Disconnected glass-glass transitions and swallowtail bifurcations in microscopic spin models with facilitated dynamics

Mauro Sellitto

Dipartimento di Ingegneria Industriale e dell’Informazione,
Seconda Università di Napoli, Real Casa dell’Annunziata, I-81031 Aversa (CE), Italy

It has been recently established that heterogeneous bootstrap percolation and related dynamic facilitation models exhibit a complex hierarchy of continuous and discontinuous transitions depending on lattice connectivity and kinetic constraints. Here the range of the previously observed phase diagram topologies and higher-order singularities is extended to disconnected glass-glass transitions and swallowtail bifurcations (generic and degenerate). The phase diagram and the order parameter for two different types of spin mixtures are analytically determined and an experimental realization of the new predictions emerging in our approach is suggested.

Soft matter enjoys a rich variety of multiphase equilibria due to the subtle interplay of energetic and entropic forces acting on different length scales. When one of the parameters controlling the system thermodynamics is suddenly changed, however, the phase formation is generally hindered for kinetic reasons and one observes amorphous states with distinct physical (as opposed to chemical) features. Such novel states of structural arrest and the glass-to-glass transition they can possibly undergo, were first predicted within schematic Mode-Coupling Theory (MCT) [1], and have been subsequently observed in short-range attractive colloids, dense copolymer micellar solutions, and molecular dynamics simulations of model systems [2–12]. Their characterization is not only technologically important for material design but is also a theoretical challenge, as there is no obvious way to discriminate on a macroscopic scale disordered patterns that are apparently featureless from a geometric standpoint.

Especially intriguing in this regard, is the existence of a peculiar glass-to-glass transition that has been recently identified in hard-sphere systems with a square-shoulder potential. In these systems the competition between the two repulsive length scales, naturally introduced by the interaction potential, makes the glass-glass transition completely disconnected from the liquid phase in a certain range of the control parameters. In this paper I show that similar features generally exist in microscopic on-lattice models with facilitated dynamics. A new prediction that emerges from our calculations is that the disconnected glass-glass transition can appear in systems with either a discontinuous or a continuous liquid-glass transition. The framework naturally suggests that the latter possibility should be realized in fluid mixtures confined in a disordered porous matrix. Our theoretical analysis, which is complementary to MCT, confirms that these features are controlled primarily by the interplay of steric or kinetic hindrance effects on different microscopic length scales (due, e.g., to particles of dissimilar size), and are therefore generally expected in multicomponents systems whenever competing packing effects are important.

Heterogeneous facilitation approach. In the past decades there has been a long lasting effort to identify valuable on-lattice models enabling a detailed analysis of the microscopic mechanism behind the glass transition. A promising approach in this direction is provided by the heterogeneous extension of bootstrap percolation and dynamic facilitation ideas [13–16]. In this framework, the coarse-grained structure of a system is represented by an assembly of mesoscopic cells. Typically, to every cell $i$ is assigned a binary spin variable, $s_i = \pm 1$, depending on the average local density (higher or lower). In the simplest case, no energetic interaction among cells is assumed, $\mathcal{H} = -h \sum_i s_i$. The crucial assumption is that the temporal evolution of the system is dictated by a kinetic constraint: fluctuations in the cell $i$ occur if and only if there is a certain number, say $f_i$, of nearby low-density cells. $f_i$ is the local facilitation (or threshold) parameter which mimics the local cage effect and can take values in the range $0 \leq f_i \leq z$, where $z$ is the lattice connectivity. The facilitation distribution $\pi(f)$ reflects the coexistence of different length scales in the system, e.g., mixtures of more or less mobile molecules, or mixtures of polymers with small and large gyration radius. In facilitated spin mixtures the average strength of kinetic constraints can be tuned smoothly by changing the populations of spins with different $f_i$, and one can thus explore a variety of different situations. Interesting results are obtained when the facilitated dynamics is cooperative, i.e., when $f_i \geq 2$. Explicit calculations and detailed numerical simulations have shown that the basic results of MCT schematic models are well reproduced within this framework [16–18]. Qualitatively, when the fraction of spins with $f_i = z - 1, z$ is larger than that with $2 \leq f_i \leq z - 2$, the liquid-glass transition is continuous (and the incipient cluster of frozen spins is fractal) while in the opposite case it is discontinuous (with a corresponding core having a compact structure). In the intermediate situation there is a crossover between the two transitions that can be either smooth [17] or abrupt [18]. In the latter case, the discontinuous transi-
tion extends deep inside the glass phase, thus generating an extra glass-glass transition [18]. As we are going to see in the remaining part of the paper, unusual features occur when a more subtle competition between clusters of frozen spins with different facilitations is present.

