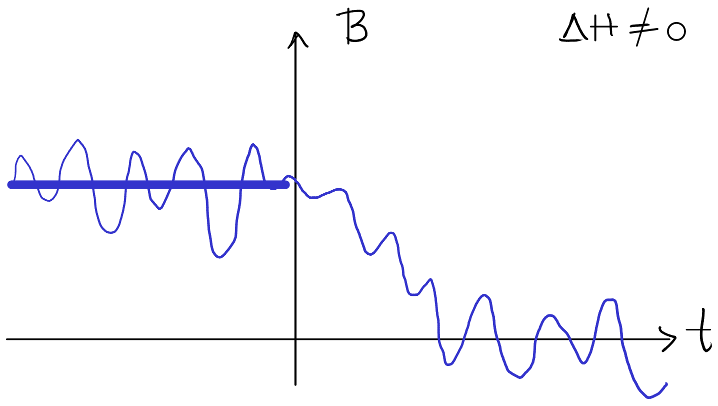
$$\phi = f \Rightarrow \Delta H = -f R_z \Rightarrow \delta l \equiv \langle R_z\rangle_p - \underbrace{\langle R_z\rangle}_{=0} = f\beta\frac{a^2N}{3} \Rightarrow \underset{\substack{\downarrow \\ \text{forza-estensione}}}{f = \frac{3k_BT}{a^2N}\delta l}$$

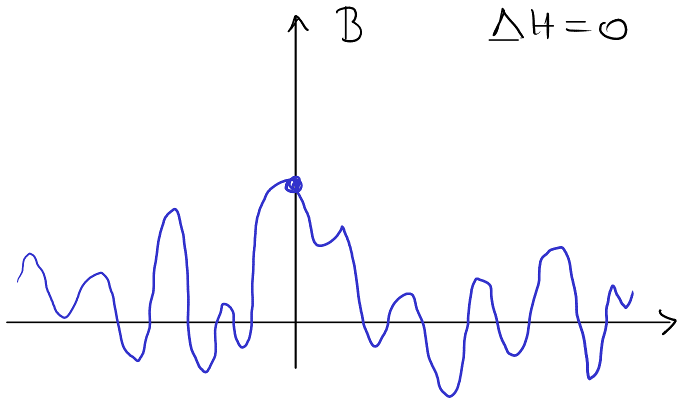
$$\vec{f} = (0,0,f)$$

Caso dinamico

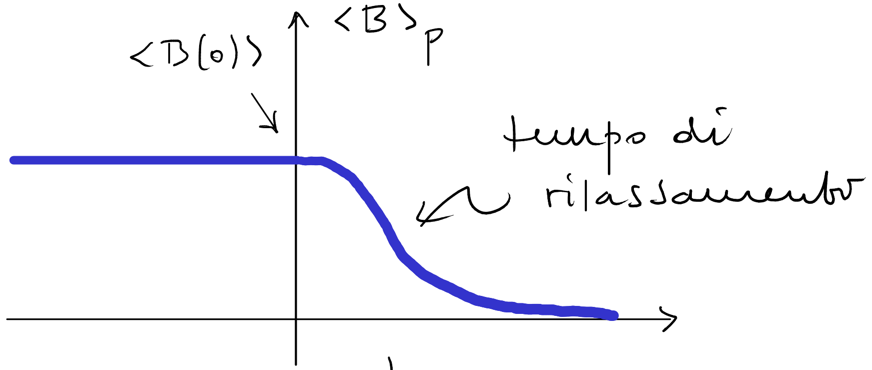
Regime lineare : $\Delta H \ll K_B T$ $\qquad \Delta H = -\phi(t)\, A \qquad A = A(\{\Gamma_i\}) \qquad B = B(\{\Gamma_i\})$

