L'Equazione di Langevin

Funzioni Memoria e Idrodinamica

Risorse:

- Balucani and Zoppi *Dynamics of the Liquid State (3.1, 3.4.3)*
- Berne and Pecora *Dynamic Light Scattering (11)*
- Hansen and Mc. Donald *Theory of simple liquids (9.1, 9.4)*
- T. Scopigno et al. *The Review of Modern Physics 77, 881, (2005)*

http://glass.phys.uniroma1.it/scopigno/RES_ACT/my_papers/Pub.htm

Alcuni richiami base

$$A(\mathbf{p}^N, \mathbf{r}^N)$$

$$C_{AB}(t,t') = \langle \delta B^*(t') \delta A(t) \rangle$$

$$\langle \cdots \rangle = \int_\Gamma d\mathbf{p}^N d\mathbf{r}^N (\cdots) \mathcal{P}(\mathbf{p}^N \mathbf{r}^N)$$

$$\rho(\mathbf{r},t) \doteq \frac{1}{\sqrt{N}} \sum_i \delta(\mathbf{r} - \mathbf{r}_i(t))$$

$$\mathbf{J}(\mathbf{r},t) \doteq \frac{1}{\sqrt{N}} \sum_i \mathbf{v}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t))$$

$$e(\mathbf{r},t) \doteq \frac{1}{\sqrt{N}} \sum_i \frac{1}{2} m v_i^2(t) \delta(\mathbf{r} - \mathbf{r}_i(t))$$

$$H = \frac{1}{2} \sum_i \frac{p_i^2}{m} + V_N(r_1, ..., r_N)$$

$$\frac{dA(t)}{dt} = \{A, \mathcal{H}\}_P = i\mathcal{L}A(t)$$

L'operatore di proiezione

$$\mathcal{P}B(t) \doteq \frac{\langle B(t)A^* \rangle}{\langle AA^* \rangle} A \qquad \mathcal{Q} = 1 - \mathcal{P}$$

$$\frac{dA(t)}{dt} = e^{i\mathcal{L}t}[\mathcal{P} + (1-\mathcal{P})]i\mathcal{L}A$$

$$R(t) = e^{i(\mathcal{QL})t}\mathcal{Q}\dot{A}$$

$$M(t) = \frac{\langle R(t)R^* \rangle}{\langle AA^* \rangle}$$

$$i\Omega = \frac{\langle i\mathcal{L}AA^* \rangle}{\langle AA^* \rangle} = \frac{\langle \dot{A}A^* \rangle}{\langle AA^* \rangle} = 0$$

$$\dot{C}_{AA}(t) \cancel{- i\Omega C_{AA}(t)} + \int_0^t M(t-t')C_{AA}(t')dt' = 0$$

Properties of $C_{AB}(t)$

1: $$C_{AB}(t,t') = C_{AB}(t-t') = C_{AB}(t)$$

2: $$C_{AB}(t) = \varepsilon_A \varepsilon_B C^*_{BA}(t)$$

3: $$\left\langle \dot{A}(t) B^*(0) \right\rangle = -\left\langle A(t) \dot{B}^*(0) \right\rangle \Rightarrow C_{\dot{A}B}(t) = -C_{A\dot{B}}(t)$$

Using 3 for A=B and t=0 $$C_{\dot{A}A}(0) \overset{(3)}{=} -C_{A\dot{A}}(0) = -C^*_{\dot{A}A}(t) \Rightarrow \mathrm{Re}[C_{\dot{A}A}(0)]$$

Using 2 and then 3 for A=B and t=0 $$C_{\dot{A}A}(0) \overset{(2)}{=} -C^*_{A\dot{A}}(0) \overset{(3)}{=} C^*_{\dot{A}A}(0) \Rightarrow \mathrm{Im}[C_{\dot{A}A}(0)]$$

$$C_{\dot{A}A}(0) = 0$$

The Markov Chain I

$$\frac{\langle A(t)A^*(0)\rangle}{\langle|A|\rangle^2} = \frac{\langle R^{(0)}(t)R^{(0)*}(0)\rangle}{\langle|R^{(0)}|\rangle^2} = \frac{M^{(0)}(t)}{M^{(0)}(0)}$$

$$\mathcal{L}^{(i)} = (1 - \mathcal{P}^{(i)})\mathcal{L}^{(i-1)}$$

$$i\Omega^{(i-1)} = \frac{\langle i\mathcal{L}^{(i-1)} R^{(i-1)} R^{(i-1)*}\rangle}{\langle R^{(i-1)} R^{(i-1)*}\rangle} = 0 \qquad M^{(i)}(t) = \frac{\langle R^{(i)}(t) R^{(i)*}\rangle}{\langle R^{(i-1)} R^{(i-1)*}\rangle}$$

$$\frac{dM^{(i-1)}}{dt} - i\Omega^{(i-1)}M^{(i-1)}(t) + \int_0^t M^{(i)}(t-t')M^{(i-1)}(t')dt' = 0$$

