

**Evidence of a glass transition induced by rigidity self-organization in a network-forming fluid**

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A Monte Carlo method is used to simulate the competition between the molecular relaxation and crystallization times in the formation of a glass. The results show that nucleation is avoided during supercooling and produces self-organization in the sense of the rigidity theory, where the numbers of geometrical constraints due to bonding and excluded volume are compared with the degrees of freedom available to the system. Following this idea, glass transitions were obtained by producing self-organization, and in the case of geometrical frustration, self-organization is naturally observed.

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**I. INTRODUCTION**

When a liquid melt is cooled, usually two things can happen: the melt crystallizes or, if the speed of cooling is high enough to avoid equilibrium, a solid without long-range order (a glass) is formed. This last process is known as the glass transition (GT), and although is very important from the fundamental and technological point of view, there are still many unsolved questions related to it.<sup>1</sup> Not all materials are able to form glasses, and many criteria have been proposed in order to explain the ability of a material to reach the glassy state.<sup>2</sup> The temperature where the GT occurs is called the glass transition temperature ( $T_g$ ). Many factors determine the  $T_g$ , but among these, the chemical composition is fundamental. Chalcogenide glasses (formed with elements of the VI column) are very useful for understanding the effects of the chemical composition.<sup>3</sup> In fact,  $T_g$  can be raised or lowered by adding impurities, and the fragility of the glass can be changed from strong to fragile.<sup>4</sup> Recently, by using stochastic matrices,<sup>5,6</sup> the empirical modified Gibbs-DiMarzio law that accounts for the relation between  $T_g$  and the concentration of modifiers<sup>7</sup> has been obtained, including the characteristic constant that appears in the law for almost any chalcogenide glass.<sup>8</sup>

The ease of glass formation in covalent glasses can be explained at least in a qualitative way by the rigidity theory, introduced first by Phillips<sup>9</sup> and further refined by Thorpe.<sup>10</sup> By considering the covalent bonding as a mechanical constraint, within this theory, the ease of glass formation is related to the proportion of available degrees of freedom and the number of constraints. If the number of constraints is lower than the degrees of freedom, there are zero-frequency vibrational modes called floppy,<sup>11</sup> and the resulting network is underconstrained. A transition occurs when the lattice becomes rigid, and at the corresponding chemical composition, the glass is easy to form. Many features of this transition have been experimentally observed.<sup>3,12</sup> Also, one of the authors proposed that rigidity can be related to the statistics of the phase-space energy landscape,<sup>13</sup> since the number of floppy modes is equal to the number of different configurations of the system with nearly equal minimal energies<sup>13</sup> and thus is a way to evaluate the function that gives the number of minima energy basins.<sup>14</sup>

In a recent paper, Thorpe *et al.*<sup>15</sup> remarked that in real

glasses, even though formed at relative high temperatures, where the entropic effects are dominant, it is not correct to fully ignore energetic contributions which can favor particular structural arrangements over others (e.g., in a binary system chemical aggregation between unlike particles favors local chemical aggregation). One interesting question that they address is how the structure itself can incorporate nonrandom features in order to minimize the free energy at the temperature of formation. They answer this question by proposing that the structure can self-organize, avoiding stress in the randomly formed network.<sup>15</sup> In the literature exists experimental evidence for self-organization in glasses;<sup>16</sup> this evidence has been associated with the intermediate phase proposed by Phillips.<sup>17,18</sup> In previous work,<sup>19</sup> we observed that in a model of an associative fluid (the Cummings-Stell model), some thermodynamics features can be associated with a rigidity transition, and in particular, it was shown that a glass transition occurs very near to the rigidity transition. Also, we showed that using the Monte Carlo (MC) step as a time parameter in an  $N$ - $P$ - $T$  ensemble, we were able to control the cooling rate of a liquid melt in a qualitative way. In this work, we go further by looking at the self-organization properties in the Cummings-Stell (CS) model, using a MC computer simulation in a grand canonical (GC) ensemble. Compared with the  $N$ - $P$ - $T$  ensemble, the GC ensemble has the advantage of reaching equilibrium faster,<sup>20</sup> given the opportunity to visit a wider range of equilibrium and nonequilibrium phases. In order to talk about the thermodynamic properties of these phases, we base our assumptions in the fact that their lifetime is larger than the observation time (averaged time).<sup>21</sup> This time is also larger than the molecular relaxation time, which we can adjust by tuning the MC steps of single-particle movements and the MC steps of the formed clusters movements. As a consequence, the slower a liquid is cooled, the longer the time available for configuration sampling at each temperature and hence the access to the homogeneous nucleation which leads to crystallization. We point out that this nucleation produces stress in the obtained structure, as a counting of floppy modes reveals. As a counterpart, the faster the liquid is cooled, there is less time available for homogeneous nucleation and hence less stress is produced in the structure, inducing a local self-organization. This framework allows us to address the question of what are the structural and thermodynamic properties of self-organized struc-