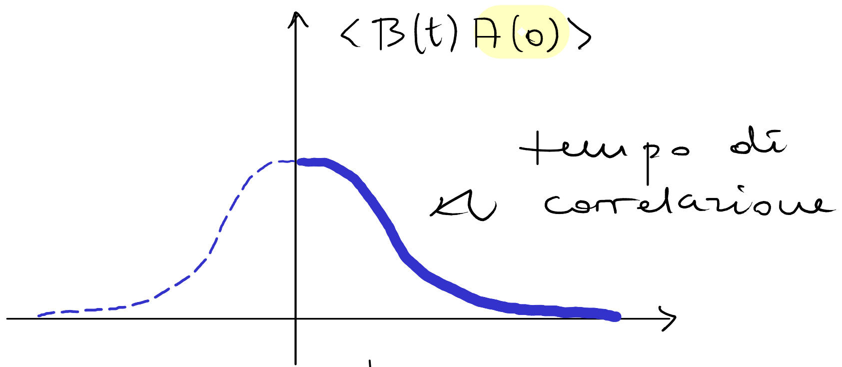






$$\phi = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$





rilassamento verso l'equilibrio

funzioni di correlazione all'equilibrio

$$\langle B(0) \rangle_p = \frac{\mathrm{Tr}\left[e^{-\beta(H+\Delta H)}\, B(0) \right]}{\mathrm{Tr}\left[e^{-\beta(H+\Delta H)} \right]}$$

$$\langle B(t) \rangle_p = \frac{\mathrm{Tr}\left[e^{-\beta(H+\Delta H)}\, B(t) \right]}{\mathrm{Tr}\left[e^{-\beta(H+\Delta H)} \right]} \qquad t > 0$$

evoluto al tempo t

$\Gamma(0) \longrightarrow \Gamma(t)$

Regime lineare : $\Delta H \ll k_B T$

$$\langle B(t) \rangle_p = \frac{Tr[e^{-\beta(H+\Delta H)} B(t)]}{Tr[e^{-\beta(H+\Delta H)}]} = \dots = \underbrace{\langle B(t) \rangle}_{\langle B \rangle} - \beta \left(\langle B(t) \Delta H \rangle - \underbrace{\langle B(t) \rangle}_{\langle B \rangle} \langle \Delta H \rangle \right) + O[(\beta \Delta H)^2]$$

$$\langle B(t) \rangle_p - \langle B \rangle = \beta \phi \left(\langle B(t) A(0) \rangle - \langle B \rangle \langle A \rangle \right) = \beta \phi \, C_{BA}(t)$$

$$\delta \bar{B}(t) \equiv \langle B(t) \rangle_p - \langle B \rangle = \beta \phi \, C_{BA}(t) \qquad \delta \bar{B}(0) = \beta \phi \, C_{BA}(0)$$

↑ risposta fuori equilibrio

↑ correlazione all'equilibrio

$$\frac{\delta \bar{B}(t)}{\delta \bar{B}(0)} = \frac{C_{BA}(t)}{C_{BA}(0)} \rightarrow \text{principio di regressione di Onsager}$$

↑ funzione correlazione normalizzata

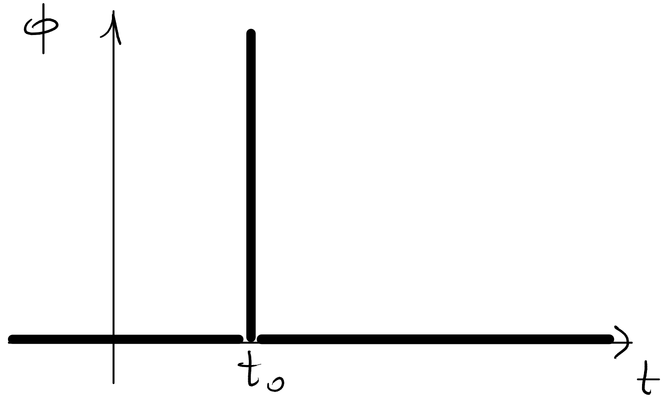
$$A = B \rightarrow \frac{\delta \bar{A}(t)}{\delta \bar{A}(0)} = \frac{C_{AA}(t)}{C_{AA}(0)}$$

