FUNZIONI DI CORRELAZIONE DIPENDENTI DAL TEMPO

$$A(\{\vec{r}(t), \vec{p}(t)\}) = A(\Gamma(t)) = A(t)$$

$$B(\{\vec{r}(t), \vec{p}(t)\}) = B(\Gamma(t)) = B(t)$$

Funzione di correlazione dinamica

$$C_{AB}(t', t'') = \langle A(t'') B(t') \rangle$$

Media d'ensemble

$$C_{AB}(t', t'') = \int d\Gamma(t')\, p(\Gamma(t'))\, A(t'') B(t') \qquad \Gamma(t') \longrightarrow \Gamma(t'')$$

Media temporale

$$C_{AB}(t', t'') = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt_0\, A(t_0 + t'') B(t_0 + t')$$

Ipotesi d'ergodicità

Equilibrio → stazionario → invarianza per traslazione temporale: $t'' - t'$

Cambio variabile: $t', t'' \to t = t'' - t', \; s = t'$

$$C_{AB}(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt_0 \, A(t_0 + s + t) B(t_0 + s)$$

$$= \langle A(s+t) B(s) \rangle \underset{s=0}{=} \langle A(t) B(0) \rangle$$

Casi limite:

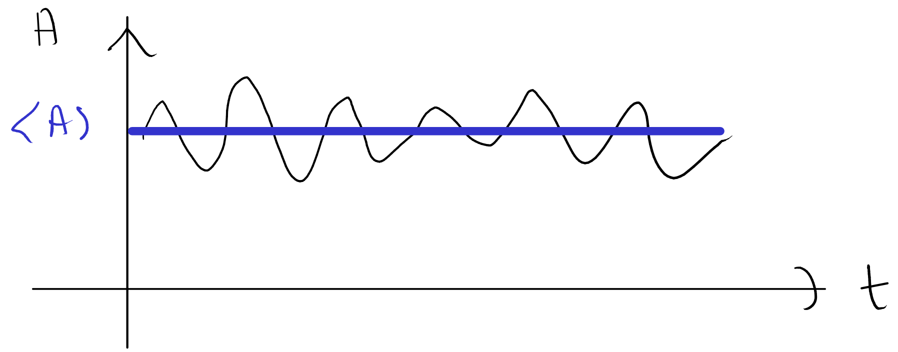
$C_{AB}(0) = \langle A B \rangle$ statica

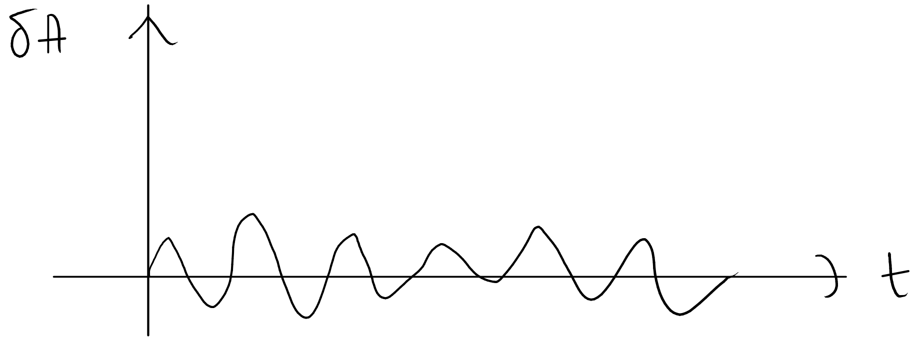
$C_{AB}(\infty) = \langle A \rangle \langle B \rangle$ ⚠

Varianti:

$$C_{AB}(t) = \langle (A(t) - \langle A \rangle)(B(0) - \langle B \rangle) \rangle = \langle \delta A(t) \, \delta B(0) \rangle$$

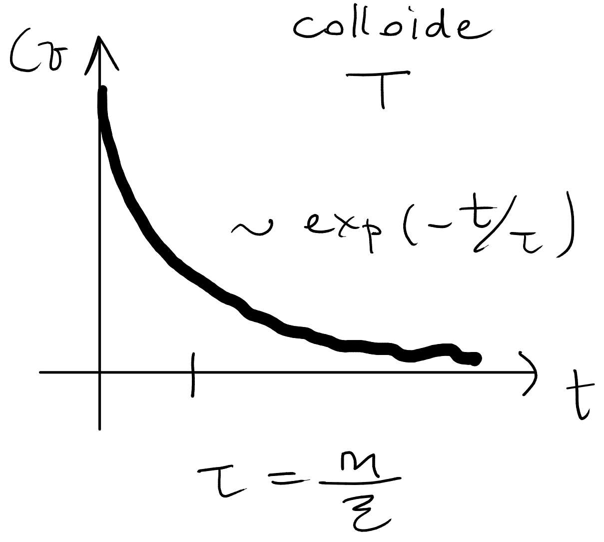
$$C_{AB}(t) = \frac{\langle A(t) B(0) \rangle}{\langle A(0) B(0) \rangle} \qquad \frac{\langle A(t) B(0) \rangle}{\langle A \rangle \langle B \rangle}$$

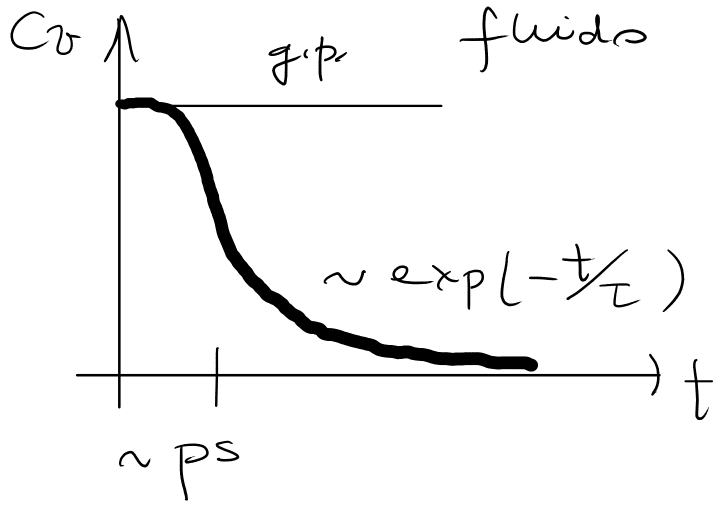


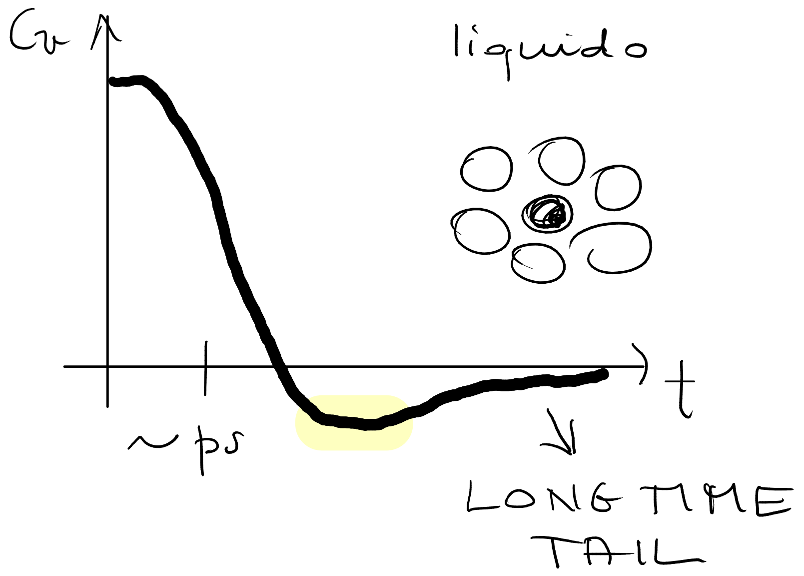


ES.: VACF autocorrelazione della velocità

$$C_v(t) = \frac{1}{3}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle = \frac{1}{3N}\sum_{i=1}^{N}\langle \vec{v}_i(t)\cdot\vec{v}_i(0)\rangle$$







Macro

Non - equilibrio

↓

Forze termodinamiche
+
correnti

↓

Coefficienti di trasporto → Relazioni di Green Kubo

regime lineare

↓

Onsager

Micro

Fluttuazioni

↓

Funzioni di correlazione dinamiche

↓

Funzioni di risposta → Relazioni di Green Kubo

regime lineare

↓

teor. di fluttuaz. dissipazione

TEORIA DELLA RISPOSTA LINEARE

Caso statico

$H + \Delta H \qquad |\Delta H| \ll K_B T \qquad A = A(\Gamma) \qquad \Gamma = \{\vec{r}, \vec{p}\}$

$\langle \ldots \rangle \rightarrow \exp(-\beta H) \rightarrow Z = \mathrm{Tr}[\exp(-\beta H)]$

$\langle \ldots \rangle_p \rightarrow \exp(-\beta(H + \Delta H))$

Regime lineare

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

$\downarrow$

$$\bar{A} \approx \frac{\mathrm{Tr}[e^{-\beta H}(1-\beta\Delta H) A]}{Z\left\{1 - \frac{\mathrm{Tr}[e^{-\beta H}\beta\Delta H]}{Z}\right\}} = \left(\langle A \rangle - \beta \langle A \Delta H \rangle\right)\left(1 + \beta \langle \Delta H \rangle\right)$$

$$= \langle A \rangle - \beta\left(\langle A \Delta H \rangle - \langle A \rangle \langle \Delta H \rangle\right)$$

