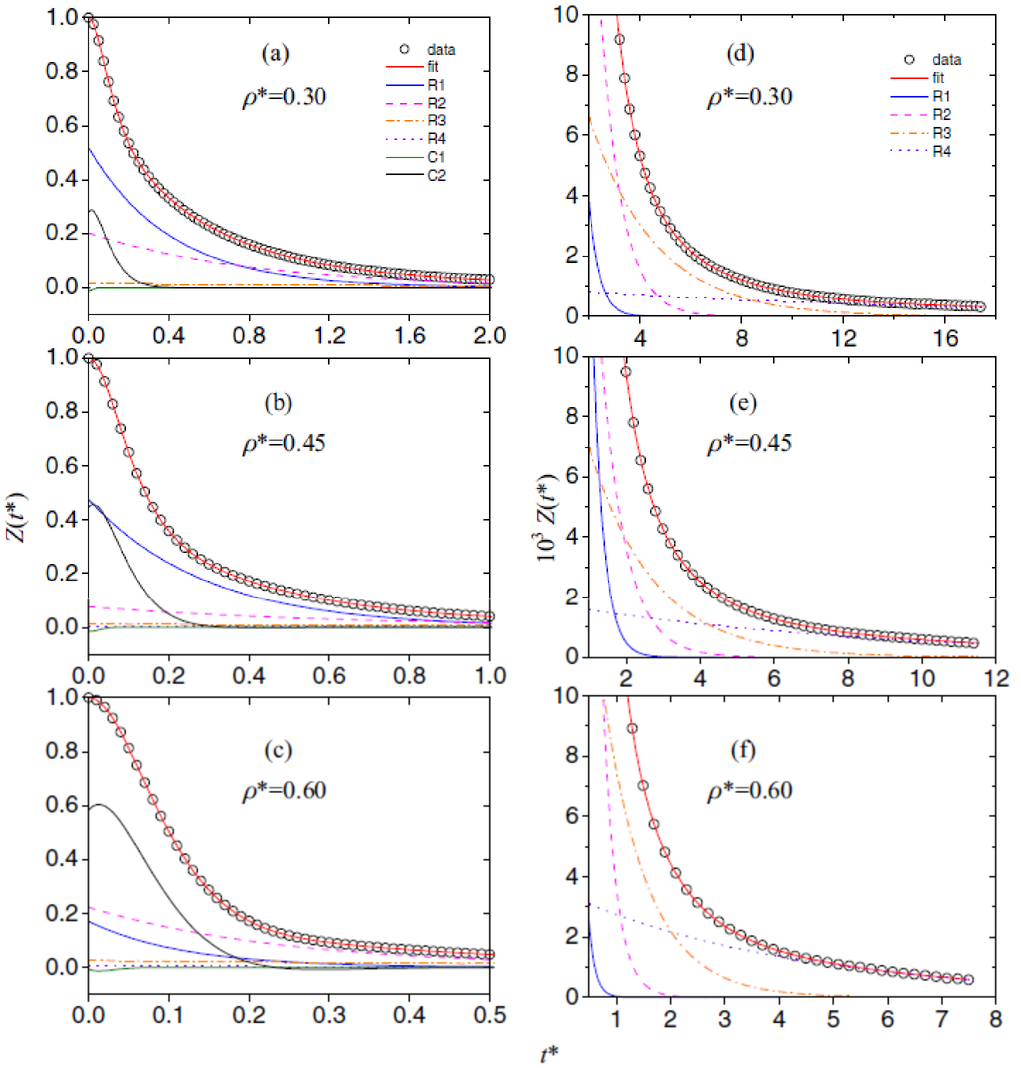
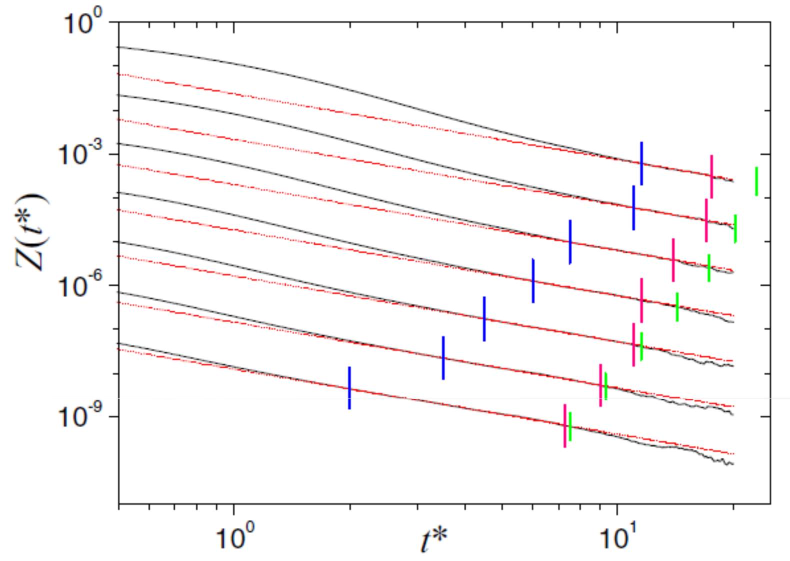
# VACF normalizzata

