FUNZIONI DI CORRELAZIONE DIPENDENTI DAL TEMPO

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

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

Funzione di correlazione

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

- media d'insieme

$\Gamma(t'')$ = evoluzione di $\Gamma(t')$

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

- 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 di ergodicità

Equilibrio: invarianza traslazione temporale $(t', t'') \to (t = t'' - t', s = t'')$

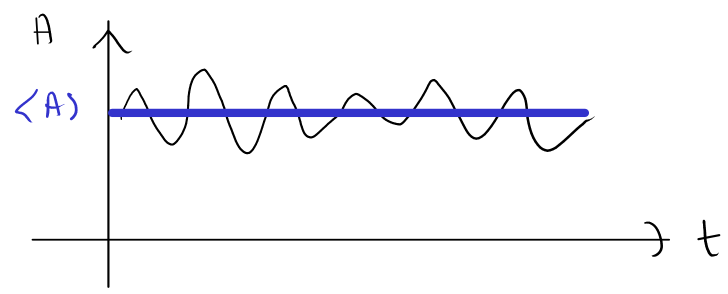
$$C_{AB}(t) = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt_0 \, A(t_0 + s + t) \, B(t_0 + s)$$

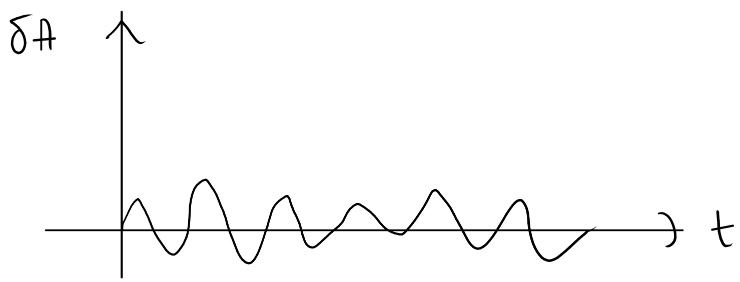
$$= \langle A(s+t) \, B(s) \rangle \underset{s=0}{\overset{\uparrow}{=}} \langle A(t) \, B(0) \rangle$$

casi limite:

$$\lim_{t \to 0} C_{AB}(t) = \langle A B \rangle \quad \text{statica}$$

$$\lim_{t \to \infty} C_{AB}(t) = \langle A \rangle \langle B \rangle \quad ⚠$$



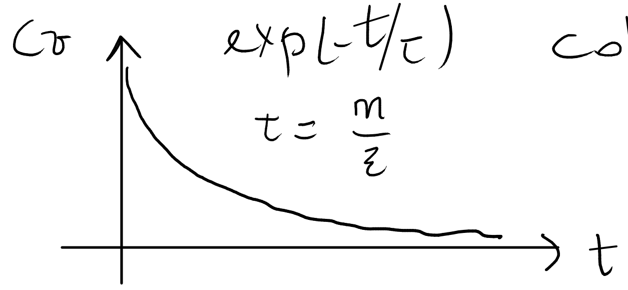


- $C_{AB}(t) = \langle [A(t) - \langle A \rangle][B(0) - \langle B \rangle] \rangle = \langle \delta A(t)\, \delta B(0) \rangle$

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

Es.: VACF funzione di autocorrelazione della velocità

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



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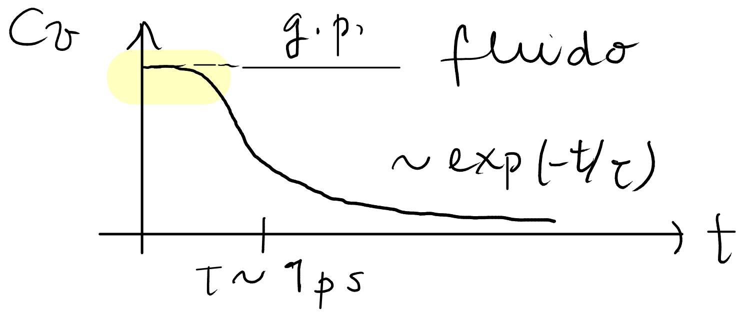
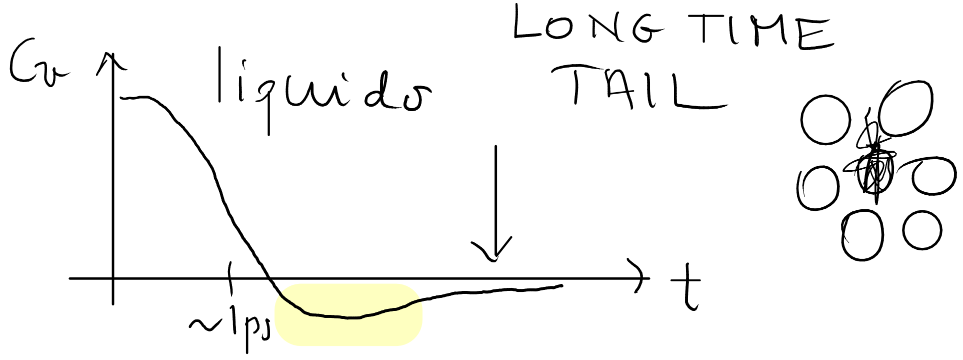




TEORIA DELLA RISPOSTA LINEARE

Caso statico

Hamiltoniana: $H + \Delta H$ $\quad |\Delta H| \ll K_B T$ $\quad \Delta H = -\phi A$ $\quad A = A(\{F\})$

Medie statistiche:

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

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

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

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

$$= \left(\langle A \rangle - \beta\langle A\Delta H\rangle\right)\left(1 + \beta\langle\Delta H\rangle\right)$$

$$= \langle A \rangle + \beta\langle A \rangle\langle \Delta H\rangle - \beta\langle A\Delta H\rangle$$

$$\langle A\rangle_p - \langle A\rangle = -\beta\left[\langle A\,\Delta H\rangle - \langle A\rangle\langle \Delta H\rangle\right] \qquad \Delta H = -\phi A$$

$$= \beta\phi\left[\langle A^2\rangle - \langle A\rangle^2\right]$$

$$\overbrace{\underbrace{\langle A\rangle_p - \langle A\rangle}_{\text{risposta}}}^{\delta\bar{A}} = \beta\phi\underbrace{\langle \delta A^2\rangle}_{\text{fluttuazioni}} + O(\phi^2)$$