The Markov Chain II

$$\phi(Q,t) = \frac{\langle \rho(Q,t)\rho^*(Q,0)\rangle}{\langle |\rho(Q)|^2\rangle} = \frac{M^{(0)}(Q,t)}{M^{(0)}(Q,0)}$$

$$\frac{dM^{(i-1)}}{dt} - i\Omega^{(i-1)} M^{(i-1)}(t) + \int_0^t M^{(i)}(t-t')M^{(i-1)}(t')dt' = 0$$

$$\tilde{\phi}(Q,s) = \left[s + \tilde{M}^{(1)}(Q,s)\right]^{-1} = \left[s + \frac{M^{(1)}(Q,t=0)}{s+\tilde{M}^{(2)}(Q,s)}\right]^{-1} = \left[s + \frac{M^{(1)}(Q,t=0)}{s+\frac{M^{(2)}(Q,t=0)}{s+.....}}\right]^{-1}$$

$$M^{(i)}(0) = -\ddot{M}^{(i-1)}(0)\cdot\left[M^{(i-1)}(0)\right]^{-1} - \left[\Omega^{(i-1)}\right]^2$$

$$M^{(1)}(Q,0) = \frac{k_B T Q^2}{mS(Q)} \qquad M^{(2)}(Q,0) = 2\frac{k_B T Q^2}{m} + \frac{\rho}{3m}\int \nabla^2 V(r) g(r) d\mathbf{r}$$

Properties of the LT

$$\mathfrak{L}\left[\frac{d}{dt}F(t)\right] = s\tilde{F}(s) - F(t=0)$$

$$\mathfrak{L}\left[\int_0^t F(t-t')G(t')dt'\right] = \tilde{F}(s)\tilde{G}(s)$$

The Markov Chain: 2^{nd} order

$$\frac{dM^{(i-1)}}{dt} - i\Omega^{(i-1)} M^{(i-1)}(t) + \int_0^t M^{(i)}(t-t')M^{(i-1)}(t')dt' = 0$$

$$\tilde{\phi}(Q,t) = \left[s + \frac{M^{(1)}(Q,t=0)}{s + \tilde{M}^{(2)}(Q,s)} \right]^{-1}$$

$$\ddot{\phi}\,(Q,t) + M^{(1)}(Q,0)\phi(Q,t) + \int_0^t M^{(2)}(Q,t-t')\,\dot{\phi}\,(Q,t')dt' = 0$$

The Multidimensional Markov Chain:

$$\mathbf{A}(t) = \mathbf{M}^{(0)}(t)$$

$$\mathcal{P}B(t) = \frac{\langle B(t)\mathbf{A}^*\rangle}{\langle \mathbf{A}\mathbf{A}^*\rangle} = \sum_{\lambda}\sum_{\nu}\langle B(t)A_{\lambda}^*\rangle[\langle AA_{\lambda}^*\rangle^{-1}]_{\lambda\nu}A_{\nu}$$

$$\frac{d\mathbf{M}^{(i-1)}}{dt} - i\mathbf{\Omega}^{(i-1)}\mathbf{M}^{(i-1)}(t) + \int_0^t \mathbf{M}^{(i)}(t-t')\mathbf{M}^{(i-1)}(t')dt' = 0$$

$$i\mathbf{\Omega}^{(i-1)} = \langle i\mathcal{L}^{(i-1)}\mathbf{R}^{(i-1)}\mathbf{R}^{(i-1)*}\rangle\langle\mathbf{R}^{(i-1)}\mathbf{R}^{(i-1)*}\rangle^{-1} = 0$$

$$\mathbf{M}^{(i)}(t) = \langle\mathbf{R}^{(i)}(t)\mathbf{R}^{(i)*}\rangle\langle\mathbf{R}^{(i-1)}\mathbf{R}^{(i-1)*}\rangle^{-1}$$