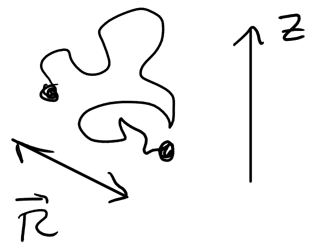
$$\delta \bar{A} = \bar{A} - \langle A \rangle = -\beta\left(\langle A \Delta H \rangle - \langle A \rangle\langle \Delta H \rangle\right) \rightarrow \text{covarianza}$$

$$\Delta H = -\phi A$$

$$\delta \bar{A} = \phi \beta \left(\langle A^2 \rangle - \langle A \rangle^2 \right)$$

$$\underbrace{\delta \bar{A}}_{\text{risposta}} = \phi \; \beta \underbrace{\langle \delta A^2 \rangle}_{\text{fluttuazioni}} \qquad \Rightarrow \qquad \delta \bar{A} = \underbrace{\beta \langle \delta A^2 \rangle}_{\substack{\chi_A \\ \text{suscettibilità}}} \cdot \phi$$

Es.: $N+1$ monomeri, dist. legame a, ideale: $\langle \vec{R} \rangle = \vec{0}$, $\langle |\vec{R}|^2 \rangle = a^2 N$



$$\delta \vec{R}_z = \delta l = \langle R_z \rangle_p - \underbrace{\langle R_z \rangle}_{=0} = \beta f \langle R_z^2 \rangle = \frac{f a^2 N}{3 k_B T} = \frac{a^2 N}{3 k_B T} f$$

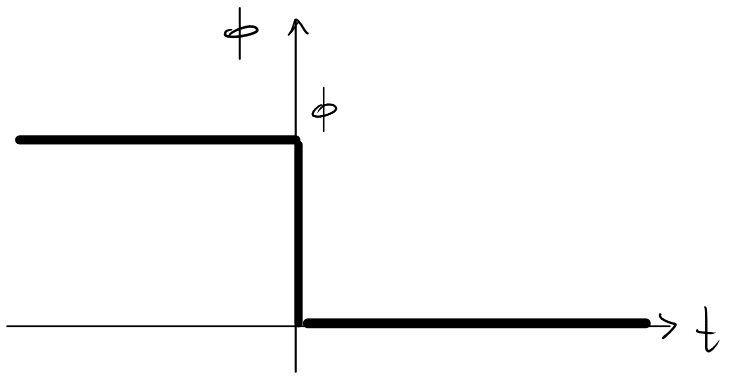
$$f = \underbrace{\frac{3 k_B T}{a^2 N}}_{\text{elasticità entropica}} \delta l$$

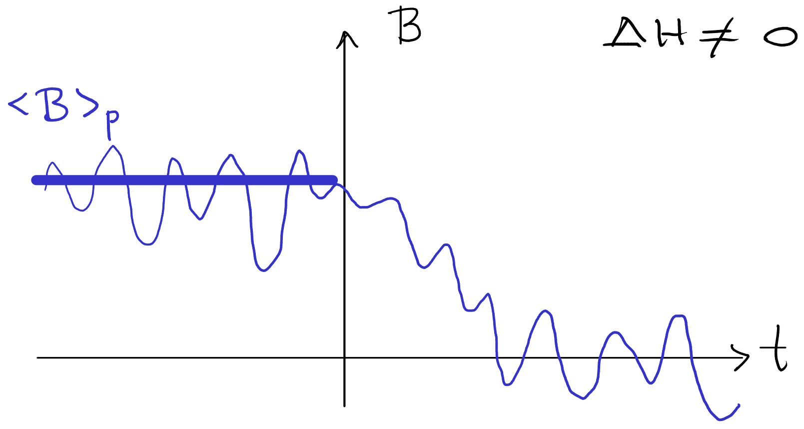
$A = R_z \quad \phi = f$

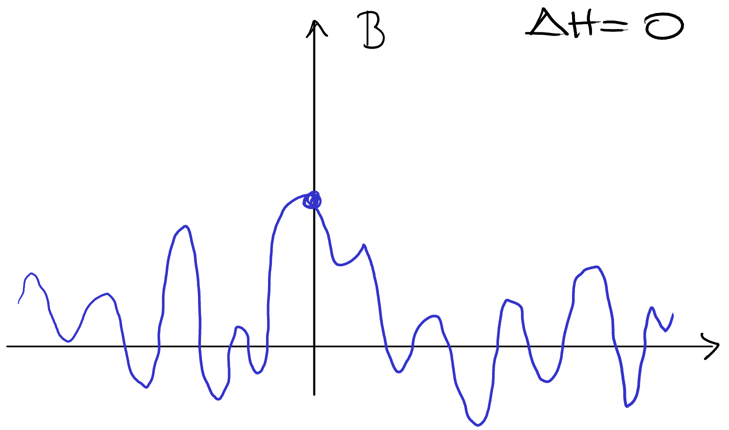
$\Delta H = -f R_z$

Caso dinamico

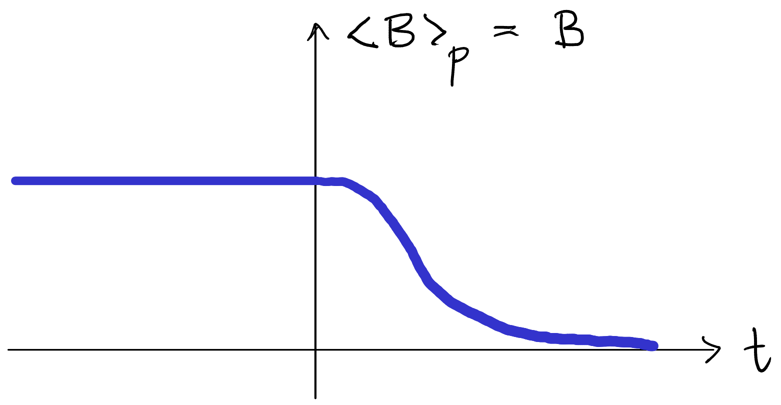
$\Delta H = -\phi(t)\, A \qquad A(t) = A(\Gamma(t)) \qquad B(t) = B(\Gamma(t)) \qquad \langle B \rangle = 0 . \quad \langle A \rangle = 0$





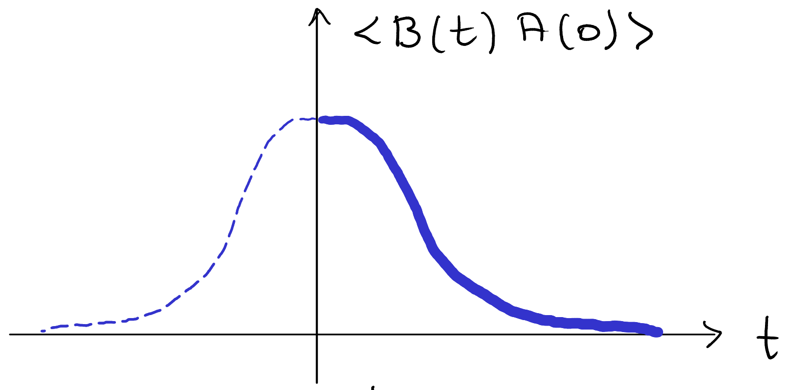


$$\phi = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$



$\downarrow$

rilassamento fuori equilibrio



$\downarrow$

funzioni di correlazione

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

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

$B(\Gamma(t))$ con $\Gamma(t)$ evoluto con H a partire da $\Gamma(0)$

$$\Delta H = -\phi A(0)$$

$$\overline{B}(t) = \dots = \langle B(t)\rangle - \beta\left(\langle B(t)\Delta H\rangle - \langle B(t)\rangle\langle \Delta H\rangle \right)$$

$$= \langle B\rangle + \beta\phi\left(\langle B(t)A(0)\rangle - \langle B\rangle\langle A\rangle \right) \qquad \langle \delta B(t)\,\delta A(0)\rangle$$

$$\delta\overline{B}(t) = \overline{B}(t) - \langle B\rangle = \beta\phi\, C_{BA}(t)$$

