Cooperative heterogeneous facilitation: multiple glassy states and glass-glass transition

Mauro Sellitto

Department of Information Engineering, Second University of Naples, I-81031 Aversa (CE), Italy

The formal structure of glass singularities in the mode-coupling theory (MCT) of supercooled liquids dynamics is closely related to that appearing in the analysis of heterogeneous bootstrap percolation on Bethe lattices, random graphs and complex networks. Starting from this observation one can build up microscopic on lattice realizations of schematic MCT based on cooperative facilitated spin mixtures. I discuss a microscopic implementation of the $F_{13}$ schematic model including multiple glassy states and the glass-glass transition. Results suggest that our approach is flexible enough to bridge alternative theoretical descriptions of glassy matter based on the notions of quenched disorder and dynamic facilitation.

Mode-coupling theory (MCT) is considered by many the most comprehensive first-principle approach to the dynamics of supercooled liquids [1]. Nevertheless, its status is rather problematic from a fundamental point of view, as the physical nature of the glass state and the microscopic interpretation of structural arrest are not yet fully elucidated. This is all the more so when we look at the higher-order glass singularities in structured and complex liquids. In this Rapid Communication, I show that multiple glassy states and glass-glass transition in MCT can be understood in terms of a generalisation of the notion of dynamic facilitation [2, 3] and bootstrap percolation [4, 5]. The latter is known to emerge in a variety of contexts including jamming of granular materials [6], NP-hard combinatorial optimization problems [7], neural and immune networks [8, 9], and evolutionary modeling [10].

The formal structure of glass singularities predicted by MCT is encoded in the self-consistent equation

$$\Phi = (1 - \Phi) M(\Phi),$$

where $\Phi$ is the asymptotic value of the correlator, and $M$ is the memory kernel describing the retarded friction effect caused by particle caging, a physical feature associated with the de Gennes narrowing. We shall be concerned in the following with one-component schematic models in which the wavevector dependence of $\Phi$ is disregarded and $M$ is a low order polynomial. Equation (1) is derived by taking the long-time of the integro-differential equation describing the evolution of the correlator of particle density fluctuations—generates a hierarchy of topologically stable glass singularities, which can be classified in terms of bifurcations exhibited by the roots of the real polynomial

$$Q(\Phi) = \Phi - (1 - \Phi) M(\Phi),$$

Following Arnol’d notation, adopted in [1], an $A_2$ glass singularity occurs when the corresponding maximum root of $Q$ has a degeneracy $\ell$, $\ell \geq 2$, and is defined by

$$\frac{d^n Q}{d\Phi^n} = 0, \quad n = 0, \cdots, \ell - 1,$$

while the $\ell$th derivative is nonzero. The polynomial $Q$ has always the trivial root $\Phi = 0$, corresponding to a liquid ergodic state, whereas nonzero values of $\Phi$ correspond to a system that is unable to fully relax and hence can be identified with a glass nonergodic state.

For two-parameter systems there are two basic singularities, $A_2$ and $A_3$, also known as fold and cusp bifurcations. They have been extensively studied by using memory kernels given by a superposition of linear and nonlinear terms. In the $F_{12}$ schematic model the memory kernel is $M(\Phi) = v_1 \Phi + v_2 \Phi^2$ while the $F_{13}$ model is defined by $M(\Phi) = v_1 \Phi + v_3 \Phi^3$. The competition between the two terms produces a variety of nonergodic behaviors: the linear term gives rise to a continuous liquid-glass transitions at which $\Phi \sim \epsilon$, while $\epsilon$ is the distance from the critical point (e.g., $\epsilon = T - T_c$), while the nonlinear term induces a discontinuous liquid-glass transition, with the well known square-root anomaly $\Phi - \Phi_c \sim \epsilon^{1/2}$. In the $F_{12}$ scenario the discontinuous line joins smoothly the continuous one at a tricritical point. In the $F_{13}$ scenario, the discontinuous transition line terminates at an $A_3$ singularity inside the glass phase generated by the continuous liquid-glass transition, and therefore inducing a glass-glass transition (see Fig. 1 for a representative phase diagram). The scaling form of the order parameter near the $A_3$ endpoint is $\Phi - \Phi_c \sim \epsilon^{1/3}$, and more generally $\Phi - \Phi_c \sim \epsilon^{1/\ell}$ for an $A_\ell$ singularity, as implied by the Taylor expansion of $Q$ near the critical surface and Eqs. (3). Thus one can observe a rich variety of nonergodic behaviors whose complexity is comparable to that of multicritical points in phase equilibria [11]. It is a nontrivial result that only bifurcation singularities of type $A_\ell$ can occur in MCT [1].