tures and how they behave as the system is cooled. With this in mind, we perform MC simulations where configurations that produce stress in the system are rejected, in a similar way to that proposed by Thorpe *et al.*<sup>15</sup> for studying rigidity self-organization. As we will see, our results are in agreement with Ref. 15, since the avoidance of stress biases the system to a glass state. The layout of this work is as follows: in Sec. II we introduce the model to be used, in Sec. III a method for indirect controlling of the various relaxation times is introduced, and in Sec. IV we discuss the effect of self-organization. Finally, in Sec. V the conclusions of the work are given.

## II. MODEL

We choose a simple model of an associative fluid: the Cummings-Stell model (CSM) of a two-component system ( $A$  and  $B$ ) of associating disks in two dimensions (2D), both of the same size.<sup>19</sup> The particles interact via a potential permitting core interpenetration of the  $A$  and  $B$  monomer disks, so that the bond length  $L$  is less than the core diameter  $\sigma$ . Without loss of generality we assume  $\sigma = 1$ . The interactions are given as follows:

$$U_{ij}(r) = U_{ij}^{hd}(r) + (1 - \delta_{ij})U_{as}(r),$$

$$U_{AA}^{hd}(r) = U_{BB}^{hd}(r) = \begin{cases} \infty, & r < 1, \\ 0, & r > 1, \end{cases}$$

$$U_{AB}^{hd}(r) = U_{BA}^{hd}(r) = \begin{cases} \infty, & r < L - 0.5w, \\ D, & L - 0.5w < r < 1, \\ 0, & r > 1, \end{cases}$$

$$U_{as}(r) = \begin{cases} 0, & r < L - 0.5w, \\ -\varepsilon_{as} - D, & L - 0.5w < r < L + 0.5w, \\ 0, & r > L + 0.5w, \end{cases}$$

where  $i$  and  $j$  stand for the species of the particles and take values  $A$  and  $B$ .  $r$  is the separation between centers,  $L$  is the bonding distance, and  $w$  is the width of the attractive intracore square well (Fig. 1). The model allows the formation of dimer species for small values of the bonding length parameter, the formation of chains, if the bonding length is slightly larger, and also vulcanization with fixed maximum coordination number for different bonding length values close to the diameter of particles, as shown in Fig. 1. In order to be able to fix a maximum coordination number in each simulation, we take  $D \rightarrow \infty$  as was done before in other works.<sup>19,22,23</sup> This choice has the effect that unlike particles avoid bond lengths between  $L + 0.5w$  and 1, and thus coordinations higher than a desired maximum are not allowed. Numerically, this condition means that in the MC simulations, we never consider bond distances in the previous range. The corresponding values for each maximum coordination number are given in Table I.