Funzione di risposta (suscettibilità)

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

$\langle R_z^2\rangle = \frac{1}{3}a^2 N$

Es: polimero ideale o gaussiano, N+1 monomeri $\vec{R} = \vec{R}_N - \vec{R}_0$; $\langle\vec{R}\rangle = \vec{0}$; $\langle|\vec{R}|^2\rangle = a^2 N$

$\vec{R}$

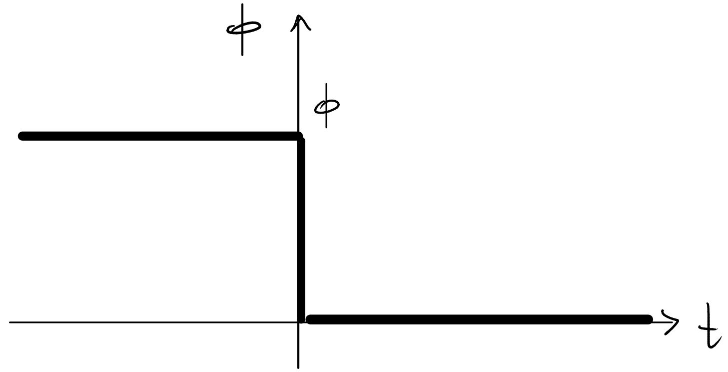
$$\Delta H = -\phi A \qquad \delta\ell \equiv \langle R_z\rangle_p - \underbrace{\langle R_z\rangle}_{=0} = \beta f\langle R_z^2\rangle = \frac{f a^2 N}{3k_B T}$$

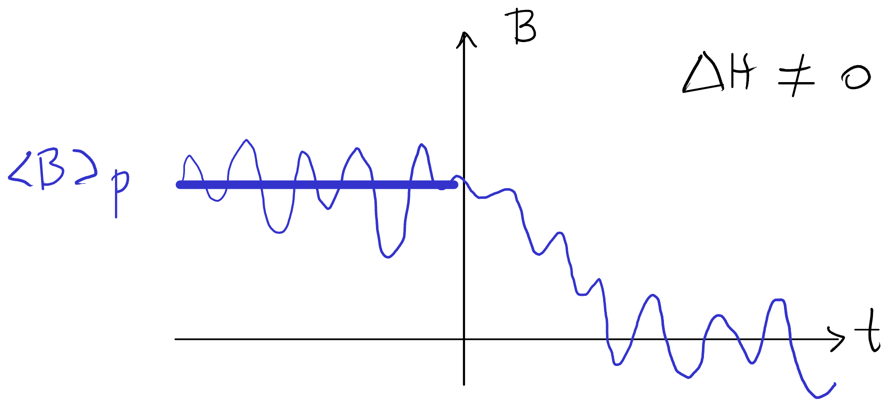
$$\phi = f\,;\; A = R_z \qquad f = \frac{3k_B T}{a^2 N}\,\delta\ell$$

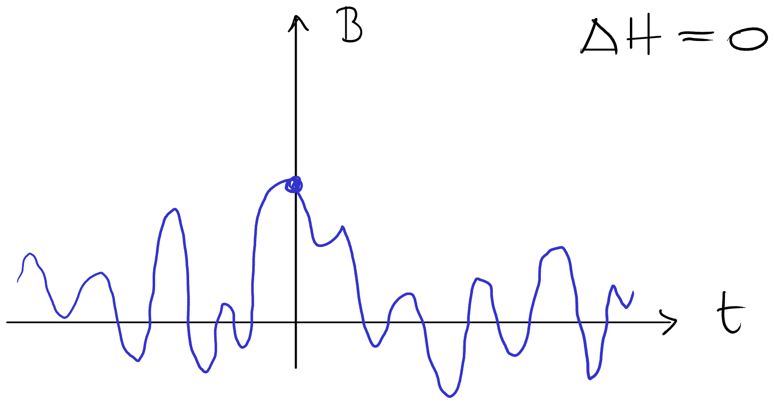
costante elastica "entropica"

Caso dinamico

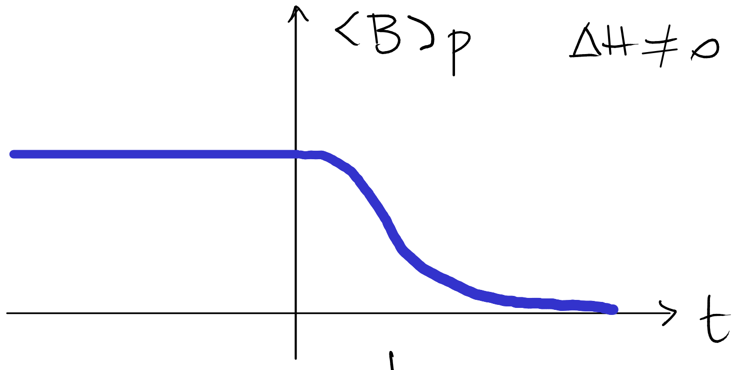
$\Delta H = -\phi(t)\, A \qquad |\Delta H| \ll K_B T \qquad A(\{\vec{r}\})\ ,\ B(\{\vec{r}\})$

