

Mode-Coupling Theory of the Glass Transition

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The **Mode-Coupling Theory (MCT)** is the only known theory about glass transition that are first-principles-based [2, 3]. It uses the Mori-Zwanzig formalism [4] to integrate out unnecessary degrees of freedom and focuses on quantities that characterize glasses.

1 A review of Mori-Zwanzig formalism

First we have a brief review of the Mori-Zwanzig formalism. It says that any time-dependent quantity A obeying the (generalized) Heisenberg equation

$$dA/dt = i\mathcal{L}A \quad (1)$$

also obeys the closed-form equation

$$\dot{A}(t) = i\Omega A(t) - \int_0^t ds K(s)A(t-s) + F(t). \quad (2)$$

The three terms on the RHS are named as the **frequency matrix**, the **memory function**, and the **fluctuating force**, respectively. The fluctuating force collects all “fast” variables that are orthogonal to A , and the memory function is the time autocorrelation function of the fluctuating force. These two terms represent how A gets connected to (in the case in a quantum theory, entangled with) the degrees of freedom that are ignored. Assuming we already have an inner product defined on physical quantities, which is usually

$$(A, B) = \langle A^* B \rangle, \quad (3)$$

we have

$$i\Omega = (A, i\mathcal{L}A)(A, A)^{-1}, \quad (4)$$

$$F(t) = e^{it(1-\mathcal{P})\mathcal{L}}i(1-\mathcal{P})\mathcal{L}A, \quad (F(t), A(0)) = 0, \quad (5)$$

and

$$K(t) = -(i\mathcal{L}F(t), A)(A, A)^{-1} = (F(0), F(t))(A, A)^{-1}, \quad (6)$$

where

$$\mathcal{P}X = (A, A)^{-1}(X, A)A. \quad (7)$$

Note that the convention of notation varies in the literature, and the two expressions of $K(t)$ in (6) can both be seen. We require A to be “slow” variables (or satisfy other conditions that somehow separate it from other degrees of freedom), or otherwise fluctuation is too strong for A to be a useful quantity.

Of course we can have several slow variables and several fast variables. Therefore, we may replace A by a vector. Note that at this time, Ω, F and K are matrices, and it can be found that (3) should be replaced by

$$\langle A, B \rangle = \langle A^* B^\top \rangle, \quad (8)$$

instead of

$$\langle A, B \rangle = \langle A^\dagger B \rangle.$$

2 The exact MCT equation

Now we go back to derive a theory about glass transition. The derivation shown below is mainly based on [3], but the notation is from [1]. Note that the spacial translation symmetry gives

$$\langle \rho(0,0)\rho(\mathbf{r},t) \rangle = \frac{1}{V} \int \frac{d^3\mathbf{k}}{(2\pi)^3} e^{-i\mathbf{k}\cdot\mathbf{r}} \langle \rho_{-\mathbf{k}}(0)\rho_{\mathbf{k}}(t) \rangle, \quad (9)$$

and since no valuable information is provided when $|\mathbf{r}| \rightarrow 0$, we will work on the correlation function in the momentum space to separate different spatial scales. What we are going to do is to find a self-consistent equation about the density-density correlation function in the small momentum region (or the large $|\mathbf{r}|$ region). We denote the correlation function as

$$F(k,t) = \frac{1}{N} \langle \rho_{-\mathbf{k}}(0)\rho_{\mathbf{k}}(t) \rangle = \frac{1}{N} \sum_{ij} \left\langle e^{-i\mathbf{k}\cdot\mathbf{r}_i(0)} e^{i\mathbf{k}\cdot\mathbf{r}_j(t)} \right\rangle, \quad (10)$$

where

$$\begin{aligned} \rho_{\mathbf{k}}(t) &= \int d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r},t) \\ &= \sum_i \int d^3\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_i(t)) \\ &= \sum_i e^{i\mathbf{k}\cdot\mathbf{r}_i(t)}. \end{aligned} \quad (11)$$

Specifically, we have

$$F(k,0) = S(k), \quad (12)$$

which is the static structural factor.