The $F_{12}$ and $F_{13}$ scenarios were first introduced with the mere intention of demonstrating the existence of higher-order singularities and glass-glass transition, and then were subsequently observed in a number of experiments and numerical simulations of realistic model systems [12–20]. It is important to emphasize that the parameters $v_i$ entering the memory kernel are smooth functions of the thermodynamic variables, e.g. temperature and density, therefore the nature of nonergodic behaviors predicted by MCT is purely dynamic. This is rather puzzling from the statistical mechanics perspective of critical phenomena where diverging relaxation time-scales are closely tied to thermodynamic singularity. It has been ar-
guessed that this unusual situation stems from uncontrolled approximations. For example, the intimate connection of some spin-glass models with MCT has brought to the fore the existence of a genuine thermodynamic glass phase at a Kauzmann temperature \( T_K \) below the putative dynamic glass transition predicted by MCT \cite{21,22}. A non-trivial Gibbs measure, induced by a replica-symmetry breaking, would therefore be actually responsible for the observed glassy behavior \cite{23}. For this reason, the nature of the MCT has been much debated since its first appearance and several approaches have been attempted to clarify its status \cite{21,30}. I will show here that the idea of dynamic facilitation \cite{3}, first introduced by Fredrickson and Andersen \cite{2}, offers some clues in this direction for its relation with bootstrap percolation provides a transparent microscopic mechanism of structural arrest \cite{4,31}. In the dynamic facilitation approach the coarse-grained structure of a supercooled liquid is represented by an assembly of higher/lower density mesoscopic cells. In the simplest version a binary spin variable, \( s_i = \pm 1 \), is assigned to every cell \( i \) depending on its solid or liquid like structure and no energetic interaction among cells is assumed, \( H = -h \sum_i s_i \). The crucial assumption is that the supercooled liquid dynamics is essentially dominated by the cage effect: fluctuations in the cells structure occur if and only if there is a certain number, say \( f \), of nearby liquid-like cells. \( f \) is called the facilitation parameter and can take values in the range \( 0 \leq f \leq z \), where \( z \) is the lattice coordination: cooperative facilitation imposes \( f \geq 2 \), while non-cooperative dynamics only requires \( f = 1 \). This very schematic representation of the cage effect gives rise to a large variety of remarkable glassy behaviors, and it has long been noticed that they are surprisingly similar to those found in the dynamic of mean-field disordered systems \cite{32,34}. It has been recently observed that in a special case, an exact mapping between facilitated and disordered models with \( T_K = 0 \), exists \cite{35}. Since such models are so utterly different in their premises, it is by no means obvious that such a correspondence is not accidental and can be extended to systems with higher-order glass singularities. To clarify this issue, I will consider a generalization of the facilitation approach \cite{36} in which every cell \( i \) is allowed to have its own facilitation parameter \( f_i \) (or, equivalently, an inhomogeneous local lattice connectivity). Physically, this situation may arise from the coexistence of different length-scales in the system, e.g., mixtures of more or less mobile molecules or polymers with small and large size, (or from a geometrically disordered environment, e.g., a porous matrix). In such facilitated spin mixtures the facilitation strength can be tuned smoothly and is generally described by the probability distribution

\[
\pi(f_i) = \sum_{\zeta=0}^{z} w_\zeta \delta_{f_i,\zeta}, \quad (4)
\]

where the weights \( \{w_\zeta\} \) controlling the facilitation strength satisfy the conditions

\[
\sum_{\zeta=0}^{z} w_\zeta = 1, \quad 0 \leq w_\zeta \leq 1. \quad (5)
\]