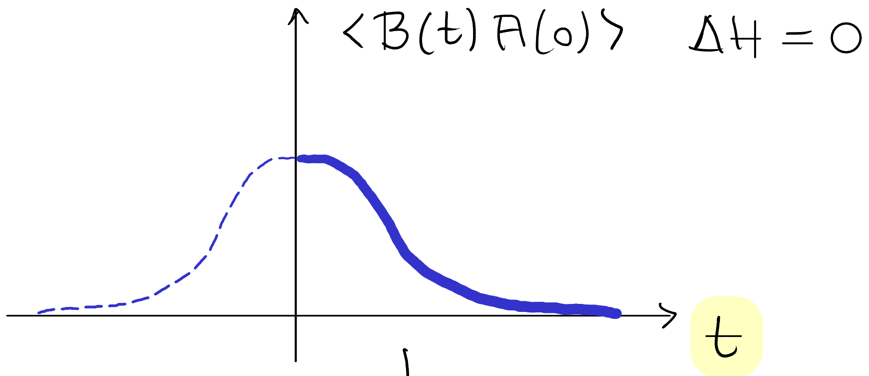






$$\phi(t) = \begin{cases} \phi & t \le 0 \\ 0 & t > 0 \end{cases}$$





rilassamento fuori equilibrio

correlazione all'equilibrio

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

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

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

Regime di risposta lineare:

$$\bar{B}(t) = \ldots \simeq \underbrace{\langle B(t)\rangle}_{\langle B\rangle} - \beta\left[\langle B(t)\,\Delta H\rangle - \underbrace{\langle B(t)\rangle}_{\langle B\rangle}\langle \Delta H\rangle\right] + O\left[(\beta\Delta H)^2\right]$$

$$\delta\bar{B}(t) \equiv \bar{B}(t) - \langle B\rangle \underset{\Delta H = -\phi A(0)}{\overset{\uparrow}{=}} \beta\phi\,[\underbrace{\langle B(t)\,A(0)\rangle - \langle B\rangle\langle A\rangle}_{\langle \delta B(t)\,\delta A(0)\rangle}] = \beta\phi\, C_{BA}(t)$$

Principio di regressione di Onsager:

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

rilassamento fuori equilibrio

correlazione all'equilibrio

tempo di correlazione = tempo di rilassamento

regime lineare

Funzione di risposta

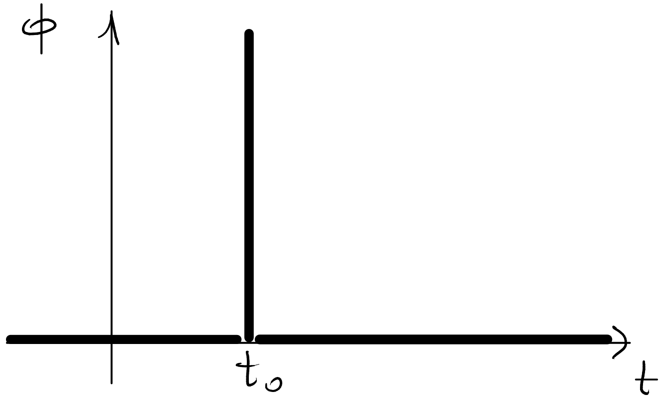
$$\delta \overline{B}(t) = \int_{-\infty}^{\infty} dt' \, \underbrace{\chi_{AB}(t,t')}_{\text{funzione di risposta}} \, \phi(t') \underset{\text{causalità: } t' \leq t}{=} \int_{-\infty}^{t} dt' \, \chi_{AB}(t,t') \, \phi(t')$$

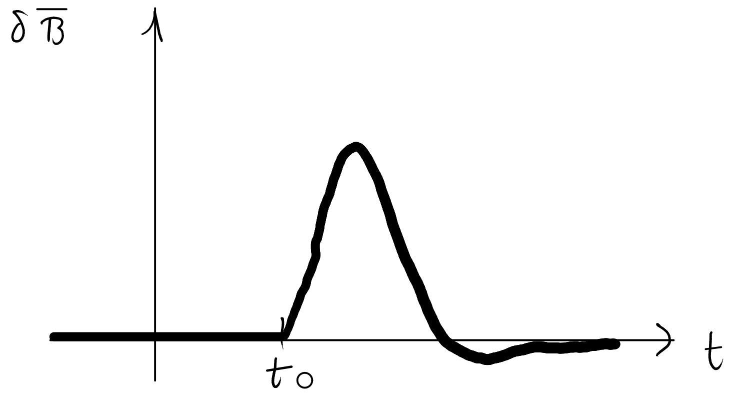
χ_{AB} non dipende da $\phi(t)$ $\Rightarrow$ $\chi_{AB}(t,t')$ è una proprietà del sistema all'equilibrio

$$\Rightarrow \quad \chi_{AB} = \chi_{A}(t-t')$$

$$\delta\overline{B}(t) = \int_{-\infty}^{t} dt' \, \chi_{AB}(t-t')\,\phi(t')$$

Es.: $\phi(t) = \phi_0\,\delta(t-t_0) \qquad \delta\overline{B}(t) = \phi_0\,\chi_{AB}(t-t_0)$





Teorema di fluttuazione - dissipazione

$$\delta\overline{B}(t) = \int_{-\infty}^{t} dt' \, \chi_{AB}(t-t')\,\phi(t') \qquad \phi(t) = \begin{cases} \phi & t \leq 0 \\ 0 & t > 0 \end{cases}$$

$$\delta \overline{B}(t) = \phi \int_{-\infty}^{0} dt' \, \chi_{AB}(t-t') \underset{s = t-t'}{=} \cancel{\phi} \int_{t}^{\infty} ds \, \chi_{AB}(s) = \beta \cancel{\phi} \, C_{BA}(t)$$

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

risposta fluttuazioni

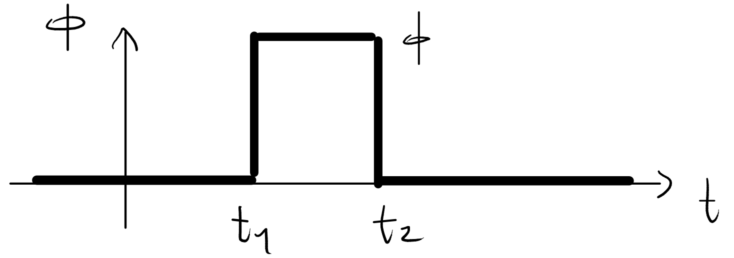
FDT

$$\chi_A(t) = -\beta \frac{dC_A}{dt} \qquad (B = A)$$

Esercizio:

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

$$C_{BA}(t) \simeq C_{AB}(0) \exp(-t/\tau)$$



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

RELAZIONI DI GREEN-KUBO

Macro

Non-equilibrio

↓

Forze termodinamiche + correnti

↓

Coeff. trasporto → Relazioni di Green Kubo

regime lineare ↓ Onsager

Micro

Fluttuazioni

↓

Funzioni di correlazione dinamiche → Relazioni di Green Kubo

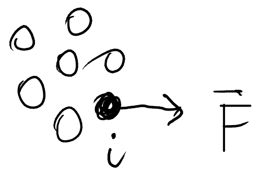
limite idrodinamico

↓

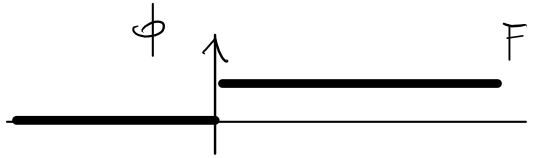
Funzioni di risposta → Relazioni di Green Kubo

regime lineare ↓ teor. di fluttuaz. dissipazione

1) Diffusione / mobilità



$$\Delta H = -\phi(t) A = -\underbrace{F\,\overset{\text{Heaviside}}{\overset{\downarrow}{\theta}}(t)}_{\phi} \cdot \underbrace{x_i(t)}_{A} \qquad \phi(t) = \begin{cases} 0 & t \leq 0 \\ F & t > 0 \end{cases}$$



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

Sistema isotropo $\rightarrow$ moto lungo x

$$B = \frac{dx_i}{dt}$$

$$\begin{cases} \delta \bar{B}(t) = \langle B(t) \rangle_p - \langle B \rangle = \int_{-\infty}^{t} dt' \, \chi_{BA}(t-t')\, \phi(t') \quad (*) \\ \chi_{BA}(t) = -\beta \dfrac{dC_{BA}}{dt} \end{cases}$$

Manipolo la derivata

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

$$= \underbrace{\frac{d}{ds} \langle B(t+s) A(s) \rangle}_{=0} - \left\langle B(t+s) \frac{dA}{ds}(s) \right\rangle$$

$$= - \langle B(t+s) \frac{dA}{ds}(s) \rangle = - \langle B(t) \frac{dA}{ds}(0) \rangle$$

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

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

$$= \beta F \int_0^t dt' \, C_v(t-t') \qquad C_v(t) = \frac{1}{3N} \sum_{i=1}^{N} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle \quad \text{VACF}$$

$$\langle |\Delta \vec{r}|^2 \rangle = 6t \int_0^t \left(1 - \frac{s}{t}\right) C_v(s)\, ds$$

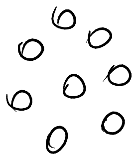
cambio var.: $\tau = t - t'$

$$\langle v_{ix}(t) \rangle_p = - \beta F \int_t^0 d\tau \, C_v(\tau) = \beta F \int_0^t d\tau \, C_v(\tau) \qquad \xrightarrow[t \to \infty]{} 6Dt$$

$$J_{deriva} = \underbrace{\lambda}_{\text{mobilità}} \rho_N F = \rho_N v_d \rightarrow \lambda = \frac{v_d}{F} \qquad \text{equilibrio: } \lambda = \frac{D}{K_B T}$$

$$\lambda = \frac{\langle v_{ix}(\infty) \rangle_p}{F} = \beta \int_0^\infty dt \, C_v(t) \implies \boxed{\underset{\text{coeff. diff.}}{D} = \int_0^\infty dt \, \underset{\text{VACF}}{C_v(t)}}$$

2. Conducibilità elettrica



q_i $\rightarrow \vec{E}$

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

$$\Delta H = -\phi(t)\, A = -\sum_{i=1}^{N} q_i \vec{E}(t)\cdot \vec{r}_i = -\underbrace{\vec{E}(t)}_{\phi}\cdot \underbrace{\left(\sum_{i=1}^{N} q_i \vec{r}_i(t)\right)}_{A}$$

dipolo elettrico totale

$$= -E\left(\sum_{i=1}^{N} q_i x_i(t)\right)$$

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

Sistema isotropo

osservabili micro $\{\vec{r}_i, \vec{p}_i\} \rightarrow \Lambda$

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

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

$$= \beta E \int_0^t dt' \langle \hat{J}_{ex}(t-t')\, \hat{J}_{ex}(0)\rangle = \beta E \int_0^t d\tau\, \overbrace{\langle \hat{J}_{ex}(\tau)\, \hat{J}_{ex}(0)\rangle}$$

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

$$\underbrace{\frac{\langle \hat{J}_{ex}(\infty) \rangle_p}{V}}_{\overline{J}_{ex}} = \underbrace{\frac{\beta}{V} \int_0^\infty dt \, \langle \hat{J}_{ex}(t) \, \hat{J}_{ex}(0) \rangle}_{\substack{\sigma \\ \text{conducibilità} \\ \text{elettrica}}} \cdot \underbrace{E}_{E}$$

$$\frac{1}{3} \langle \vec{\hat{J}}_e(t) \cdot \vec{\hat{J}}_e(0) \rangle$$

$\bar{J}_E = -\kappa_T \bar{\nabla} T$

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

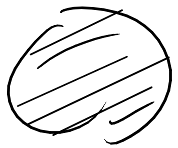
Caso statico

osservabili micro $\{\vec{r}_i, \vec{p}_i\}$

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

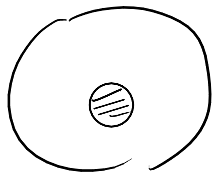
Es: densità micro $a_i = 1$

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



V

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



Σ_0

$$\int_{\Sigma_0^3} d\vec{r}\, \hat{\rho}(\vec{r}) = \begin{cases} 0 \\ 1 \end{cases}$$

Media d'ensemble

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

$$\neq \rho_N(\vec{r})$$

Sistema omogeneo:

