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Relationship between glass transition and rigidity in a binary associative fluid

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Abstract

Using Monte Carlo simulations in a binary associative fluid, we study the effects of connectivity on the glass transition. The results show that this transition occurs near the rigidity transition, when the number of geometrical constraints due to bonding and excluded volume in a given temperature of the simulation, is equal to the degrees of freedom available in the configurational space. These results are interpreted within the energy landscape paradigm. We also show that the average coordination number is a good parameter to describe many thermodynamical properties of the glass formation. © 2002 Published by Elsevier Science B.V.

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Glass transition (GT) is a process where an amorphous solid is formed by supercooling a melt, and remains as one of the most fascinating problems in solid state [1]. Not all materials are able to form glasses, and many semi-empirical criteria have been proposed in order to explain the ability of a material to reach the glassy state [2], because there are many factors involved in the process. Of these, one important is the speed of cooling. A slow speed means that the system has time to explore different states of the phase space and a glass cannot be formed, since the crystal has a lower free energy. To form a glass, the melt must be cooled fast enough. The GT is not considered as a true

phase transition, although there are jumps in the specific heat or in the thermal expansion coefficient [3].

A lot of attention has been given to the problem of finding the physical and chemical factors that determine the temperature where it occurs, called GT temperature (T_g). Among these factors, the chemical composition is fundamental. Chalcogenide glasses (formed with elements of the VI column) are a benchmark test for understanding the effects of the chemical composition [4]. For example, T_g can be raised or lowered by adding impurities, and the fragility of the glass can be changed from strong to fragile [5]. For these changes, a method based on the statistics of agglomeration [6,7] succeeded in obtaining the empirical modified Gibbs–DiMarzio law that accounts for the relation between T_g and the concentration of modifiers [8]. The method predicts the characteristic constant that appears in the law for almost any chalco-

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genide glass [9], and gives a topological explanation to the phenomena.

In all of these problems, the rigidity theory introduced first by Phillips [10] and further refined by Thorpe [11] has a fundamental role. By considering the covalent bonding as a mechanical constraint, within this theory, the ease of glass formation is related with the proportion of available degrees of freedom and the number of constraints. When the glass has an average atom coordination ($\langle r \rangle$) below 2.4 in three dimensions (3D), there are zero frequency vibrational modes called floppy [12]. Although this theory has been very successful in explaining qualitative features of GT, and many experiments confirmed the validity of the theory [13], not so much effort has been done to test the theory in a quantitative way. More recently, it has been proposed that the number of floppy modes is related with the statistics of the phase space landscape [14], since the number of floppy modes is equal to the number of different configurations of the systems with nearly equal minimal energies. From this, a free energy is defined, and many thermodynamical properties can be calculated. Using this approach, the jump in specific heat during GT for the glass $As_yGe_xSe_{1-x-y}$ has been obtained as a function of x and y without using any free parameter [14]. However, still it is not clear how rigidity affects T_g, i.e., if a rigidity transition has an effect in a glass transition [15], although these effects are now slowly emerging from experiments, as in the case of the Ge–S–I system [16], and the Si–Se binary glass [4]. In this Letter, we address this question by performing Monte Carlo (MC) simulations for a binary associative model, which allows to explore the role of connectivity in the GT.

As starting point, we choose the Cummings–Stell model of a two component system (A and B) of associating disks in 2D, all of the same size [17,18]. We restrict our attention to the case where the number density of each component is the same, i.e., $\rho_A = \rho_B = 0.5\rho$ where ρ is the total number density. The particles interact via a potential permitting core interpenetration of the A and B monomer discs, so that the bond length L is less than the core diameter σ. Without loss of generality we assume $\sigma = 1$. The interactions are given as follows:

