



Rigidity aspects of the glass transition

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Abstract

By using a model for an associative fluid, we perform Monte-Carlo simulations to observe that at the glass transition, there is also an underlying rigidity transition. This last transition occurs very close to the value predicted by a mean-field theory and serves as an starting point to determine the effects of rigidity in the glass transition temperature.

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1. Introduction

Crystallization is not the only possible outcome of supercooling a liquid. If the speed of cooling is fast enough, a disordered solid is formed at a certain temperature. This process is known as the glass transition (GT), and still poses many challenging problems in solid state physics [1] since the time-dependent nature of the GT [2] means that the GT is not a true phase transition [3]. The chemical composition is fundamental to determine the minimum speed of cooling and the temperature where it occurs (called T_g). This GT temperature can be raised or lowered by adding impurities [4], and the fragility of the glass can be changed from strong to fragile [5]. In 1979, Phillips proposed a

relationship between the rigidity of the glassy network and the ability to form a glass [6], obtained from the speed of cooling, that was further refined by relating the elastic properties with rigidity [7]. By considering the covalent bonding as a mechanical constraint, the ease of glass formation is then 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 [7]. This theory has been successful in explaining general qualitative features of GT, and many experiments confirmed the validity of the theory [4], but not so much effort has been done to test the theory in a quantitative way and more importantly; only very recently have the effects on the thermodynamics been considered [8]. In this work, we explore the relationship between the GT thermodynamics and the rigidity theory by performing Monte-Carlo simulations (MC) for a simple model fluid.

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2. Model and simulations

We use the Cummings–Stell model of a two component system [9,10] (A and B) of associating disks in 2D, where the number density of each component is the same, i.e. $\rho_A = \rho_B = 0.5\rho$. The particles interact via a potential permitting core interpenetration of A and B disks, so the bond length L is less than the core diameter σ (here we take $\sigma = 1$). 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 (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, chains, and vulcanization with fixed maximum coordination number, by tuning L with values close to the diameter of the particles. To fix a maximum coordination number (r_{max}), we take $D \rightarrow \infty$. Then we applied a Metropolis MC in the isobaric–isothermal ensemble (NPT), but allowing a quite long thermal equilibrium keeping the volume fixed (NVT ensemble) between successive changes of volume in the NPT procedure. The MC step of the NPT cycle was used as a time parameter [11]. Starting from a fluid, the temperature was slowed down every certain MC steps of the NPT loop for fixed NVT steps, and we obtained the volume (V) as a function of the scaled temperature, ($T^* = kT/\varepsilon_{as}$) for the potential condition that allows $r_{max} = 3$ (cpx3). The results show a characteristic GT (see inset in Fig. 1). We confirmed this GT by looking at the jump in the specific heat, the

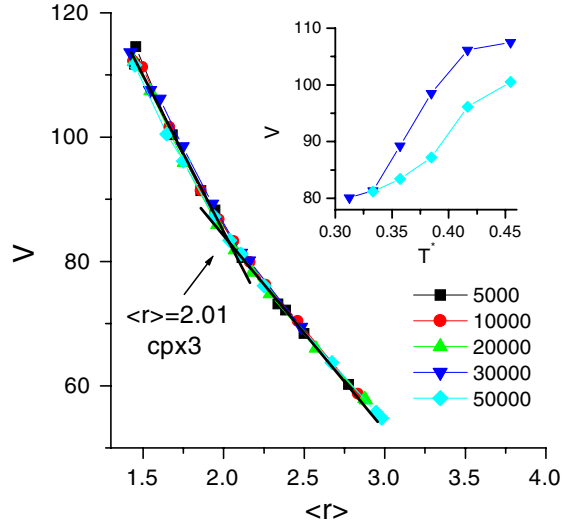


Fig. 1. Dependence of the volume as a function of the average coordination number for models with maximum coordination 3 (cpx3) for the indicated MC steps. Inset: V versus T^* for different cooling rates.

radial distribution function and a direct inspection of the structures. In Fig. 1 we present the results from these simulations, but instead of plotting V as a function of T^* , we show V versus the average coordination number, defined as, $\langle r \rangle = \sum_r r x_r$, where x_r is the fraction of particles that are bonded with coordination r . The volume follows an isocoordination rule (see Fig. 1), in the sense that is a universal function of $\langle r \rangle$ for different cooling rates. Fig. 1 shows a clear transition in the slope that occurs at the critical value $\langle r \rangle = 2.01$, obtained by fitting two straight lines. This point also corresponds to the GT observed in the volume and specific heat. The value 2.01 suggests a connection with rigidity, since within 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 allow one to calculate the fraction of floppy modes (f) in a mean-field approximation, known as the Maxwell counting that goes as follows: 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, that gives