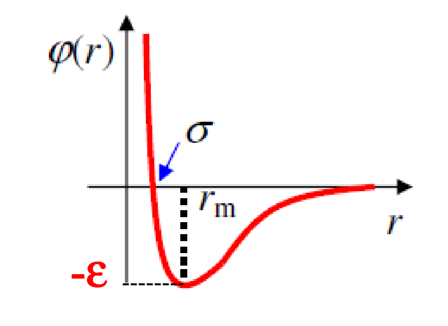



## Long time tail phenomenon

## (Vortici nei fluidi)



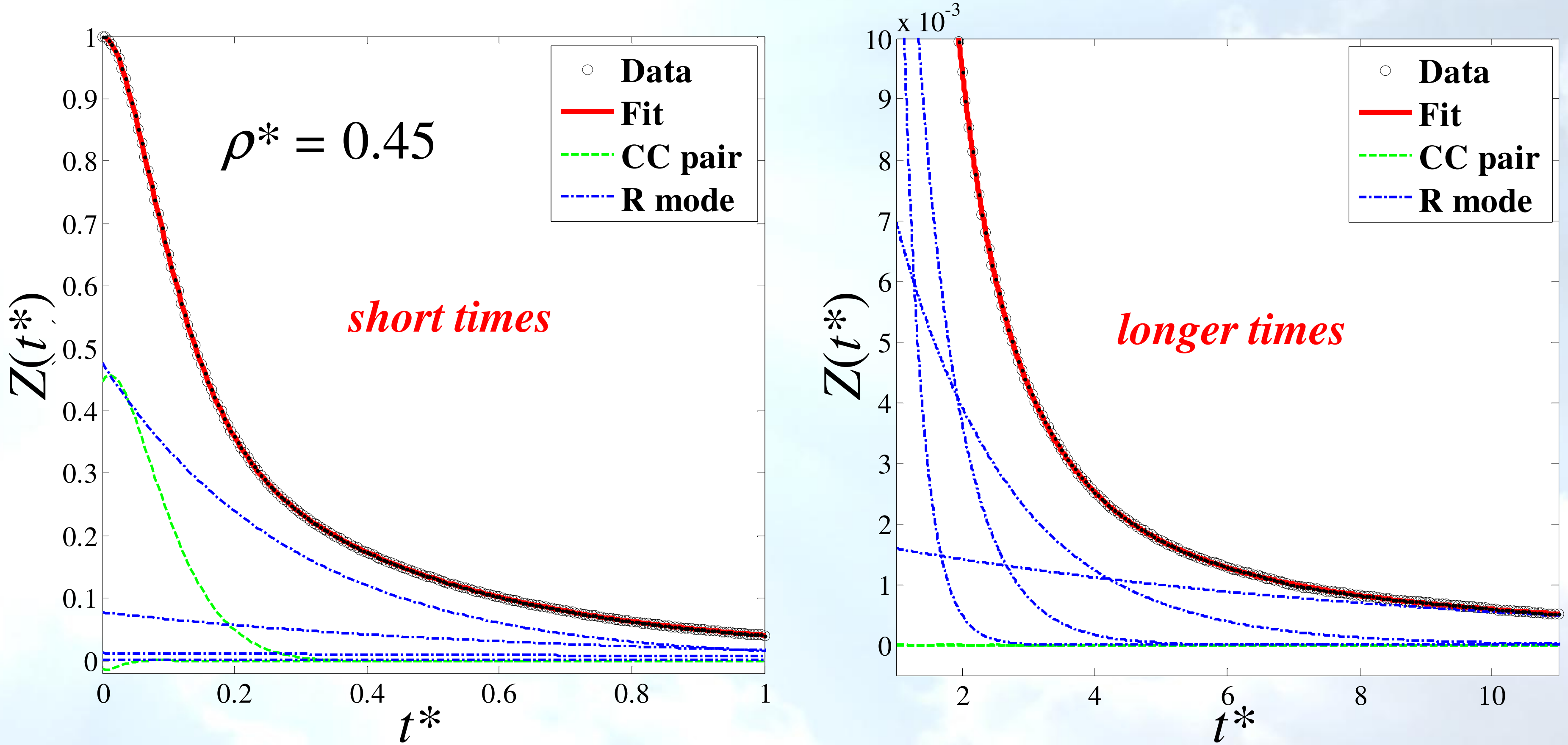

$$t^* = t/\sqrt{m\sigma^2/\epsilon}$$




$$\frac{\langle \boldsymbol{v}(0)\cdot\boldsymbol{v}(t)\rangle}{\langle v(0)^2\rangle} \quad