Outline

1. Some preliminaries - simple classical liquids, correlation functions and structure functions.
2. Exact dynamics via the Mori-Zwanzig approach.
3. The mode-coupling theory (MCT) of glasses.
4. Other "mode-coupling" theories.
5. Successes and Failures of mode-coupling.
6. Is the MCT a mean-field theory?
7. MCT, higher-order correlations and dynamical heterogeneity.
8. Final remarks.

The 1st 3 parts of these lectures will follow closely the lecture notes of J. Stat. Mech. (2005) P. 05013. Useful references after that will be mentioned as we go...

1) Some preliminaries:

In the following we want to develop theory for (Generally classical) time correlation functions

$$C(t) = \langle A(t)A(0)\rangle \equiv \int d\underline{p}\, d\underline{q}\; \rho(\underline{p},\underline{q})\left(\exp(i\mathcal{L}t)\,A(\underline{p},\underline{q})\right)A(\underline{p},\underline{q})$$

where the integral is over the entire phase space, $\rho(\underline{p},\underline{q})$ is the (canonical) equilibrium distribution function, and the operator $\mathcal{L}$ is the classical Liouville operator:

$$H = \sum_i \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2}\sum_{i\neq j}\phi(|\vec{r}_i - \vec{r}_j|)$$

(H: Hamiltonian; $|\vec{r}_i - \vec{r}_j|$: can assume more general forms)

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

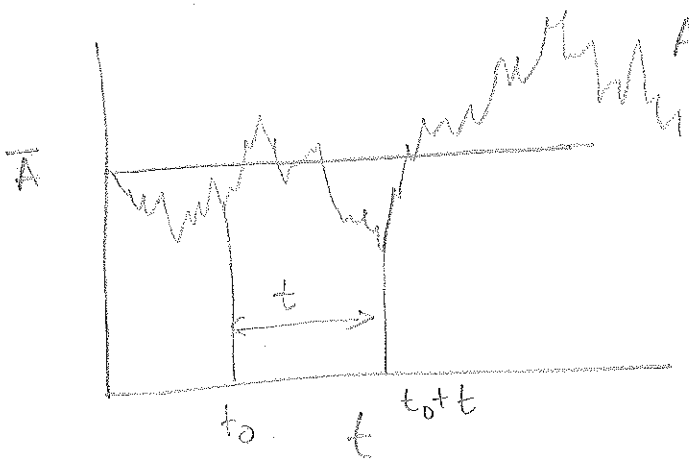
$$\{A,B\} \equiv \sum_i \left(\left(\frac{\partial A}{\partial \vec{r}_i}\right)\cdot\left(\frac{\partial B}{\partial \vec{p}_i}\right) - \left(\frac{\partial A}{\partial \vec{p}_i}\right)\cdot\left(\frac{\partial B}{\partial \vec{r}_i}\right)\right)$$ [Poisson Bracket]

and thus:

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

Note that while our definition of $C(t)$ is theoretically useful how to calculate it is not, for example, how it is done on the computer!

Here we envision a canonical distribution function $\rho(\underline{p}, \underline{q}) \sim e^{-H(\underline{p},\underline{q})/k_B T}$, while on the computer it is simplest to work at fixed energy and not temperature. Further, on the computer we calculate correlations directly from trajectories + time averaging



$$\overline{A(t_0)\,A(t_0+t)} \sim C(t)$$

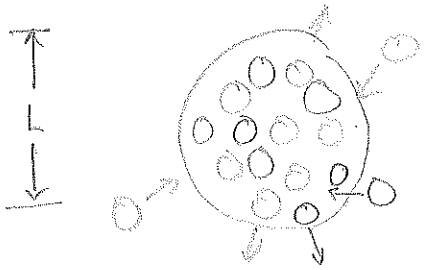
in equilibrium average over all time origins t_0

Thus our theory will assume that we can interchange canonical + Microcanonical ensemble (good as $N \to$ large generally) and that the ergodic hypothesis holds, at least if we want to compare with simulations!

For a large part of these lectures we will want to look at density correlation functions.

Density $\Rightarrow$ $A(t) = \rho(r,t) = \sum_i \delta(\vec{r} - \vec{r}_i(t))$

Might want to look at dynamics of total number of particles that enter + leave a specified volume (or over some lengthscale)



Information same as $\delta\rho(\vec{r},t) \sim \rho(\vec{r},t) - \bar{\rho}$

These kinds of fluctuations can be probed by neutron scattering, light scattering, etc.

Often it is advantageous to Fourier transform $\rho(\vec{r},t)$ and work in $\vec{k}$-space:

$$\rho_{\vec{k}}(t) = \sum_i \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \delta(\vec{r} - \vec{r}_i(t)) = \sum_i e^{i\vec{k}\cdot\vec{r}_i(t)}.$$

The specific correlator then that we focus on for now is

$$F(\vec{k},t) = \frac{1}{N}\left\langle \rho_{-\vec{k}}(t)\rho_{\vec{k}}(0)\right\rangle = \frac{1}{N}\sum_{ij}\left\langle e^{-i\vec{k}\cdot\vec{r}_i(0)}\, e^{i\vec{k}\cdot\vec{r}_j(t)}\right\rangle$$

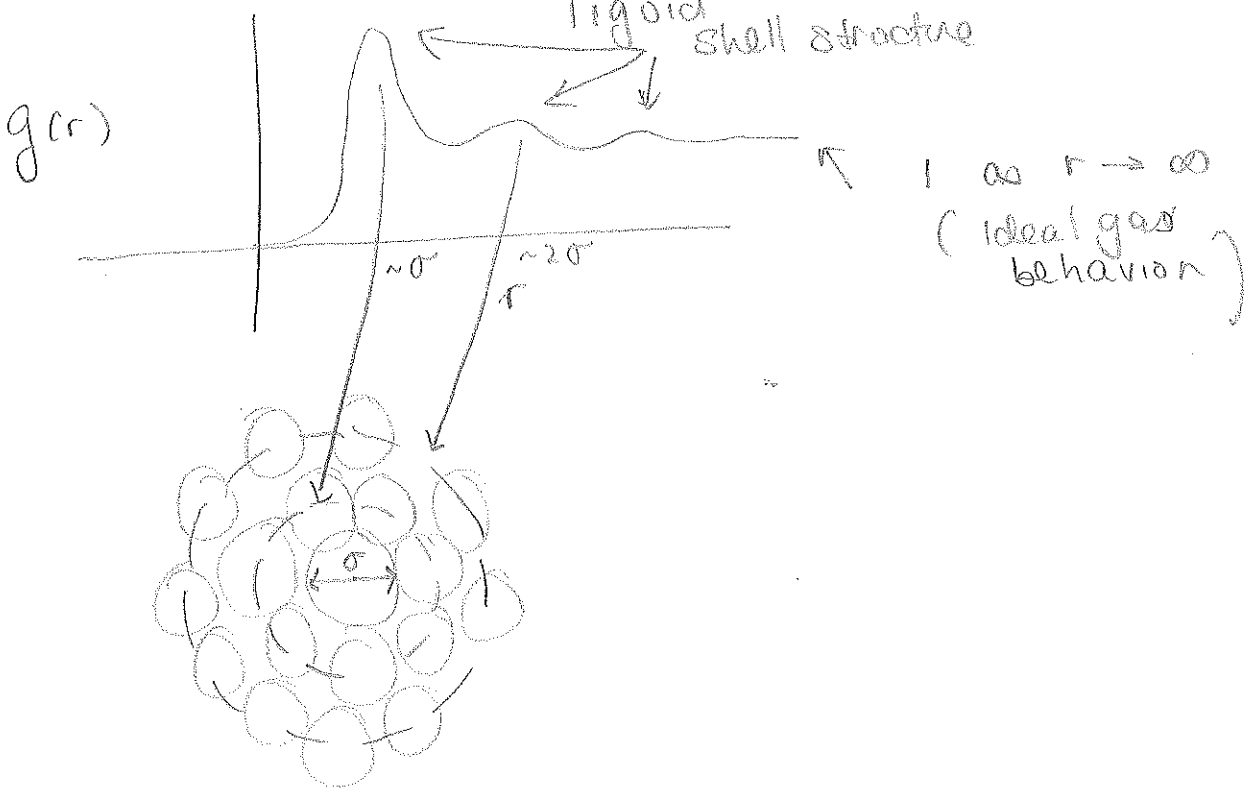
Note that we need to always conserve momentum ($\vec{k}$) if our system is translationally invariant so $\sum_i \vec{k}_i = 0$, thus the "$-$" sign.

