17/07/2017 DAVID REICHMANN MODE COUPLING THEORY → NOTES ONLINE

OUTLINE:
1. Simple background
2. Exact dynamics via Mori-Zwanzig Eqn.
3. MCT for glasses (approximation)
4. Other MCTs if time allows
5. Success / Failures
6. Is MCT a MF theory? A correct MF?
7. MCT for dynamical heterogeneity

→ EVERYTHING FOR EQUILIBRIUM!!

1 SIMPLE BACKGROUND

We wish to calculate a correlation function: $C(t) = \int dp\, dq\, \rho(q,p) \left(e^{i\mathcal{L}t} A(q,p) \right) A(q,p)$.

$\rho(q,p) = e^{-H(q,p)/T}$; $\mathcal{L}$: Liouville op. $\frac{dA}{dt} = i\mathcal{L} A(t)$

$\mathcal{L} = \{A(t), H\}$. ← poisson braket $\{A,B\} = \sum_i \frac{\partial A}{\partial \vec{r}_i}\frac{\partial B}{\partial \vec{p}_i} - \frac{\partial A}{\partial \vec{p}_i}\frac{\partial B}{\partial \vec{r}_i}$

with pairwise interactions $H = \sum_{i=1} \frac{p_i^2}{2m_i} + \frac{1}{2}\sum_{i \neq j} \phi(|\vec{r}_i - \vec{r}_j|)$

$\Rightarrow i\mathcal{L} = \frac{1}{m}\sum_i \left(\vec{p}_i \cdot \frac{\partial}{\partial \vec{r}_i}\right) - \sum_{i\neq j}\left(\frac{\partial \phi(|\vec{r}_i - \vec{r}_j|)}{\partial \vec{r}_i}\right)\frac{\partial}{\partial \vec{p}_i}$

propagator $\Rightarrow A(t) = A(0)\, e^{i\mathcal{L}t}$

We are assuming Newtonian dynamics ($\neq$ Langevin). In the end would be equivalent, but it is not so obvious why it is so.

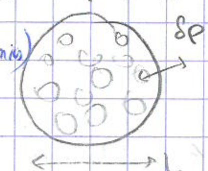
what to calculate?

→ classical density field: $\rho(\vec{r},t) = \sum_i \delta(\vec{r} - \vec{r}_i)$

FT $\int dr\, e^{i\vec{k}\cdot\vec{r}} \rho(\vec{r},t) = \rho_k(t) = \sum_i e^{i\vec{k}\cdot\vec{r}_i(t)}$ density mode

→ canonical correlation function: $F(\vec{k},t) = \frac{1}{N}\langle \rho_{-\vec{k}}(0)\, \rho_{\vec{k}}(t)\rangle$ — conservation of momentum, if $\vec{k}_1 + \vec{k}_2 \neq 0$ → trivial

how should we think of $\vec{k}$: → high $\vec{k}$ small length scale (fast dynamics)
(slow vs fast modes) → small $\vec{k}$ hydrodynamic l.s.

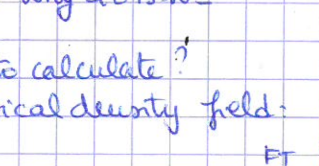


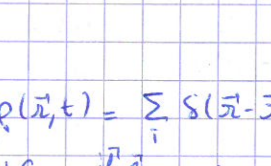
↳ time derivative $\dot{\rho}_k(t) = i\vec{k}\cdot\sum_i \vec{v}_i(t)\, e^{i\vec{k}\cdot\vec{r}_i(t)} = i|k|\, j^L_k(t)$ (velocity)

longitudinal current: $\sum_i \frac{\vec{k}}{|\vec{k}|}\cdot\vec{v}_i(t)\, e^{i\vec{k}\cdot\vec{r}_i(t)} = j^L_k(t)$ ($= \hat{k}$)

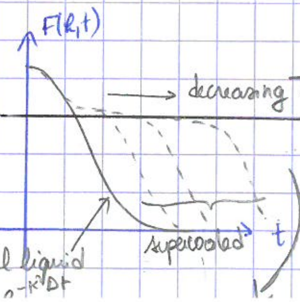
More precisely: static structure function $S(\vec{k}) = F(\vec{k},0) = \frac{1}{N}\langle \rho_{-\vec{k}}(0), \rho_{\vec{k}}(t=0)\rangle$

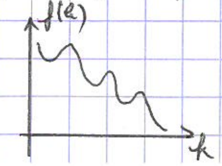
$= 1 + \rho\int e^{i\vec{k}\cdot\vec{r}}\, g(r)\, d^3r$ ← pair correlation function





↳ what to expect in glass forming liquids?