By tuning the weights one can thus explore a variety of different situations. Generally, one observes that when the fraction of spins with facilitation \( f = z - 1, z \) is larger than that with \( 2 \leq f \leq z - 2 \), the glass transition is continuous while in the opposite case it is discontinuous. One advantage of the facilitation approach is that when the lattice topology has a local tree-like structure, one can compute exactly some key quantities, such as the critical temperature and the arrested part of correlation and its scaling properties near criticality. This can be done by exploiting the analogy with bootstrap percolation. Let \( p \) be the density of up spins in thermal equilibrium,

\[
p = \frac{1}{1 + e^{-h/k_B T}}, \quad (6)
\]

for a generic spin mixture on a Bethe lattice with branching ratio \( k = z - 1 \). As usual, one arranges the lattice as a tree with \( k \) branches going up from each node and one going down, and then proceeds downwards. In analogy with the heterogeneous bootstrap percolation problem, the probability \( B \) that a cell is in, or can be brought into, the liquid-like state by only rearranging the state of \( k \) cells above it \( \Phi \), can be cast in the form

\[
1 - B = B p \left\langle \sum_{i=k-f+1}^{k} \binom{k}{i} B^{k-i-1} (1-B)^i \right\rangle_f, \quad (7)
\]

where \( \langle \cdots \rangle_f \) represents the average over the probability distribution Eq. (4). The right-hand side of Eq. (7) is a polynomial of \( 1 - B \), and hence the formal structure of Eq. (7) is similar to that of schematic MCT (once \( 1 - B \) is formally identified with \( \Phi \)). Singularities can therefore be classified according to the criteria already mentioned in the introduction. Nevertheless, it should be noticed that what would be the analog of the MCT kernel in Eq. (7) can also have negative coefficients (besides containing an extra term of the form \( (1 - B)^k / B \)), while the polynomial coefficients of the MCT memory kernel are restricted to non-negative ones. In fact, the sets of critical states which specify some \( A_g \) glass-transition singularity are not identical to those describing the full bifurcation scenario of real polynomials of degree \( \ell \), because the coefficients of the admissible polynomials \( Q \) form only a subset of all real coefficients. This observation means that the correspondence between MCT and the heterogeneous facilitation approach is not an identity, but this still leaves enough room for building up models with MCT features, although some ingenuity may be required. It has already been shown, for example, that the \( F_{13} \) scenario is faithfully reproduced in this framework \cite{35,37,38}. To substantiate the above observation, I will now focus on the next higher-order glass singularity, which is the \( F_{13} \) scenario.
Let us consider, for simplicity, a binary mixture on a Bethe lattice with $z = 5$ and

$$\pi(f_i) = (1-q)\delta_{f_i,2} + q\delta_{f_i,4}. \quad (8)$$

For such a mixture, denoted here as (2,4), the probability $B$ obeys the fixed-point equation:

$$1 - B = p \left[ q(1-B^4) + (1-q)(1-B)^3(1+3B) \right]. \quad (9)$$

This equation is always satisfied by $1 - B = 0$, while an additional solution with $1 - B > 0$ is found by solving