$F(k, t=0) = \frac{1}{N}\langle \rho_{-\vec{k}}(0)\rho_{\vec{k}}(0)\rangle \equiv S(k)$ is called the static structure factor. It is easily measured by scattering, and is directly related to simple static structure of the liquid: (assume in our system function of $|\vec{k}|$ only)

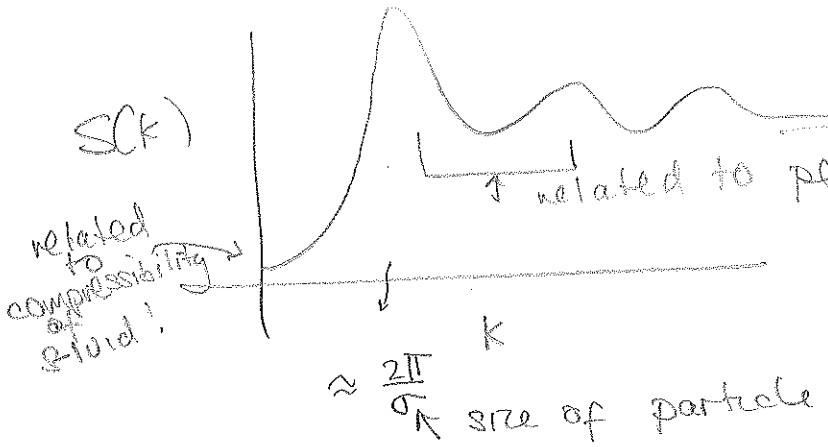
$$S(k) = 1 + \rho \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\, g(r)$$

ρ: density $\frac{N}{V}$

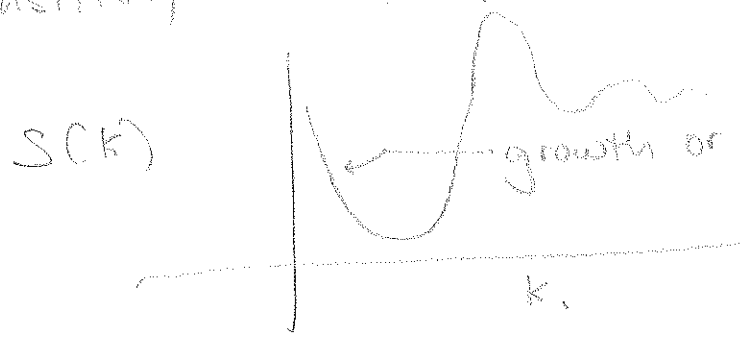
$g(r)$: pair distribution function $\propto$ prob. of finding a particle a distance r away from another.



Given that $g(r)$ looks like this, $S(k)$ will look like



$S(k \to 0)$ related to long lengthscale structure + compressibility of liquid. Near 2nd order phase transition, or in system with sharp interfaces



Recall in general: large k ⟶ small lengthscales
small k ⟶ large lengthscales

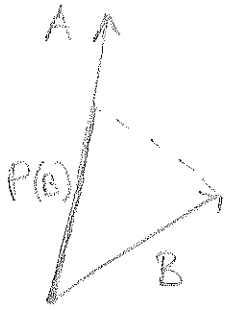
O.k. Now, we have $F(k,t)$ [called, B.T.W., the "intermediate scattering function,"] what to do w/ it?

The Mori–Zwanzig approach:

Define scalar product $(A,B) = \langle A^* B \rangle$ of two observables A & B (could both be $\rho_{\vec{k}}$, for example; note $\rho_{\vec{k}}^* = \rho_{\vec{k}}$).

Now define a projection operator $\mathcal{P} \equiv (A,\dots)\cdot(A,A)^{-1}\cdot A$

If A is a vector, (A,A) is a matrix. Note $\mathcal{P}^2 A = \mathcal{P}A = A$. In geometrical terms, the projection operator finds the component of some variable along a chosen "direction" A



Consider $\rho_{\vec{k}}(t) = \sum_i e^{i\vec{k}\cdot\vec{r}_i(t)}$. Its time derivative is $\dot{\rho}_{\vec{k}}(t) = i\vec{k}\cdot\sum_i \frac{\vec{p}_i}{m}(t)\, e^{i\vec{k}\cdot\vec{r}_i(t)} = i\vec{k}\cdot\vec{j}_{\vec{k}}(t) =$

$ik\, j^{\parallel}_{\vec{k}}(t)$, where $j^{\parallel}_{\vec{k}}(t)$ is the longitudinal current (current along $\vec{k}$).

$J_{\vec{k}}^{L}(t)$ can be written as $\frac{1}{m}\sum_i (\hat{k}\cdot\vec{P}_i(t))\, e^{i\vec{k}\cdot\vec{r}_i(t)}$.

We will make use of these two variables in a bit to define our $A(t)$.

We want in general to find an equation of motion for $A(t)$ (which we will denote as $\underline{A}(t)$, since it will be a vector in the case we study):

$$\frac{d\underline{A}(t)}{dt} = i\gamma\,\underline{A}(t) = e^{i\gamma t}\left[P + (1-P)\right] i\gamma\,\underline{A}(0).$$

This can be seen since $i\gamma\underline{A}(t) = i\gamma\, e^{i\gamma t}\underline{A}(0) = e^{i\gamma t}\, i\gamma\underline{A}(0) = e^{i\gamma t}\left[1\right] i\gamma\underline{A}(0)$.

Then, $\frac{d\underline{A}(t)}{dt} = i\underline{\underline{\Omega}}\cdot\underline{A}(t) + e^{i\gamma t}(1-P)\, i\gamma\underline{A}(0)$

where $i\underline{\underline{\Omega}} = (\underline{A}, i\gamma\underline{A})\cdot(\underline{A},\underline{A})^{-1}$.

(both are matrices)

Next let's write

$$e^{i\gamma t} \equiv e^{i\gamma t\hat{\Theta}(t)} + e^{i(1-\Theta)\gamma t}$$

We can find $\hat{O}(t)$ by differentiating both sides of this eqn:

$$i\mathcal{L}e^{i\mathcal{L}t} = i\mathcal{L}e^{i\mathcal{L}t}\hat{O}(t) + e^{i\mathcal{L}t}\frac{d\hat{O}(t)}{dt} + i[(1-\rho)\mathcal{L}]e^{i(1-\rho)\mathcal{L}t}$$

$$i\mathcal{L}\left(e^{i\mathcal{L}t}\hat{O}(t) + e^{i(1-\rho)\mathcal{L}t}\right) = i\mathcal{L}e^{i\mathcal{L}t}\hat{O}(t) + e^{i\mathcal{L}t}\frac{d\hat{O}}{dt}(t) + i[(1-\rho)\mathcal{L}]e^{i(1-\rho)\mathcal{L}t}$$

$$i\mathcal{L}\hat{O}(t) + e^{i(1-\rho)\mathcal{L}t} = i\mathcal{L}e^{i\mathcal{L}t}\hat{O}(t) + \frac{d\hat{O}}{dt}(t) + i[(1-\rho)\mathcal{L}]e^{i(1-\rho)\mathcal{L}t}$$

Thus

$$e^{i\mathcal{L}t}\frac{d\hat{O}(t)}{dt} = i\rho\mathcal{L}e^{i(1-\rho)\mathcal{L}t}$$

$$\boxed{\hat{O}(t) = i\int_0^t d\tau\, e^{i\mathcal{L}t}\rho\mathcal{L}e^{i(1-\rho)\mathcal{L}\tau}}$$

where we used $\hat{O}(0) = 0$. Thus

$$\boxed{e^{i\mathcal{L}t}i(1-\rho)\mathcal{L}\underline{A} = \int_0^t d\tau\, e^{i\mathcal{L}(t-\tau)}i\rho\mathcal{L}f(\tau) + f(t)}$$

where $f(t)$ is the <u>fluctuating force</u>

$$f(t) = e^{i(1-\rho)\mathcal{L}t}i(1-\rho)\mathcal{L}\underline{A}$$

what is meaning of fluctuating force?

$1-\rho \equiv Q$ is a projection operator that projects to the space orthogonal to that of ρ - namely $P\cdot Q = Q\cdot P = 0$

This means that $1-P$ removes the $\underline{A}$ character of a function. The f.f. thus can be interpreted as:

a) remove the "A" character of $\mathring{A}$

b) propagate the remainder of $\mathring{A}$ in this orthogonal subspace.

In other words, if A is a "slow" variable (one that takes a long time to decay) then $f(t)$ is the "fast" component of $\mathring{A}$ propagated in the space of other "fast" variables. Thus, it is rapidly fluctuating.

Note $i(\underline{A}, \mathcal{L} f(t)) = i(\mathcal{L}\underline{A}, f(t)) = i((1-\mathcal{P})\mathcal{L}\underline{A}, f(t)) =$

$-(f(0), f(t))$.