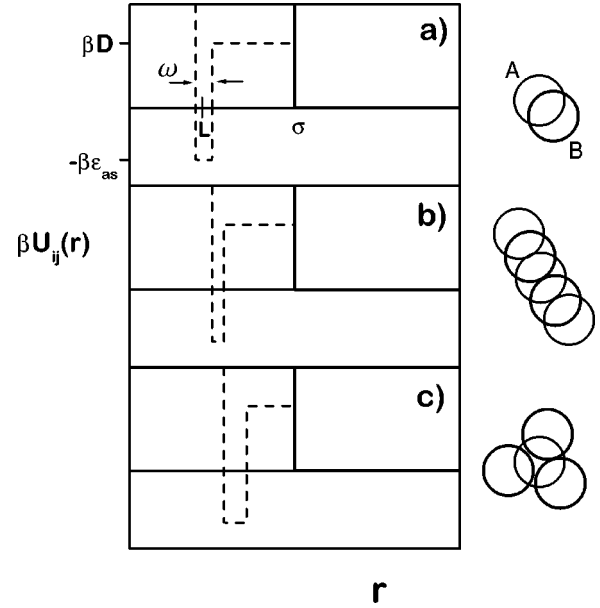


FIG. 1. Cummings-Stell model. (a) Max. coordination one, (b) two, (c) and three.

## III. GLASS TRANSITION BY CONTROLLING RELAXATION TIMES

We start by pointing out that a supercooled liquid phase is metastable with respect to the crystalline state, and this supercooling can be achieved if nucleation is inhibited during cooling.<sup>21</sup> One way of inhibiting nucleation is by performing a rapid quench of the liquid; in these terms, two characteristic times  $\tau_1$  (the time required for crystallization) and  $\tau_2$  (the time corresponding to molecular relaxation) compete between crystallization and vitrification.<sup>21</sup> In this work, we simulate this effect in two different ways, which we will show that at the end turn out to be very similar: one is to use the MC steps as a time parameter in the GC ensemble,<sup>24</sup> where we tune the ratio between  $\tau_1$  and  $\tau_2$  in an indirect way, by controlling the ratio between steps of particle and cluster rearrangements, since the first is the most important factor for molecular relaxation, while the second optimizes crystallization. The second way which we observed that leads to supercooling is the self-organization of rigidity, as we will see in the next section.

To implement supercooling using the MC steps by indirect control of the relaxation times, we use a GC Metropolis Monte Carlo method.<sup>25</sup> The procedure has two nested loops. In the inner one, the particles are moved inside the volume, and an interchange of particles with the particle reservoir is

TABLE I. Parameters of the CS model that fix the maximum coordination of the particles as used in this work. The notation cpx  $r$  means a complex of particles with maximum coordination  $r_{\max}$ .

$r_{\max}$	$L$	$w$
cpx 3	0.65	0.1
cpx 4	0.78	0.1
cpx 5	0.91	0.1

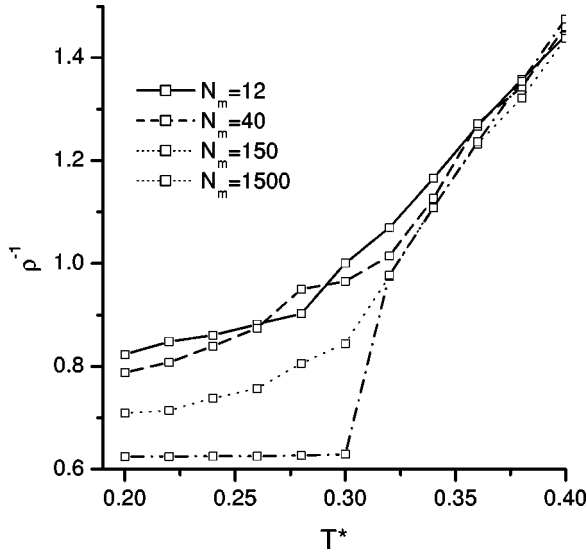


FIG. 2. Inverse of the density ( $\rho^{-1}$ ) as a function of the scaled temperature ( $T^*$ ) for different values of  $N_m$ .

allowed. This loop is performed  $N_m$  times. The particle movements inside the volume allow us to rearrange the structure, and thus this is related to the molecular relaxation of the structure ( $\tau_2$ ). In the outer loop, cluster rearrangements and the average of the thermodynamical quantities are performed, each time that  $N_m$  cycles of the inner loop are finished. The external loop is related to crystallization, since cluster movements promote the growth of bigger clusters. It is clear that if  $N_m$  is high enough, the probability of having local cluster nucleation is high, and thus cluster movements allow us to form a crystal by successive aggregation of small clusters. When  $N_m$  is small, the local configurations are not in equilibrium, and hence the cluster movements promote the generation of a random network.