We are going to apply the Mori-Zwanzig formalism to $F(k,t)$. We need to find some slow variables and apply (2) to them to find their dynamics, and then we are able to find the dynamics of $F(k,t)$. It can be easily noticed that since we are interested in the small k region, the time derivative

$$\dot{\rho}_{\mathbf{k}} = \sum_i \frac{i\mathbf{k} \cdot \mathbf{p}_i}{m} e^{i\mathbf{k}\cdot\mathbf{r}_i}$$

is also small, and therefore $\rho_{\mathbf{k}}(t)$ is a slow variable. Then we also find that

$$i|\mathbf{k}|j_{\mathbf{k}}^L = i\mathbf{k} \cdot \underbrace{\sum_i \frac{\mathbf{p}_i}{m} e^{i\mathbf{k}\cdot\mathbf{r}_i}}_{j_{\mathbf{k}}}$$

is a slow variable. So the slow variable set is

$$\mathbf{A} = \begin{pmatrix} \delta\rho_{\mathbf{k}} \\ j_{\mathbf{k}}^L \end{pmatrix}, \quad (13)$$

where

$$\delta\rho_{\mathbf{k}} = \rho_{\mathbf{k}} - \langle \rho_{\mathbf{k}} \rangle = \sum_i e^{i\mathbf{q}\cdot\mathbf{r}_i} - (2\pi)^3 \rho \delta(\mathbf{q}). \quad (14)$$

Applying (2) to \mathbf{A} , we have

$$\dot{\mathbf{A}}(t) = i\Omega\mathbf{A}(t) - \int_0^t ds \mathbf{K}(s)\mathbf{A}(t-s) + \mathbf{F}(t),$$

and since

$$\langle \mathbf{A}(0), \mathbf{F}(t) \rangle = \langle \mathbf{A}(0)^* \mathbf{F}(t)^\top \rangle = 0,$$

which is a result in the Mori-Zwanzig formalism, we have

$$\dot{\mathbf{C}} = i\Omega\mathbf{C}(t) - \int_0^t ds \mathbf{K}(s)\mathbf{C}(t-s), \quad (15)$$

where we have

$$\mathbf{C}(t) = \langle \mathbf{A}(0)^* \mathbf{A}(t)^\top \rangle = \begin{pmatrix} \langle \delta \rho_{-\mathbf{q}}(0) \delta \rho_{\mathbf{q}}(t) \rangle & \langle \delta \rho_{-\mathbf{q}} j_{\mathbf{q}}^L(t) \rangle \\ \langle j_{-\mathbf{q}}^L(0) \delta \rho_{\mathbf{q}}(t) \rangle & \langle j_{-\mathbf{q}}^L(0) j_{\mathbf{q}}^L(t) \rangle \end{pmatrix}, \quad (16)$$

$$\begin{aligned} i\Omega &= \langle \mathbf{A}, \dot{\mathbf{A}} \rangle \langle \mathbf{A}, \mathbf{A} \rangle^{-1} \\ &= \begin{pmatrix} \langle \delta \rho_{-\mathbf{q}} \delta \dot{\rho}_{\mathbf{q}} \rangle & \langle \delta \rho_{-\mathbf{q}} \delta \dot{j}_{\mathbf{q}}^L \rangle \\ \langle \delta j_{-\mathbf{q}}^L \delta \dot{\rho}_{\mathbf{q}} \rangle & \langle \delta j_{-\mathbf{q}}^L \delta \dot{j}_{\mathbf{q}}^L \rangle \end{pmatrix} \begin{pmatrix} \langle \delta \rho_{-\mathbf{q}} \delta \rho_{\mathbf{q}} \rangle & \langle \delta \rho_{-\mathbf{q}} \delta j_{\mathbf{q}}^L \rangle \\ \langle \delta j_{-\mathbf{q}}^L \delta \rho_{\mathbf{q}} \rangle & \langle \delta j_{-\mathbf{q}}^L \delta j_{\mathbf{q}}^L \rangle \end{pmatrix}^{-1} \end{aligned} \quad (17)$$

Note that unitarity guarantees that the $\langle \mathbf{A}, \mathbf{A} \rangle$ factor in (17) is constant, and therefore we have

$$\begin{pmatrix} \langle \delta \rho_{-\mathbf{q}} \delta \rho_{\mathbf{q}} \rangle & \langle \delta \rho_{-\mathbf{q}} \delta j_{\mathbf{q}}^L \rangle \\ \langle \delta j_{-\mathbf{q}}^L \delta \rho_{\mathbf{q}} \rangle & \langle \delta j_{-\mathbf{q}}^L \delta j_{\mathbf{q}}^L \rangle \end{pmatrix} = \begin{pmatrix} NS(q) & 0 \\ 0 & \frac{Nk_B T}{m} \end{pmatrix},$$

where

$$\langle \delta \rho_{-\mathbf{q}} \delta j_{\mathbf{q}}^L \rangle \propto \mathbf{q} \cdot \langle \mathbf{p} \rangle = 0,$$

and Here and below we calculate all expectations with the assumption that the translational symmetry is not broken, and therefore the probabilistic distributions of positions and momenta are independent.

References

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