Thus, our eqn of motion for $\underline{A}(t)$ may be expressed

$$\boxed{\frac{d\underline{A}(t)}{dt} = i\underline{\underline{\Omega}} \cdot \underline{A}(t) - \int_0^t d\tau\, \underline{\underline{K}}(t) \cdot \underline{A}(t-\tau) + f(t)}$$

where we define the memory matrix

$$\underline{\underline{K}}(t) = (f(0), f(t)) \cdot (\underline{A}, \underline{A})^{-1}$$

This is an Exact Langevin Eqn!

Now, we can define the correlation matrix

$$\underline{\underline{C}}(t) = \langle \underline{A}^*(0)\,\underline{A}(t)\rangle = (\underline{A}, \underline{A}(t)), \text{ using}$$

$$(\underline{A}, f(t)) = 0 \quad \text{(show!)}$$

$$\boxed{\frac{d\,\underline{\underline{C}}(t)}{dt} = i\underline{\underline{\Omega}}\cdot\underline{\underline{C}}(t) - \int_0^t d\tau\, \underline{\underline{K}}(\tau)\cdot\underline{\underline{C}}(t-\tau)}$$

This is the Mori-Zwanzig eqn. It is one of the most useful results in studying relaxation behavior in statistical mechanics.

Now let's specialize to studying density correlations

take $\underline{A} = \begin{bmatrix} \delta\rho_{\vec{q}} \\ j^L_{\vec{q}} \end{bmatrix}$, where $\delta\rho_{\vec{q}} = \rho_{\vec{q}} - \underbrace{\langle\rho_{\vec{q}}\rangle}_{(2\pi)^3\rho\delta(\vec{q})}$.

and $j^L_{\vec{q}} = \frac{1}{m}\sum_i (\hat{q}\cdot\vec{p}_i)e^{i\vec{q}\cdot\vec{r}_i}$

Then $\underline{\underline{C}}(t) = \langle \underline{A}^*\,\underline{A}(t)\rangle =$

$$\begin{bmatrix} \langle \delta\rho_{-\vec{q}}(0)\,\delta\rho_{\vec{q}}(t)\rangle & \langle \delta\rho_{-\vec{q}}(0)\, j^L_{\vec{q}}(t)\rangle \\ \langle j^L_{-\vec{q}}(0)\,\delta\rho_{\vec{q}}(t)\rangle & \langle j^L_{-\vec{q}}(0)\, j^L_{\vec{q}}(t)\rangle \end{bmatrix}$$

The upper left corner is $NF(q,t)$, and the other entries are related to time derivatives of $F(q,t)$.

at $t=0$ $\quad \underline{\underline{C}}(0) = \begin{bmatrix} NS(q) & 0 \\ 0 & \frac{NkT}{m} \end{bmatrix}$

where we used $\langle \delta\rho_{\vec{q}} j^L_{\vec{q}} \rangle = 0$ at $t=0$

and $\langle V_{z,i}^2 \rangle = \frac{kT}{m}$, where $V_{z,i} = \hat{q} \cdot \vec{P}_i$.

Next, we show $i\underline{\underline{\Omega}} = \langle \underline{A}^* \cdot \dot{\underline{A}} \rangle \cdot \langle \underline{A}^* \underline{A} \rangle^{-1} =$

$$\begin{bmatrix} \langle \delta\rho_{-\vec{q}} \dot{\delta\rho}_{\vec{q}} \rangle & \langle \delta\rho_{\vec{q}} \frac{dj^L_{\vec{q}}}{dt} \rangle \\ \langle j^L_{-\vec{q}} \delta\rho_{\vec{q}} \rangle & \langle \frac{dj^L_{-\vec{q}}}{dt} \delta\rho_{\vec{q}} \rangle \end{bmatrix} \cdot \begin{bmatrix} \frac{1}{NS(q)} & 0 \\ 0 & \frac{m}{NkT} \end{bmatrix} =$$

$$\begin{bmatrix} 0 & \frac{iNqkT}{m} \\ \frac{iNqkT}{m} & 0 \end{bmatrix} \begin{bmatrix} \frac{1}{NS(q)} & 0 \\ 0 & \frac{m}{NkT} \end{bmatrix} = \begin{bmatrix} 0 & iq \\ \frac{iqkT}{mS(q)} & 0 \end{bmatrix}$$

$q \equiv |\vec{q}|$. We used integration of the time derivative terms by parts and fact $\langle \alpha \dot{\alpha} \rangle = 0$ where $\alpha = \delta\rho_{\vec{q}}, j^L_{\vec{q}}$ and fact that $\langle j^L_{-\vec{q}} \dot{\delta\rho}_{\vec{q}} \rangle =$

$$\frac{i}{m} \sum_{ij} \langle (\hat{q} \cdot \vec{P}_i) e^{-i\vec{q} \cdot \vec{r}_i} (\vec{q} \cdot \vec{P}_j) e^{i\vec{q} \cdot \vec{r}_j} \rangle = \frac{iq}{m} \sum_i \langle m V_i^2 \rangle =$$

$$\frac{iqNkT}{m}.$$

Now for the fluctuating force

$$f(0) = (1-\mathcal{P})\dot{\underline{A}} = \begin{bmatrix} \delta\dot{\rho}_{\vec{q}} \\ \frac{dj^{\perp}_{\vec{q}}}{dt} \end{bmatrix} - \begin{bmatrix} 0 & iq \\ \frac{iqkT}{mS(q)} & 0 \end{bmatrix} \begin{bmatrix} \delta\rho_{\vec{q}} \\ j^{\perp}_{\vec{q}} \end{bmatrix} = \begin{bmatrix} 0 \\ R_{\vec{q}} \end{bmatrix}$$

where $R_{\vec{q}} = \frac{dj^{\perp}_{\vec{q}}}{dt} - \frac{iqkT}{mS(q)}\delta\rho_{\vec{q}}$.

Note $\underline{\underline{K}}(t) = \begin{bmatrix} 0 & 0 \\ 0 & \langle R_{-q}(0) R_q(t)\rangle \end{bmatrix} \begin{bmatrix} \frac{1}{NS(q)} & 0 \\ 0 & \frac{m}{NkT} \end{bmatrix} =$

$$\begin{bmatrix} 0 & 0 \\ 0 & \frac{m}{NkT}\langle R_{-q}(0) R_q(t)\rangle \end{bmatrix} \quad \text{where } R_q(t) = e^{i\mathcal{Q}t} R_q .$$

We now have all the components. Focusing on the $\underline{\underline{K}}(2,1)$ component of the matrix $\underline{\underline{C}}(t)$, namely

$$\left(\frac{d\underline{\underline{C}}(t)}{dt}\right)_{21} = i\underline{\underline{\Omega}}_{2\alpha}\,\underline{\underline{C}}_{\alpha 1}(t) - \int_0^t d\tau\, \underline{\underline{K}}(\tau)_{2\alpha}\cdot\underline{\underline{C}}_{\alpha 1}(t-\tau)$$

gives

$$\frac{d^2F(q,t)}{dt^2} + \frac{q^2kT}{mS(q)}F(q,t) + \frac{m}{NkT}\int_0^t d\tau \langle R_{-q}(0) R_q(\tau)\rangle \frac{dF(q,t-\tau)}{dt} = 0$$

Where we used fact that

$$\int_0^t d\tau\, \alpha(t-\tau)\beta(\tau) = \int_0^t d\tau\, \alpha(\tau)\beta(t-\tau).$$

The eqn. derived is an exact equation of motion for the intermediate scattering function $F(q,t)$. It has the form of a damped, retarded harmonic oscillator eqn. However the Memory function $\langle R_{\vec{q}}(0) R_{\vec{q}}(\tau)\rangle$ is complicated, and its behavior is unknown.

Let's look at the meaning of the fluctuating force term $R_{\vec{q}}$:

$$R_{\vec{q}} = \frac{dj_{\vec{q}}^{\,L}}{dt} - \frac{i q^2 kT}{m S(q)} \rho_{\vec{q}}\,; \quad \frac{dj_{\vec{q}}^{\,L}}{dt} = \frac{d}{dt}\left(\frac{1}{m}\sum_i (\hat{q}\cdot\vec{p}_i)\, e^{i\vec{q}\cdot\vec{r}_i}\right) =$$

$$\frac{1}{m}\sum_i \left(\hat{q}\cdot\frac{d\vec{p}_i}{dt}\right) e^{i\vec{q}\cdot\vec{r}_i} + \frac{i}{m^2}\sum_i (\hat{q}\cdot\vec{p}_i)^2 e^{i\vec{q}\cdot\vec{r}_i}$$

↑ Force on particle i

↑ like Kinetic energy → fluctuates quickly and decays — not important

Note that Force

$$\frac{d\vec{p}_i}{dt} \sim -\sum_{i\neq j} \nabla \phi(|\vec{r}_i - \vec{r}_j|) = \sum_{\vec{k}} i\,\phi_{\vec{k}}\, \rho_{\vec{k}}\, \rho_{-\vec{k}}$$

↑ pair potential

↑ $\phi_{\vec{k}} = \int d\vec{r}\, e^{i\vec{k}\cdot\vec{r}}\, \phi(\vec{r})$.

