Mode-Coupling Theory of the Glass Transition

Jinyuan Wu

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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

$$\mathrm{d}A/\mathrm{d}t = \mathrm{i}\mathcal{L}A \tag{1}$$

also obeys the closed-form equation

$$\dot{A}(t) = \mathrm{i}\Omega A(t) - \int_0^t \mathrm{d}s\, K(s) A(t-s) + F(t). \tag{2}$$

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

$$(A, B) = \langle A^* B \rangle\,, \tag{3}$$

we have

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

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

and

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

where

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

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.

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

$$\langle \rho(0, 0)\rho(\boldsymbol{r}, t)\rangle = \frac{1}{V}\int \frac{\mathrm{d}^3\boldsymbol{k}}{(2\pi)^3}\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}\langle \rho_{-\boldsymbol{k}}(0)\rho_{\boldsymbol{k}}(t)\rangle\,, \tag{8}$$

and since no valuable information is provided when $|\boldsymbol{r}| \to 0$, 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 $|\boldsymbol{r}|$ region). We denote the correlation function as

$$F(k,t) = \frac{1}{N} \langle \rho_{-\boldsymbol{k}}(0)\rho_{\boldsymbol{k}}(t)\rangle = \frac{1}{N} \sum_{ij} \left\langle \mathrm{e}^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i(0)} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_j(t)} \right\rangle, \tag{9}$$

where

$$\begin{aligned} \rho_{\boldsymbol{k}}(t) &= \int \mathrm{d}^3\boldsymbol{r}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \rho(\boldsymbol{r},t) \\ &= \sum_i \int \mathrm{d}^3\boldsymbol{r}\, \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}} \delta\left(\boldsymbol{r} - \boldsymbol{r}_i(t)\right) \\ &= \sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_i(t)}. \end{aligned} \tag{10}$$

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

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

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

$$\mathrm{i}|\boldsymbol{k}|\, j^{\mathrm{L}}_{\boldsymbol{k}} = \mathrm{i}\boldsymbol{k} \cdot \underbrace{\sum_i \frac{\boldsymbol{p}_i}{m} \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}}}_{\boldsymbol{j}_{\boldsymbol{k}}}$$

is a slow variable. So the slow variable set is

$$\mathbf{A} = \begin{pmatrix} \delta\rho_{\boldsymbol{k}} \\ j^{\mathrm{L}}_{\boldsymbol{k}} \end{pmatrix}, \tag{11}$$

where

$$\delta\rho_{\boldsymbol{k}} = \rho_{\boldsymbol{k}} - \langle \rho_{\boldsymbol{k}} \rangle = \sum_i \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_i} - (2\pi)^3 \rho \delta(\boldsymbol{q}). \tag{12}$$

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

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

and since

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

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

$$\dot{\mathbf{C}} = \mathrm{i}\boldsymbol{\Omega}\mathbf{C}(t) - \int_0^t \mathrm{d}s\, \mathbf{K}(s)\mathbf{C}(t-s), \tag{13}$$

where we define

$$\mathbf{C}(t) = \langle \mathbf{A}^\dagger(0)\mathbf{A}(t) \rangle = \begin{pmatrix} \langle \delta\rho_{-\boldsymbol{q}}\delta\rho_{\boldsymbol{q}}(t) \rangle & \left\langle \delta\rho_{-\boldsymbol{q}} j^{\mathrm{L}}_{\boldsymbol{q}}(t) \right\rangle \\ \left\langle j^{\mathrm{L}}_{-\boldsymbol{q}} \delta\rho_{\boldsymbol{q}}(t) \right\rangle & \left\langle j^{\mathrm{L}}_{-\boldsymbol{q}} j^{\mathrm{L}}_{\boldsymbol{q}}(t) \right\rangle \end{pmatrix}. \tag{14}$$

Viscosity may be viewed as

References

[1] Shankar P. Das. Mode-coupling theory and the glass transition in supercooled liquids. *Rev. Mod. Phys.*, 76:785–851, Oct 2004.

[2] Liesbeth M. C. Janssen. Mode-coupling theory of the glass transition: A primer. *Frontiers in Physics*, 6, Oct 2018.

[3] David R Reichman and Patrick Charbonneau. Mode-coupling theory. *Journal of Statistical Mechanics: Theory and Experiment*, 2005(05):P05013, May 2005.

[4] Wikipedia. Mori-zwanzig formalism. https://en.wikipedia.org/wiki/Mori-Zwanzig_formalism. Accessed: 2021-11-18 09:30:13.