→ we'll come out that a and b are not independent: $\frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}$

↳ compared to numerical simulations: "not grossly wrong".

2 EXACT DYNAMICS VIA MORI-ZWANZIG EQUATIONS.

Start by defining a scalar function → Scalar product $(A, B) \equiv \langle A^* B \rangle$ ← canonical average

(might find for quantum problems: $\frac{1}{\beta\hbar}\int_0^{\beta\hbar} d\tau \langle A(-i\hbar\tau) B(0) \rangle$, with $e^{\tau H} A e^{-\tau H}$)

→ projection operator: $P(B) \equiv (A, B)(A, A)^{-1} A$ — A can be a matrix, in which case $(\,)^{-1}$ is a matrix inverse

→ equation of motion: * $\frac{dA(t)}{dt} = i\mathcal{L}A(t) = i\mathcal{L}e^{i\mathcal{L}t}A(0)$

$= e^{i\mathcal{L}t}(P + (1-P))\, i\mathcal{L}A(0)$

- P: projection op — projector on A(0)
- (1−P) = Q: complementary projection operator to P, (PQ) = 0

$P(i\mathcal{L}A(0)) = (A, \dot{A})(A, A)^{-1} A(0) = i\Omega A(0)$, with $\dot{A}(0) = i\mathcal{L}A(0)$ — def $i\Omega$ → static $t=0$

$= i\Omega A(t) + e^{i\mathcal{L}t}(1-P)\, i\mathcal{L}A(0)$

(hydrodynamic free streaming)

We make an ansatz: $e^{i\mathcal{L}t} = e^{i\mathcal{L}t}\hat{\Theta}(t) + e^{i(1-P)\mathcal{L}t}$ → find $\hat{\Theta}(t)$, $\hat{\Theta}(0) = 0$ given definition

($e^{i(1-P)\mathcal{L}t}$: evolution in the fast space)

↳ to find $\hat{\Theta}$ take derivatives: $i\mathcal{L}e^{i\mathcal{L}t} = i\mathcal{L}e^{i\mathcal{L}t}\hat{\Theta}(t) + e^{i\mathcal{L}t}\dot{\hat{\Theta}}(t) + i(1-P)\mathcal{L}e^{i(1-P)\mathcal{L}t}$

$= i\mathcal{L}\left(e^{i\mathcal{L}t}\hat{\Theta}(t) + e^{i(1-P)\mathcal{L}t}\right)$

$\Rightarrow \dot{\hat{\Theta}}(t) = e^{-i\mathcal{L}t} P\mathcal{L} e^{i(1-P)\mathcal{L}t}$

$\int dt$, $\hat{\Theta}(0) = 0 \Rightarrow e^{i\mathcal{L}t}\Theta(t) = \int_0^t d\tau\, e^{i(t-\tau)\mathcal{L}}(iP\mathcal{L})e^{i(1-P)\mathcal{L}\tau}$

Using this we have: $e^{i\mathcal{L}t} i(1-P)\mathcal{L}A(0) = \int_0^t d\tau\, e^{i\mathcal{L}(t-\tau)}\, iP\mathcal{L} f(\tau) + f(t)$

$*$ (second term RHS)

FLUCTUATING FORCE:

$f(t) = e^{i(1-P)\mathcal{L}t}\, i(1-P)\mathcal{L}A(0)$

if P projects to slow modes, 1−P to all the fast modes.

