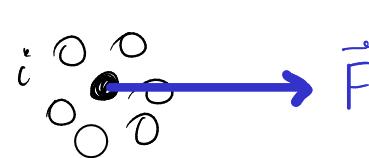


RELAZIONI DI GREEN - KUBO

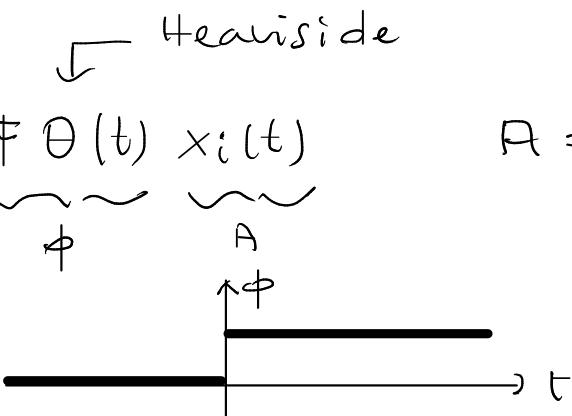
Coefficienti di trasporto \leftrightarrow funzioni di correlazione

1) Diffusione / mobilità



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

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



$$\left\{ \langle B(t) \rangle_p - \langle B \rangle = \int_{-\infty}^t x_{BA}(t-t') \phi(t') dt' = \delta \bar{B}(t) \right.$$

$$\left. \left\{ \begin{aligned} x_{BA}(t) &= -\beta \frac{dC_{BA}}{dt} & \frac{d}{dt} \langle B(t+s) A(s) \rangle &= \langle \frac{dB}{dt}(t+s) A(s) \rangle = \langle \frac{dB}{ds}(t+s) A(s) \rangle \\ && &= -\langle B(t+s) \frac{dA}{ds}(s) \rangle = -\langle B(t) \frac{dA}{ds}(0) \rangle \end{aligned} \right. \right.$$

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

stationarietà

$$\langle v_{ix}(t) \rangle_p = \beta F \int_{-\infty}^t \langle v_{ix}(t-t') v_{ix}(0) \rangle \theta(t') dt' = \beta F \int_0^t \langle v_{ix}(t-t') v_{ix}(0) \rangle dt' \quad \tau = t-t'$$

$$= -\beta F \int_t^0 \langle v_{ix}(\tau) v_{ix}(0) \rangle d\tau = \beta F \underbrace{\int_0^t \langle v_{ix}(\tau) v_{ix}(0) \rangle d\tau}_{\text{funz. autocorrelazione}}$$

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

Velocità per $t \rightarrow \infty$:

$$[J_{\text{deriva}} = \lambda f_N F = f_N \cdot v \rightarrow \lambda = \frac{D}{k_B T}]$$

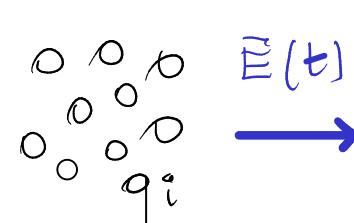
$$\langle v_{ix}(\infty) \rangle_p = \beta F \int_0^\infty C_V(t) dt$$

$$\lambda = \frac{\langle v_{ix}(\infty) \rangle}{F} = \beta \int_0^\infty C_V(t) dt = \beta D \rightarrow D = \int_0^\infty C_V(t) dt$$

↑
mobilità

relazione di Green-Kubo
coeft. di diffusione

2) Condutività elettrica



$$\Delta H = - \sum_{i=1}^N q_i \vec{E}(t) \cdot \vec{r}_i(t) = - \vec{E}(t) \cdot \sum_{i=1}^N q_i \vec{r}_i(t)$$

→ momento di dipolo totale

$$\vec{E} = (E_x, 0, 0) \rightarrow = - \vec{E}(t) \sum_{i=1}^N q_i x_i(t) \rightarrow A = \sum_{i=1}^N q_i x_i(t)$$

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

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

≈ corrente elettrica totale

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

\uparrow funzione di autocorrelazione della corrente elettrica

Corrente elettrica per $t \rightarrow \infty$

$$\underbrace{\frac{\langle \hat{j}_{ex}(0) \rangle}{\sqrt{}}}_{J_e} = \underbrace{\frac{\beta}{\sqrt{}} \int_0^\infty \langle \hat{j}_{ex}(t) \hat{j}_{ex}(0) \rangle dt}_{\sigma} \cdot E \rightarrow \bar{j}_e = \sigma \vec{E}$$