Thus, we see that while we expected the fluctuating force to only have "fast" components like $\frac{i}{m^2}\sum_i (\vec{q}\cdot\vec{p}_i)^2 e^{i\vec{q}\cdot\vec{r}_i}$ it also has slow components like δp, $\delta p\cdot\delta p$!

This is the key insight of mode-coupling theory as invisioned by Fixman, Kawasaki, Kadanoff/Swift:

If δp is "slow," so is $\delta p\cdot\delta p$, $\delta p\cdot\delta p\cdot\delta p$ ....

The above analysis suggests a 2-step approximation scheme:

1) Replace $e^{iQ\mathcal{L}t} \longrightarrow P_2 e^{i\mathcal{L}t} P_2$ where P_2 (as described below) projects the fluctuating force onto pairs of density variables.

This approximation is (somewhat) justified by fact that the projection P_2 picks out dominant slow part of $R\vec{q}_1$, and then propagate it in its full space ($1-P \approx 1$ since projection has already happened).

2) Factorize 4-point density correlation functions into products of 2-point ones

So we take $P_2 B = \sum_{\vec{k}_1\vec{k}_2\vec{k}_3\vec{k}_4} A_{\vec{k}_1,\vec{k}_2} \langle A^*_{\vec{k}_3,\vec{k}_4} B \rangle \langle A^*_{\vec{k}_1,\vec{k}_2} A_{\vec{k}_3,\vec{k}_4} \rangle^{-1}$

where $A_{\vec{k}_1\vec{k}_2} = \delta\rho_{\vec{k}_1}\delta\rho_{\vec{k}_2}$.

Using this,

$$\mathcal{Q}_2 R_{\vec{q}} = \sum_{\vec{k}_1,\vec{k}_2} V_{\vec{q}}(\vec{k}_1,\vec{k}_2)\,\delta\rho_{\vec{k}_1}\,\delta\rho_{\vec{k}_2}$$

where $V_{\vec{q}}(\vec{k}_1,\vec{k}_2) = \sum_{\vec{k}_3\vec{k}_4} \langle \delta\rho_{\vec{k}_1}\delta\rho_{\vec{k}_2} R_{\vec{q}}\rangle \cdot \langle \delta\rho_{\vec{k}_1}\delta\rho_{\vec{k}_2}\delta\rho_{\vec{k}_3}\delta\rho_{\vec{k}_4}\rangle^{-1}$

Calculating the explicit form of V is straightforward but tedious; its details are found in the referenced review. Here I will just write it down. Due to translational invariance we can write

$$V_{\vec{q}}(\vec{k}_1,\vec{k}_2) = V_{\vec{k}_1,\vec{q}-\vec{k}} \qquad (\vec{k} \equiv \vec{k}_1 - \vec{k}_2).$$

$$V_{\vec{k}_1,\vec{q}-\vec{k}} = \frac{i\rho kT}{2mN}\left((\hat{q}\cdot\vec{k})\,c(k) + \hat{q}\cdot(\vec{q}-\vec{k})\,c(|\vec{k}-\vec{q}|)\right)$$

where $c(k) = \frac{1}{\rho}\left(1 - \frac{1}{S(k)}\right)$ ("direct" correlation function)

and $\rho = N/V$.

Thus

$$\langle (\mathcal{Q}_2 R_{\vec{q}}(0))^* (\mathcal{Q}_2 R_{\vec{q}}(t))\rangle = \sum_{\vec{k}\vec{k}'} |V^*_{\vec{k},\vec{q}-\vec{k}}\, V_{\vec{k}',\vec{q}-\vec{k}'}| \langle \delta\rho_{\vec{k}}\,\delta\rho_{\vec{k}'-\vec{q}}\,\delta\rho_{\vec{q}-\vec{k}}(t)\,\delta\rho_{\vec{q}-\vec{k}'}(t)\rangle$$

Factoring

$$\approx \sum_{\vec{k},\vec{k}'} |V^*_{\vec{k},\vec{q}-\vec{k}}\, V_{\vec{k}',\vec{q}-\vec{k}'}| N^2 F(k,t) F(|\vec{q}-\vec{k}|,t)\left(\delta_{\vec{k},\vec{k}'} + \delta_{\vec{k}'-\vec{q},\vec{k}}\right)$$

(product of intermediate scattering functions; conserving momentum)

$$= \frac{\rho^2 (kT)^2}{2m^2} \sum_{\vec{k}} |\hat{V}_{\hat{q}\cdot\vec{k},\vec{k}}|^2 F(k,t) F(|\vec{q}-\vec{k}|,t)$$

where $\tilde{V}_{\vec{q}-\vec{k},\vec{k}} = \left((\hat{q}\cdot\vec{k})c(k) + \hat{q}\cdot(\vec{q}-\vec{k})c(|\vec{q}-\vec{k}|) \right)$ (17)

Finally sending $\sum_{\vec{k}} \to \frac{V}{(2\pi)^3}\int d\vec{k}$ we get Final MCT eqn. For density fluctuations

$$\frac{d^2F(q,t)}{dt^2} + \frac{q^2kT}{mS(q)}F(q,t) + \int_0^t d\tau\, K(q,t-\tau)\frac{\partial F}{\partial \tau}(q,\tau) = 0$$

with $K(q,t) = \frac{\rho kT}{16\pi^3 m}\int d\vec{k}\, |V_{\vec{q}-\vec{k},\vec{k}}|^2 F(|q-k|,t)F(k,t)$.

Note - the eqn. is now closed! It only depends on static thermodynamic + structural input (like $S(q)$, kT, ρ ...) and can then be solved for $F(k,t)$. However it is a complicated non-linear integro-differential eqn. That can have some surprising behavior.

First, let's note that the memory term in the integral acts as a friction which slows the decay of $F(q,t)$. As $F(q,t)$ starts to decay slowly the memory function develops a long tail in time. As we now show, this can give rise to an ergodic - non-ergodic transition.

May have no time to cover, but these notes may prove useful. The Mori-Zwanzig approach is useful in many contexts - e.g. the study of the conductivity of metals (Götze + Wölfle, PRB, 6, 1226, 1972) and the dynamics of quantum spin chains (see, e.g., Sirker, Pereira + Affleck, PRB, 83, 035115, 2011). In fact even in conjunction with mode-coupling theories the utility goes far beyond glasses. Here I sketch an example - the Frohlich polaron problem.

Frohlich (and others) were interested in the behavior of a charge (electron) in a polar crystal. In such a dielectric medium the Hamiltonian of the electron interacting with the lattice can be expressed as:

$$\hat{H} = \frac{\hat{p}^2}{2m} + \sum_{\vec{k}}' \hbar\omega_{\vec{k}} a^\dagger_{\vec{k}} a_{\vec{k}} + \sum_{\vec{k}}' \left(V_{\vec{k}} a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + V^*_{\vec{k}} a^\dagger_{\vec{k}} e^{-i\vec{k}\cdot\vec{r}} \right)$$

where p is the momentum operator of the electron, m is its (bare) mass, r is its position operator, $\omega_{\vec{k}}$ is the frequency of the mode of the phonons w/ wavevector $\vec{k}$, $a_{\vec{k}}$ ($a^\dagger_{\vec{k}}$) destroys (creates) a phonon with said $\vec{k}$, and V_k is the electron-phonon coupling strength - left unspecified here.

The coupling between the electron and lattice will result in a new quasi-particle – an electron surrounded by a cloud of phonons. As the phonons drag on the electron, the effective mass of this quasi-particle increases with increasing V_k.

The mobility of the electron was studied by Feynman with path integrals and by Kadanoff w/ the Boltzmann eqn these approaches are complicated! Here we derive Feynman's result via Mori-Zwanzig + a mode coupling factorization.

The frequency-dependent mobility can be found by subjecting the system to an electric field $\vec{E}_\omega(t) = E_0 e^{i\omega t} \hat{e}_x$ and the current in x-direction is

$$J_\omega(t) = \frac{1}{Z(\omega)} E_\omega(t)$$

where $Z(\omega)$ is the impedance function.

The mobility of the electra is

$$\mu(\omega) = \mathrm{Re}\left(\frac{1}{Z(\omega)}\right)$$

which is related to the Laplace transform of the "velocity-velocity" correlation function:

$$\underline{\Phi}(z) = \left(\dot{x}, \frac{1}{z-\mathcal{L}}\dot{x}\right), \quad \text{namely}$$

$$\underline{\Phi}(t) = \left(\dot{x}, e^{i\mathcal{L}t}\dot{x}\right)$$

Lastly, $$\frac{1}{Z(\omega)} = ie \lim_{\epsilon \to 0} \underline{\Phi}(\omega + i\epsilon)$$

with $z = \omega + i\epsilon$, $\epsilon > 0$, and e is the charge of the electron.