$\uparrow$ risposta

$\uparrow$ fluttuazioni

Principio di regressione di Onsager

$$\frac{\delta \bar{B}(t)}{\delta \bar{B}(0)} = \frac{C_{BA}(t)}{C_{BA}(0)}$$

regime lineare

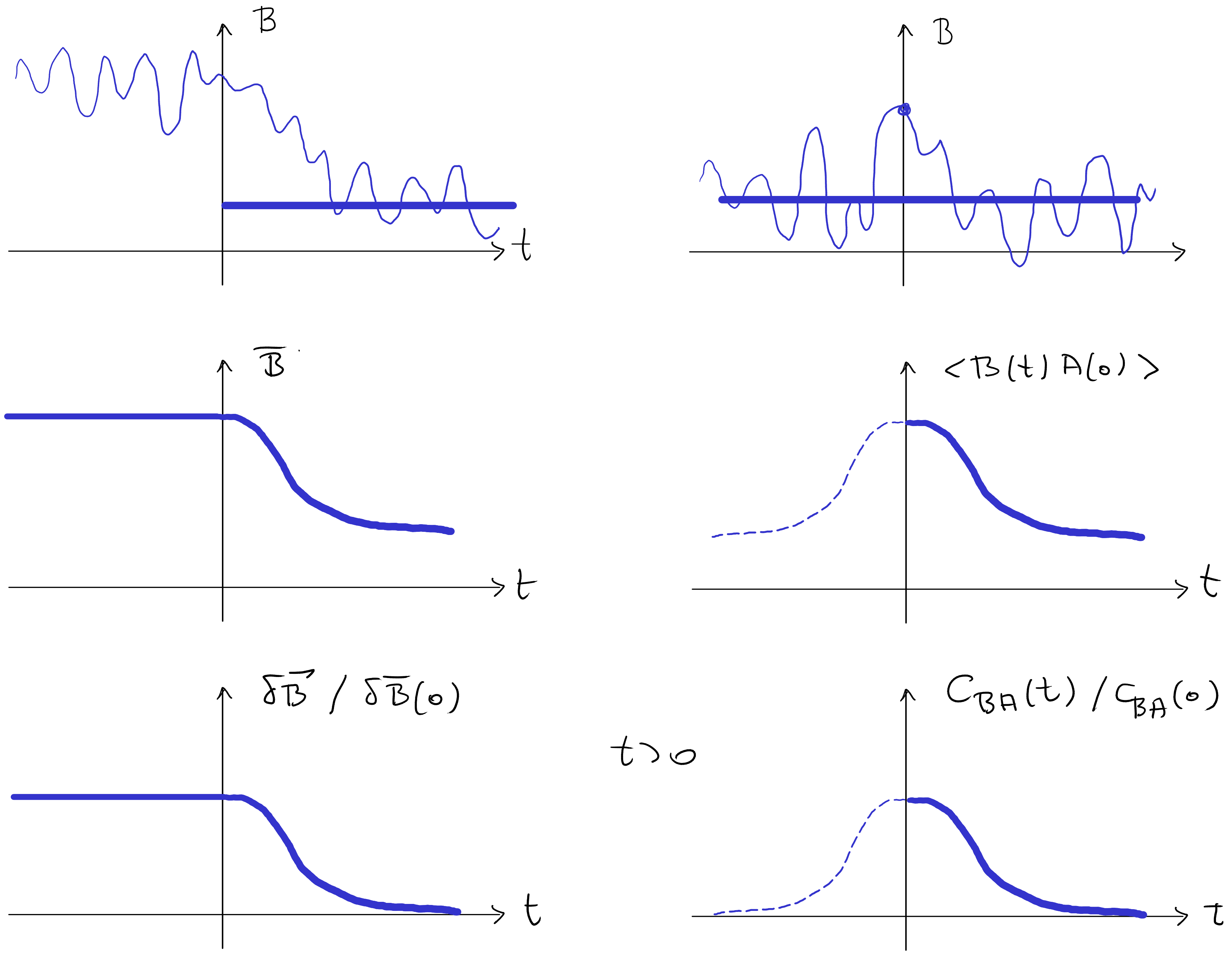
↓ rilassamento verso l'eq.

↓ fluttuazioni all'eq.

tempo di rilassamento

$\simeq$

tempo di correlazione



Funzione di risposta

$\left[\delta \bar{B} = \chi \phi \quad \text{statico} \right]$ $\qquad \Delta H = -\phi(t) A$

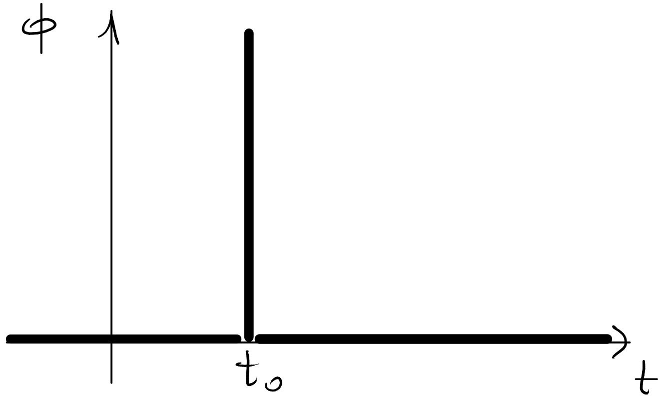
$$\delta \bar{B}(t) = \underbrace{\int_{-\infty}^{\infty} dt' \, \chi_{BA}(t,t') \, \phi(t')}_{\substack{\chi_{BA}:\ \text{suscettibilità} \\ \text{funzione di risposta}}} \underset{\text{causalità}}{=} \int_{-\infty}^{t} dt' \, \chi_{BA}(t,t') \, \phi(t') \qquad t' < t$$

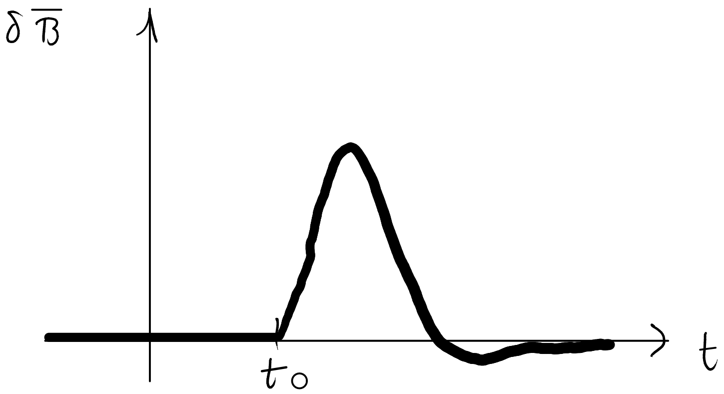
χ_{BA} non dipende da ϕ $\rightarrow$ χ_{BA} è una proprietà del sistema all'equilibrio

$\Rightarrow \quad \chi_{BA}(t,t') = \chi_{BA}(t-t')$

Es.: campo impulsivo $\phi(t) = \phi_0 \, \delta(t-t_0)$ $\Rightarrow$ $\delta \bar{B}(t) = \phi_0 \int_{-\infty}^{t} dt' \, \chi_{BA}(t-t') \, \delta(t'-t_0)$

$$= \phi_0 \, \chi_{BA}(t-t_0)$$





Teorema di fluttuazione - dissipazione

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

$s = t - t' \qquad dt' = -ds$

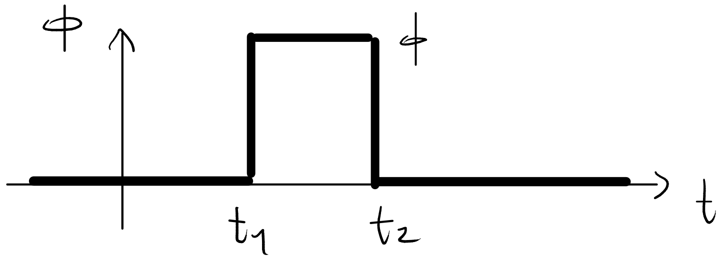
$$\begin{cases} \delta\bar{B}(t) = \int_{-\infty}^{t} dt' \, \chi_{BA}(t-t') \, \phi(t') = \phi \int_{-\infty}^{0} dt' \, \chi_{BA}(t-t') = -\phi \int_{\infty}^{t} ds \, \chi_{BA}(s) \\ \delta\bar{B}(t) = \beta \phi \, c_{BA}(t) \end{cases}$$

$$\frac{d}{dt}\left(-\int_{\infty}^{t} ds \, \chi_{BA}(s) \right) = \beta \frac{dc_{BA}}{dt}$$

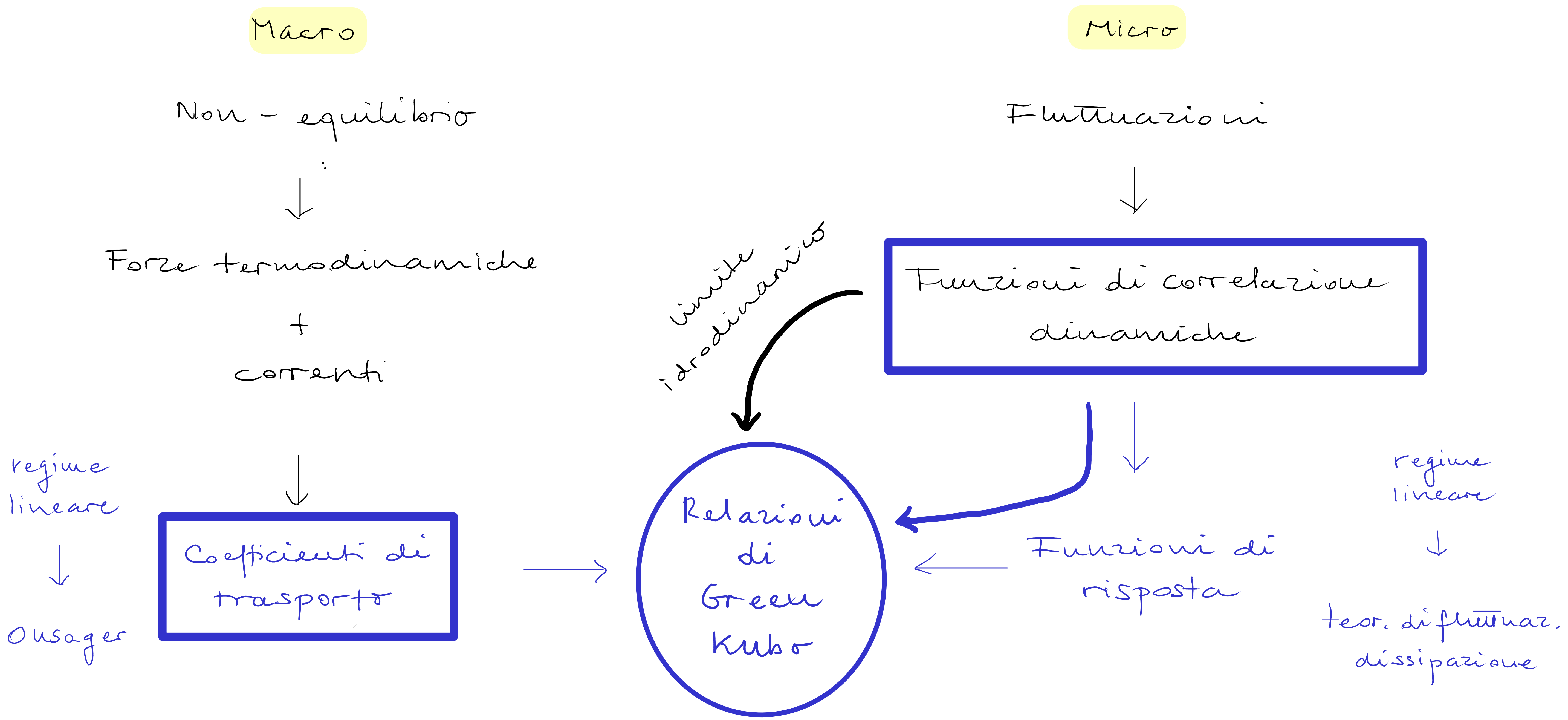
$$\boxed{\chi_{BA}(t) = -\beta \frac{dc_{BA}}{dt}} \qquad \text{TFD}$$