↳ properties of the fluctuating force:
- always orthogonal to A: $(f(t), A(0)) = 0$ — ∈ image 1−P by definition

⇒ rewriting of $*$

$$\frac{dA}{dt} = i\Omega A(t) - \int_0^t d\tau\, K(\tau) A(t-\tau) + f(t) \quad \text{EXACT LANGEVIN EQ!}$$

MEMORY FUNCTION: autocorrelation of f normalized by AA overlap

$iP\mathcal{L}f(\tau) = i(A, \mathcal{L}f(\tau))\cdot(A,A)^{-1}A(0)$

$i((1-P)\mathcal{L}A, f(\tau))(A,A)^{-1}\cdot A(0)$

$-\underbrace{(f(0), f(\tau))(A,A)^{-1}}_{=K(\tau)} A(0)$

$\langle *, A(0) \rangle = \langle \frac{dA}{dt} A(0) \rangle = \langle i\Omega A(t) A(0) \rangle - \int_0^t d\tau K(\tau) \langle\ \rangle + \langle f(t) A(0) \rangle$ (→ 0)

$$\Rightarrow \frac{dC(t)}{dt} = i\underline{\Omega}\, \underline{C}(t) - \int_0^t d\tau\, \underline{K}(\tau)\, \underline{C}(t-\tau) \quad **$$

EXACT

In the following, we will consider a vector $A(t) = \begin{pmatrix} \delta\rho_{\vec{k}} \\ j^L_{\vec{k}} \end{pmatrix} = \begin{matrix} \sum_i e^{i\vec{k}\cdot\vec{r}_i(0)} - (2\pi)^3 \rho\, \delta(\vec{k}) / \langle\delta\rho\rangle \\ = \frac{1}{m}\sum_i \hat{k}\, \vec{p}_i(0)\, e^{i\vec{k}\cdot\vec{r}_i(0)} \end{matrix}$

$\hat{k}$ → unit vector.

$$\Rightarrow C(t) = \begin{pmatrix} \langle \delta\rho_{\vec{k}}(t)\,\delta\rho_{\vec{k}}(0)\rangle & \langle \delta\rho(0)\, j(t)\rangle \\ \langle j(0)\,\delta\rho(t)\rangle & \langle j(0)\, j(t)\rangle \end{pmatrix}$$

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reminding our notations:

$$\begin{cases} PB = (A,B)\cdot(A,A)^{-1}A, \quad Q = 1-P \\ f = e^{iQ\mathcal{L}t}\, Q\dot{A} \\ K(t) = (f(0), f(t))\cdot(A,A^{-1}) \\ \quad = \langle f^*(0)\, e^{iQ\mathcal{L}t} f(t)\rangle (\underline{A},\underline{A}^{-1}) \\ i\underline{\underline{\Omega}} = (\underline{A},\underline{\dot{A}})(\underline{A},\underline{A})^{-1} \end{cases}$$

⚠ $\begin{cases} A = A(0) \\ A(t) \text{ otherwise} \end{cases}$

$$(A,A) = \begin{pmatrix} \langle a_1^2\rangle & \langle a_1 a_2\rangle \\ \langle a_2 a_1\rangle & \langle a_2^2\rangle \end{pmatrix}$$

For our choice of A: $\underline{\underline{C}}(t) = \begin{pmatrix} \langle \delta\rho_{-\vec{k}}(0)\,\delta\rho_{\vec{k}}(t)\rangle & \langle \delta\rho_{\vec{k}}(0)\, j^L_{\vec{k}}(t)\rangle \\ \langle j^L_{-\vec{k}}(0)\,\delta\rho_{\vec{k}}(t)\rangle & \langle j^L_{-\vec{k}}(0)\, j^L_{\vec{k}}(t)\rangle \end{pmatrix} = \begin{pmatrix} F(k,t) & \alpha\dot{F} \\ \alpha\dot{F} & \end{pmatrix}$

intermediate scattering function F → $\langle \delta\rho_{-\vec{k}}(0)\,\delta\rho_{\vec{k}}(t)\rangle$