**Formalism.** Exploiting the analogy with heterogeneous bootstrap percolation on a locally tree-like random graphs [13–17] one can see that the probability $B$ that a cell is, or can be brought, in the lower density state by only rearranging the state of the nearby $z-1$ cells obeys a self-consistent polynomial equation $Q(B) = 0$ where

$$Q(B) = 1 - B - p \Psi_{z-1}(1 - B),$$

and we have defined the auxiliary function

$$\Psi_f(X) = \left\langle \sum_{n=0}^{f-1} \left( \frac{z}{n} \right) X^{z-n}(1 - X)^n \right\rangle.$$  

(2)

Here $p$ is the fraction of high-density cells in thermal equilibrium at temperature $T$, $p^{-1} = 1 + \exp(-h/k_B T)$, and the angular brackets, $\langle \cdots \rangle$, represents the average over the probability distribution, $\pi(f)$, of kinetic constraints. Quite generally, one finds that at high temperature every cell can always change state, $B = 1$, while at low temperature there is a fraction of spins which is unable to change state, $B < 1$, and the system is therefore a glass. The detailed topology of the phase diagram at low temperature depends on the coefficients of the polynomial $Q(B)$ and can be rather intricate. Interestingly, the self-consistent equation $Q(B) = 0$ has a formal structure quite similar to that satisfied by the long-time limit of the form factor in MCT. Accordingly, one can immediately draw the conclusion that $Q(B)$ exhibits the same hierarchy of bifurcations, $A_e$, of schematic MCT. They occur when the corresponding maximum root of $Q$ has a degeneracy $\ell$ ($\ell \geq 2$) and

$$\frac{d^n Q}{dB^n} = 0, \ n = 0, \ldots, \ell - 1; \quad \frac{d^\ell Q}{dB^\ell} \neq 0.$$  

(3)

The Taylor expansion of $Q$ near the critical surface and Eqs. (3), immediately implies that the scaling form of the order parameter near an $A_e$ bifurcation goes like $e^{1/\ell}$, where $\epsilon$ is the distance from the critical surface (e.g., $\epsilon = T - T_c$). Singularities of type $A_e$ can be further distinguished in generic and degenerate depending on whether the order parameter, $\Phi$, changes abruptly or smoothly near the transition. To denote this latter case, we shall use the notation $A_e^*$. In the following, we shall focus on ternary mixtures with facilitation distribution

$$\pi(f_i) = (1 - q)\delta_{f_i,a} + (q - r)\delta_{f_i,b} + r\delta_{f_i,c}$$

(4)

For such ternary mixtures, denoted here with $(a, b, c)$, we shall consider two distinct situations corresponding to small and large facilitation variance per spin population $\sigma_q^2 = ((f^2) - (f)^2)/3$. For each situation, we determine the phase diagram and compute the fraction of permanently frozen spins, $\Phi$, which represents the actual order parameter in this framework. It is directly related to $B$ through the general relation

$$\Phi = p \Psi_f(B) + (1 - p)\Psi_f(p\Psi_{f-1}(B)).$$  

(5)

For sake of simplicity we shall consider hereafter only random graphs with fixed connectivity, i.e. Bethe lattices. Similar results are expected in more general random graphs with variable connectivity [16, 19, 20].

**Mixture with small $\sigma_q^2$.** Let us first consider the $(2, 3, 4)$ mixture on a Bethe lattice with $z = 5$. For such a mixture, the fixed-point equation obeyed by $B$ is:

$$1 = 1 - B - 5B^2 + 3B^3 + 6qB^2(1 - B) + 4rB^3.$$  

(6)

The continuous glass transition, $T_c(r) = -1/\ln(4r - 1)$, is obtained by setting $B = 1$ in Eq. (6). Therefore, it does not depend on $q$ and is limited to the range $1/2 \geq r \geq 1/4$ (we do not consider here the case of negative temperature). Setting the first-order derivative of Eq. (6) is zero, we get

$$r = \frac{9B^2 + 10B - 1 - 12rB^2}{12B - 18B^2};$$  

(7)

and thus the discontinuous transition is obtained by plotting Eqs. (6) and (7) parametrically in terms of $B$. A section of the phase diagram illustrating the distinct topologies of the transition lines obtained for different values of $r$ (i.e., the fraction of spins with $f = 4$), is shown in the
and we expect they should be observed in other systems, which we observe the disconnected glass-glass transition. The order parameter with for a value of $r$ something more interesting happens: we observe that the glass-to-glass transition departs from the continuous liquid-glass transition and becomes completely disconnected from the liquid phase. This departure generates an extra endpoint singularity corresponding to a generic cusp bifurcation, $A_3$. The range of $q$ values over which the transition is disconnected widens until the the glass-glass transition eventually disappears.