$\uparrow$ dissipazione $\qquad$ $\uparrow$ fluttuazioni

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



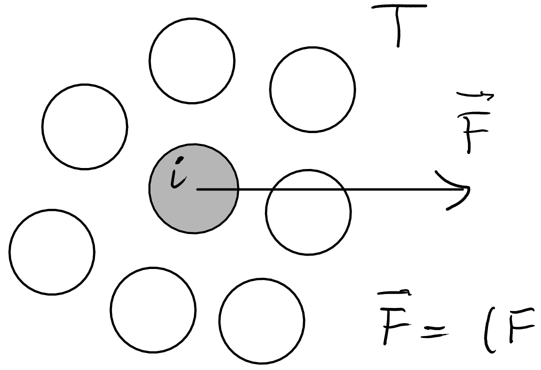
$$\phi(t) = \begin{cases} 0 & t < t_1 \\ \phi & t_1 \leq t \leq t_2 \\ 0 & t > t_2 \end{cases} \Rightarrow \begin{cases} \chi_{BA} = ? \\ \delta\overline{B}(t) = ? \end{cases}$$


Macro
Micro
Non-equilibrio
Fluttuazioni
Forze termodinamiche
+
correnti
limite idrodinamico
Funzioni di correlazione dinamiche
regime lineare
Onsager
Coefficienti di trasporto
Relazioni di Green Kubo
Funzioni di risposta
regime lineare
teor. di fluttuaz. dissipazione

RELAZIONI DI GREEN-KUBO

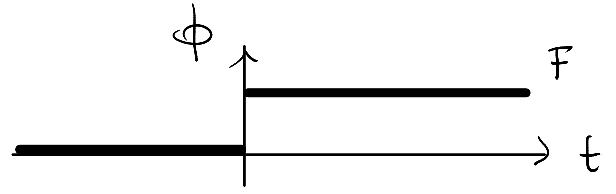
Relazioni integrali tra f. di correlazione e coeff. trasporto

1. Coefficiente di diffusione (mobilità)



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

$$\Delta H = - \underbrace{F\,\theta(t)}_{\phi}\ \underbrace{x_i(t)}_{A} \qquad A = x_i(t) \quad \Rightarrow \quad B = v_{ix}(t) = \frac{dx_i}{dt}$$



$$\begin{cases} \delta \bar{B}(t) = \langle B(t) \rangle_p - \langle B \rangle = \displaystyle\int_{-\infty}^{t} dt'\, \chi_{BA}(t-t')\, \phi(t') \\ \chi_{BA}(t) = -\beta \dfrac{d C_{BA}(t)}{dt} = -\beta \dfrac{d}{dt} \langle B(t) A(0) \rangle \end{cases}$$

Manipolo la derivata:

$$\frac{d}{dt} \langle B(t+s) A(s) \rangle = \left\langle \frac{dB(t+s)}{dt} A(s) \right\rangle = \left\langle \frac{dB(t+s)}{ds} A(s) \right\rangle$$

$$= \underbrace{\frac{d}{ds} \langle B(t+s)\, A(s) \rangle}_{=0} - \langle B(t+s) \frac{dA}{ds}(s) \rangle = - \langle B(t+s) \frac{dA}{ds}(s) \rangle \underset{s=0}{\overset{\uparrow}{=}} - \langle B(t) \frac{dA}{dt}(0) \rangle$$

$$\chi_{BA}(t) = \beta \langle B(t) \frac{dA}{dt}(0) \rangle$$

$$\langle v_{ix}(t) \rangle_p = \beta F \int_0^t dt' \langle v_{ix}(t-t')\, v_{ix}(0) \rangle$$

$$\underset{s=t-t'}{=} -\beta F \int_t^0 ds \underbrace{\langle v_{ix}(s)\, v_{ix}(0) \rangle} = \beta F \int_0^t ds\, C_v(s)$$

$$C_v(t) = \frac{1}{3N} \sum_{i=1}^{N} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle$$

Limite $t \to \infty$

$$\langle v_{ix}(\infty) \rangle_p = \beta F \int_0^\infty ds\, C_v(s)$$

Corrente di deriva

$$J_{deriva} = \lambda \rho_N F = \rho_N v_d \leftarrow \text{velocità di deriva}$$

$$v_d = \lambda F$$

Mobilità

$$\lambda = \beta \int_0^\infty ds\, C_v(s)$$

Equilibrio : $\lambda = \frac{1}{\xi} \Rightarrow D = \frac{K_B T}{\xi} \Rightarrow \lambda = \frac{D}{K_B T}$

Relazione di GK :

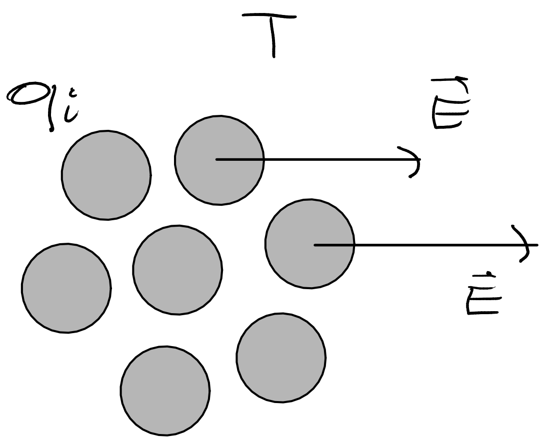
$$D = \int_0^\infty ds\, C_v(s)$$

Relazione di Einstein :

$$\langle |\Delta \bar{r}|^2 \rangle \xrightarrow[t\to\infty]{} 6Dt \qquad \langle |\Delta \bar{r}|^2 \rangle = 6t \int_0^t ds \left(1 - \frac{s}{t}\right) C_v(s)$$

2. Conducibilità elettrica

$\{\vec{r}, \vec{p}\}$

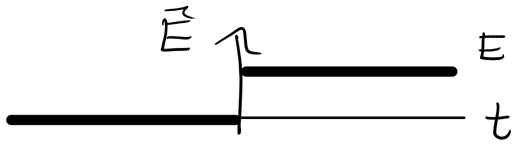


campo elettrico

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

$$\Delta H = -\phi(t) A$$

$$\Delta H = -\sum_{i=1}^{N} q_i \vec{E} \cdot \vec{r}_i = -\underbrace{\vec{E}}_{\phi} \cdot \underbrace{\left(\sum_{i=1}^{N} q_i \vec{r}_i\right)}_{\text{momento di dipolo elettrico totale}} = -E \underbrace{\sum_{i=1}^{N} q_i x_i(t)}_{A}$$



Corrente elettrica totale microscopica ($\to \wedge$)

$$\hat{\vec{J}}_e = \sum_{i=1}^{N} q_i \vec{v}_i(t) \rightarrow \hat{J}_{ex} = \sum_{i=1}^{N} q_i v_{ix}(t) = B$$

$$\langle \hat{J}_{ex}(t) \rangle_p = \beta E \int_0^t dt' \langle \hat{J}_{ex}(t-t') \frac{d}{dt}\left(\sum_{i=1}^{N} q_i x_i(0)\right) \rangle$$

$$= \beta E \int_0^t dt' \langle \hat{J}_{ex}(t-t') \hat{J}_{ex}(0) \rangle = \beta E \int_0^t ds \overbrace{\langle \hat{J}_{ex}(s) \hat{J}_{ex}(0) \rangle}^{\frac{1}{3} \langle \bar{\hat{J}}_e(s) \bar{\hat{J}}_e(0) \rangle}$$

Limite $t \to \infty$

$$\langle \hat{J}_{ex}(\infty) \rangle_p = \beta E \int_0^\infty ds \langle \hat{J}_{ex}(s) \hat{J}_{ex}(0) \rangle$$

Legge di Ohm : $\vec{J}_e = \sigma \vec{E} \rightarrow J_{ex} = \sigma E$

$$\underbrace{\frac{\langle \hat{J}_{ex}(\infty) \rangle}{V}}_{J_{ex}} = \underbrace{\frac{\beta}{V} \int_0^\infty ds \langle \hat{J}_{ex}(s) \hat{J}_{ex}(0) \rangle}_{\substack{\text{conducibilità elettrica} \\ \text{(relazione GK)} \\ \sigma}} \cdot E$$