Since we are dealing with a quantum problem, we have to define our inner-product a bit differently.

Previously we said $(A, B) = \langle A^* B \rangle$. (classical functions)

Now we define $(\hat{A}, \hat{B}) = \int_0^{\beta} d\lambda \langle (e^{\lambda H} \hat{A} t), \hat{B} \rangle$ (quantum operators)

this is called the Kubo-transform. It turns quantum averages into things that have classical properties — but still exact quantum mechanically

Recall our eqn of motion is from the Mori-Zwanzig approach

$$\boxed{\frac{d\underline{\Phi}(t)}{dt} + \Omega \cdot \underline{\Phi}(t) + \int_0^t d\tau\, \Sigma(t-\tau)\cdot\underline{\Phi}(\tau) = 0}$$

$$\Sigma(t) = \left(\mathcal{Q}\dot{x},\ e^{i\mathcal{Q}\mathcal{L}t}\,\mathcal{Q}\mathcal{L}\dot{x}\right)/\chi$$

↑ memory function

$$\chi = (\dot{x},\dot{x}), \quad \Omega = (\dot{x},\mathcal{L}\dot{x})/\chi$$

This is exactly as before, but now we are just projecting onto $\dot{x}$ so do not have a matrix eq. This is, again, exact.

Also, it is easy to show $e^{i\mathcal{Q}\mathcal{L}t}\,\mathcal{Q}\mathcal{L}\dot{x} = e^{i\mathcal{Q}\mathcal{L}\mathcal{Q}t}\,\mathcal{Q}\mathcal{L}\dot{x}$

since $\mathcal{Q}^2 = \mathcal{Q}$.

The eqn in $\boxed{\ }$ above can be Laplace transformed; it now reads

$$\underline{\Phi}(z) = \frac{\chi}{z - \Omega - \Sigma(z)}$$

since $PA = \dfrac{(\dot{x},A)\dot{x}}{\chi}$ it is straightforward to show

$$\chi = (\dot{x},\dot{x}) = \frac{i}{m}(p_x,\mathcal{L}x) = \frac{i}{mi\hbar}\langle[p_x,x]\rangle = \frac{1}{m}$$

and $\Omega = (\dot{x},\mathcal{L}\dot{x})/\chi = 0$

And the memory function is

$$\Sigma(z) = \sum_{\vec{k}} \frac{k^2}{3m} |V_{\vec{k}}|^2 \left[\Phi^{++}_{\vec{k}}(z) + \Phi^{--}_{\vec{k}}(z) + \Phi^{+-}_{\vec{k}}(z) + \Phi^{-+}_{\vec{k}}(z) \right]$$

with $$\Phi^{++}_{\vec{k}}(z) = \left(b^{\dagger}_{\vec{k}}, \frac{1}{z - \Omega_{\vec{k}} Q} b^{\dagger}_{\vec{k}} \right)$$

$$\Phi^{--}_{\vec{k}}(z) = \left(b_{\vec{k}}, \frac{1}{z - \Omega_{\vec{k}} Q} b_{\vec{k}} \right)$$

and $$\Phi^{+-}_{\vec{k}}(z) = \left(b^{\dagger}_{\vec{k}}, \frac{1}{z - \Omega_{\vec{k}} Q} b_{\vec{k}} \right); \quad \Phi^{-+}_{\vec{k}}(z) = \left(b_{\vec{k}}, \frac{1}{z - \Omega_{\vec{k}} Q} b^{\dagger}_{\vec{k}} \right)$$

where $$b^{\dagger}_{\vec{k}} = a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}}$$

Now, note $$\Phi^{++}_{\vec{k}}(z) = -i \int_0^{\infty} dt\, e^{izt} \left(b^{\dagger}_{\vec{k}}(t), b_{\vec{k}}(0) \right)$$

with $b^{\dagger}_{k}(t) = e^{i\Omega_{\vec{k}} Q} b_{k}(0)$; by integrating by parts $$\Phi^{++}_{\vec{k}}(z) = \frac{1}{z} \left(b^{\dagger}_{\vec{k}}(0), b^{\dagger}_{\vec{k}}(0) \right) - \frac{i}{z} \int_0^{\infty} dt\, e^{izt} \left(\dot{b}^{\dagger}_{\vec{k}}(t), b^{\dagger}_{\vec{k}}(0) \right)$$

where we used the property $Q b_{\vec{k}} = b_{\vec{k}}$ and assume ergodicity $\left(\lim_{t \to \infty} \left(b^{\dagger}_{\vec{k}}(t), b_{\vec{k}}(0) \right) = 0 \right)$.

From here it can be shown

$$\Phi^{++}_{\vec{k}}(z) = \frac{i}{\hbar z} \int_0^{\infty} dt \left(1 - e^{izt} \right) \langle \left[b_{\vec{k}}(t), b^{\dagger}_{\vec{k}}(0) \right] \rangle$$

Similar expressions can be derived for the other Φ functions. We thus find

$$\Sigma(z) = \frac{1}{z}\int_0^\infty dt\,(1-e^{izt})\,\mathrm{Im}\,F(t)$$

with $$F(t) = -\sum_{\vec{k}} \frac{2k^2}{3m\hbar}|V_k|^2\left(\langle[b_{\vec{k}}(t), b^\dagger_{\vec{k}}(0)]\rangle + \langle[b_{\vec{k}}(t), b_k(0)]\rangle\right).$$

We now make a mode-coupling approx

$$\langle b_{\vec{k}}(t)\, b^\dagger_{\vec{k}}(0)\rangle \approx \underbrace{\langle a_{\vec{k}}(t)\, a^\dagger_{\vec{k}}(0)\rangle}_{\text{assume average over free phonons} = [1+n(\omega_{\vec{k}})]e^{-i\omega_{\vec{k}}t}} \underbrace{\langle e^{i\vec{k}\cdot\vec{r}(t)}\, e^{-i\vec{k}\cdot\vec{r}(0)}\rangle}_{\text{assume Feynman model — Gaussian approx holds}\ e^{-k^2D(-t)}}$$

In Gaussian Feynman model can easily calculate $D(t) = \langle \vec{r}(t)\vec{r}(0)\rangle$ but won't do so here

Similarly, $\langle b^\dagger_{\vec{k}}(0)\, b_{\vec{k}}(t)\rangle = n(\omega_{\vec{k}})\, e^{-i\omega_{\vec{k}}t}\, e^{-k^2D(t)}$

and $\langle b_{\vec{k}} b_{\vec{k}}(t)\rangle = \langle b_{\vec{k}}(t)\, b_{\vec{k}}\rangle = 0.$

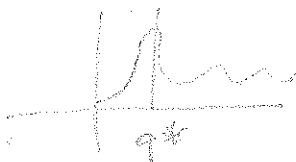
Under these approximations:

$$\boxed{\begin{aligned}\Sigma(z) &= \frac{1}{z}\int_0^\infty dt\,(1-e^{izt})\,\mathrm{Im}\,S(t)\\ S(t) &= \sum_{\vec{k}} \frac{2k^2}{3m\hbar}|V_k|^2\, e^{-k^2D(t)}\left([1+n(\omega_k)]e^{i\omega_k t} + n(\omega_k)e^{-i\omega_k t}\right)\end{aligned}}$$

This is the famed Feynman-Hellwarth-Iddings-Platzman (1962) result!

OK - Back to liquid state MCT - lets simplify:

The "vertex" constant $|V_{\vec{q}-\vec{k},\vec{k}}|^2$ is dominated by wave vectors near the peak of $S(q)$



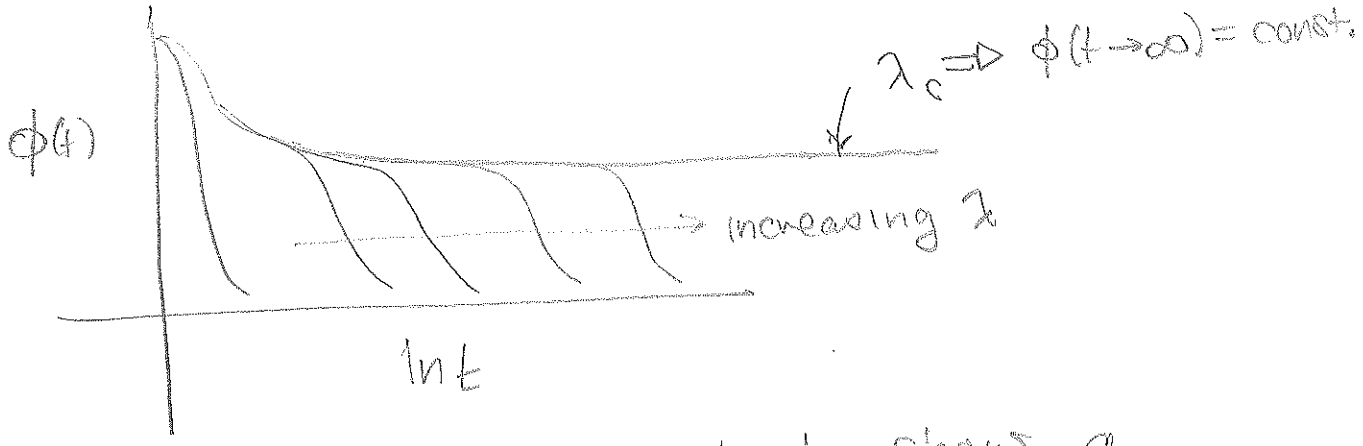
. If we take

$S(q) \approx A\delta(q-q^*)$, then we can effectively make a model where all wave-vectors are suppressed. This then gives

$$F(q^*,t) \sim \phi(t)$$

$$\ddot{\phi}(t) + \Omega^2\phi(t) + \lambda\int_0^t d\tau\, \phi(t-\tau)^2 \cdot \frac{\partial\phi}{\partial\tau}(\tau) = 0$$

