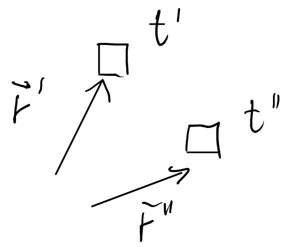
FUNZIONI DI CORRELAZIONE DELLA DENSITÀ MICROSCOPICA



sistema omogeneo $\to \vec{r}$

stazionario $\to t$

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

Caso statico

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

$$\vec{r}', \ \vec{r} = \vec{r}'' - \vec{r}' \to \vec{r}'' = \vec{r}' + \vec{r}$$

$$G(\vec{r}) = \frac{1}{N}\int_V d\vec{r}'\, G(\vec{r}', \vec{r}' + \vec{r}) = \frac{1}{N}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N} \int d\vec{r}'\, \delta(\vec{r}' - \vec{r}_j)\, \delta(\vec{r}' + \vec{r} - \vec{r}_i) \right\rangle - \underbrace{\frac{\rho^2}{N}V}_{\rho}$$

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

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

miscele

$g_{\alpha\beta}(\vec{r})$

$\uparrow$

$\leftarrow$ funzione di distribuzione di coppia o radiale

$g(r)$

$$= \rho\,[g(\vec{r}) - 1] + \delta(\vec{r})$$

Caso dinamico

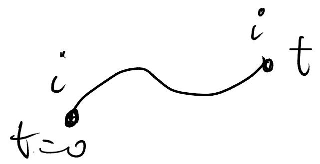
stazionario $t = t'' - t'$

$$G(\vec r, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \int d\vec r' \, \delta(\vec r - \vec r_j(0)) \, \delta(\vec r' + \vec r - \vec r_i(t)) \right\rangle - \rho \qquad G(\vec r', \vec r'', t', t'')$$

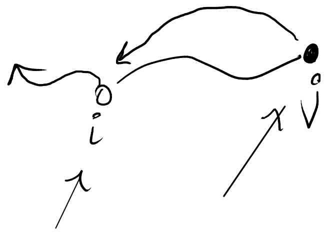
$$= \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\vec r - (\vec r_i(t) - \vec r_j(0))) \right\rangle - \rho$$

$$= G_s(\vec r, t) + G_d(\vec r, t) - \rho \quad \rightarrow \text{ f. correlazione di van Hove}$$

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



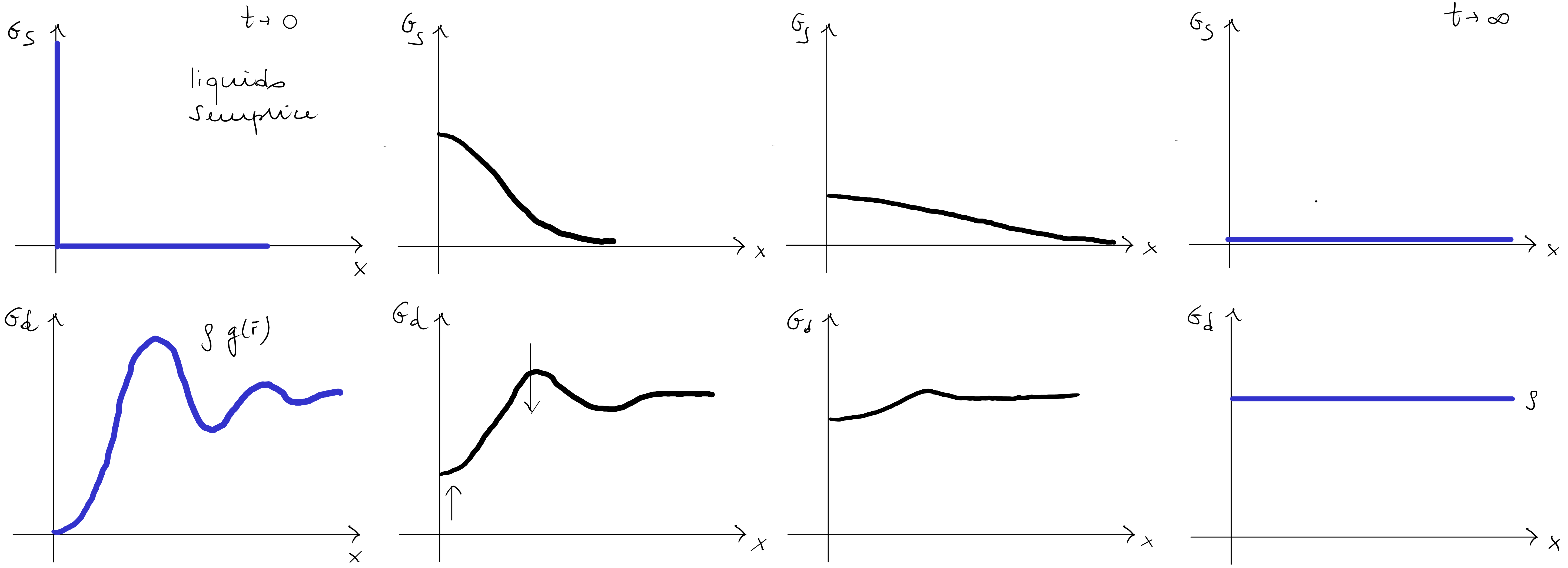
$$G_d(\vec r, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} {\sum_{j=1}^{N}}' \delta(\vec r - (\vec r_i(t) - \vec r_j(0))) \right\rangle \quad \rightarrow \text{ distinct}$$