The endpoints of the glass-glass transition lines define a set of generic cusp singularities, $A_3$, whereas the crossing points between the continuous and discontinuous liquid-glass transitions correspond to degenerate cusp singularities, $A_3^*$. They are respectively given by

$$\frac{1}{T(q)} = \begin{cases} \ln(15 - 18q), & A_3; \\ -\ln(2q - 1), & A_3^* \end{cases}$$

Either curves possess an unstable branch and are represented in the $(T, q)$ plane in Fig. 2. One can easily check that they coalesce smoothly in a degenerate swallowtail singularity, $A_3^*$, which is exactly located at $q = 2/3$, $r = 1/3$, and $T = 1/\ln 3$. Notice that these values of $q$ and $r$ corresponds to a mixture with an exactly balanced composition of each components $(1 - q - r = r = 1/3)$. For completeness we also show, in Fig. 3, the variation of the order parameter with for a value of $r$ in the range in which we observe the disconnected glass-glass transition.

The above findings have not been previously reported and we expect they should be observed in other systems, e.g., in fluid mixtures confined in porous media. In fact, building on the observations of Refs. [21, 22], spin-glass models with $p + q$ multispin interaction terms when supplemented with an extra random field should reproduce the structure of MCT for a fluid binary mixture in a random environment. However, the kinetic analogue of the three Hamiltonian interaction terms correspond just to the facilitated terms entering the model studied above.

**Mixture with large $\sigma^2_\text{f}$.** – Next we consider, for comparison, the $(2, 5, 7)$ mixture with probability distribution Eq. (4) on a Bethe lattice with $z = 12$. Evidently, since there is no spin population with $f_i = z - 1, z$, the order parameter cannot vanish continuously and so no degenerate singularity is expected. A section of the phase diagram obtained in this case is reported in the Fig. 3 for several values of $r$ illustrating the different topologies of the transition lines we obtain. For $r < 0.4$ we find that there is only a discontinuous liquid-glass transition, i.e., a fold bifurcation, $A_3$ singularity. For $r > 0.4$ it appears an additional cusp bifurcation, $A_3^*$, corresponding to the end point of a glass-glass transition line. The crossover between these two behaviors occurs via a swallowtail bifurcation, $A_4$, which is located at $q \approx 0.773, T \approx 0.296, r \approx 0.40369$. Upon increasing further $r$ the glass-glass transition becomes eventually disconnected from the liquid phase, see the curve $r = 0.68$ in Fig. 3. Therefore, also in this case, spin populations with different values of $f_i$, with $2 \leq f_i \leq z - 2$, compete with each other to produce a disconnected glass-glass transition. As we can observe in Fig. 3 this occurs when the fraction $1 - q$ of spins with $f = 2$ become smaller than that with $f = 7$ (i.e., $r$) and, correspondingly, the fraction of spins with intermediate value of $f_i = 5$, becomes pretty small, $q \approx r$. The variation of the order parameter $\Phi$ with the temperature, $T$, is shown in Fig. 4 for $r$ in the range in which we observe the disconnected glass-
glass transition and several values of $q$. As expected we find that $\Phi$ exhibits a single or a double jumps depending on whether the system crosses one or two transition lines upon lowering the temperature.

The results we find here are qualitatively similar to those obtained in hard-sphere systems with the square-shoulder potential $^{11}$. Nevertheless, in the latter case, there is an interesting extra feature which is not reproduced in our approach: It is the counter-intuitive melting-by-cooling often associated with higher-order singularities. It would be interesting to ascertain the influence of these singularities in the present context, whether they are entropic or energetic in origin.

It is also interesting to notice that the phase diagram we have derived above shares some similarities with that of the spherical $p + q$ spin-glass models (see Fig. 1 in Ref. $^{23}$). The disconnected glass-glass transition, however, is not observed in this spin-glass model. Since a $p$--spin interaction term plays the same role of a facilitated dynamics with $z - 2 \geq f_i \geq 2$, our approach suggests that an additional multispin interaction term in the $p + q$ Hamiltonian is required to observe a disconnected glass-glass transition. Nevertheless, the analysis of this latter case could be rather awkward as it involves delicate aspects of replica symmetry breaking calculations $^{24}$.

Conclusions.— To summarise, I have shown that disconnected glass-glass transitions take place in systems with either a continuous or a discontinuous liquid-glass transition and that the related swallowtail bifurcation can be degenerate or generic, respectively. Such features are controlled primarily by the competition between packing effects on different microscopic length scales, as opposed to system-specific details of the molecular interactions, and are therefore expected in a range of soft matter systems including fluid mixtures confined in porous media, and colloidal and polymer gels. The fact that, starting from very different premises, we reach conclusions quite similar to those obtained in more realistic model systems is neither obvious nor coincidental, and should lend further support to the universality of both MCT and the present framework.