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

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

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

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

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. 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 the 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 $D \to \infty$ as was done before in other works [18,19]. 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.
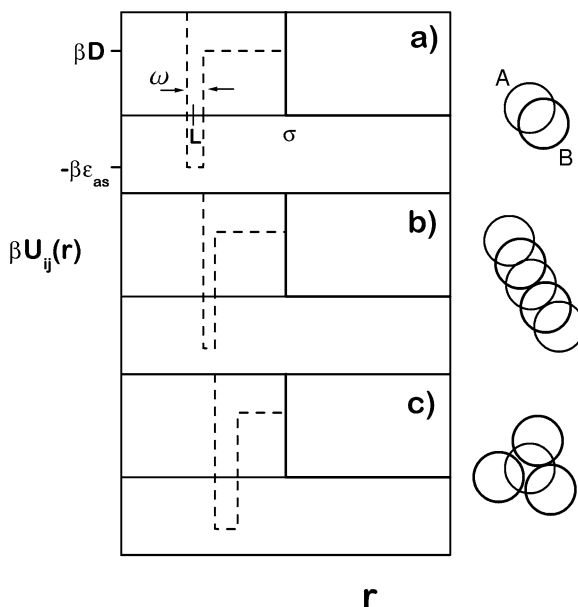

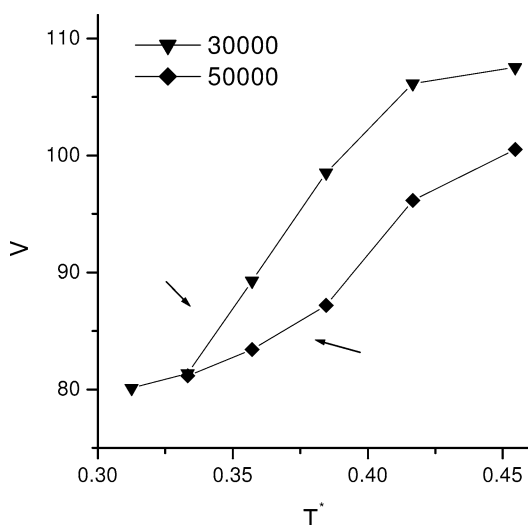Fig. 1. Schematic representation of the Cummings–Stell model.

Fig. 2. Change of the volume as a function of the scaled temperature. The symbols specified in the legend correspond to different cooling rates (30000 and 50000 MC-steps) of a model with maximum coordination three (cpx3).

Fig. 3. Energy fluctuations against reduced temperature for the two models described in the text.

To study the model we have applied the Metropolis Monte Carlo sampling technique in the isobaric-isothermal ensemble (NPT). Some minor changes in the scheme of the MC procedure was applied comparing with previous works [18]. The first consists in permitting the variation in the length of the unit cell in x and y directions in order to give the opportunity to access configurations near close packed structures. The second is to permit a quite long thermal equilibrium keeping the volume fixed (NVT ensemble) between successive changes of volume of the usual NPT procedure. Using the Monte Carlo step of the NPT cycle as a time parameter [20], we try to reproduce in a qualitative way the effect of the experimental cooling rate at constant pressure that allows the possibility of visiting the configurational space accessible in the short time in which is it cooled. Starting from a fluid temperature configuration, we gradually slowed down the temperature every certain MC steps of the NPT procedure for a fixed NVT steps previously determined.

In Fig. 2, we show the volume of the system as a function of the scaled temperature ($T^* = kT/\varepsilon_{as}$) for the potential condition that allows maximum coordination three (cpx3). We can observe that for different cooling rates, there is a characteristic inflexion that is a
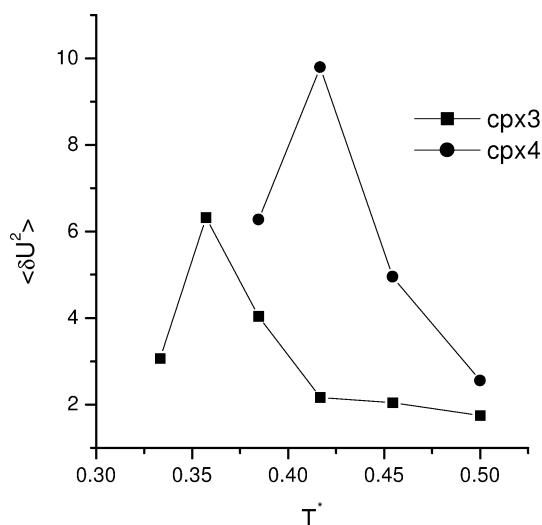
feature of a GT. To check if this is a GT, we have calculated the energy fluctuations (which give the main contribution to the specific heat in the NPT ensemble under these conditions) against T^*, as shown in Fig. 3. As can be seen, these fluctuations have also jump in the same values of T^*. In Fig. 5(b), we show a plot of the fluctuations as a function of the average coordination that we will define later, the temperature region where the jump occurs corresponds to that observed at the change of slopes in Fig. 2. Furthermore, by using the radial distribution function and a direct inspection of the resulting structures, we have verified that the high density phase is a glass and not a crystal. Thus, the inflexion that appears in Fig. 2 can be associated with a GT.