$\dot{F}$ → $\langle j^L_{-\vec{k}}(0)\,\delta\rho_{\vec{k}}(t)\rangle$

At initial time: $\underline{\underline{C}}(0) = \begin{pmatrix} N S(\vec{k}) & \langle \delta\rho_{\vec{k}}(0)\, j^L_{\vec{k}}(0)\rangle \, (=0) \\ \langle j^L_{-\vec{k}}(0)\,\delta\rho_{\vec{k}}(0)\rangle \, (=0) & \langle j^L_{-\vec{k}}(0)\, j^L_{\vec{k}}(0)\rangle \end{pmatrix} \Rightarrow (A,A)^{-1} = \begin{pmatrix} \frac{1}{NS(\vec{k})} & 0 \\ 0 & \frac{m}{NkT} \end{pmatrix}$

$$\langle v_i^x v_j^x\rangle = \delta_{ij}\frac{kT}{m}\ \Big\langle \Big(\sum_i \hat{k}\, \dot{r}_i\, e^{-i\vec{k}\cdot\vec{r}_i}\Big)\Big(\sum_j \hat{k}\, \dot{r}_j\, e^{i\vec{k}\cdot\vec{r}_j}\Big)\Big\rangle = \frac{NkT}{m}$$

$$i\Omega = (\underline{A},\underline{\dot{A}})\cdot \begin{pmatrix} 1/NS(k) & 0 \\ 0 & m/NkT \end{pmatrix} = \begin{pmatrix} \langle \delta\rho_{-k}\,\dot{\delta\rho}_k\rangle \ (=0) & \langle \delta\rho_{-k}\,\frac{dj^L_k}{dt}\rangle \ (= i N|k|\, k_BT/m) \\ \langle j^L_{-k}\,\dot{\delta\rho}_k\rangle \ (= iN|k|\,k_BT/m) & \langle \frac{dj^L_k}{dt}\,\dot{\delta\rho}_k\rangle \ (=0) \end{pmatrix}\begin{pmatrix} & \\ & \end{pmatrix}$$

$$= \begin{pmatrix} 0 & i|k| \\ \frac{i|k|\,k_BT}{mS(k)} & 0 \end{pmatrix}$$

fluctuating force

$$f(0) = Q\dot{A}(0) = \underline{\dot{A}} - i\underline{\underline{\Omega}}\,\underline{A} = \begin{bmatrix} \dot{\delta\rho}_k \\ \frac{dj^L_k}{dt} \end{bmatrix} - \begin{pmatrix} 0 & i|k| \\ \frac{i|k|\,k_BT}{mS(k)} & 0 \end{pmatrix}\begin{pmatrix} \delta\rho_k \\ j^L_k \end{pmatrix} = \begin{bmatrix} 0 \\ R_{\vec{k}} \end{bmatrix}$$

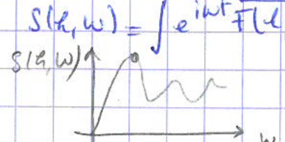
$$\boxed{R_{\vec{k}} = \frac{dj^L_k}{dt} - \frac{i|\vec{k}|\,k_BT}{mS(\vec{k})}\,\delta\rho_{\vec{k}}}$$

$$\underline{\underline{K}}(t) = \begin{bmatrix} 0 & 0 \\ 0 & \frac{m}{Nk_BT}\langle R_{-\vec{k}}\, e^{iQ\mathcal{L}t} R_{\vec{k}}\rangle \end{bmatrix} = (f(0), e^{i\mathcal{L}t} f(0))(A,A)^{-1}$$

21 element of ★★

$$\boxed{\frac{d^2F(k,t)}{dt^2} + \frac{k^2 k_BT}{mS(k)}F(k,t) + \frac{m}{Nk_BT}\int_0^t d\tau\, \langle R_{-\vec{k}}(0)\, e^{iQ\mathcal{L}t} R_{\vec{k}}(0)\rangle\, \frac{dF}{dt}(k, t-\tau) = 0}$$

$S(k,\omega) = \int e^{i\omega t} F(k,t)\, dt$ dynamic structure factor.



force term moving slowly & term fluctuating fast