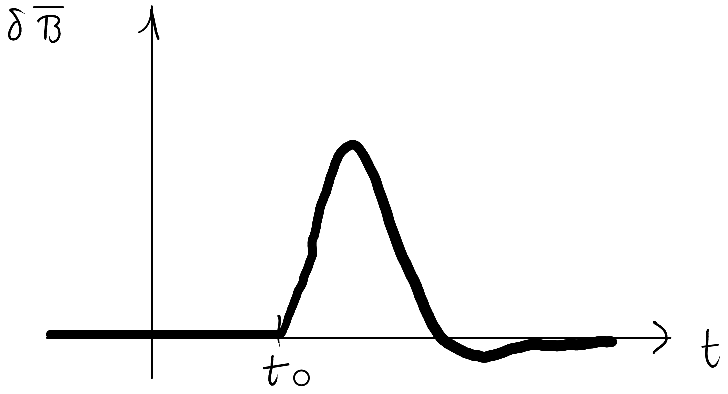
Funzione di risposta $\qquad \Delta H = -\phi(t)\,A \qquad$ regime lineare

$$\delta\bar{B}(t) = \int_{-\infty}^{\infty} dt'\,\phi(t')\,\chi_{BA}(t',t) \underset{\substack{t'<t \\ \text{causalità}}}{=} \int_{-\infty}^{t} dt'\,\phi(t')\,\chi_{BA}(t',t) = \int_{-\infty}^{t} dt'\,\phi(t')\,\chi_{BA}(t-t')$$

χ_{BA} è una proprietà all'equilibrio

ES.: campo impulsivo $\quad \phi(t) = \phi_0\,\delta(t-t_0) \rightarrow \delta\bar{B}(t) = \phi_0\,\chi_{BA}(t-t_0)$





Caso particolare:

$$\phi(t) = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$

$$\delta\bar{B}(t) = \beta\,\phi\,C_{BA}(t) \quad (*)$$

$$= \int_{-\infty}^{t} dt'\,\phi(t')\,\chi_{BA}(t-t') = \phi \int_{-\infty}^{0} dt'\,\chi_{BA}(t-t')$$

$$\underset{s = t - t'}{\uparrow}{=}\ \cancel{\phi} \int_t^{\infty} ds\, \chi_{BA}(s) \ \underset{*}{\uparrow}{=}\ \cancel{\phi}\, \beta\, C_{BA}(t)$$

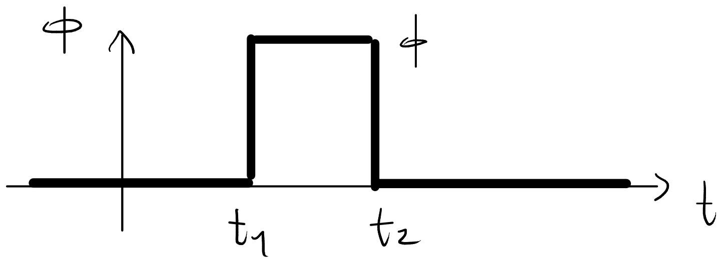
Teorema di fluttuazione – dissipazione

$$\chi_{BA}(t) = -\beta \frac{dC_{BA}}{dt}$$

$\uparrow$ risposta $\qquad$ $\uparrow$ funzione di correlazione

$A = B$: $\quad \chi(t) = -\beta \dfrac{dC}{dt}$

Esercizio : $\quad \Delta H = -\phi(t) A \qquad C_{BA}(t) \simeq C_{AB}(0) \exp(-t/\tau)$



$$\phi(t) = \begin{cases} 0 & t < t_1 \\ \phi & t_1 \le t \le t_2 \\ 0 & t > t_2 \end{cases} \Rightarrow \begin{cases} \chi_{BA} = ? \\ \delta \overline{B}(t) = ? \end{cases}$$