This eqn can be solved a bunch of ways, even simply iterating numerically. What is found is



as λ increases $\phi(t)$ starts to show a 2-step relaxation with the appearance of a plateau. At a critical λ $\phi(t)$ no longer decays!

We can argue that at this critical λ, the system has transformed into a glass. Why? When the full q-dependant MCT Eqn is solved with input of T, ρ and S(q) (itself a function of T & ρ) then the same behavior occurs. However the S(q) we input is that of the liquid, perhaps supercooled, and not the crystal. Still- a nonergodic solution is found where dynamics are completely arrested. We call this a glass.

→ MCT has been shown to have a remarkable set of features and some clear successes and failures which we now discuss:

Advantages/successes

1) Fully microscopic – only true 1st principles theory of glass transition.

2) Because of this, detailed – and often remarkably accurate – predictions of dynamical behavior, Debye-Waller factor and the like can be made. See the attached examples.

3) some surprising relaxation patterns have been predicted and confirmed in Expt.

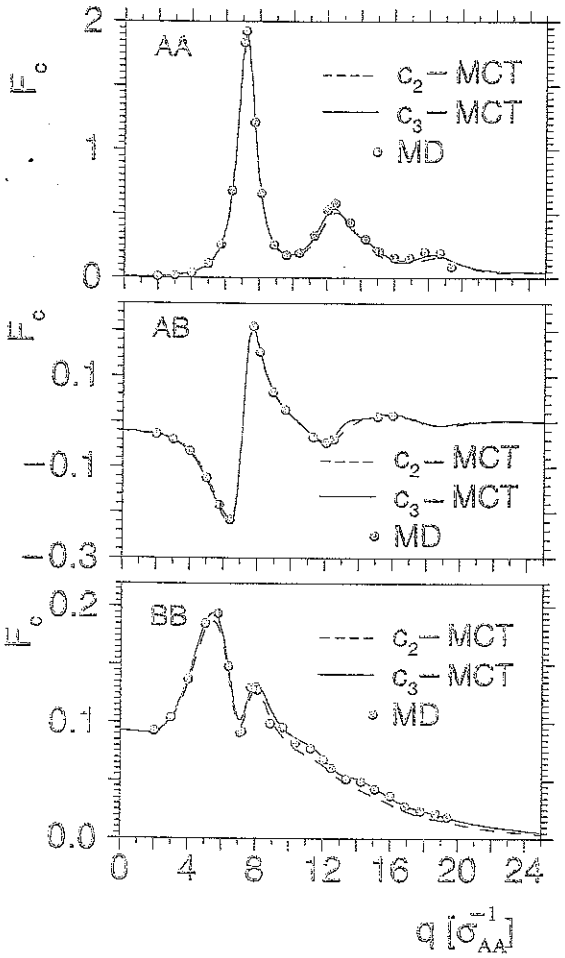


Fig. 4. Wave vector dependence of the NEPs for the BMLJ system. The circles are the result of the simulation, the dashed line is the theoretical prediction if the three point correlation function is set to zero, and the full line is the theoretical prediction if this function is taken into account.

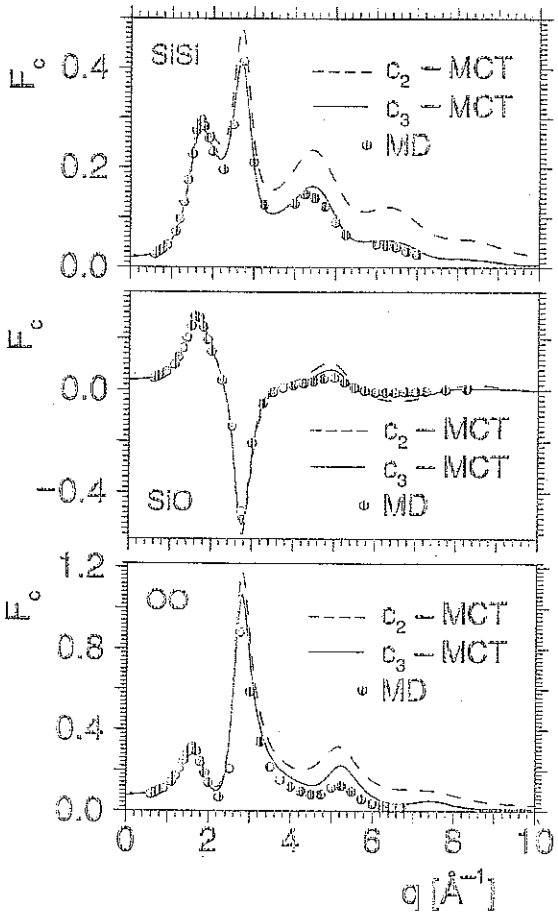


Fig. 5. Same as Fig. 4 but for the case of silica.

PHYSICAL REVIEW E 82, 011504 (2010)

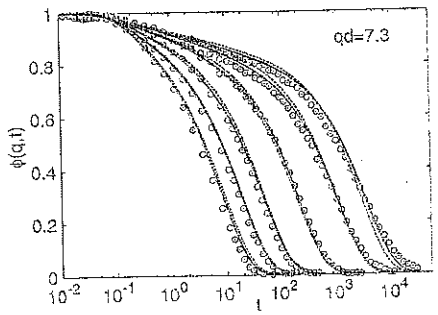


FIG. 13. (Color online) MCT fits of the simulated collective density correlation functions (shown as circles) using the simulated static structure factors binned into $M=1$ (dashed lines), $M=3$ (solid lines), and $M=5$ (dashed-dotted lines) components to approximate the simulated polydispersity distribution. Packing fractions in the simulation are $\varphi=0.5$, 0.53, 0.55, 0.57, 0.58, and 0.585. The curves have been fitted by adjusting only φ_{MCT} as described in conjunction with Fig. 12; we get $\varphi_{MCT,M=1}=0.473$, 0.502, 0.52, 0.54, 0.554, and 0.558; $\varphi_{MCT,M=3}=0.449$, 0.472, 0.493, 0.5122, 0.5234, and 0.5289; and $\varphi_{MCT,M=5}=0.45$, 0.47, 0.49, 0.509, 0.5207, and 0.5259.

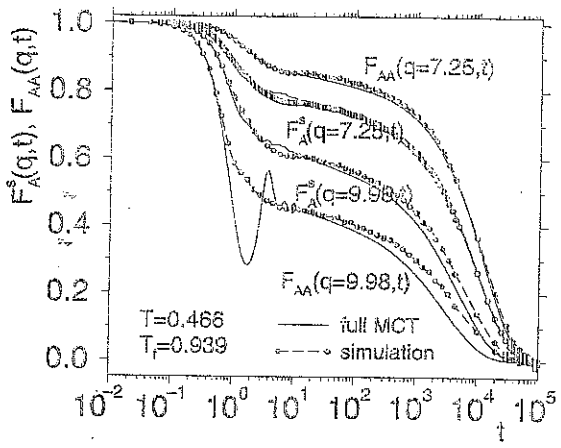
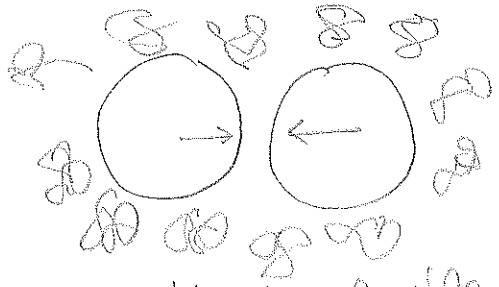


Fig. 3. Same as Fig. 2 but now for $T = 0.466$.