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

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

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

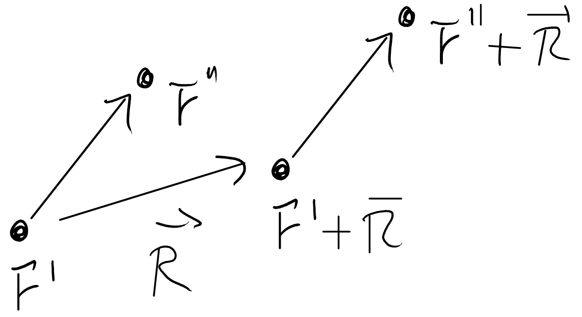
Funzioni di correlazioni

$$C_{AB}(\vec{r}',\vec{r}'') = \langle \hat{A}(\vec{r}')\,\hat{B}(\vec{r}'')\rangle$$

$$C_{AB}(\vec{k}',\vec{k}'') = \langle \hat{A}_{\vec{k}'}\,\hat{B}^{*}_{\vec{k}''}\rangle = \langle \hat{A}_{\vec{k}'}\,\hat{B}_{-\vec{k}''}\rangle$$

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

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



$$\langle \hat{A}(\vec{r})\rangle = A(\vec{r})$$

Simmetrie:

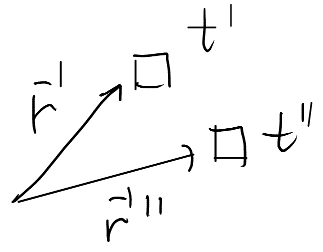
- stazionarietà : $t = t' - t''$
- omogeneità : $\vec{r} = \vec{r}' - \vec{r}''$; $\vec{k} = \vec{k}' = \vec{k}''$
- omogeneità + isotropia : $|\vec{r}|$; $|\vec{k}|$

$$\hat{J}_{ex} = \sum_{i=1}^{N} q_i v_{ix} \qquad \langle \hat{J}_{ex}(t)\, \hat{J}_{ex}(0) \rangle = \sum_{i=1}^{N} q_i^2 \langle v_{ix}(t)\, v_{ix}(0) \rangle$$

$$+ \sum_{i}^{N} \sum_{j \neq i}^{N} q_i q_j \langle v_{ix}(t)\, v_{jx}(0) \rangle$$

FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA

$\hat{\rho}(\vec{r}, t)$ sistema stazionario e omogeneo



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

Caso statico

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

$$\vec{r} = \vec{r}'' - \vec{r}' \quad \Rightarrow \quad \vec{r}'' = \vec{r} + \vec{r}'$$

$$G(\vec{r}) = \frac{1}{N} \int_V d\vec{r}'\, G(\vec{r}', \vec{r}' + \vec{r})$$

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

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

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

funzione di correlazione di coppia

$g(r) \rightarrow$ funzione di distribuzione radiale

Funzioni di correlazione parziali per miscela A-B

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

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

Caso dinamico

$$G(\vec r\,', \vec r\,'', t', t'') \longrightarrow \quad \vec r = \vec r\,'' - \vec r\,' \; ; \quad t = t'' - t'$$

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

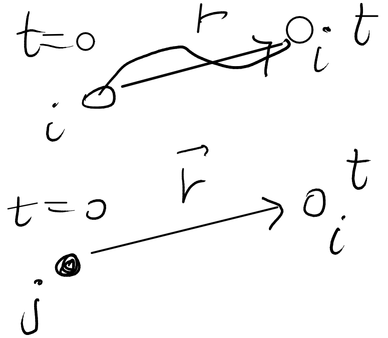
$$G(\bar r, t) = \frac{1}{N} \int_V d\vec r\,' \left\langle \left(\hat\rho(\vec r\,', 0) - \rho\right)\left(\hat\rho(\vec r\,' + \vec r, t) - \rho\right)\right\rangle = \ldots =$$