con \ \ valore \ \ iniziale \ \langle v(0)^2\rangle = \frac{2}{m}E_K = \frac{2}{m}\frac{3}{2}k_BT = \frac{3k_BT}{m}$$

# Velocity Autocorrelation Function of a LJ fluid

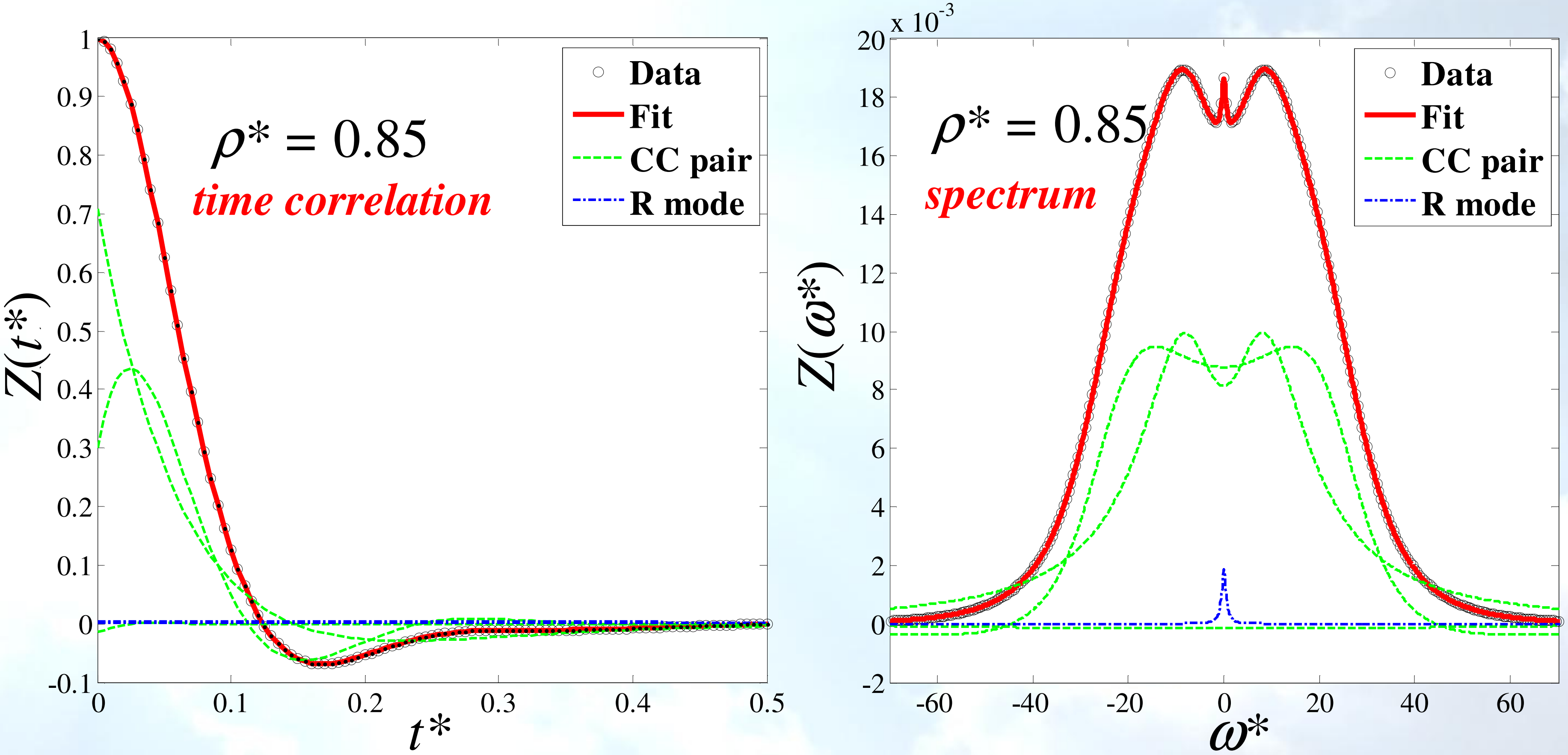
## Gaseous low-density ($\rho^* = 0.45$) state at $T \gtrsim T_c$