For example in colloidal hard-sphere suspensions, short ranged attractions can be tuned in by the addition of polymer which induces depletion interactions



MCT predicts that if the range of the attraction (which depends on the radius of gyration of the polymer) is short enough then the system will first exhibit Faster dynamics until the attraction strength is strong enough, and then dynamics will arrest again. Near this reentrant change of dynamics, the decay of $F(q,t)$ will be logarithmic in time. All of these features were observed in experiments & simulations after these predictions were made.

Failures

1) MCT predicts a complete dynamical arrest at temperatures that are way too high or densities that are far too low. In this sense MCT is not really a theory of the glass transition at all! Indeed much of the slowing near T_g involves dynamical processes that cannot be captured by MCT, as we will discuss. This is expected of a mean-field theory - as we will also discuss.

2) Because of its mean-field nature MCT does not properly describe local relaxation processes that lead to the break-down of the Stokes-Einstein relation, sizable non-Gaussian parameters, etc...

How should we view MCT; is it a proper dynamical mean-field Theory?

I. The view from spin-Glasses:

As you likely learned in the lectures of Biroli & Cugliandolo, there is a class of mean field spin-glass models whose behavior appears to be strikingly close to that of real glasses.

For example, consider

$$H_3 = g \sum_{\alpha<\beta<\gamma} J_{\alpha\beta\gamma}\, \phi_\alpha \phi_\beta \phi_\gamma$$

(one can easily generalize to more ϕ's as in

$$H_4 = g \sum_{\alpha<\beta<\gamma<\delta} J_{\alpha\beta\gamma\delta}\, \phi_\alpha \phi_\beta \phi_\gamma \phi_\delta \ldots$$
)

Here, the couplings $J_{\alpha\beta\gamma\delta}$ are independent Gaussian random variables with $\overline{J} = 0$ and $\overline{J^2_{\alpha\beta\gamma\delta}} = \frac{1}{N^3}$. Similar considerations hold for any number of coupled ϕ's. Then $\overline{J^2_{\alpha\beta\ldots}}^{\text{k+1 indices}} = \frac{1}{N^k}$

We can define the equation of motion for the ϕ variables

$$\frac{\partial \phi_\alpha}{\partial t} = -\mu(t)\phi_\alpha - 4g \sum_{\beta<\gamma<\delta} J_{\alpha\beta\gamma\delta}\phi_\beta\phi_\gamma\phi_\delta + \eta_\alpha$$

with $\langle \eta_\alpha(t)\eta_{\alpha'}(t')\rangle = 2\delta_{\alpha\alpha'}T\delta(t-t')$,

$\mu(t)$ acts to keep $\frac{1}{N}\sum_{\alpha=1}^{N}\phi_\alpha(t)^2 = 1$

and $C(t,t') = \frac{1}{N}\sum_{\alpha=1}^{N}\overline{\langle \phi_\alpha(t)\phi_\alpha(t')\rangle}$ ← average over disorder.

In equilibrium (where $C(t,t') = C(t-t')$ and the response function is not needed to close the dynamical eqns)

Then it can be shown that the exact eqn of motion for $C(t)$ is

$$\frac{\partial C(t)}{\partial t} + \mu(t) C(t) + \int_0^t d\tau\, M(t-\tau) \frac{\partial C(\tau)}{\partial \tau} = 0$$

with (in the case of 3-coupled ϕ's)

$$M(t) = \frac{g^2}{2} C(t)^2.$$

This is nearly identical to the standard schematic MCT eqn we obtained from liquid state theory with some big approximations! It can be shown that the behavior is the same regardless of $\frac{\partial C}{\partial t}$ vs $\frac{\partial^2 C}{\partial t^2}$ — so what we have is a model where MCT is exact!

As you have already learned (likely) when studying a model like

$$H_3 = g \sum_{\alpha<\beta<\delta} J_{\alpha\beta\gamma} \phi_\alpha \phi_\beta \phi_\gamma$$ - what we know:

1) Above the temperature where MCT predicts dynamical arrest, MCT exactly describes dynamics as we have discussed previously. Here the configurational entropy is zero.
2) at the transition the configurational entropy jumps up and becomes finite; the free energy landscape forms distinct states. In mean field the system gets stuck in these states, but in a "real"

system activation from one state to another occurs, and this process dominates relaxation

3) The configurational entropy continues to decrease until it becomes subextensive ("zero") at temperature T_K.

In this picture - MCT works in the regime of trivial configurational Entropy. Even so, within this mean-field picture there is a growing dynamical length scale above the temperature where MCT freezes. We will (hopefully) return to this at end.

Before coming back to how MCT as derived from Liquid State theory is or is not a true mean-field theory, want to mention one interesting speculation concerning mean-field spin glasses, MCT and the like.

Consider a quantum version of the same type of mean-field models. For Example

$$\hat{H} = g \sum_{\alpha\beta\gamma\delta} J_{\alpha\beta\gamma\delta} \chi_\alpha \chi_\beta \chi_\gamma \chi_\delta \qquad (*)$$

where instead of classical dynamical fields ϕ we have fermions - and in this case we choose Majorana fermions. Normally $\{c_i, c_j^\dagger\} = \delta_{ij}$ for fermions, but Majorana fermions are their own anti-particles, so $\chi_i \sim c_i \sim c_i^\dagger$ (or $\chi_i = \chi_i^\dagger$) and $\{\chi_i, \chi_j\} = 2\delta_{ij}$. This seems weird but what we discuss now would hold also for normal fermions and their c's & c†'s.

The model (*) is known as the Sachdev-Ye-Kitaev model, and has come under very close scrutiny in the last few years because of a possible connection to black holes. The properties of interest are

1) a finite entropy at $T = 0$
2) Maximally chaotic (The decay of a particular "out-of-time" 4-point correlator $\sim \langle \chi_i(t)\chi_j(0)\chi_i(t)\chi_j(0)\rangle \sim e^{Kt}$, $K = \frac{2\pi}{\beta\hbar}$. This correlator "measures" chaotic divergence of dynamics, and a bound [Maldacena] says $K \leq \frac{2\pi}{\beta\hbar}$).
3) at strong coupling, low $T \to$ conformal invariance.

All of these properties are shared by simple models of black holes, down to the details. It is believed that the SYK model is holographically dual to these models, but there is no proof of this.

Why bring this up? Interestingly in the Fermionic SYK model there appears to be no transition a-la MCT to a non-ergodic state, but the (exact) Eqn of motion is precisely of the MCT type, albeit w/ Fermonic boundary conditions. We (with Biroli/Kurchan) speculate that effectively the MCT transition in the model is occuring at $T=0$, and the Entropy at $T=0$ is really the standard configurational Entropy at the transition. We have ample evidence for this, although work still needs to be done. If true - maybe we can say that MCT/mean-field spin glasses tell the secrets of black holes!

O.k. back to (quasi) reality:

O.K. - so it would seem all is good and MCT is the "correct" mean-field dynamical theory of a liquid. I will first present results that support this. Then results that say - "not quite."

1) support for this notion - Simulation of liquids in high dimensions.

It is natural that if you want to see mean-field behavior in a system, the first thing to explore is what the behavior of your system is as $d \to \infty$.

So let's ask - if we simulate a glass forming liquid (LJ spheres, hard spheres, etc.) in high dimensions what do we see/expect?

Recall what MCT would say:

1) Should show 2-step relaxation with very well-defined plateau. Over the span of this slowing down MCT predicts $\tau \sim (T - T_c)^{-\gamma}$. We should find that fits to the MD agree with this such that as d gets larger the T_c and γ more and more coincide when comparing simulation and Theory.

2) The violation of the Stokes-Einstein relation should be more and more suppressed. It is useful to express this as

$D \sim \tau^{-1+\gamma}$. $\gamma = 0$ gives SE relation,

$\gamma \neq 0$ is SE-violating.

3) particle hopping (local dynamical heterogeneity) should be suppressed.

A series of computer simulations show this all to be the case.

- Eaves & Reichman PNAS 2009 (LJ in 4d)
- Charbonneau et al JCP 2013 (HS in up to 10 d!)
- Ikeda & Miyazaki JCP 2011 (long ranged system of gaussian core particles in 3D!)

So basically the gross behavior is as expected: in high dimension there is an extended range of T or p for which we see strong slowing down where the dynamics looks "mean-field" like. So is liquid-state MCT exact (as suggested by Kirkpatrick & Wolynes in 1987)?

Not so fast...

What happens if we solve the very same MCT equations themselves (P. 17) in $d \to \infty$? The behavior becomes unphysical!

See, for example Ikeda + Miyazaki PRL 2010. Here it is shown that in high d $\langle \delta[r - |\vec{R}_i(t) - \vec{R}_i(0)|] \rangle$ develops negative regions - which is unphysical (and does not occur in 3d).

It would appear that MCT:

1) describes some aspects of glass formation in 3d well
2) Has the general flavor of a dynamical mean-field theory and is thus qualitatively consistent with true behavior exposed in high d in real liquids.
3) But also becomes unphysical in some regards as $d \to \infty$. Paradoxically in some ways MCT is better in $d = 3$ than $d = \infty$!