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

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

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

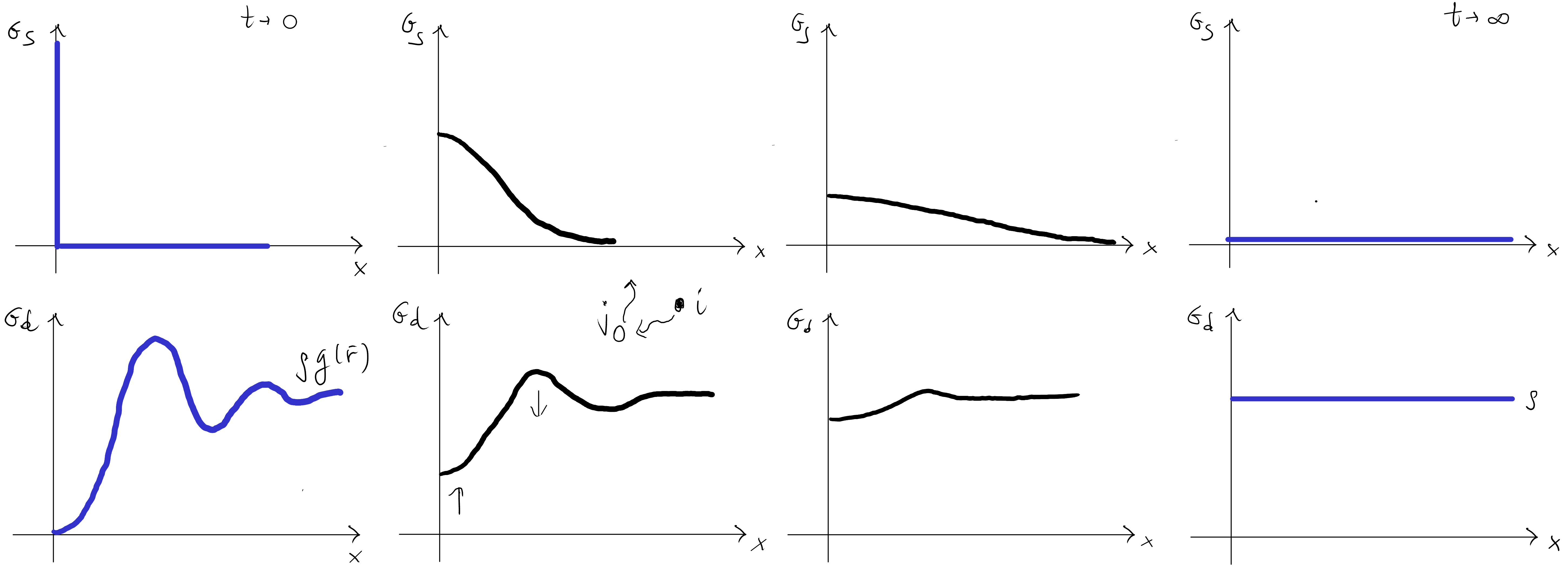
funzione di van Hove



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: SPAZIO DI FOURIER

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

Caso statico

Stazionario, omogeneo $\to$ $\vec{k}$ $\qquad \langle \hat{\rho}_k \hat{\rho}_{-\vec{k}} \rangle \qquad \vec{k}' = \vec{k}'' = \vec{k}$

$S(\vec{k}) = \frac{1}{N} \langle \hat{\rho}_{\vec{k}} \hat{\rho}_{-\vec{k}} \rangle$ **fattore di struttura**

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

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

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

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

$$S(\vec{k}) = 1 + \rho \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \underbrace{[g(\vec{r}) - 1]}_{h(\vec{r})} + \rho\, \delta(\vec{k})$$

Caso dinamico

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

$$F(\vec{k},t) = \frac{1}{N} \langle \hat{\rho}_{\vec{k}}(t)\, \hat{\rho}_{-\vec{k}}(0) \rangle$$ funzione intermedia di scattering

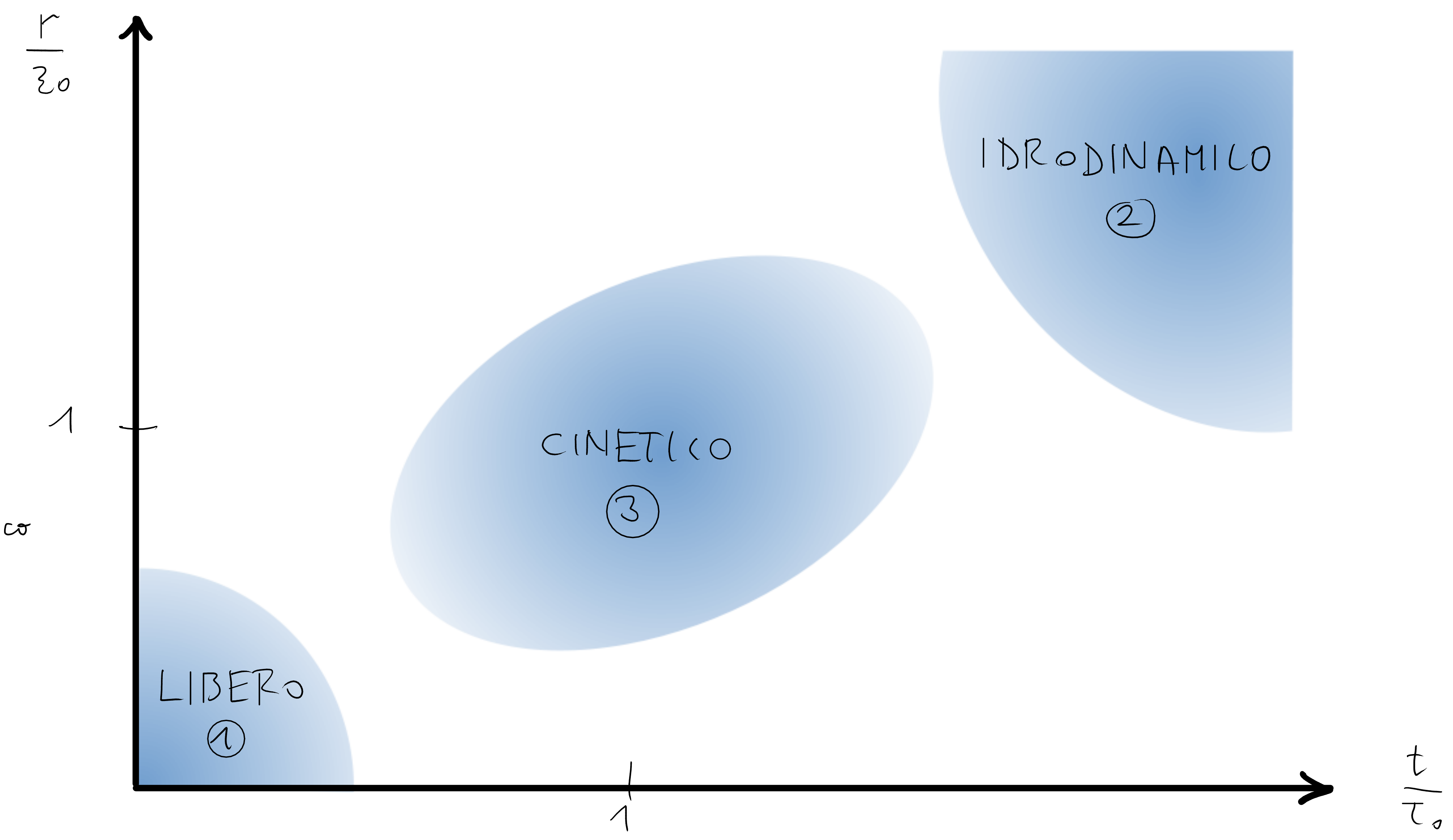
$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, G(\vec{r},t) + \rho\, \delta(\vec{k})$$

$$F_s(\vec{k},t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, G_s(\vec{r},t) \qquad (\text{self})$$

$$= \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{-i\vec{k}\cdot[\vec{r} - (\vec{r}_i(t) - \vec{r}_i(0))]} \right\rangle$$

casi limite: $F(\vec{k},0) = S(\vec{k})$; $F_s(\vec{k},\infty) = F(\vec{k},\infty) = 0$ (ergodico)