Although the dynamical behavior of facilitated systems can be numerically studied with a relatively modest effort (using continuous-time algorithms) it would be certainly interesting, from a theoretical perspective, to rationalise the anomalous logarithmic relaxation near higher-order singularities through the dynamics of minimal size rearrangements $^{25}$. Similarly, one should be able to identify the conditions under which the parameter exponent, typically denoted with $\lambda$ in MCT, can be derived in the present starting from the “facilitated” analogue of the MCT functional $^{18}$. That would provide an alternative route to the determination of $\lambda$ by-passing the computation of multispin correlation functions recently suggested in Ref. $^{26}$. Work in these directions is in progress and we hope to report on such issues in the near future.

FIG. 4. A section of the phase diagram for the mixture $f = (2, 5, 7)$ on a Bethe lattice with connectivity $z = 12$. The lines represent discontinuous transitions. In this figure, the glass-glass transition occurs for $r = 0.52$, $0.6$ and $0.68$. In the latter case it is disconnected from the liquid phase. Higher-order singularities with cusp and swallowtail structures are denoted with $A_3$ and $A_4$ respectively.

FIG. 5. The order parameter, $\Phi$, representing the fraction of frozen spins vs temperature, $T$, at $r = 0.7$ and for several values of $q$, in the $(2, 5, 7)$ mixture with $z = 12$. The double jump of $\Phi$ for $q = 0.74$ and $0.76$ corresponds to a liquid-glass transition followed by a glass-glass transition upon lowering the temperature.

[1] W. Götze, Complex dynamics of glass-forming liquids, (Oxford University Press, Oxford, 2009).
[2] K. Dawson, G. Foffi, M. Fuchs, W. Götze, F. Sciortino, M. Sperl, P. Tartaglia, T. Voigtmann, and E. Zaccarelli, Phys. Rev. E 63, 011401 (2000).
[3] K.N. Pham, A.M. Puertas, J. Bergenholz, S.U. Egelhaaf, A. Moussaid, P.N. Pusey, A.B. Schofield, M.E. Cates, M. Fuchs, and W.C. Poon, Science 296, 104 (2002).
[4] T. Eckert and E. Bartsch, Phys. Rev. Lett. 89, 125701 (2002).
[5] S. H. Chen, W. R. Chen, and F. Mallamace, Science 300, 619 (2003).
[6] F. Sciortino, P. Tartaglia, and E. Zaccarelli, Phys. Rev. Lett. 91, 268301 (2003).
[7] S.H. Chong, A.J. Moreno, F. Sciortino, W. Kob, Phys. Rev. Lett. 94, 215701 (2005).
[8] V. Krakoviack, Phys. Rev. Lett. 94, 065703 (2005).
[9] J. Kurzidim, D. Coslovich and G. Kahl, Phys. Rev. Lett. 103, 138303 (2009).
[10] K. Kim, K. Miyazaki, and S. Saito, Europhys. Lett. 68, 36002 (2009).
[11] M. Sperl, E. Zaccarelli, F. Sciortino, P. Kumar, and H. E. Stanley, Phys. Rev. Lett. 104, 145701 (2010).
[12] Th. Voigtmann, Europhys. Lett. 96, 36006 (2011).
[13] G.H. Fredrickson and H.C. Andersen, Phys. Rev. Lett. 53, 1244 (1984).
[14] J. Chalupa and P. L. Leath and G. R. Reich, J. Phys. C: Solid State Phys. 12, L31 (1979).
[15] N.S. Branco, J. Stat. Phys. 70, 1035 (1993).
[16] M. Sellitto, D. De Martino, F. Caccioli, and J.J. Arenzon, Phys. Rev. Lett. 105, 265704 (2010).
[17] J. J. Arenzon and M. Sellitto, J. Chem. Phys. 137, 084501 (2012).
[18] M. Sellitto, Phys. Rev. E 86, 030502(R) (2012).
[19] G.J. Baxter, S.N. Dorogovtsev, A.V. Goltsev, and J.F.F. Mendes, Phys. Rev. E 82, 011103 (2010).
[20] D. Cellai and J.P. Gleeson, arXiv 1301.4556; D. Cellai, A. Lawlor, K.A. Dawson, and J.P. Gleeson, Phys. Rev. Lett. 107, 175703 (2011).
[21] S. Ciuchi and A. Crisanti, Europhys. Lett. 49, 754 (2000).
[22] V. Krakoviack, Phys. Rev. E 75, 031503 (2007).
[23] V. Krakoviack, Phys Rev. B 76, 136401 (2007).
[24] A. Crisanti and L. Leuzzi, Phys. Rev. B 76, 136402 (2007).
[25] A. Montanari and G. Semerjian, J. Stat. Phys. 124, 103 (2006).
[26] F. Caltagirone, U. Ferrari, L. Leuzzi, G. Parisi, F. Ricci-Tersenghi, T. Rizzo, Phys. Rev. Lett. 108, 085702 (2012).