Can the uniquely correct solution to $d = \infty$ dynamics for glass formers be determined?

Yes! See: Maimbourg, Kurchan and Zamponi PRL - 2016.

These authors make use of a dynamical virial expansion. In $d = \infty$ only 2 terms survive.

The final result is an Eqn. of motion that produces results nearly identical to MCT: $\tau \sim (T - T_c)^{\gamma}$, power-law near the plateau... and prediction of a mild kind of Stokes-Einstein violation consistent with $d \to \infty$ behavior seen by Charbonneau et al in 2013. The non-ergodic factors (Debye-Waller factors) look different than MCT.

The theory is significantly worse in 3D in a quantitative sense than standard MCT, but "infinitely" better in $d = \infty$ (it is exact) and is fully consistent with the static / thermodynamic approach in $d \to \infty$. Thus all is good in RFOT-land, but standard MCT is not really the correct mean-field dynamics

---

What about growing length scales? MCT says nothing about static lengths like the point-to-set length discussed in, e.g., the lectures of Biroli. However it does say something about growing dynamical lengths...

Consider (see, e.g. Glotzer + coworkers ~1998–2003) the 2-point, 2-time order parameter in a liquid:

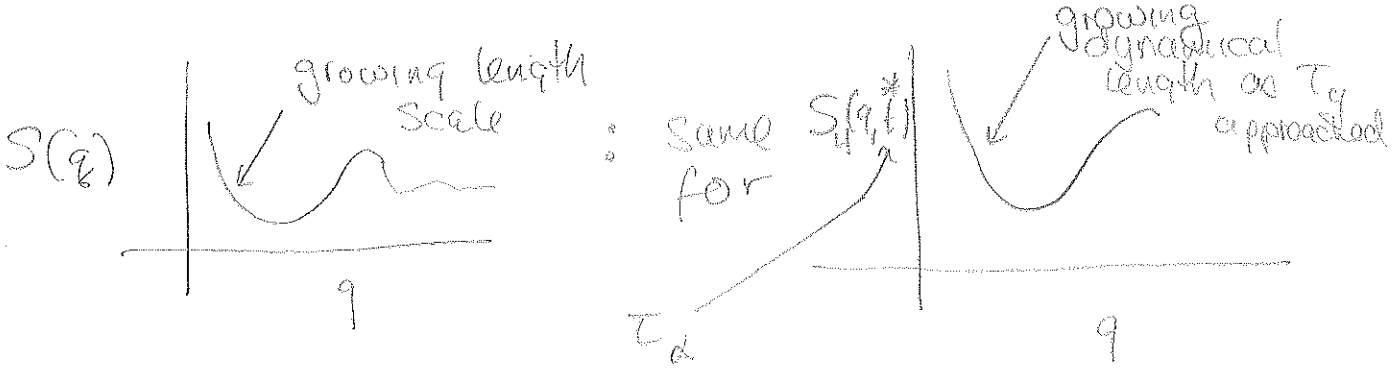
$$Q_k(t) = \sum_{ij} \theta(|r_i(0) - r_j(t)|) e^{i\vec{k}\cdot\vec{r}_i(0)}$$

where θ is a step function such that if $|r_i - r_j(t)|$ is $\leq a$, say a fraction of a particle diameter, count 1, otherwise 0.

Then consider the "structure factor"

$$S_4(\vec{k}, t) = \frac{1}{Np} \langle Q_{-k}(t) Q_k(t) \rangle .$$

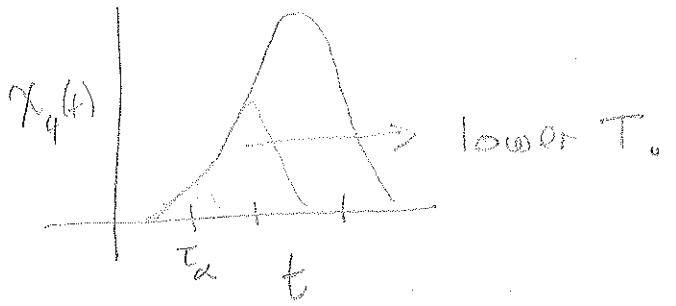
This is just like Static structure factor $S(k)$ but with a more elaborate order parameter. As discussed early in these notes, near a 2nd-order phase transition



Indeed, just as the static susceptibility diverges as, say, we approach the critical point in the Ising model, the analogous susceptibility

$$\chi_4(t) \sim \frac{1}{Np}\left(\langle Q(t)^2\rangle - \langle Q(t)\rangle^2\right);$$

$$Q(t) = \sum_{ij} \theta(|r_i - r_j(t)|) \quad \text{grows as } T \to T_g$$



This signifies a growing dynamical correlation as T gets lower. This is predicted to occur in the p-spin mean-field model as well: In this case χ_4 diverges at T_c.

How about from liquid state MCT? What are the predictions?

Via standard techniques it is quite hard to compute something like $S_4(k,t)$ directly (although see Biroli & Bouchaud EPL 2004).

He we (Biroli, Bouchaud, Miyazaki & Reichman, PRL 2006) take a different strategy:

a) consider the application of an external, spatially varying potential $U(x)$.

b) This field breaks translational invariance. With Field on, the intermediate scattering function would be a function of $\vec{k}_1$ & $\vec{k}_2$

e.g. $F(\vec{k}_1, \vec{k}_2, t) = \frac{1}{N} \langle \delta\rho_{\vec{k}_1}(t) \delta\rho_{\vec{k}_2}(0) \rangle$

$\vec{k}_1 + \vec{k}_2 + \vec{q} = 0$

$\vec{q}$: field

c) From this regular MCT can be used. Find

$$\frac{\partial^2}{\partial t^2} F(k_1, k_2, t) + \int d\vec{k}' \, \Omega(k_1, k') F(k', k_2, t)$$
$$+ \int d\vec{k}' \int dt' \, M(k_1, k', t - t') \frac{\partial}{\partial t'} F(k', k_2, t') = 0$$

Within MCT the Memory function and other terms specifically prescribed.

d) In analogy with critical phenomena - instead of computing "equilibrium" fluctuations in absence of field, compute susceptability (of dynamics) to field:

$$\chi_q(k,t) \propto \left.\frac{\delta F(k, q+k, t)}{\delta U(q_s)}\right|_{u=0}$$

It is argued theoretically in Berthier, Biroli, Bouchaud, Kob, Miyazaki & Reichman JCP (2007), and demonstrated numerically by molecular dynamics in Kim, Saito, Miyazaki, Biroli and Reichman, J.P.C.B (2013) that this contains very same information of $S_q(k,t)$.

e) The form of the resulting equations are complicated. They are something like

$$\frac{\partial^2 \chi_q(k,t)}{\partial t^2} + \frac{kTk^2}{mS(k)}\chi_q(k,t) + \int_0^t dt'\, M_0(k, t-t')\frac{\partial \chi_q(k,t')}{\partial t'}$$

$$+ \int_0^t dt' \frac{kTpk}{m|\vec{k}+\vec{q}|}\int d\vec{k}'\, v_k(\vec{k}', \vec{k}-\vec{k}')\, v_{\vec{k}+\vec{q}}(\vec{k}-\vec{k}', \vec{q}+\vec{k}')\, \chi_q(\vec{k}', t-t') \cdot$$

$$F_0(|\vec{k}-\vec{k}'|, t-t')\frac{\partial F_0(|\vec{k}+\vec{q}|, t')}{\partial t'} = S_q(\vec{k}, t)$$

where quantities like F_0, M_0 are the standard MCT ones & $v_{\vec{k}}$ is of the standard MCT form for the vertex. $S_{\vec{q}}(\vec{k},t)$ is a source term – its form does not influence the description of growing dynamical length scales.

From these equations one can calculate in detail scaling behavior and extract info on a growing dynamical correlation length.

Here is what we learn:

1) a unique, diverging length scale grows as $\xi \sim |T - T_c|^{1/4}$.

2) the length-time scaling behavior is $\tau \sim \xi^z$, $z \sim 4\gamma$, since $\gamma \sim 1.8 - 2.8$ z is large so the growth is slow.

3) specific scaling form changes from early ("β") to late ("α") times

this change implies that dynamically correlated regions get more compact ("thicker") with time even though the same length governs growth for all times. The fact that the short time regime already shows the non-trivial correlations in dynamics is interesting.

The thickening of dynamically correlated regions has been observed in Appignanesi et al, PRL, (2006). The fact that even the β-regions shows non-trivial correlation has been detailed in Karmakar, Dasgupta and Sastry, PRL (2016).

Overall, the predictions of the BBBMR (IMCT) theory are in reasonable qualitative (but not quantitative) agreement with detailed simulations.