In Fig. 2, we show the results of the inverse density ( $\rho^{-1}$ ) against reduced temperature [ $T^* = (\beta \epsilon_{as})^{-1}$ ] for several  $N_m$  cycles which simulate different  $\tau_2$  times. In this figure, we fixed the parameters of the CSM that allows as maximum coordination four (cpx4),  $L=0.78, w=0.1$ , restricted to equimolar concentration  $\beta \mu_A = \beta \mu_B = -0.4$ . Finally, after each  $N_m$  steps of the inner cycle, we allow the possibility of one cycle cluster rearrangement. In order to simulate the same cooling rate with several  $\tau_2$  times, we fix the outer cycle for 100 steps during the quasiequilibrium run and 2000 times for a productive run. In such a way, we averaged over the same number of configurations for each different,  $N_m$ . As can be seen, for  $N_m = 1500$  a crystallization is observed, while for the other values, a glass transition is obtained, as is revealed by the figure and by a direct inspection of the resulting structures. In all the procedure, MC steps are controlled to have an acceptance ratio between 20% and 30%.

An interesting observation is that the fraction of particles with maximum coordination  $\chi_4$  depends strongly on  $N_m$ . In Table II, we show this fraction against temperature for the same simulations presented in Fig. 2. When the crystal is formed,  $\chi_4$  is nearly 1, while for the supercooled liquid at the

TABLE II. Fraction of maximum coordinated particles as a function of the reduced temperature ( $T^*$ ) and molecular relaxation time, controlled by the parameter  $N_m$ .

$T^*$	$N_m=12$	$N_m=40$	$N_m=150$	$N_m=1500$
0.40	0.0011	0.001 13	0.0025	0.0019
0.38	0.0046	0.001 03	0.0053	0.0040
0.36	0.0022	0.004 04	0.0043	0.0079
0.34	0.0007	0.012 87	0.0152	0.0188
0.32	0.0077	0.016 77	0.0495	0.0591
0.30	0.0108	0.043 76	0.1353	0.9395
0.28	0.0258	0.053 91	0.1538	0.9786
0.26	0.0366	0.051 38	0.2229	0.9666
0.24	0.0725	0.074 17	0.3100	0.9487
0.22	0.1057	0.083 55	0.3292	0.9622
0.20	0.1116	0.077 62	0.3496	0.9617

same temperature,  $\chi_4$  remains at the same order of magnitude. We can understand this effect as follows: if full thermal equilibrium of the system is not allowed, it is not possible to access the global minimum of the energy potential,<sup>26</sup> and hence the nucleation is prohibited, with the consequence that the supercooled liquid is structurally arrested at a finite temperature and restricted to explore the configurational space correspondent to a single basin in the energy landscape. In the next section, we use this idea to relate this observation with the self-organization of rigidity.

#### IV. GLASS TRANSITION BY THE SELF-ORGANIZATION OF RIGIDITY

The fact that the maximum coordination is not achieved for most of the particles in the supercooled liquid means that inhibiting nucleation is a natural way of inhibiting crystallization, as was discussed in the Introduction. This simple idea can be put in contact with the rigidity ideas of Phillips<sup>17</sup> and Thorpe.<sup>11</sup> As we mentioned before, in this theory, the ability for making a glass is optimized when the number of freedom degrees, in this case  $2N$ , where  $N$  is the number of particles, is equal to the number of mechanical constraints ( $N_c$ ) that are given by the bond length and angles between bonds.