**4 Real modes + 4 Complex modes (2 CC pairs)**

# VACF & spectrum of a LJ fluid

## Liquid high-density ($\rho^* = 0.85$) state at $T \gtrsim T_c$




**2 Real modes + 6 Complex modes (3 CC pairs)**

# Spostamento quadratico medio

$$\delta r^2(t)=\left\langle\left[\boldsymbol{R}_\alpha(t)-\boldsymbol{R}_\alpha(0)\right]^2\right\rangle=\frac{1}{N}\sum_{\alpha=1}^{N}\left\langle\left[\boldsymbol{R}_\alpha(t)-\boldsymbol{R}_\alpha(0)\right]^2\right\rangle=\int d\boldsymbol{r}\;\; r^2\,\frac{1}{N}\sum_{\alpha=1}^{N}\left\langle\delta\left[\boldsymbol{r}-\left(\boldsymbol{R}_\alpha(t)-\boldsymbol{R}_\alpha(0)\right)\right]\right\rangle=\int d\boldsymbol{r}\, r^2\;\, G_{self}(r,t)$$

Infatti avevamo

$$G(\boldsymbol{r},t)=\frac{1}{N}\int d\boldsymbol{r}_1\left\langle\rho(\boldsymbol{r}_1,t_1)\rho(\boldsymbol{r}_1+\boldsymbol{r},t_1+t)\right\rangle=\frac{1}{N}\int d\boldsymbol{r}_1\sum_{\alpha=1}^{N}\;\sum_{\beta=1}^{N}\;\left\langle\delta\left(\boldsymbol{r}_1-\boldsymbol{R}_\alpha(t_1)\right)\delta\left(\boldsymbol{r}_1+\boldsymbol{r}-\boldsymbol{R}_\beta(t_1+t)\right)\right\rangle$$

$$per\;\;\alpha=\beta\;\;diventa\;\;(t_1=0)$$

$$G_{self}(\boldsymbol{r},t)=\frac{1}{N}\int d\boldsymbol{r}_1\sum_{\alpha=1}^{N}\;\left\langle\delta\left(\boldsymbol{r}_1-\boldsymbol{R}_\alpha(0)\right)\delta\left(\boldsymbol{r}_1+\boldsymbol{r}-\boldsymbol{R}_\alpha(t)\right)\right\rangle=\frac{1}{N}\sum_{\alpha=1}^{N}\;\left\langle\delta\left(\boldsymbol{R}_\alpha(0)+\boldsymbol{r}-\boldsymbol{R}_\alpha(t)\right)\right\rangle$$