$J_E = - \kappa \vec{\nabla} T$

Fourier

TABLE 8.1. *Green–Kubo relations for the transport coefficients in the form of Eqn* (8.4.18)

$$K = \int_0^\infty \langle J(t) J(0) \rangle \, dt$$

K	$J(t)$	Name of current	Eqn
D	$u_{ix}(t) = \frac{d}{dt} x_i(t)$	Particle velocity	(7.2.8)
$Vk_B T\eta$	$\sigma_0^{xz}(t) = \frac{d}{dt} m \sum_{i=1}^{N} u_{ix}(t) z_i(t)$	Off-diagonal component of stress tensor	(8.4.10)
$Vk_B T(\frac{4}{3}\eta + \zeta)$	$\sigma_0^{zz}(t) - PV = \frac{d}{dt} m \sum_{i=1}^{N} u_{iz}(t) z_i(t) - PV$	Diagonal component of stress tensor	(8.5.13)
$Vk_B T^2 \lambda$	$J_0^{ez}(t) = \frac{d}{dt} \sum_{i=1}^{N} z_i(t) \left\{ \frac{1}{2} m u_i^2(t) + \frac{1}{2} \sum_{j \neq i}^{N} v[r_{ij}(t)] \right\}$	Energy current	(8.5.27)
$\left(\frac{\partial^2 (\beta G/N)}{\partial c^2} \right)_{P,T} D_{12}$	$j_x^c(t) = \frac{d}{dt} \left\{ (1-c) \sum_{i=1}^{N_1} x_{i1}(t) - c \sum_{i=1}^{N_2} x_{i2}(t) \right\}$	Interdiffusion current	(8.6.31)
$Vk_B T\sigma$	$j_x^Z(t) = \frac{d}{dt} \sum_{i=1}^{N} q_i x_i(t)$	Electrical current	(7.8.10)

Note: $c = N_1/(N_1 + N_2)$; q_i is the charge carried by particle i.

Hansen MacDonald

FUNZIONI DI CORRELAZIONE DIPENDENTI DALLO SPAZIO E DAL TEMPO

2 punti nel tempo t', t'' → tempo; spazio-tempo

2 punti nello spazio $\vec{r}', \vec{r}''$ → spazio-tempo; spazio

tempo, spazio-tempo } dinamiche

spazio → statiche

spazio reale $\vec{r}$	tempo t
spazio reciproco $\vec{k}$	frequenze ω

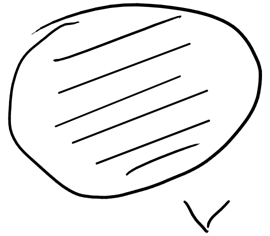
Caso statico

Osservabili microscopiche: $\{\vec{r}, \vec{p}\}$

$$\hat{A}(\vec{r}) = \sum_{i=1}^{N} a_i\, \delta(\bar{r} - \bar{r}_i) \qquad \hat{A}_{\bar{k}} = \int \hat{A}(\bar{r})\, e^{-i\bar{k}\cdot\bar{r}}\, d\vec{r} = \sum_{i=1}^{N} a_i\, e^{-i\bar{k}\cdot\bar{r}_i}$$

Es.: $a_i = 1$ densità microscopica

$$\hat{\rho}(\bar{r}) = \sum_{i=1}^{N} \delta(\bar{r} - \bar{r}_i) \qquad \hat{\rho}_{\bar{k}} = \sum_{i=1}^{N} e^{-i\bar{k}\cdot\bar{r}_i}$$



$$\int_V d\bar{r}\, \hat{\rho}(\bar{r}) = N$$

$$\int_{\varepsilon_0^3} d\bar{r}\, \hat{\rho}(\bar{r}) = \begin{cases} 1 \\ 0 \end{cases}$$

Media d'ensemble

$$\langle \hat{\rho}(\bar{r}) \rangle = \rho(\bar{r}) \quad \text{densità locale}$$
$$\neq \rho_N(\bar{r})$$

Sistema omogeneo

$$\rho(\bar{r}) = \rho = \frac{N}{V} = \text{cost}$$

Caso dinamico

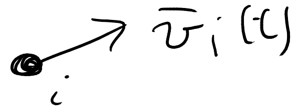
$$\hat{A}(\vec{r},t) = \sum_{i=1}^{N} a_i(t)\, \delta(\vec{r}-\vec{r}_i(t)) \qquad \hat{A}_{\vec{k}}(t) = \sum_{i=1}^{N} a_i(t)\, e^{-i\vec{k}\cdot\vec{r}_i(t)}$$

Es. densità micro $a_i = 1$

$$\hat{\rho}(\vec{r},t) = \sum_{i=1}^{N} \delta(\vec{r}-\vec{r}_i(t)) \qquad \hat{\rho}_{k}(t) = \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i(t)}$$

Es. corrente micro $a_i = \vec{v}_i(t)$

$$\hat{J}(\vec{r},t) = \sum_{i=1}^{N} \vec{v}_i(t)\, \delta(\vec{r}-\vec{r}_i(t))$$



Funzioni di correlazione

$$\left.\begin{aligned} C_{AB}(\vec{r}',\vec{r}'') &= \langle \hat{A}(\vec{r}')\,\hat{B}(\vec{r}'') \rangle \\ C_{AB}(\vec{k}',\vec{k}'') &= \langle \hat{A}_{\vec{k}'}, \hat{B}^{*}_{\vec{k}''} \rangle = \langle \hat{A}_{\vec{k}'}, \hat{B}_{-\vec{k}''} \rangle \end{aligned}\right\} \text{statiche}$$

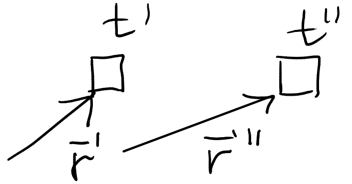
$$C_{AB}(\vec r', \vec r'', t', t'') = \langle \hat A(\vec r', t')\, \hat B(\vec r'', t'')\rangle$$
$$C_{AB}(\vec k', \vec k'', t', t'') = \langle \hat A_{\vec k'}(t')\, \hat B_{-\vec k''}(t'')\rangle$$

} dinamiche

Simmetrie :

- stazionarietà : $t = t' - t''$
- omogeneità : $\vec r = \vec r' - \vec r''$; $\vec k = \vec k' = \vec k''$
- omogeneità + isotropia : $|\vec r| = |\vec r' - \vec r''|$; $|\vec k| = |\vec k'| = |\vec k''|$

FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA: SPAZIO REALE



sistema stazionario e omogeneo

$t'' - t', \quad \vec{r}'' - \vec{r}'$

$$\hat{\rho}(\vec{r}, t) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i(t))$$

Caso statico:

$$\hat{\rho}(\vec{r}) = \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \quad \to \quad \vec{r} = \vec{r}'' - \vec{r}' \qquad \langle \hat{\rho}(\vec{r}) \rangle = \rho$$

$$G(\vec{r}', \vec{r}'') = \langle (\hat{\rho}(\vec{r}') - \rho)(\hat{\rho}(\vec{r}'') - \rho) \rangle = \langle \hat{\rho}(\vec{r}')\, \hat{\rho}(\vec{r}'') \rangle - \rho^2$$

$$G(\vec{r}) = \frac{1}{N} \int_V d\vec{r}' \langle \hat{\rho}(\vec{r}')\, \hat{\rho}(\vec{r}' + \vec{r}) \rangle - \rho$$

$$= \frac{1}{N} \int_V d\vec{r}' \left\langle \left(\sum_{j=1}^{N} \delta(\vec{r}' - \vec{r}_j) \right) \left(\sum_{i=1}^{N} \delta(\vec{r}' + \vec{r} - \vec{r}_i) \right) \right\rangle - \rho$$

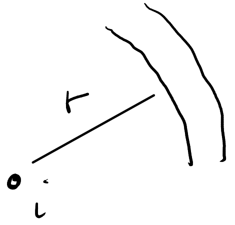
$$= \frac{1}{N} \left\langle \int_V d\vec{r}' \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec{r}' - \vec{r}_j)\, \delta(\vec{r}' + \vec{r} - \vec{r}_i) \right\rangle - \rho$$

$$= \underbrace{\frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec{r} - (\vec{r}_i - \vec{r}_j)) \right\rangle}_{} - \rho = \underset{i=j}{G_s(\vec{r})} + \underset{i \neq j}{G_d(\vec{r})} - \rho$$

$$= \delta(\bar{r}) + \rho\, g(\bar{r}) - \rho = \rho\,[\underbrace{g(\bar{r}) - 1}_{h(\bar{r})}] + \delta(\bar{r})$$

Funzione di distribuzione radiale

$$g(\bar{r}) = \frac{1}{N\rho} \left\langle \sum_{i=1}^{N} \sum_{j \neq i} \delta(\bar{r} - (\bar{r}_i - \bar{r}_j)) \right\rangle$$



Funzioni di distribuzione radiale parziali

$g_{\alpha\beta}(\bar{r}) \quad \alpha, \beta = A, B$

Caso dinamico

$$\hat{\rho}(\bar{r}, t) = \sum_{i=1}^{N} \delta(\bar{r} - \bar{r}_i(t)) \qquad \bar{r} = \bar{r}'' - \bar{r}' \,; \quad t = t'' - t'$$