$(2N - N_c)/2N$  gives the fraction of cyclic variables of the Hamiltonian and also corresponds to the number of vibrational modes with zero frequency ( $f$ ), called floppy modes, with respect to the total number of vibrational modes. The counting of floppy modes in a mean field, known as Maxwell counting, goes as follows: since each of the  $r$  bonds in a site of coordination  $r$  is shared by two sites, there are  $r/2$  constraints due to the distance fixing between neighbors. If the angles are also rigid, in 2D there are  $(r-1)$  constraints, to give,

$$f = \frac{2N - N_c}{2N} = 1 - \frac{\langle r \rangle}{4} - \sum_r (r-1)x_r,$$

where the last term corresponds to the angular constraints,  $\chi_r$  is the fraction of particles with coordination  $r$ , and  $\langle r \rangle$  is the average coordination number, defined as

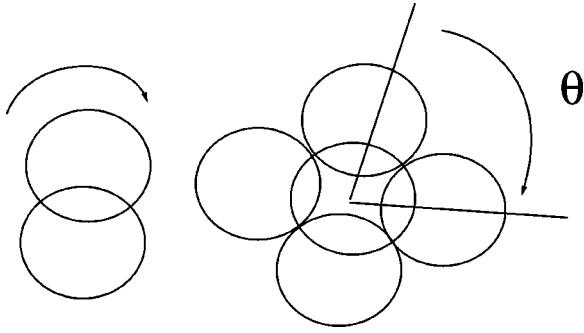


FIG. 3. Counting of angular constraints in the Cummings-Stell model. A cluster of two particles has no angular constraints, since one of the particles can rotate  $360^\circ$  around the other, while in a cluster with coordination 4 the angle between particles is fixed, which leads to three angular constraints.

$$\langle r \rangle = \sum_r r x_r.$$

A rigidity transition occurs when  $f=0$  and the system passes from a floppy network to a rigid one. If  $f$  is a negative number, i.e., if there are more constraints than degrees of freedom, the lattice is overconstrained and  $f$  is the number of stressed bonds. In 2D, the rigidity transition leads to the critical value  $\langle r \rangle = 2.0$  if all angular constraints are considered and  $\langle r \rangle = 4.0$  if the angular restoring forces are not strong.

Within the Cummings-Stell model, rigidity comes from the association of particles: each bond generates a constraint, and the angular constraints are only produced by geometrical hindrance; i.e., the angles between particles can change without a cost in energy, but within certain limits imposed by the restriction of the hard-core interaction between like particles, as shown in Fig. 3. For maximum coordination 4, this means that only sites with coordination 4 have a contribution to angular constraints. It is true that sites with coordination 2 and 3 in principle should provide extra angular constraints, since the hard-core interaction gives a minimum angle between particles. However, the angles are not fixed and they have a wide region to allow particle movements, and thus do not contribute to the restriction counting.

Taking into account the geometrical hindrance of the model, the number of floppy modes is now given by

$$f = 1 - \frac{\langle r \rangle}{4} - \sum_r \delta_{r, r_{\max}} (r-1) x_r,$$

where  $r_{\max}$  is the maximum allowed coordination, and  $\delta_{r, r_{\max}}$  is a Kronecker delta. From here, it is clear that when in a cluster we have a site with maximum coordination, rigidity rises since the  $\delta$  function is different from zero and more constraints are added that overconstrain the cluster. Thus, sites with maximum coordination nucleate rigidly and produce stress in the lattice. For example, in a crystal with coordination 4,  $\chi_4 = 1$  and  $f = -3/2$ , which means that the lattice is overconstrained. According to Phillips, when  $f=0$ , it is easy to form a glass, since the material is neither overconstrained (which produces explosive exothermic crystalliza-

