$G(\bar r, t) \rightarrow$ f. corr. van Hove

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

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

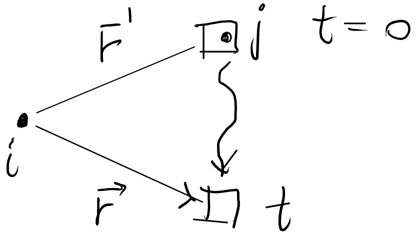
1) libero $\quad r/\xi_0 \ll 1 \quad t/\tau_0 \ll 1$

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

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

$t=0$: $\quad G_d(\bar r, 0) = \rho\, g(\bar r)$

prob. di uno spost. $\bar r$ dopo t della particella j $\quad \rho\, g(\bar r') \cdot W(\vec r - \bar r', t)$



<u>Approssimazione di Vineyard</u> (~ 58) : $\quad W(\bar r - \bar r', t) \approx G_s(\bar r - \bar r', t)$

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

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

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

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

$\uparrow$

$\bar k \neq 0$

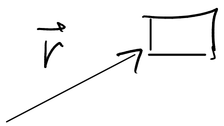
$\downarrow$

$$F(\bar k, t) = F_s(\bar k, t) + (S(\bar k) - 1)\, F_s(\bar k, t) = S(\bar k)\, F_s(\bar k, t)$$

2) Regime idrodinamico $r/\xi_0 \gg 1$ $k\xi_0 \ll 1$ $t/\tau_0 \gg 1$

variabili idrodinamiche : eq. continuità + eq. costitutiva   es. $\rho_N(\bar r,t) \to D$

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



$v = dx\,dy\,dz$

$$\rho_N(\bar r,t) = \frac{1}{v}\int_v d\bar r'\,\hat\rho(\bar r'-\bar r)$$

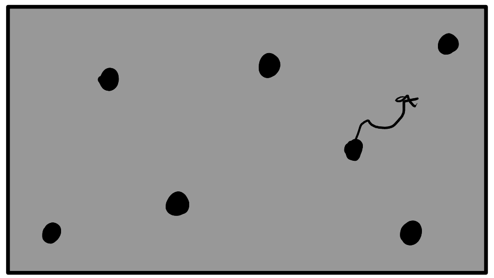
$$\rho_{N,\bar k}(t) = \int e^{-i\bar k\cdot\bar r}\,\rho_N(\bar r,t)\,d\bar r \qquad |\bar k| \lesssim \frac{2\pi}{v^{1/3}}$$

$$\langle \rho_{N,\bar k}(t)\,\rho_{N,-\bar k}(0)\rangle \underset{\uparrow}{=} \lim_{\substack{k\xi\ll 1\\ t/\tau_0\gg 1}} \langle \hat\rho_{\bar k}(t)\,\rho_{-\bar k}(0)\rangle \quad \to \quad \text{BH } 11.5$$

$$\bar J_N = -D\,\bar\nabla\rho_N$$

$$\frac{\partial\rho_N}{\partial t} = -\nabla\cdot(-D\,\bar\nabla\rho_N) = D\nabla^2\rho_N$$

Dinamica singola particella $\to$ $G_s(\bar r,t)$, $F_s(\bar k,t)$



$N_0 \ll N$ $\to$ regime diluito : $\rho_N(\bar r,t) \longrightarrow \dfrac{\partial\rho_N}{\partial t} = D\nabla^2\rho_N$

$\uparrow$

"tagged particles"

$$\rho_{N,\bar k}(t) = \rho_{N,\bar k}(0)\,e^{-D|\bar k|^2 t}$$

$$\underbrace{\frac{1}{N_0} \langle \rho_{N,\bar{k}}(t)\, \rho_{N,-\bar{k}}(0) \rangle}_{\substack{\lim \\ k\xi_0 \ll 1 \\ t/\tau_0 \gg 1} F_s(\bar{k},t)} = \underbrace{\frac{1}{N_0} \langle \rho_{N,\bar{k}}(0)\, \rho_{N,-\bar{k}}(0) \rangle}_{=1} e^{-D|\bar{k}|^2 t}$$

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

$$F_s(\bar{k},t) = e^{-D|\bar{k}|^2 t}$$

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

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

Approssimazione gaussiana

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

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

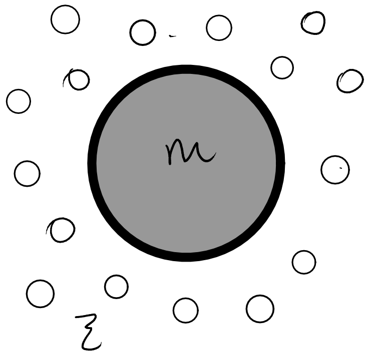
$$\int d\bar{r}\, |\bar{r}|^2 G_s(\bar{r},t) = \int d\bar{r}\, |\bar{r}(t) - \bar{r}(0)|^2 G_s(\bar{r},t) = \langle |\bar{r}(t) - \bar{r}(0)|^2 \rangle$$

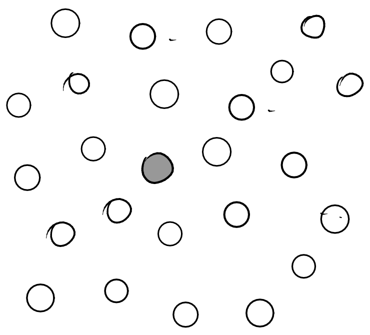
$$\int d\bar{r}\, |\bar{r}|^2 \left(\frac{\alpha(t)}{\pi}\right)^{3/2} e^{-\alpha(t)|\bar{r}|^2} = 3 \int_{-\infty}^{\infty} dx\, x^2 \left(\frac{\alpha(t)}{\pi}\right)^{1/2} e^{-\alpha(t)x^2} = 3 \cdot \frac{1}{2\alpha(t)}$$

$$\alpha(t) = \frac{3}{2\langle |\bar{r}(t) - \bar{r}(0)|^2 \rangle}$$

$$F_s(\bar{k},t) = e^{-\frac{1}{4\alpha(t)}|\bar{k}|^2} = e^{-\frac{1}{6}|\bar{k}|^2 \langle |\bar{r}(t) - \bar{r}(0)|^2 \rangle}$$