In order to understand the relationship between the connectivity of the system with some thermodynamical properties, in Fig. 4 we plot the volume as a function of the average coordination number, defined as

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

where r is the coordination and x_r is the fraction of particles that are bonded. These proportions are functions of the temperature, since each new bond that is formed changes the energy by a fixed amount. As a consequence, is clear that the total energy is proportional to the number of bonds formed in each step of the agglomeration process that occurs when the

temperature is lowered, and thus is also proportional to the average coordination number. From Fig. 4, we observe that for all cooling rates, the volume follows an isocoordination rule, in the sense that is a universal function of $\langle r \rangle$ for different cooling rates. Furthermore, from Fig. 4 is clear that there is a change of regime in the behavior of the volume. The transition occurs at the critical value $\langle r \rangle = 2.01$, obtained by two straight-line fits as shown in the figure. This point also corresponds to the previous transition observed in the volume (the corresponding transitions for the coordination number are marked with arrows in Fig. 2) and energy fluctuations as a function of the temperature. The value 2.01 suggests a strong connection with the rigidity theory of Phillips and Thorpe for the following reason. 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. These two numbers allows to calculate the fraction of floppy modes (f) in a mean-field approximation, known as the Maxwell counting. This 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. If the angles are also rigid, in 2D there are $(r-1)$ constraints, to give

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

where the last term corresponds to the angular constraints. The rigidity transition occurs when $f = 0$. In 2D, this lead 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. Although the value $\langle r \rangle$ is very close to the one obtained from our MC simulations, care must be taken because in the Cummings–Stell model, the rigidity transition is complicated due to the fact that 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. In the case of maximum coordination three, this means that only sites with coordination two and three have a contribution to angular constraints. To obtain the fraction of floppy modes in our MC simulation, we used the mean-field approximation given by Eq. (1),
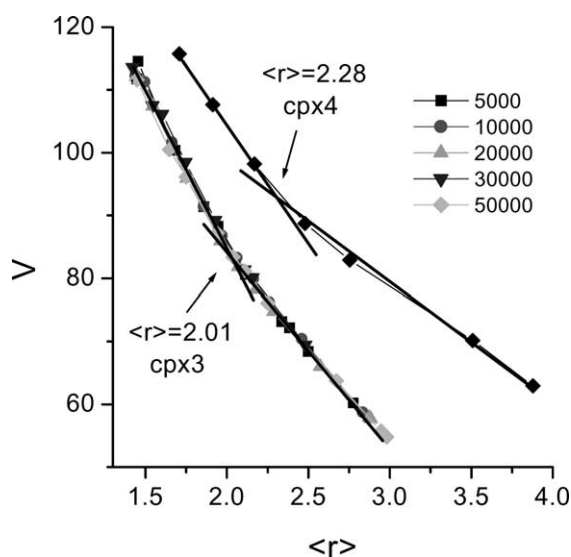

Fig. 4. Dependence of the volume as a function of the average coordination number for models with maximum coordination three (cpx3) and four (cpx4) for the indicated MC-steps.

although a more refined calculation requires the use of the pebble game algorithm [12]. The contributions x_r were found directly from the concentrations of sites with coordination two and three given by the MC simulations. Fig. 5(a) shows a plot of the fraction of floppy modes as a function of $\langle r \rangle$ calculated in this way. As can be seen, the value where $f = 0$ is $\langle r \rangle = 1.99$, in close agreement with the value obtained from the GT.