$$p^{-1} = 1 + B - 5B^2 + 3B^3 + 2qB^3(3-B). \quad (10)$$

A continuous glass transition is obtained by setting $B = 1$ in the previous equation, giving: $p_c = 1/4q$. Using the relation between $T$ and $p$ (and setting $h/k_n = 1$), one gets $T_c(q) = -1/\ln(4q - 1)$, implying that the continuous transition exists in the range $1/2 \geq q \geq 1/4$. The discontinuous transition instead occurs when Eq. (10) is satisfied and its first derivative with respect to $B$ vanishes. The latter condition implies

$$q = \frac{(9B - 1)(1-B)}{6B(2-B)}, \quad (11)$$

and naturally leads to the square-root scaling near the discontinuous transition line. Thus the discontinuous transition can be graphically represented by Eqs. (10) and (11) in parametric form in terms of $B$. The phase diagram in the plane $(T, q)$ is shown in the Fig. 1. It exhibits two crossing glass transition lines, with continuous and discontinuous nature, corresponding to a degenerate and generic $A_3$ singularities. The discontinuous branch extends into the glass region below the continuous line up to a terminal endpoint which corresponds to an $A_3$ singularity. The location of the endpoint is found by simultaneously solving equation

$$B = \frac{5 - 6q}{9 - 6q}, \quad (12)$$

(which is obtained by setting the second derivative of Eq. (11) to zero), along with Eqs. (10) and (11). The discontinuous branch located between the crossing point and the endpoint corresponds to a transition between two distinct glass states, called here glass 1 and glass 2. They are respectively characterized by a fractal and compact structure of the spanning cluster of frozen particles. The passage from one glass to the other can take place either continuously or without meeting any singularity, i.e. by circling around the endpoint (in a way much similar to liquid-gas transformation). The existence of two transitions in bootstrap percolation was first discovered by Fontes and Schonmann [38] in homogeneous trees and then found in Erdős-Rényi graphs and complex networks in [39, 40]. However, its relation with glass-glass transition and MCT went unnoticed. In fact, the correspondence between Eqs. (1) and (7) naturally suggests the existence of further singularities in bootstrap percolation and cooperative facilitated models.

Fig. 2 reports the behavior of the fraction of frozen spins, which is the analog of the nonergodicity parameter in the facilitation approach, when the temperature crosses the liquid-glass continuous transition and the glass-glass transition. This quantity can be exactly computed from $B$ [36, 37], and its expression is not reported here—we only notice that its general features, and in particular the scaling properties near the critical states, are similar to those of $B$. We observe that the fraction of frozen spins first increases smoothly at the liquid-glass continuous transition and then suddenly jumps at the glass-glass transition. The jump decreases when $q$ approaches the endpoint and eventually disappears. At this special point, the additional condition that the second-
order derivative of Eq. [10] with respect to $B$ vanishes, implies a cube-root scaling near the endpoint. These scaling features are exactly those expected from the $F_{13}$ scenario, and we obtain similar results for the mixtures (3,5) on a Bethe lattice with $z = 6$.

To summarise, a close relationship exists between the structure of glass singularities in MCT and that of heterogeneous bootstrap percolation. This allows the construction of microscopic realizations of MCT scenarios based on the heterogeneous cooperative facilitation approach and provides further insights into the degree of universality of MCT. The role of the linear and nonlinear terms in the MCT memory kernel is played in facilitated spin mixtures by the fraction of spins with facilitation $f = k, k + 1$ and $k - 1 \geq f \geq 2$, respectively.

Their competition generates continuous and discontinuous liquid-glass transitions, while the order of singularity is primarily controlled by the lattice connectivity. This leads to multiple glassy states, glass-glass transition and more complex glassy behaviors. In this framework, the mechanism of structural arrest can be geometrically interpreted in terms of the formation of a spanning cluster of frozen spin having fractal or compact structure depending on the continuous or discontinuous nature of the glass transition. Finally, from the relation between MCT and mean-field disordered systems [21, 22] it follows that quenched disorder and cooperative facilitation are two complementary, rather than alternative, descriptions of glassy matter, and this contributes to the long sought unifying approach to glass physics.

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