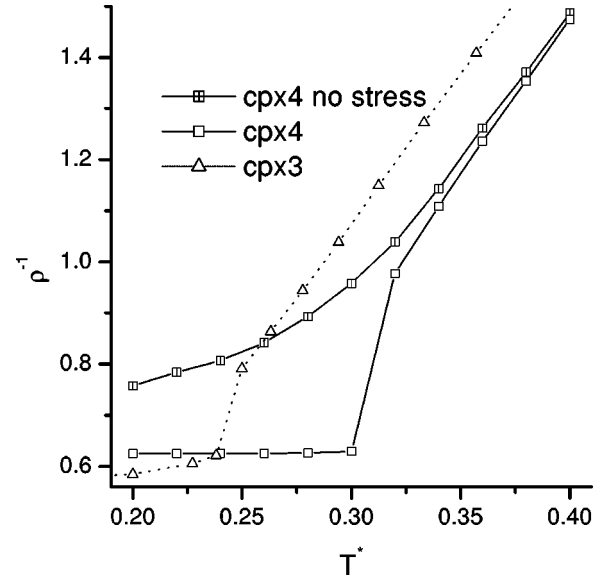


FIG. 4. The same as Fig. 2 for the case of stress-free nucleation for a system with maximum allowed coordination 4 (cpx4), with and without stress (squares and dashed squares). We include a simulation for maximum coordination 3 (cpx3) with stress.

tion due to strain energy<sup>27</sup>) nor underconstrained (leading to the formation of a molecular crystal), the system is trapped in a configurational limbo,<sup>27</sup> where fluctuations do not provide a pathway to the crystalline phase.

Furthermore, in the last section we have shown that the fraction of particles with maximum coordination is in close connection with the molecular relaxation time, which in other words means that to form a glass, nucleation of stress must be prevented. From our previous results, we can observe that the probability of formation of a nucleated structure is small due to the high molecular relaxation time. We decided to follow these ideas by proceeding in the opposite way than in the last section; i.e., we inhibit rigidity nucleation by rejecting configurations with maximum coordination and then we see if we are able to bias the system to a glassy state in such a way that we simulate long molecular relaxation times. Observe that rejecting configurations that produce stress is the same process of self-organization that was considered by Thorpe *et al.* in order to form stress-free lattices.<sup>15</sup> In that sense, we look if self-organization of rigidity is able to produce a glass transition. This kind of simulation is usually called a biased Monte Carlo simulation.<sup>28</sup>

To study the effect of self-organization, we made the same MC procedure described in the previous section, but with  $N_m$  fixed to the value that gives crystallization ( $N_m = 1500$ ). The only difference with the previous case is that now we reject particle movements that produce a site with maximum coordination.

In Fig. 4, we present the behavior of the inverse of the density ( $\rho^{-1}$ ) as a function of the reduced temperature  $T^* = (\beta \epsilon_{as})^{-1}$ , with the condition that allows a maximum of four neighbors (cpx4), restricted to equimolar concentration  $\beta \mu_A = \beta \mu_B = -0.4$  (open squares). As the temperature is slowed down, we can observe a continuous decrease in  $\rho^{-1}$ . However, for reduced temperatures lower than 0.30, a jump in  $\rho^{-1}$  is observed when all the configurations are allowed.

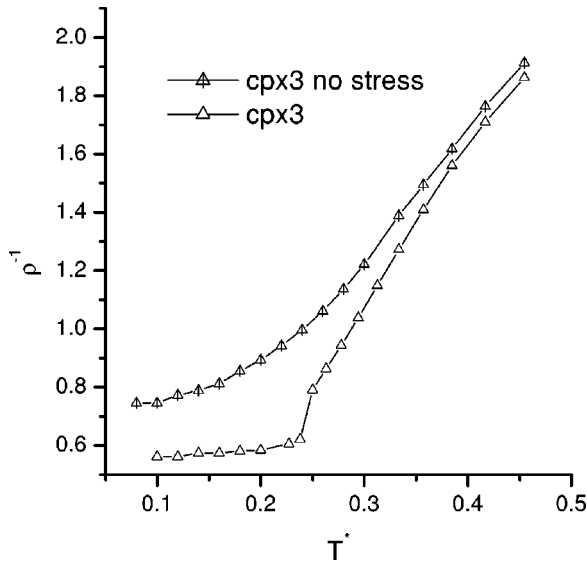


FIG. 5. Inverse of the density ( $\rho^{-1}$ ) as a function of the scaled temperature ( $T^*$ ) for maximum coordination 3 with and without stress (triangles and dashed triangles).