The Multidimensional Markov Chain: a Hydrodynamic set I

$$\mathbf{A}(t) = [\rho(t), J_L(t), T(t)] = \mathbf{R}^{(0)}(t)$$

$$T(Q) = \frac{1}{m\rho c_V(Q)}\left[E(Q) - \frac{\langle E^*(Q)\rho(Q)\rangle}{\langle \rho^*(Q)\rho(Q)\rangle}\rho(Q)\right]$$

$$\tilde{M}_{eff}(Q,s)$$

$$\tilde{\phi}(Q,s) = \cfrac{1}{s + \cfrac{\omega_0^2(Q)}{s + \tilde{M}_{JJ}^{(1)}(Q,s) - \cfrac{[\tilde{M}_{JT}^{(1)}(Q,s) - i\Omega_{JT}^{(0)}][\tilde{M}_{TJ}^{(1)}(Q,s) - i\Omega_{TJ}^{(0)}]}{s + \tilde{M}_{TT}^{(1)}(Q,s)}}},$$

The first level Markov chain of the 3-variables set leads to an equation for the DAF formally equivalent to a second level 1-variable chain with an appropriate equivalent (scalar) memory function

$$\ddot{\phi}(Q,t) + \omega_0^2(Q)\phi(Q,t) + \int_0^t M_{eff}(Q,t-t')\,\dot{\phi}(Q,t')dt' = 0$$

The Multidimensional Markov Chain: a Hydrodynamic set II

$$\mathbf{A}(t) = [\rho(t), J_L(t), T(t)] = \mathbf{R}^{(0)}(t)$$

$$i\mathbf{\Omega}^{(0)} = \begin{pmatrix} 0 & -iQ & 0 \\ -\frac{iQ}{S(Q)}\frac{k_B T}{m} & 0 & -\frac{\left\langle \dot{J}_L(Q)T^*(Q)\right\rangle}{\left\langle T(Q)T^*(Q)\right\rangle} \\ 0 & -\frac{\left\langle T(Q)\dot{J}_L^*(Q)\right\rangle}{Nk_B T/m} & 0 \end{pmatrix}$$

•The diagonal terms are 0
The non diagonal terms vanish with Q

$$i\mathbf{M}^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & M_{22}(Q,t) & M_{32}(Q,t) \\ 0 & M_{23}(Q,t) & M_{33}(Q,t) \end{pmatrix}$$

•The random force of ϱ is 0
The 22-33 terms vanish with Q^2
The 23-32 terms vanish with Q^4

$$R_\lambda^{(1)}(t) = e^{i(1-\mathcal{P})\mathcal{L}t}[\dot{A}_\lambda - \sum_\nu i\Omega_{\lambda\nu}A_\nu]$$

The Multidimensional Markov Chain: a Hydrodynamic set III

The dynamical problem is now reduced to the determination of M_{22} and M_{33}

$$i\mathbf{M}^{(1)} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & M_{22}(Q,t) & M_{32}(Q,t) \\ 0 & M_{23}(Q,t) & M_{33}(Q,t) \end{pmatrix}$$

•The random force of ϱ is 0
The 22-33 terms vanish with Q^2
The 23-32 terms vanish with Q^4

$$R_\lambda^{(1)}(t) = e^{i(1-\mathcal{P})\mathcal{L}t}[\dot{A}_\lambda - \sum_\nu i\Omega_{\lambda\nu}A_\nu]$$

MARKOVIAN APPROXIMATION:

Under the hypothesis that all the QUASI conserved ("slow") variables have been included in the coupled set that we have chosen, we can assume an instantaneous decay of the memory functions

$$\tilde{\mathbf{M}}(Q,s) \approx \tilde{\mathbf{M}}(Q,s=0)$$

Expected to hold in the Q=0 limit

The Multidimensional Markov Chain: a Hydrodynamic set IV

$$\tilde{M}^{(1)}_{JJ}(Q \to 0, s) = D_V Q^2$$

$$\tilde{M}^{(1)}_{TT}(Q \to 0, s) = \gamma D_T Q^2$$

$$\Omega^{(0)}_{JT}(Q \to 0)\Omega^{(0)}_{TJ}(Q \to 0) = (\gamma - 1)\omega_0^2(Q)$$

$$D_V = \frac{1}{2\rho m}\left[\frac{4}{3}\eta_s + \eta_B\right]$$

$$\gamma = \frac{c_P}{c_V},$$

$$D_T = \frac{\kappa}{\rho m C_p},$$

$$\tilde{M}_{eff}(Q \to 0, s) = D_V Q^2 + \frac{(\gamma - 1)\omega_0^2(Q)}{s + \gamma D_T Q^2}$$

$$M_{eff}(Q \to 0, t) = 2 D_V Q^2 \delta(t) + \omega_0^2(Q)(\gamma - 1)e^{-\gamma D_T Q^2 t}$$

$$\ddot{\phi}(Q, t) + \omega_0^2(Q)\phi(Q, t) + \int_0^t M_{eff}(Q, t - t')\,\dot{\phi}(Q, t')dt' = 0$$