REGIMI DINAMICI



ξ_0 distanza interatomica

$\sim 10^{-10}\,m$

τ_0 tempo microscopico

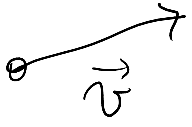
$\sim 10^{-12}\,s$

1 Regime libero

$t \ll \tau_0 \qquad |\bar{r}| \ll \xi_0 \qquad |\bar{k}|\,\xi_0 \gg 1 \qquad \omega\tau_0 \gg 1$

$$\begin{cases} G_d(\bar{r},t) = \rho \\ G_s(\bar{r},t) \sim P_{MB}\left(\frac{\bar{r}}{t}\right) \qquad \bar{r} = \bar{v}\,t \end{cases}$$

gas perfetto

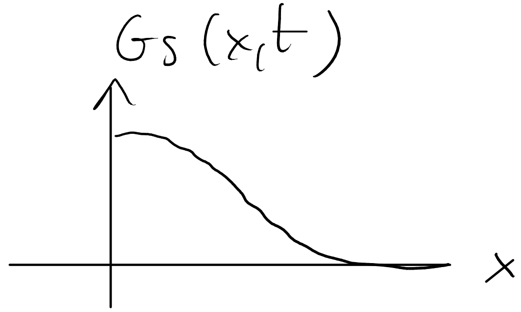


$\vec{r} = \vec{v}\,t$

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

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

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



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

$G(\bar r, t) \to$ f. di van Hove

$F(\bar k, t) \to$ f. intermedia di scattering

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

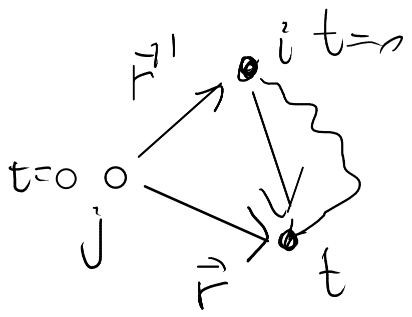
1) libero $r/\xi_0 \ll 1$ $\quad t/\tau_0 \ll 1$

2) cinetico $r/\xi_0 \sim 1$ $\quad t/\tau_0 \sim 1$

3) idrodinamico $r/\xi_0 \gg 1$ $\quad t/\tau_0 \gg 1$

① Libero : $G_d(\bar r, t) = \rho$

$$S(\bar k) = \frac{1}{N}\langle \rho_{\bar k}\, \rho_{-\bar k} \rangle$$



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

$t=0$: densità di prob. di trovare i a distanza $\vec r$ da j $\to \rho\, g(\vec r\,')$

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

approssimazione di Vineyard

$W \approx G_s$

convoluzione

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

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

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

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

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

② Regime idrodinamico

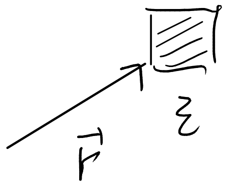
$t/\tau_0 \gg 1 \quad r/\xi_0 \gg 1 \quad k\xi_0 \ll 1$

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

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

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

eq. locale

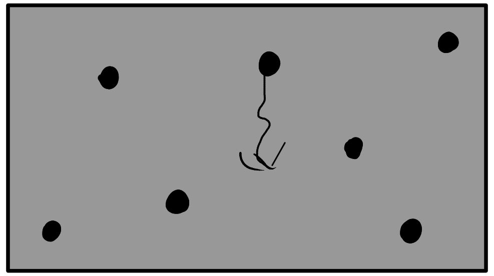


$$\rho_N(\bar{r},t) = \frac{1}{\xi^3}\int_{\xi^3} d\bar{r}'\, \hat{\rho}(\bar{r}'-\bar{r})$$

Ipotesi! $\quad t/\tau_0 \gg 1 \quad k\xi_0 \ll 1$

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

BH 11.5



$N_0 \ll N$ tagged particle dynamics, diluito $\quad \rho_{\bar{k}}(t) = \sum_{i=1}^{N_0} e^{-i\bar{k}\cdot\bar{r}_i(t)}$

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

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

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

NB: $\rho_{N,\bar{k}}$ è la densità di tagged particles (non interagenti)

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

③ Regime cinetico $\quad r/\xi_0 \sim 1 \quad t/\tau_0 \sim 1 \quad k\xi_0 \sim 1$

Approssimazione gaussiana

$$G_S(\bar{r},t) = \left(\frac{\alpha(t)}{\pi}\right)^{3/2} \exp\left(-\alpha(t)\,|\bar{r}|^2\right)$$ α non dipende da $\vec{r}$

regime libero : $\alpha(t) = \dfrac{m}{2K_BT\,t^2}$ $\quad$ regime idrodinamico : $\alpha(t) = \dfrac{1}{4Dt}$

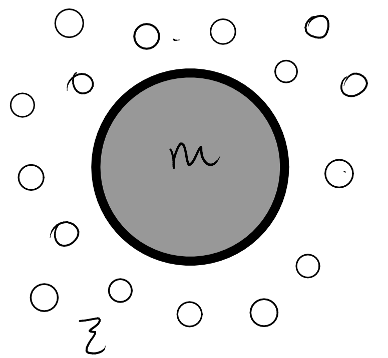
$$\langle|\Delta\bar{r}(t)|^2\rangle = \int d\bar{r}\,|\bar{r}|^2\,G_S(\bar{r},t) = 3\int dx\,x^2\,G_S(x,t)$$ $\leftarrow$ assumo isotropia

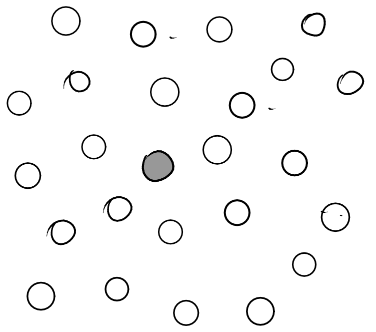
$$= 3\int dx \left(\frac{\alpha(t)}{\pi}\right)^{1/2} x^2 \exp\left(-\alpha(t)\,x^2\right) = \frac{3}{2\alpha(t)}$$