This jump corresponds to the crystallinelike phase transition, as can be argued by the shape of the transition, from an inspection of the configuration obtained, and by the radial distribution function. Due to the fact that it is possible to keep the system without stress, we develop the same simulation as before but rejecting in the simulation every configuration that contains a particle with coordination 4. The results are presented in Fig. 4 with dashed squares. In that case, the system remains as a supercooled fluid. Moreover, the system cannot form a crystal structure as occurs in the simulation in which we allow stress, and thus do not present a usual phase transition; instead a glasslike transition is observed. These results show that self-organization of rigidity is able to produce a glass.

An important remark is that avoiding configurations with maximum coordination is not equivalent to considering a CSM without self-organization but with a lower maximum coordination. For example, in Fig. 4 we plot the results of a simulation without rejection for a CSM that allows maximum coordination 3 (cpx3). As can be seen, the model also presents crystallization.

In Fig. 5, we present the results for the same kind of simulation but for a system that allows maximum coordination 3 (cpx3). As can be seen, the rejection of stressed configurations also leads to a glasslike transition.

Now we turn our interest to the condition of maximum coordination 5 (cpx5), as shown in Fig. 6. As can be seen, in this case the glass transition is produced even when the stressed configurations are not rejected. This fact can be understood in terms of rigidity in the following way: when  $r_{\max}=5$ , it is impossible to have a crystal due to geometric frustration at an equimolar condition  $\beta\mu_A = \beta\mu_B = -0.4$  and  $\chi_5 \ll 1$ . Since the rigidity transition without angular restrictions occurs only when  $\langle r \rangle = 4$ , most of the configurations do not produce stress and the system behaves freely (i.e., we do not need to reject any configuration) as a self-organized sys-

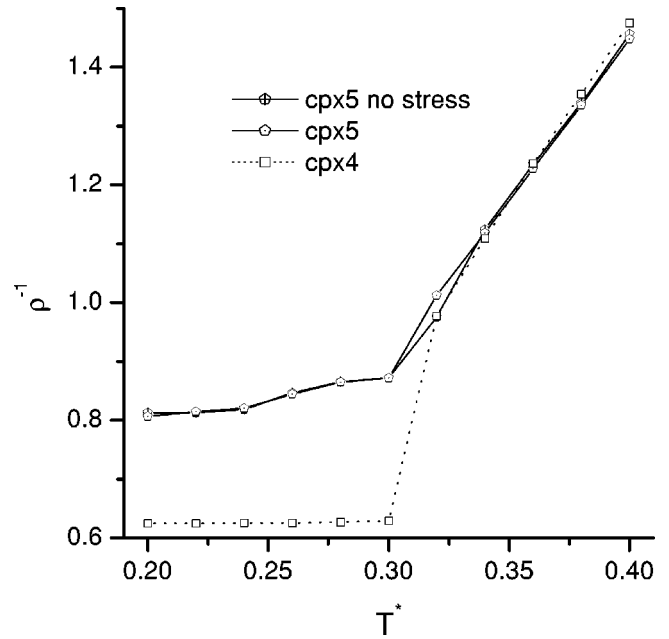


FIG. 6. Inverse of the density ( $\rho^{-1}$ ) as a function of the scaled temperature ( $T^*$ ) for maximum coordination 5 (cpx5) with and without stress (pentagons and dashed pentagons). For comparison purposes, we include a simulation of cpx4 without rejecting configurations (squares).

tem. In this sense, geometric frustration induces self-organization of the system. As a corroboration of this fact, in Fig. 7 we show the number of floppy modes as a function of the average coordination number, using the Maxwell counting. We remark that each coordination corresponds to a certain temperature of the simulation. For example, at high temperatures, all models with different maximum coordination fall in the same line, since in the liquid the probability of