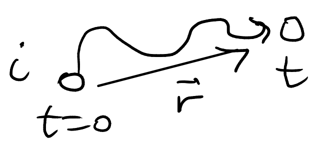
$$G(\bar{r}', \bar{r}'', t', t'')$$

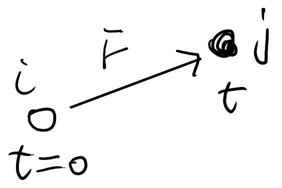
$$G(\bar{r}, t) = \frac{1}{N} \int_V d\bar{r}' \langle \hat{\rho}(\bar{r}', 0)\, \hat{\rho}(\bar{r}' + \bar{r}, t) \rangle - \rho = \ldots =$$

$$= \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\bar{r} - (\bar{r}_i(t) - \bar{r}_j(0))) \right\rangle - \rho$$

$$= G_s(\bar{r}, t) + G_d(\bar{r}, t) - \rho \rightarrow$$ funzioni di Van Hove

self	distinta
$G_s(\bar{r}, t)$	$G_d(\bar{r}, t)$

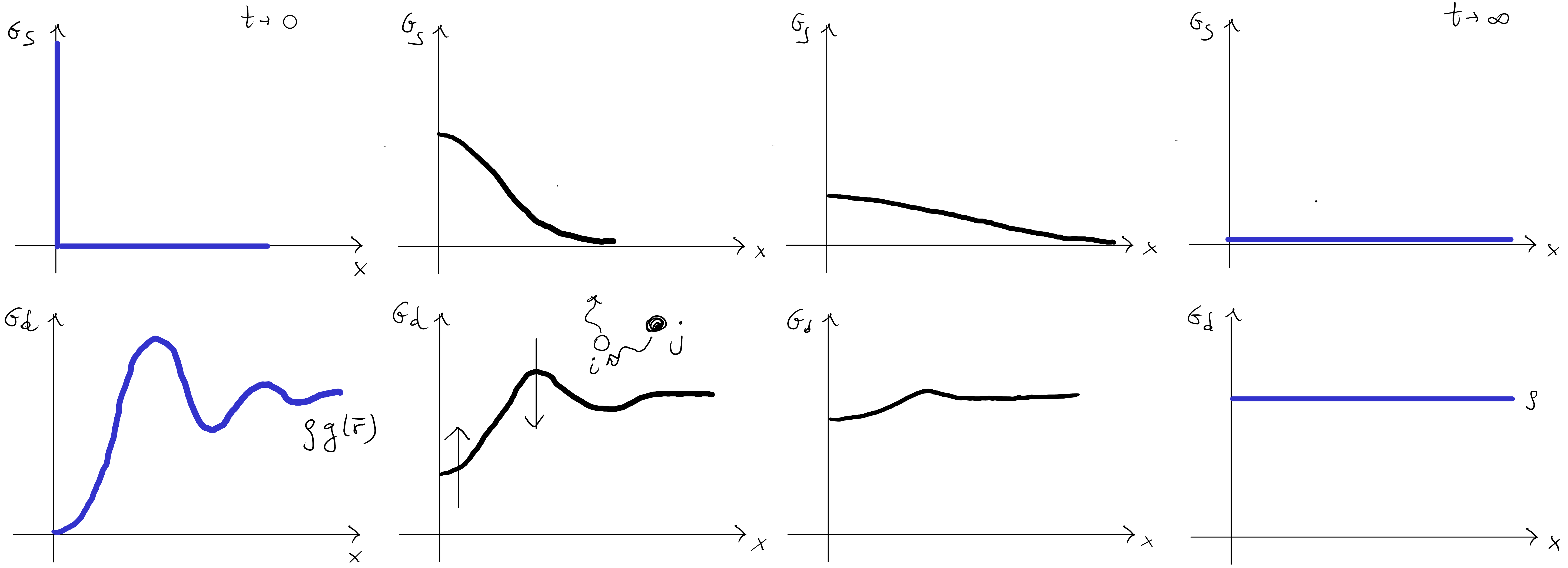




Casi limite

$$\lim_{t\to 0} G_s(\vec r,t) = \delta(\vec r) \qquad \int_V d\vec r\, G_s(\vec r,t) = 1 \qquad \lim_{t\to\infty} G_s(\vec r,t) = \frac{1}{V} \approx 0$$

$$\lim_{t\to 0} G_d(\vec r,t) = \rho\, g(\vec r) \qquad \int_V d\vec r\, G_d(\vec r,t) = N-1 \qquad \lim_{t\to\infty} G_d(\vec r,t) = \frac{N-1}{V} \approx \rho$$



FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA: SPAZIO DI FOURIER

Sistema stazionario e omogeneo $\qquad \hat{\rho}_{\vec{k}} = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \hat{\rho}(\vec{r}) = \sum_{i=1}^{N} e^{-i\vec{k}\cdot\vec{r}_i}$

Caso statico

$$S(\vec{k}) = \frac{1}{N} \langle \hat{\rho}_{\vec{k}}\, \hat{\rho}_{-\vec{k}} \rangle$$

fattore di struttura

$$= \frac{1}{N} \int d\vec{r}\,'' e^{-i\vec{k}\cdot\vec{r}\,''} \int d\vec{r}\,' e^{i\vec{k}\cdot\vec{r}\,'} \langle \hat{\rho}(\vec{r}\,') \hat{\rho}(\vec{r}\,'') \rangle \qquad \begin{aligned} \vec{r} &= \vec{r}\,'' - \vec{r}\,' \\ \vec{r}\,'' &= \vec{r}\,' + \vec{r} \end{aligned}$$

$$= \frac{1}{N} \int d\vec{r}\,' \int d\vec{r}\,'' e^{-i\vec{k}\cdot(\vec{r}\,'' - \vec{r}\,')} \langle \hat{\rho}(\vec{r}\,') \hat{\rho}(\vec{r}\,'') \rangle$$

$$= \frac{1}{N} \int d\vec{r}\,' \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \langle \hat{\rho}(\vec{r}\,') \hat{\rho}(\vec{r}\,' + \vec{r}) \rangle$$

$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \underbrace{\frac{1}{N} \int d\vec{r}\,' \langle \hat{\rho}(\vec{r}\,') \hat{\rho}(\vec{r}\,' + \vec{r}) \rangle}_{G(\vec{r}) + \rho} = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} G(\vec{r}) + \rho\, \delta(\vec{k})$$

$$= \rho \int d\bar{r}\, e^{-i\bar{k}\cdot\bar{r}} \left[g(\bar{r}) - 1 \right] + 1 + \rho\, \delta(\bar{k})$$

$$= 1 + \rho\, h(\bar{k}) + \rho\, \delta(\bar{k})$$

$$S(\bar{k}) = \frac{1}{N} \langle \hat{\rho}_k \hat{\rho}_{-k} \rangle \qquad \hat{\rho}_k = \sum_{i=1}^{N} e^{-i\bar{k}\cdot\bar{r}_i}$$

Caso dinamico

$$F(\bar{k},t) = \frac{1}{N} \langle \hat{\rho}_k(t)\, \hat{\rho}_{-\bar{k}}(0) \rangle \ \dots = \qquad \hat{\rho}_k(t) = \sum_{i=1}^{N} e^{-i\bar{k}\cdot\bar{r}_i(t)}$$

funzione intermedia di scattering

$$= \int d\bar{r}\, e^{-i\bar{k}\cdot\bar{r}}\, G(\bar{r},t) + \rho\, \delta(\bar{k}) \qquad G(\bar{r},t) = G_s(\bar{r},t) + G_d(\bar{r},t)$$

$$F_s(k,t) = \int d\bar{r}\, e^{-i\bar{k}\cdot\bar{r}}\, G_s(\bar{r},t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{-i\bar{k}\cdot(\bar{r}_i(t) - \bar{r}_i(0))} \right\rangle$$

[Fattore struttura dinamico $S(\vec{k},\omega)$]

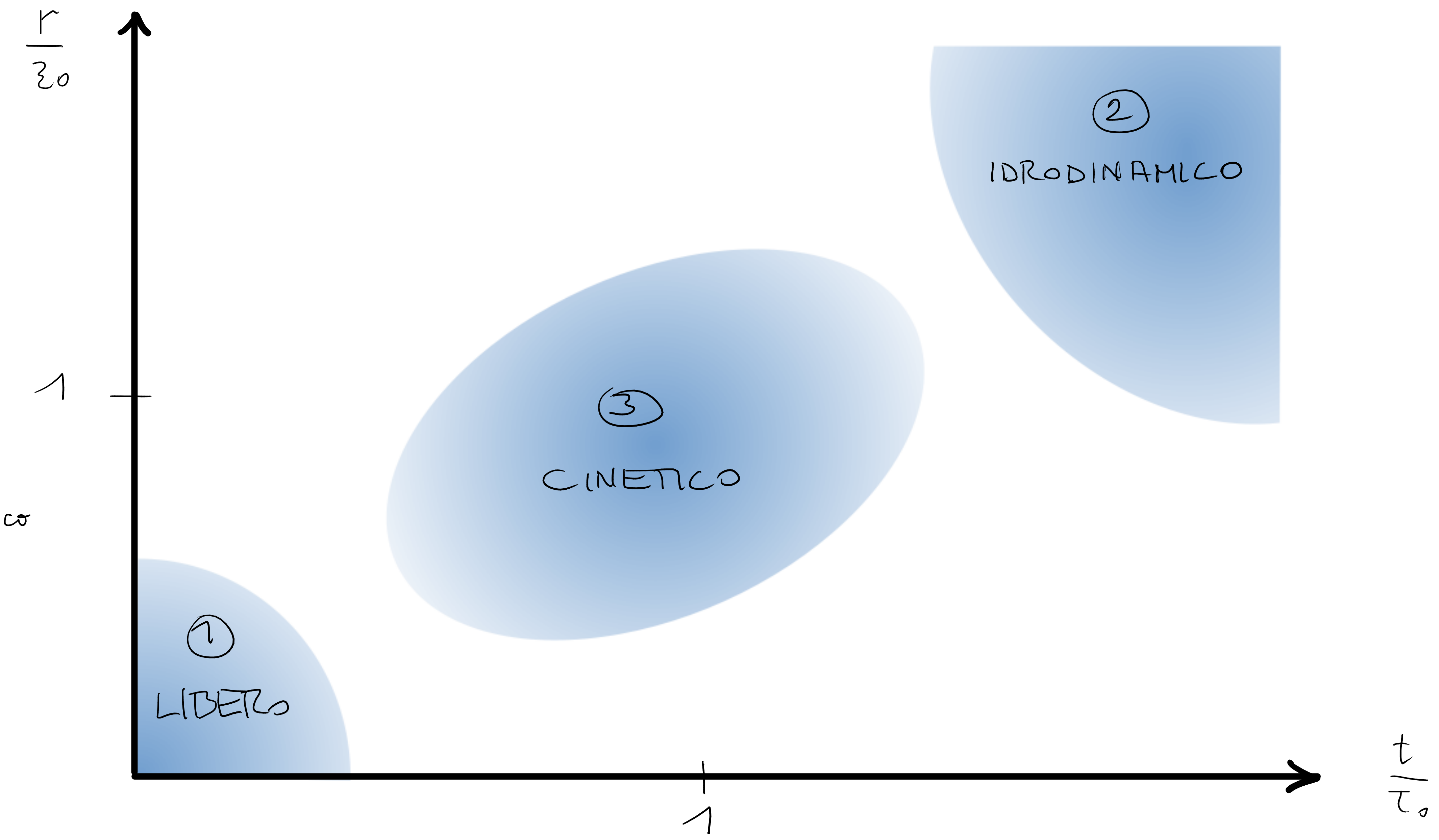
Casi limite:

- $F(\vec{k}, t=0) = S(\vec{k})$
- $F(\vec{k}, t\to\infty) = F_s(\vec{k}, t\to\infty) = 0$

REGIMI DINAMICI

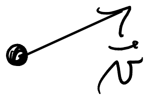
ξ_0 distanza interatomica 10^{-10} m

τ_0 tempo microscopico 10^{-12} s



① **Regime libero** $\quad t \ll \tau_0 , \quad |\vec{r}| \gg \xi_0 , \quad |\vec{k}|\,\xi_0 \gg 1 \quad \rightarrow \quad$ g.p.

$$\begin{cases} G_d(\vec{r},t) = \rho \\ G_s(\vec{r},t) \sim p_{MB}\left(\dfrac{\vec{r}}{t}\right) \end{cases}$$



equilibrio T $\qquad \vec{r} = \vec{v}\,t$

$$G_s(\vec{r},t) \sim \exp\left(- \frac{m}{2 k_B T t^2} |\vec{r}|^2 \right)$$

$$G_s(\vec{r},t) = \left(\frac{m}{2\pi k_B T t^2} \right)^{3/2} \exp\left(- \frac{m}{2 k_B T t^2} |\vec{r}|^2 \right)$$

$$F_s(\vec{k},t) = \exp\left(- \frac{2 k_B T |\vec{k}|^2}{m} t^2 \right) = F(\vec{k},t)$$

$G(\bar r,t)$ → funzione di Van Hove

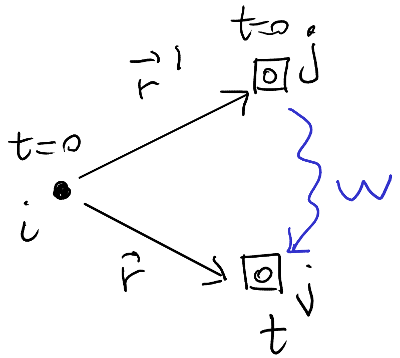
$F(\bar k,t)$ → funzione intermedia di scattering

$S(\bar k,\omega)$ → fattore di struttura dinamico

1)	libero	$r/\xi_0 \ll 1$	$t/\tau_0 \ll 1$	$k\xi_0 \gg 1$
2)	cinetico	$r/\xi_0 \sim 1$	$t/\tau_0 \sim 1$	$k\xi_0 \sim 1$
3)	idrodinamico	$r/\xi_0 \gg 1$	$t/\tau_0 \gg 1$	$k\xi_0 \ll 1$

Approssimazione di Vineyard

$$G_d(\bar r,t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} \sum_{j\neq i} \delta\left(\bar r - (\bar r_j(t) - \bar r_i(0))\right)\right\rangle$$



prob. di trovare j in $\bar r'$ $\sim$ $\rho g(\bar r)$

$$G_d(\bar r,t) = \int_V d\bar r' \, \rho g(\bar r') \cdot W(\bar r-\bar r',t)$$

$$\approx \rho \int_V d\bar r' \, g(\bar r') \, G_s(\bar r-\bar r',t)$$

i e j indipendenti

$$F(\bar{k},t) = F_s(\bar{k},t) + F_d(\bar{k},t)$$

$$= F_s(\bar{k},t) + \rho \int d\vec{r}\, e^{-i\bar{k}\cdot\bar{r}} \int_V d\bar{r}'\, g(\bar{r}')\, G_s(\bar{r}-\bar{r}',t)$$

$$= F_s(\bar{k},t) + \rho \int d\bar{r}\, e^{-i\bar{k}\cdot\bar{r}}\, g(\bar{r}) \cdot F_s(\bar{k},t)$$

convoluzione

$$S(\bar{k}) = 1 + \rho \int d\bar{r}\, e^{-i\bar{k}\cdot\bar{r}}\, g(\bar{r}) \qquad \bar{k} \neq 0$$

$$F(\bar{k},t) = F_s(\bar{k},t) + \left[S(\bar{k}) - 1 \right] F_s(\bar{k},t) = S(\bar{k})\, F_s(\bar{k},t)$$

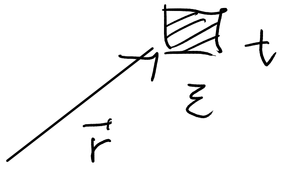
$\square$

3) Regime idrodinamico $\quad |\bar{r}|/\xi_0 \gg 1 \quad t/\tau_0 \gg 1 \quad |\bar{k}|\xi_0 \ll 1$

$$\hat{\rho}(\bar{r},t) = \sum_{i=1}^{N} \delta(\bar{r}-\bar{r}_i(t))$$

$\rho_N(\bar{r},t)$ equilibrio locale

$$\langle \hat{\rho}(\bar{r},t) \rangle = \rho(\bar{r},t)$$



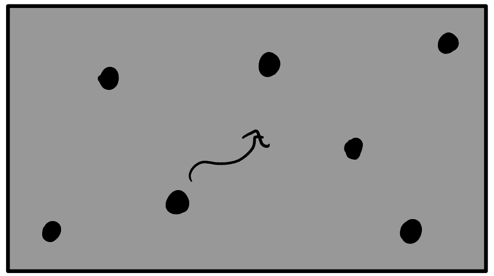
$$\rho_N(\bar{r},t) = \frac{1}{\xi^3}\int_{\xi} d\bar{r}'\,\hat{\rho}(\bar{r}'-\bar{r},t)$$

$$\hat{\rho}_{\bar{k}}(t) \to \langle \hat{\rho}_{\bar{k}}(t) \rangle \qquad \rho_{N,\bar{k}}(t)$$

Ipotesi: $|\bar{k}|\xi_0 \ll 1 \quad t/\tau_0 \gg 1$

$$\langle \rho_{N,\bar{k}}(t)\,\rho_{N,-\bar{k}}(0) \rangle = \langle \hat{\rho}_{\bar{k}}(t)\,\hat{\rho}_{-\bar{k}}(0) \rangle \qquad (\text{Onsager})$$

No tagged particles



$N_0 \ll N$

$$F_s(\bar{k},t) = \frac{1}{N_0}\langle \hat{\rho}_{\bar{k}}(t)\,\hat{\rho}_{-k}(0) \rangle = \frac{1}{N_0}\langle \rho_{N,\bar{k}}(t)\,\rho_{N,-\bar{k}}(0) \rangle$$

$$\frac{\partial \rho_N}{\partial t} = D\nabla^2\rho_N \Rightarrow \rho_{N,\bar{k}}(t) = \rho_{N,\bar{k}}(0)\exp(-Dk^2t)$$

$$F_s(\bar{k},t) = \underbrace{\frac{\langle \delta_{N,\bar{k}}(0)\, \delta_{N,-\bar{k}}(0) \rangle}{N_0}}_{=1} \exp(-Dk^2 t) = \underbrace{\exp(-Dk^2 t)}_{\text{diffusione}} \qquad k^2 = |\bar{k}|^2$$

$$G_s(\bar{r},t) = \left(\frac{1}{4\pi D t} \right)^{3/2} \exp\left(- \frac{1}{4Dt} |\bar{r}|^2 \right)$$

2) <u>Regime cinetico</u> $\quad |\bar{r}| \sim \xi_0 \quad t \sim \tau_0 \quad |\bar{k}| \sim 1/\xi_0$

<u>Approssimazione gaussiana</u>

$$G_s(\bar{r},t) = \left(\frac{\alpha(t)}{\pi} \right)^{3/2} \exp\left(-\alpha(t) |\bar{r}|^2 \right)$$