The Dynamic Structure Factor

From knowledge of $\tilde{\phi}(Q,s)$ one straightforwardly obtains $S(Q,\omega)=[S(Q)/\pi]\mathrm{Re}\{\tilde{\phi}(Q,s=i\omega)\}$ in terms of the real (M') and imaginary ($-M''$) parts of the Fourier-Laplace transform of the memory function:

$$\ddot{\phi}(Q,t) + \omega_0^2(Q)\phi(Q,t) + \int_0^t M(Q,t-t')\,\dot{\phi}(Q,t')dt' = 0$$

↓

$$S(Q,\omega) = \frac{S(Q)}{\pi}\frac{\omega_0^2(Q)M'(Q,\omega)}{[\omega^2-\omega_0^2-\omega M''(Q,\omega)]^2+[\omega M'(Q,\omega)]^2}.$$

Simple Hydrodynamics I

$$\tilde{M}_{eff}(Q \to 0, s) = D_V Q^2 + \frac{(\gamma - 1)\omega_0^2(Q)}{s + \gamma D_T Q^2}$$

Defining: $c_t = \frac{\omega(Q \to 0)}{Q^2} = \frac{k_B T}{mS(0)}$

$$\tilde{\phi}(Q, s) = \frac{s^2 + As + B}{s^3 + As^2 + Cs + D}$$

$$\begin{aligned}
A &= \gamma D_T Q^2 + D_V Q^2 \\
B &= \gamma D_T D_V Q^4 + (\gamma - 1) c_t^2 Q^2 \\
C &= \gamma D_T D_V Q^4 + \gamma c_t^2 Q^2 \\
D &= \gamma D_T c_t^2 Q^4
\end{aligned}$$

Simple Hydrodynamics II

$$M_{eff}(Q \to 0, t) = 2D_V Q^2 \delta(t) + \omega_0^2(Q)(\gamma - 1)e^{-\gamma D_T Q^2 t}$$

In the Q=0 limit the timescale $\tau_{th}=1/\gamma D_T Q^2$ is much longer than the characteristic time of the density fluctuations $1/\omega_B$

$$\omega_B \tau_{th} = \frac{cQ}{D_T Q^2} \xrightarrow{Q \to 0} \infty$$

In a light scattering experiment ($Q\sim10^{-2}$ nm^{-1}) and for ordinary, non conductive fluids ($D_T\sim10^{-6}$ m^2/s) one has

$Q\sim10^{-2}$ nm^{-1}

$D_T\sim10^{-6}$ m^2/s

$\gamma\sim1$

c~1000m/s

$$\omega_B \tau_{th} \approx 100$$

The poles of Φ can then be approximated to the leading term (up to O(Q²)):

$$\begin{aligned} s_0 &= -D_T Q^2 \\ s_\pm &= \pm i\sqrt{\gamma} c_t Q - \frac{1}{2}\left[D_V + (\gamma-1)D_T\right] \end{aligned}$$

and the Dynamic Structure Factor reads:

$$\begin{aligned} S(Q,\omega) &= \frac{NK_BT}{2\pi V}\frac{k_T}{\gamma}\left[\frac{2(\gamma-1)D_TQ^2}{\omega^2+D_T^2Q^4} + \right. \\ &+ \frac{\Gamma Q^2}{(\omega+c_SQ)^2+\Gamma^2Q^4} + \frac{\Gamma Q^2}{(\omega-c_SQ)^2+\Gamma^2Q^4} + \\ &+ \left. [\Gamma + D_T(\gamma-1)]\frac{Q}{c_S}\left(\frac{\omega+c_SQ}{(\omega+c_SQ)^2+\Gamma^2Q^4} - \frac{\omega-c_SQ}{(\omega-c_SQ)^2+\Gamma^2Q^4}\right)\right] \end{aligned}$$

Having defined

$$\begin{aligned} c_s &= \sqrt{\gamma} c_t \\ \Gamma &= \frac{1}{2}\left[D_V + (\gamma-1)D_T\right] \\ k_T &= -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \end{aligned}$$

Simple Hydrodynamics IV

$$\frac{S(Q,\omega)}{S(Q)} = \left[f_Q \delta(\omega) + \frac{1-f_Q}{\pi} \frac{\Omega^2(Q)\Gamma(Q)}{(\omega^2 - \Omega^2(Q))^2 + \omega^2 \Gamma^2(Q)} \right],$$