In regime idrodinamico (diffusivo) sappiamo che $F^{diff}{}_{self}(\boldsymbol{Q},t)=e^{-DQ^2|t|}$ allora

$$G_{self}(\boldsymbol{r},t)=\frac{1}{(2\pi)^3}\int d\boldsymbol{Q}\;\; e^{-i\boldsymbol{Q}\cdot\boldsymbol{r}}\;\; e^{-DQ^2|t|}$$

svolgendo l'integrale in coordinate sferiche

$$G_{self}(\boldsymbol{r},t)=\frac{1}{(2\pi)^3}(2\pi)\int_0^{+\infty}dQ\int_0^{\pi}d\theta\; Q^2\;\; e^{-iQr\cos\theta}\;\; e^{-DQ^2|t|}$$

e sfruttando il cambiamento di variabile η=cosθ

$$G_{self}(\boldsymbol{r},t)=\frac{1}{(2\pi)^2}\int_0^{+\infty}dQ\;Q^2\,e^{-DQ^2|t|}\;\int_{-1}^{1}d\eta\;\;\; e^{-iQr\eta}=\frac{1}{(2\pi)^2}\int_0^{+\infty}dQ\;Q^2\,e^{-DQ^2|t|}\,2\frac{\sin Qr}{Qr}=\cdots=\left(\frac{1}{4\pi\;D\;|t|}\right)^{\frac{3}{2}}e^{-\frac{r^2}{4D|t|}}$$

Dunque in regime idrodinamico (diffusivo) vale $\delta r^2(t>>\tau)=\int d\boldsymbol{r}\;\; r^2\, G_{self,diff}(r,t)=6\,D|t|$

# Spostamento quadratico medio e diffusione e VACF

Con vari calcoli si può anche dimostrare che in regime idrodinamico vale

$$\delta r^2(t >> \tau) = 2\left[\int_0^{+\infty} dt' \,\langle \boldsymbol{v}_\alpha(0)\cdot \boldsymbol{v}_\alpha(t')\rangle\right] t = 6\,D\,t$$

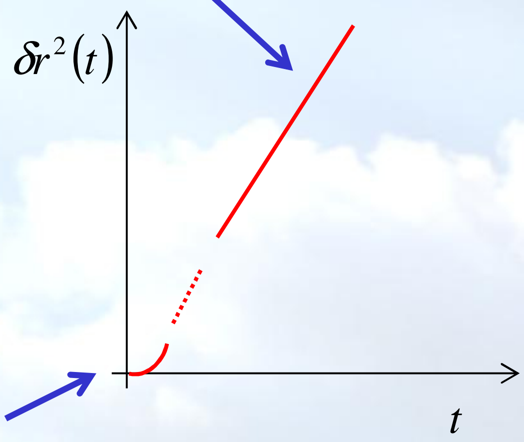
da cui l'importante relazione

$$D = \frac{1}{3}\left[\int_0^{+\infty} dt' \,\langle \boldsymbol{v}_\alpha(0)\cdot \boldsymbol{v}_\alpha(t')\rangle\right]$$

Questo è uno degli esempi più semplici di *relazioni di Green-Kubo*, ovvero relazioni che legano coefficienti di trasporto all'integrale di una opportuna funzione di correlazione temporale

Più in generale vale

$$D(t) = \frac{1}{3}\left[\int_0^{t} dt' \,\langle \boldsymbol{v}_\alpha(0)\cdot \boldsymbol{v}_\alpha(t')\rangle\right] \xrightarrow[t\to\infty]{} D$$




A tempi brevi, cioè in regime cinetico vale

$$\delta r^2(t << \tau) = \left\langle \left[\boldsymbol{R}_\alpha(t) - \boldsymbol{R}_\alpha(0)\right]^2 \right\rangle \cong \left\langle \left[\boldsymbol{v}_\alpha(0)t\right]^2 \right\rangle = \left\langle v_\alpha(0)^2 \right\rangle t^2 = \frac{3k_BT}{m} t^2$$