Casi limite

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

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



FUNZIONI DI CORRELAZIONE DELLA DENSITÀ: SPAZIO DI FOURIER

Esperimenti: scattering neutroni → FT di G_s e G_d → $\vec{k}, \omega$ — liquidi atomici e molecolari

spin echo → $\vec{k}, t$

dynamic light scattering → $\vec{k}, t$ — colloidi

confocal microscopy → $\vec{r}, t$

Caso statico

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

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

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

$$G(\vec{r}) = \frac{1}{N} \int d\vec{r}\,' \left[\langle \hat{\rho}(\vec{r}\,') \hat{\rho}(\vec{r}\,' + \vec{r}) \rangle - \rho^2 \right]$$

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

cambio variabili $\vec{r} = \vec{r}\,' - \vec{r}\,''$, $\vec{r}\,'$ (sistema omogeneo)

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

$$= \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} \left[G(\vec{r}) + \frac{1}{N} \rho^2 \right] = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}} G(\vec{r}) + \underbrace{N\rho\,\delta(\vec{k})}_{\text{irrilevante}}$$

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

$$G(\vec{r}) = \rho \left[g(\vec{r}) - 1 \right] + \delta(\vec{r}) \qquad h(\vec{r}) = g(\vec{r}) - 1 \quad \text{funzioni di correlazione totale}$$

Caso dinamico stazionario $t', t'' \rightarrow t = t'' - t'$

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

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

funzione intermedia di scattering (coerente)

$$F_s(\vec{k}, t) \equiv \frac{1}{N} \left\langle \sum_{i=1}^{N} e^{-i\vec{k}\cdot(\vec{r}_i(t) - \vec{r}_i(0))} \right\rangle \quad \text{self (incoerente)}$$

Casi limite

$$F(\vec{k}, t \to 0) = S(\vec{k}) \qquad F(\vec{k}, t \to \infty) = F_s(\vec{k}, t \to \infty) = 0 \quad \text{ergodico (liquido)}$$