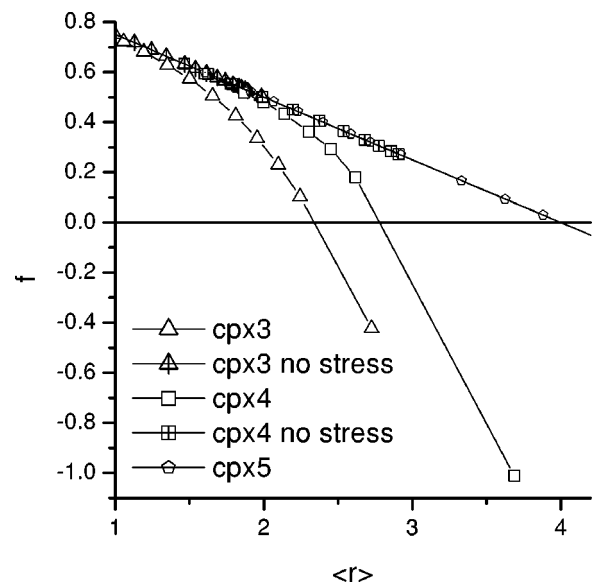


FIG. 7. Number of floppy modes as a function of the coordination number ( $\langle r \rangle$ ) for each of the models with different maximum coordination number.

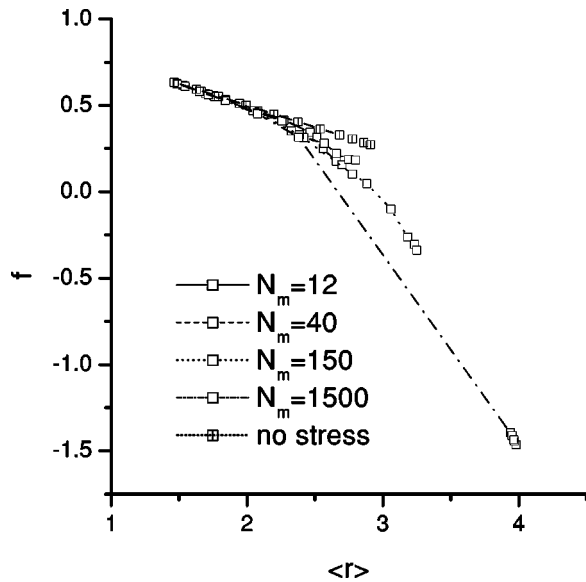


FIG. 8. Number of floppy modes as a function of  $\langle r \rangle$  for several  $N_m$  relaxation times without rejecting any configuration.

nucleation is very low. However, for the cases of cpx5, cpx3, and cpx4 without stress, all simulations fall again in the same line even for low temperatures, since self-organization means that the clusters grow without angular constraints (stress free). When this line is extrapolated to  $f=0$ , we obtain  $\langle r \rangle = 4$ , which is the value for a rigidity transition without angular constraints. If angular constraints are allowed, the simulations for low temperatures falls outside the line determined by self-organization, and the rigidity transition occurs at lower values of  $\langle r \rangle$ . Finally, we can compare these results to the floppy mode counting made for the glass transition using the method of tuning the different relaxation times. In

Fig. 8, we present the number of floppy modes as a function of  $\langle r \rangle$ . As can be seen, when  $N_m$  is high, there is a transition of rigidity due to nucleation, while for low  $N_m$  the system tends to stay in the line of self-organization.

## V. CONCLUSIONS

In this work, we have explored the connection between the self-organization of rigidity and the supercooling of a liquid to form a glass. By considering an associative fluid model, we showed that the competition between two different characteristic times—molecular relaxation and crystallization times—can be modeled using a MC simulation, where the number of cycles between particle and cluster moves is controlled. The results of these simulations suggested that nucleation is avoided during supercooling and produces self-organization in the sense of the rigidity theory. This idea was also tested by making MC simulations but avoiding stressed configurations. As a result, we were able to produce glass transitions using self-organization. In a model (cpx5) with geometrical frustration, this self-organization is provided by geometry, and thus the glass transition occurs without rejecting configurations. All of the results of this article are in agreement with the idea of Phillips that the glass transition is related to rigidity due to the lack of a pathway to crystallization.<sup>27</sup> Many of these facts can also be studied from an energy landscape point of view, as we will show in future works.

## ACKNOWLEDGMENTS

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