Funzioni di memoria





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

forza stocastica

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

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

funzione di memoria

Langevin generalizzata : $m \frac{d\vec{v}}{dt} = -\int_{-\infty}^{t} M(t-t')\,\vec{v}(t')\,dt' + \vec{\theta}(t)$

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

$\langle \vec{\theta}(t) \cdot \vec{v}(0) \rangle = 0 \qquad t>0$

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

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

Formalismo operatore proiezione → HM, Zwanzig

Ansatz :

$M(t) = M(0)\, e^{-t/\tau}, \qquad t>0$ HM 7.3

Ω_0 : frequenza di Einstein $t \ll \tau_0$

$C_v(t) = 1 - \frac{1}{2}\Omega_0^2 t^2 + O(t^4)$ $\quad \Omega_0 \to \langle |\vec{F}|^2 \rangle$

$$C_v(t) = \frac{k_B T}{m(\alpha_+ - \alpha_-)} \left(\alpha_+ e^{-\alpha_- |t|} - \alpha_- e^{-\alpha_+ |t|} \right) \qquad \alpha_\pm = \frac{1}{2\tau} \left[1 \mp \left(1 - 4 \Omega_0^2 \tau^2 \right)^{1/2} \right]$$

$\tau < \frac{1}{2\Omega_0} \rightarrow$ esponenziali decrescenti

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

$F(\bar{k}, t)$

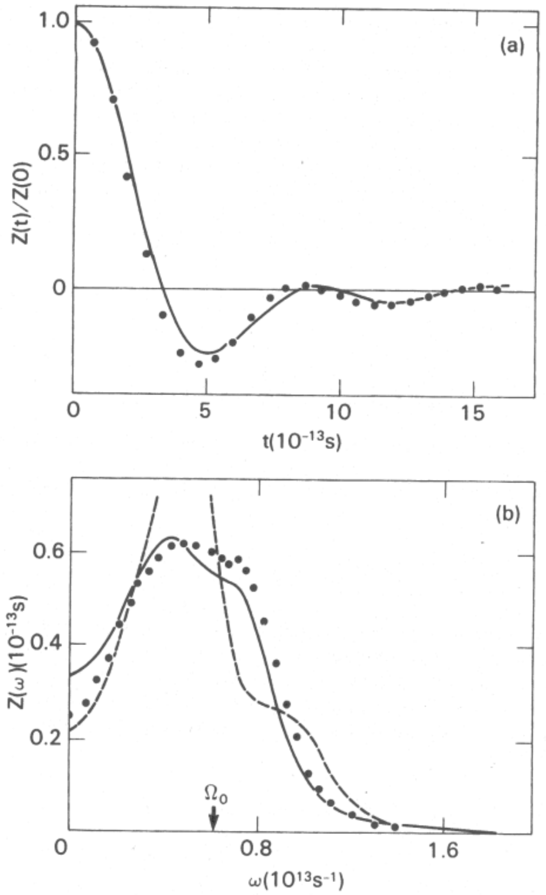


FIG. 9.5. Velocity autocorrelation function (a) and the associated power spectrum (b) of a model of liquid rubidium. The points are molecular dynamics results (Rahman, 1974b), the full curves correspond to the theory of Gaskell and Miller (1978a) (see Eqn (9.5.9)) and the dashed curve in (b) is calculated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

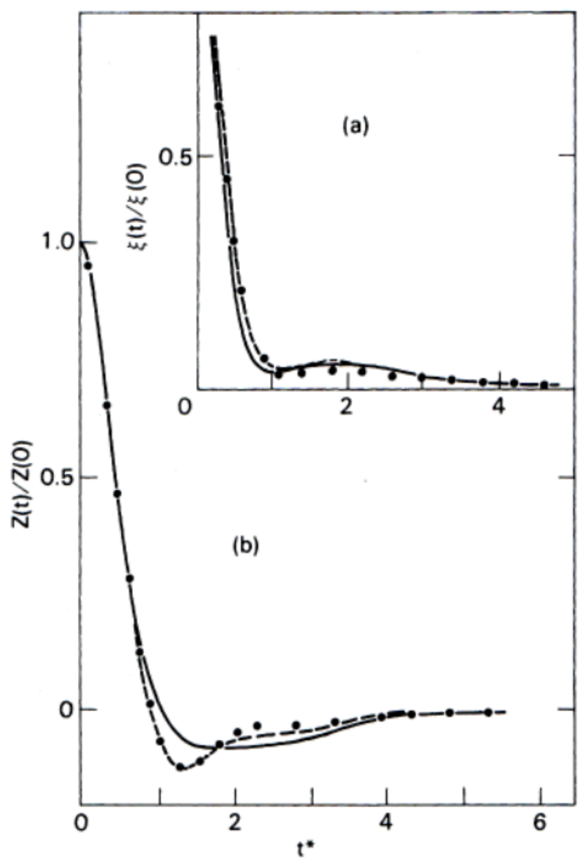


FIG. 9.7. Velocity autocorrelation function and the associated memory function (inset) of the Lennard-Jones fluid near the triple point. The points are molecular dynamics results of Levesque and Verlet (1970), and the curves are calculated from the kinetic theory of Sjögren (1980a) before (full lines)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