α non dipende da $\bar{r}$

libero: $\alpha(t) = \dfrac{m}{2k_B T t^2}$ $\qquad$ idrodinamico: $\alpha(t) = \dfrac{1}{4Dt}$

$$\langle |\Delta \bar{r}(t)|^2 \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle |\bar{r}_i(t) - \bar{r}_i(0)|^2 \rangle$$

isotropia

$$= \int d\bar{r}\, |\bar{r}|^2 G_s(\bar{r},t) = 3 \int_{-\infty}^{\infty} dx\, x^2 G_s(x,t)$$

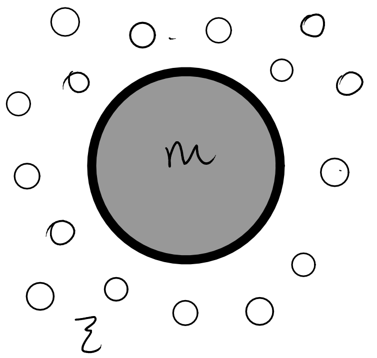
$$= 3 \int_{-\infty}^{\infty} dx \; x^2 \left(\frac{\alpha(t)}{\pi} \right)^{3/2} \exp\left(- \frac{2}{2} \alpha(t) \, x^2 \right)$$

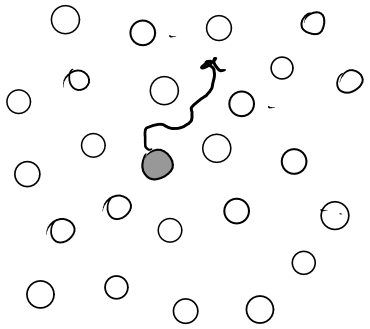
$$= 3 \cdot \frac{1}{2 \alpha(t)}$$

$$\Rightarrow \quad \alpha(t) = \frac{3}{2 \langle |\Delta \bar{r}(t)|^2 \rangle}$$

$$F_s(\bar{k}, t) = \exp\left(- \frac{1}{4 \alpha(t)} |\bar{k}|^2 \right) = \exp\left(- \frac{1}{6} \langle |\Delta \bar{r}(t)|^2 \rangle |\bar{k}|^2 \right)$$

Funzioni di memoria





Langevin : $m\frac{d\vec{v}}{dt} = -\xi\vec{v} + \vec{\theta}(t)$

forza stocastica : $\langle\vec{\theta}(t)\rangle = \vec{0}$

$$\langle\theta_\alpha(t')\,\theta_\beta(t'')\rangle = 2\theta_0\,\delta_{\alpha\beta}\,\delta(t'-t'')$$

Eq. di Langevin generalizzata ← operatore di proiezione (Mori - Zwanzig)

$$m\frac{d\bar{v}}{dt} = -\int_{-\infty}^{t} dt'\, M(t-t')\,\bar{v}(t') + \bar{\theta}(t) \qquad \langle\bar{\theta}(t)\rangle = \vec{0} \qquad \langle\bar{\theta}(t)\cdot\bar{v}(0)\rangle = 0$$

funzione di memoria

$$\left\langle m\frac{d\bar{v}}{dt}\cdot\bar{v}(0)\right\rangle = -\int_{-\infty}^{t} dt\, M(t-t')\,\langle\bar{v}(t')\cdot\bar{v}(0)\rangle + \underbrace{\langle\bar{\theta}(t)\cdot\bar{v}(0)\rangle}_{=0}$$

$$\frac{d\langle\bar{v}(t)\cdot\bar{v}(0)\rangle}{dt} = -\frac{1}{m}\int_{-\infty}^{t} dt\, M(t-t')\,\langle\bar{v}(t')\cdot\bar{v}(0)\rangle \Rightarrow \frac{dC_v}{dt} = -\frac{1}{m}\int_{-\infty}^{t} dt\, M(t-t')\,C_v(t')$$

$$C_v(t) = \frac{k_B T}{m(\alpha_+ - \alpha_-)}\left(\alpha_+ e^{-\alpha_-|t|} - \alpha_- e^{-\alpha_+|t|}\right)$$

$$M(t) = M(0)\exp(-t/\tau)$$

Hansen - MacDonald

$$\alpha_\pm = \frac{1}{2\tau}\left[1 \mp (1 - 4\Omega_0^2\tau^2)^{1/2}\right]$$

$\tau < \frac{1}{2\Omega_0}$: esponenziale decrescente

$\tau > \frac{1}{2\Omega_0}$: oscillazioni smorzate

$$C_v(t) = 1 - \frac{1}{2}\Omega_0^2 t^2 + O(t^4)$$

$\langle |F| \rangle$

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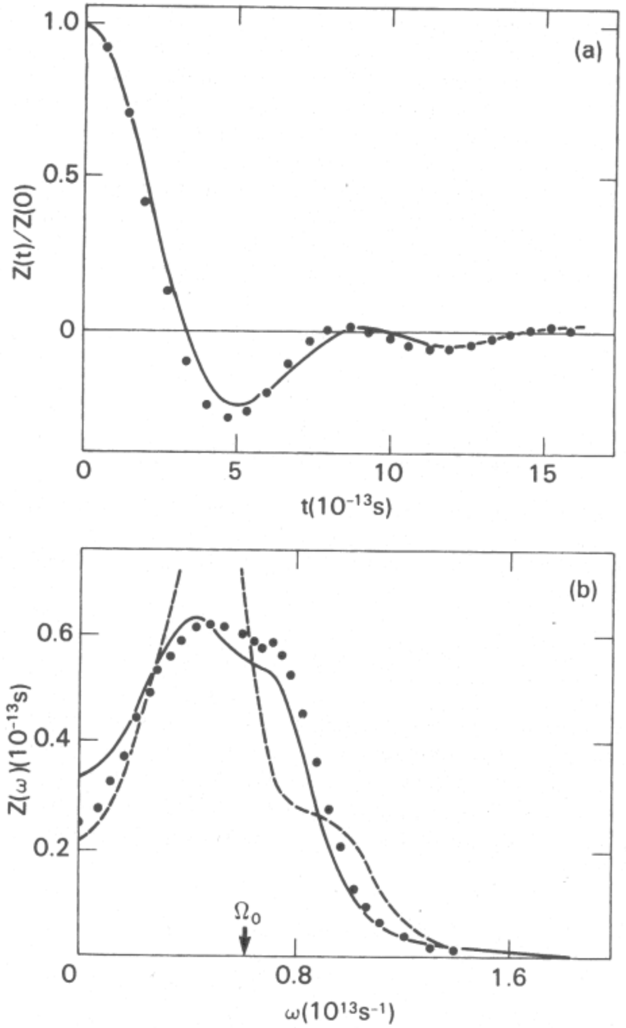

FIG. 9.5. Velocity autocorrelation function (a) and the associated power spectrum (b) of a model of liquid rubidium. The points are molecular dynamics results (Rahman, 1974b), the full curves correspond to the theory of Gaskell and Miller (1978a) (see Eqn (9.5.9)) and the dashed curve in (b) is calculated from the theory of Bosse *et al.* (1978d) (see Eqns (9.5.16)). The low-frequency peak in $Z(\omega)$ arises from the coupling to the transverse current and the shoulder at higher frequencies comes from the coupling to the longitudinal current.

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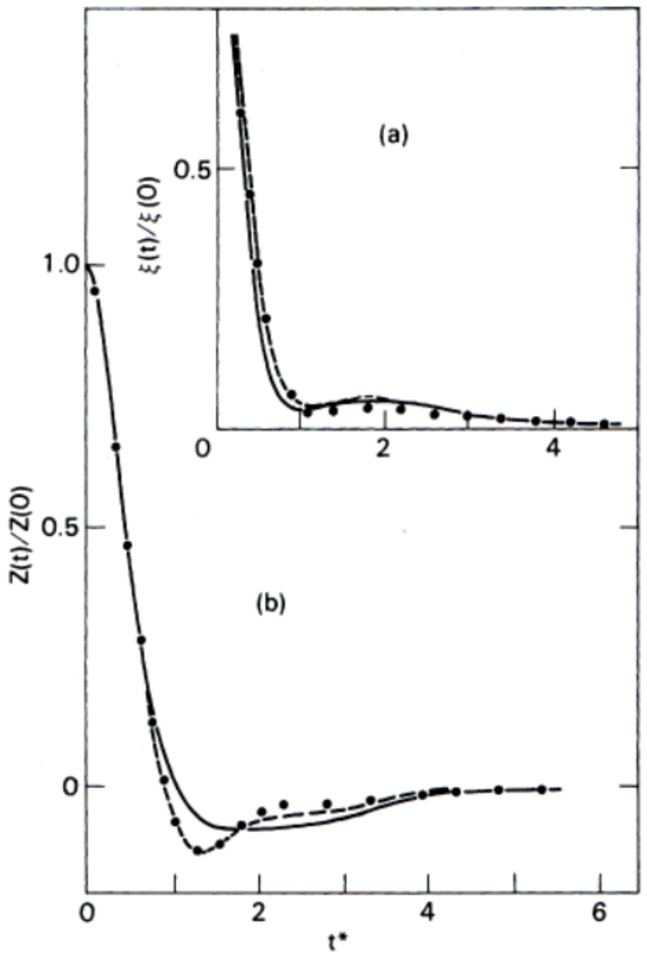

FIG. 9.7. Velocity autocorrelation function and the associated memory function (inset) of the Lennard-Jones fluid near the triple point. The points are molecular dynamics results of Levesque and Verlet (1970), and the curves are calculated from the kinetic theory of Sjögren (1980a) before (full lines) and after (dashed lines) modification of the binary-collision term in the memory function (see text). The unit of time is the quantity τ_0 defined by Eqn (3.3.5). After Sjögren (1980a).