In order to check the validity of this result, we performed the same calculations in a system that allows as maximal coordination four (cpx4 model). When the maximal coordination is two, we were not able to obtain a glass, but the rigidity transition is also not possible (due to a limitation of the model or a peculiarity of 2D). Fig. 4 shows that for the cpx4 model, there is a transition that occurs at $\langle r \rangle = 2.28$, which is also reflected in the energy fluctuations (Fig. 6(b)). This value is higher than the expected from the rigidity transition, and this means that some angular constraints must be broken. To clarify this point, Fig. 6(a) shows a plot of f as a function of $\langle r \rangle$—obtained as described for the cpx3 model—except that now only sites with coordination three and four contribute to the angular constraints. Now, the corresponding rigidity transition occurs at $\langle r \rangle = 2.27$, which is very similar to the value obtained from the thermodynamical quantities. This
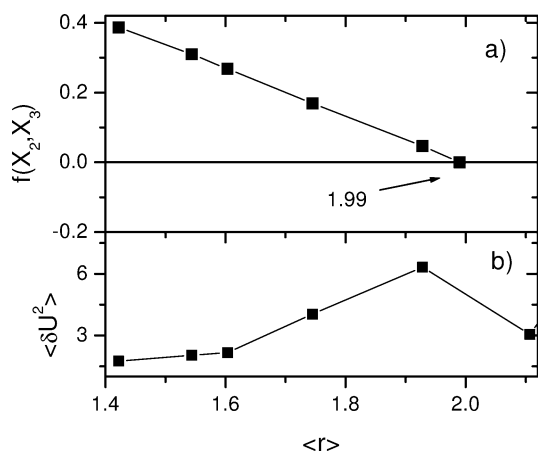
Fig. 5. (a) Number of floppy modes and (b) energy fluctuations as a function of the coordination number for a model with maximum coordination three (cpx3).
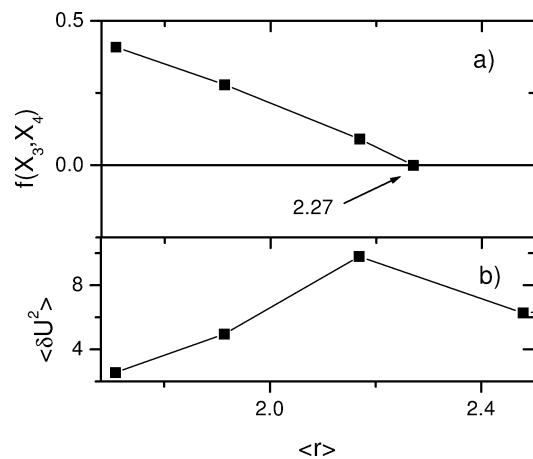

Fig. 6. The same as in Fig. 5, but for a model with maximum coordination four (cpx4).

confirms the fact that sites with coordination two have broken constraints, due to the wider angular flexibility allowed by the parameters in the cpx4 case ($\sim 212°$), compared with the cpx3 case ($\sim 177°$). The geometrical features of the model in question restrict the angular flexibility of the structures, and this promotes the self-organization of the particles, as Thorpe remark in his recent paper [21].

We can understand the relationship between rigidity and glass transition using the statistics of the energy landscape [22,23]. The landscape is the allowed region of the phase space for a given temperature. The glass explores this landscape, but as the temperature is lowered, it begins to be trapped inside basins, until it breaks the ergodicity by staying only on a certain region of the space. This breaking of ergodicity occurs at the glass transition. At low temperatures, the free energy contains contributions from the depth and number of the basins, and the dynamics inside them [14]. It is possible to separate the configurational contribution to thermophysical properties, an a Helmholtz free energy is then given by [22], $A = N(\bar{\phi} - kT\sigma(\bar{\phi}) + a^v)$ where $\bar{\phi}$ is the depth of the basins in the phase space explored by the glass at a given temperature, $\sigma(\bar{\phi})$ is the number of basins of a given depth, and the last term is the contribution form the vibrational component. The present approach suggest a strong connection between the number of floppy modes and $\sigma(\bar{\phi})$. This connection seems to be natural, since the number of floppy modes is also the number of different structures with nearly the same minimal energy [21], and thus $\sigma(\bar{\phi})$ is a function of f, i.e., there are f different pockets in the phase space. The number of states in the phase space in a volume V and N particles has the following form, $\Omega(N, V) = ((1 + f)N)!\Omega(N_1, V_1)$ where $(1 + f)!$ accounts for the f different minima, and $\Omega(N_1, V_1)$ is the contribution in each minima. However, much more work is required to further clarify this point.

In conclusion, we have observed that the glass transition occurs near the rigidity transition in a Monte Carlo simulation cooling of a simple associative fluid. This fact is consistent with the landscape energy model. These results also show that the isocoordination rule is very useful as a parameter in this kind of simulations.

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