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

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

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. Langevin generalizzata $\longrightarrow$ operatore di proiezione Mori e Zwanzig

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

funzione di memoria

$$\frac{d}{dt}\langle \vec{v}(t)\cdot\vec{v}(0)\rangle = -\frac{1}{m}\int_{-\infty}^{t} dt'\, M(t-t')\,\langle \vec{v}(t')\cdot\vec{v}(0)\rangle + \underbrace{\langle \vec{v}(0)\cdot\vec{\theta}(t)\rangle}_{=0}$$

$$\frac{dC_v}{dt} = -\frac{1}{m}\int_{-\infty}^{t} dt'\, M(t-t')\, C_v(t')$$

Ansatz! $M(t) = M(0)\,e^{-t/\tau}$

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

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

↳ $\langle |\vec{F}| \rangle$, $k_B T$

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

$\tau < \frac{1}{2\Omega_0}$ → esponenziale semplice

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

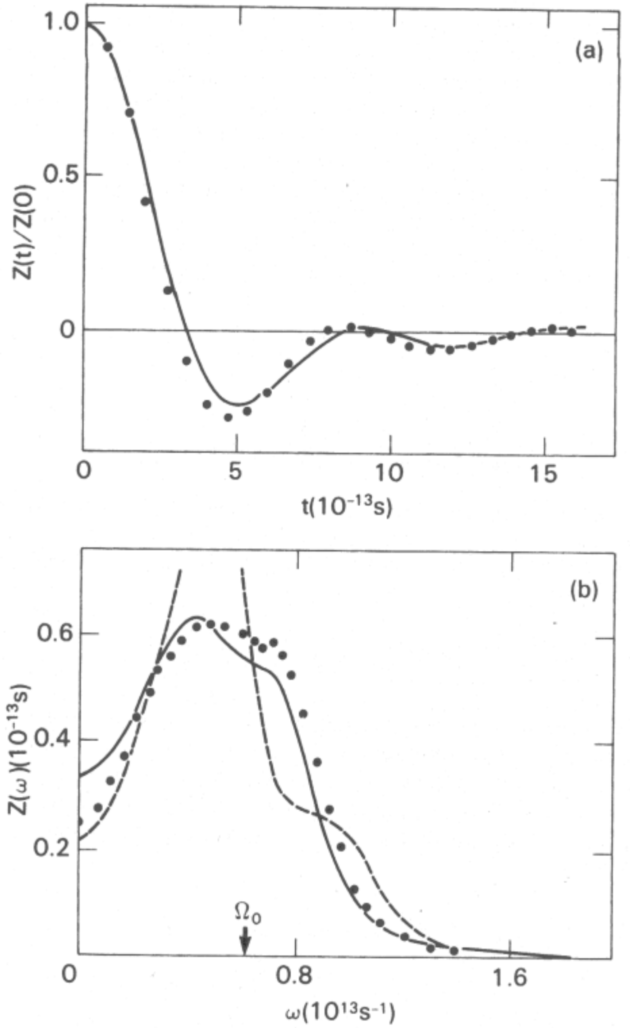


FIG. 9.5. Velocity autocorrelation function (a) and the associated power spectrum (b) of a model of liquid rubidium. The points are molecular dynamics results (Rahman, 1974b), the full curves correspond to the theory of Gaskell and Miller (1978a) (see Eqn (9.5.9)) and the dashed curve in (b) is calculated 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.

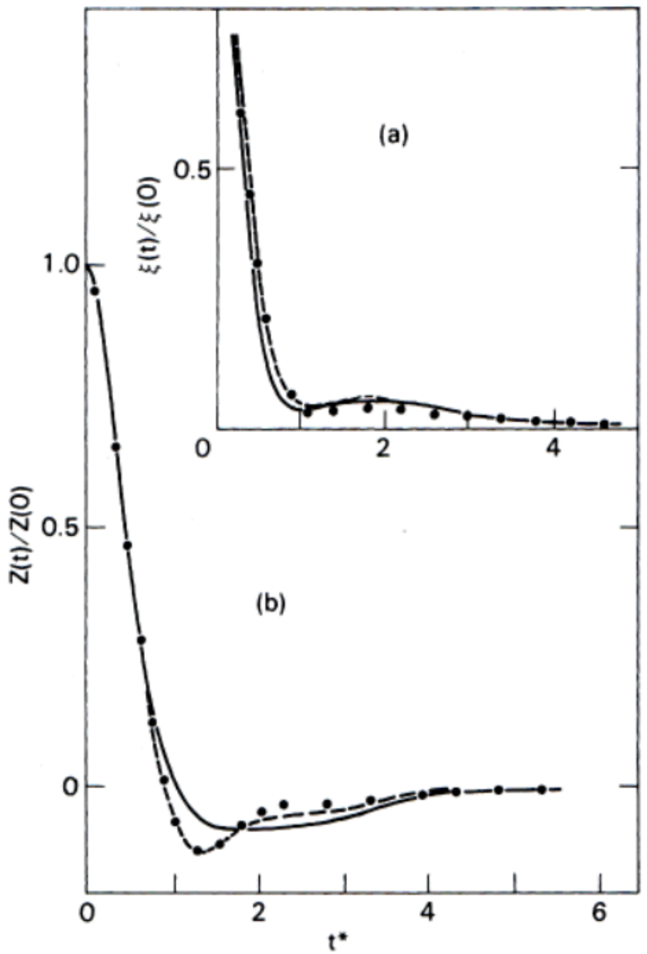


FIG. 9.7. Velocity autocorrelation function and the associated memory function (inset) of the Lennard-Jones fluid near the triple point. The points are molecular dynamics results of Levesque and Verlet (1970), and the curves are calculated from the kinetic theory of Sjögren (1980a) before (full lines) 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).