σ

E

condutività elettrica

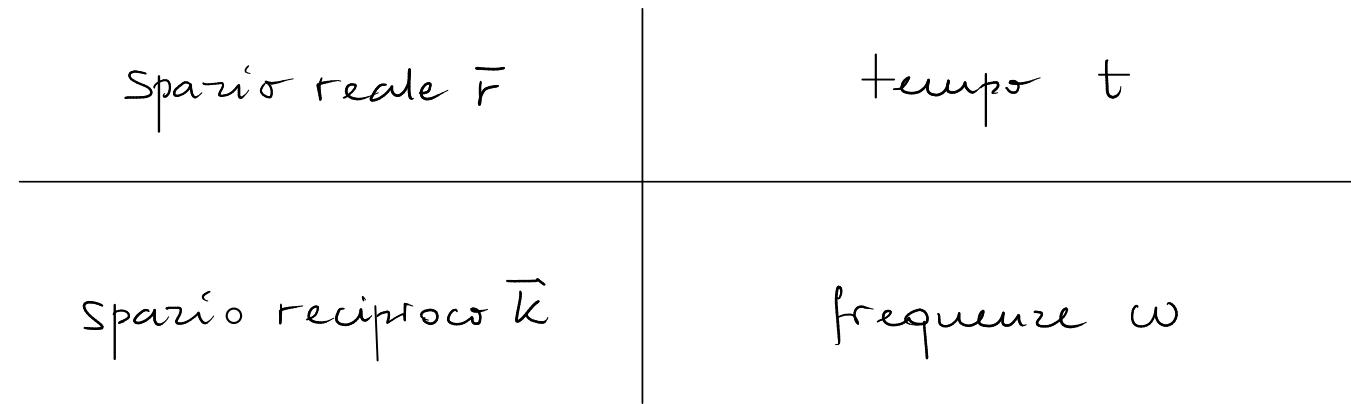
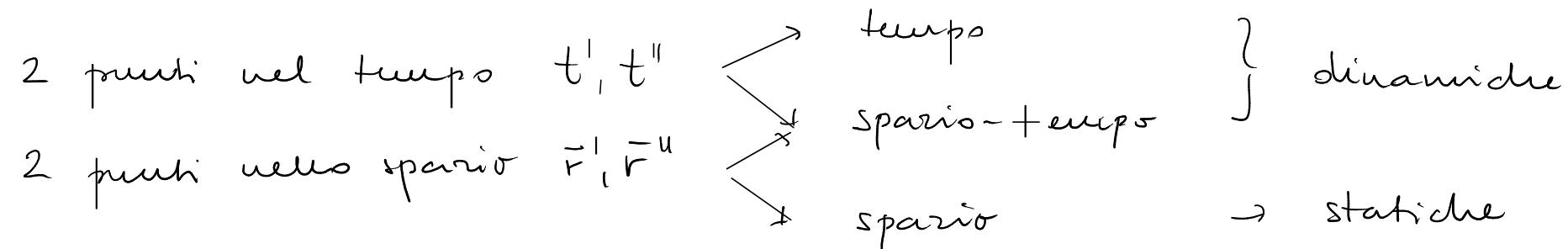
$$\sigma = \frac{\beta}{\sqrt{}} \int_0^\infty \langle \hat{j}_{ex}(t) \hat{j}_{ex}(0) \rangle dt \quad \left(\frac{1}{2} \langle \bar{j}_e(t) \cdot \bar{j}_e(0) \rangle \right) \text{ relazione di Green-Kubo}$$

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

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)
$Vk_B T^2 \lambda$	$J_0^{ez}(t) = \frac{d}{dt} \sum_{i=1}^N z_i(t) \left\{ \frac{1}{2}mu_i^2(t) + \frac{1}{2} \sum_{j \neq i}^N v[r_{ij}(t)] \right\}$	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 .

FUNZIONI DI CORRELAZIONE DIPENDENTI DALLO SPAZIO E DAL TEMPO



Caso statico

Osservabili $\rightarrow \{\vec{r}_i, \vec{p}_i\}$ microscopiche

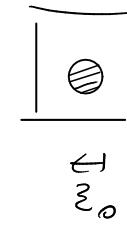
$$\hat{A}(\vec{r}) = \sum_{i=1}^N a_i \delta(\vec{r} - \vec{r}_i) \quad \hat{A}_{\vec{k}} = \int A(\vec{r}) e^{-i\vec{k} \cdot \vec{r}} d\vec{r} = \sum_{i=1}^N a_i e^{-i\vec{k} \cdot \vec{r}_i}$$

Ese: densità microscopica $a_i = 1$

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



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



$$\int_{V_0} \hat{g}(\vec{r}) d\vec{r} = 1$$

Media statistica

$$\langle \hat{g}(\vec{r}) \rangle = g(\vec{r}) \text{ densità locale} \leftrightarrow g_N(\vec{r})$$

Sistema omogeneo

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

Caso dinamico

$$\vec{r}_i \rightarrow \vec{r}_i(t) \quad \vec{p}_i \rightarrow \vec{p}_i(t)$$

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

Ese: densità microscopica

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

$$\rightarrow \frac{\partial \hat{g}}{\partial t} + \vec{\nabla} \cdot \vec{j} = 0 \quad \text{eq. continuità}$$

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

corrente microscopica

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

Funzioni di correlazione

$\rightarrow \delta A, \delta B$

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

$$C_{AB}(\vec{k}', \vec{k}'') = \langle A_{\vec{k}'} B_{\vec{k}''}^* \rangle = \langle A_{\vec{k}'} B_{-\vec{k}''} \rangle$$

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

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

Simmetrie

- stazionarietà : invarianza traslazione temporale $\rightarrow t = t' - t''$
- omogeneità : $\rightarrow \vec{r} = \vec{r}' - \vec{r}''$ invarianza spaziale $\rightarrow \vec{k} = \vec{k}' - \vec{k}''$
- isotropia : invarianza rotazionale $\rightarrow |\vec{r}|, |\vec{k}|$