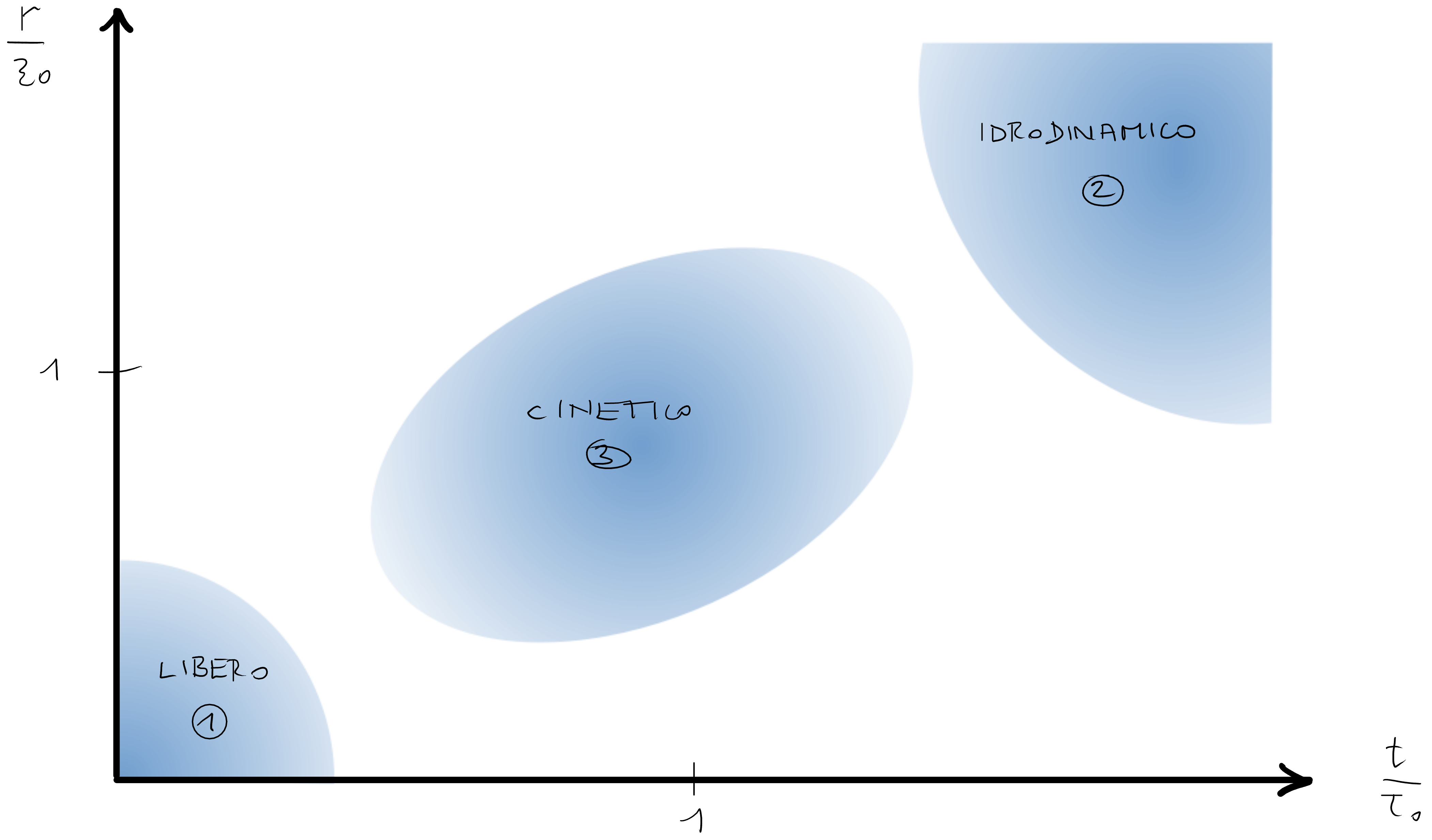
REGIMI DINAMICI

ξ_0 distanza interatomica

$\sim 10^{-10}$ m

τ_0 tempo microscopico

$\sim 10^{-12}$ s



Regime libero

$r/\xi_0 \ll 1 \qquad t/\tau_0 \ll 1 \qquad k\xi_0 \gg 1 \qquad \omega\tau_0 \gg 1$

→ gas perfetto

$$\begin{cases} G_d(\bar r, t) = \rho \\ G_s(\vec r, t) \sim p(\vec v) \text{ con vincolo } \vec r = \vec v t \end{cases}$$

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

$$G(\vec r,t) = G_s(\vec r,t) + G_d(\vec r,t) - \rho = G_s(\vec r,t)$$

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