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

where the last term corresponds to the angular constraints. A rigidity transition (RT) occurs when $f = 0$. In 2D, this gives $\langle r \rangle = 2.0$ if 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. In the case of $r_{\max} = 3$, this means that only sites with coordination 2 and 3 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 f . The contributions x_r were found directly from the concentrations of sites with coordination 2 and 3 given by the MC simulations. The obtained value for $f = 0$ is $\langle r \rangle = 1.99$, in close agreement with the GT. In order to check the validity of this result, we performed calculations in a system that allows $r_{\max} = 4$ and similar results were found. If the allowed r_{\max} is higher, rigidity can arise even if the particles are not bonded, due to jamming. For example, when $D \rightarrow \infty$ and $U_{as}(r) \rightarrow 0$, we get a one component hard-disk system (HDS). Here there is no rigidity due to association, and a glass transition is difficult to observe because the system crystallize. However, rigidity comes from the contact between dynamical jammed disks. To clarify this point, we made calculations in a MC grand-canonical ensemble. The problem is how to define a contact in a MC. However, seven disks in an heptagon are not able to jam a central disk, and this defines a circular contact region around a disk delimited by an hexagon (with radius $R = \sigma$) and an heptagon ($R = \sigma/2\pi \sin(2\pi/14)$). Using this idea, we found that the fluid–solid phase transition occurs at $\langle r \rangle = 4$, which is the same value predicted at the RT. By imposing the condition of not allowing more than six particles in the contact region, we produced a glass transition (Fig. 2).

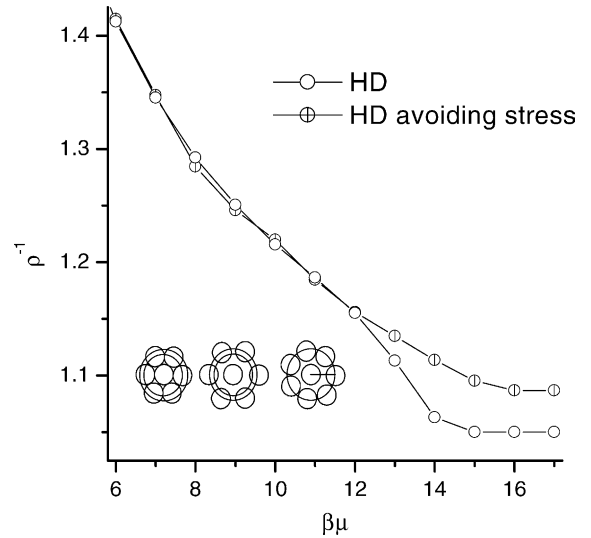


Fig. 2. The inverse of the numerical density as a function of the chemical potential for the hard-disk system with and without of stress as indicated. The inset shows an schematic representation of the contact region.

3. Conclusions

We have observed, from our MC simulations on an associative fluid, that rigidity plays an important role in the GT and also for the freezing in a HDS. Also, the present calculations suggest that the structural relaxation time increases at the RT, due to particle jamming, controlling from the molecular point of view T_g . Nevertheless, in a particular material, the value of $\langle r \rangle$ at the RT depend on the chemical structure, since the constraints can be broken according to the energy involved in a particular kind of bond.

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References

- [1] P.W. Anderson, Science 267 (1995) 1615.
- [2] J. Jackle, Rep. Prog. Phys. 49 (1986) 171.

- [3] S.R. Elliot, *Physics of Amorphous Materials*, Wiley, New York, 1998.
- [4] D. Selvanathan, W.J. Bresser, P. Boolchand, *Phys. Rev. B* 61 (2000) 15061.
- [5] R. Kerner, G.G. Naumis, *J. Phys.: Condens. Matter* 12 (2000) 1641.
- [6] J.C. Phillips, *J. Non-Cryst. Solids* 34 (1979) 153.
- [7] M.F. Thorpe, *J. Non-Cryst. Solids* 57 (1983) 355.
- [8] G.G. Naumis, *Phys. Rev. B* 61 (2000) R92605.
- [9] P.T. Cummings, G. Stell, *Molec. Phys.* 51 (1984) 253.
- [10] A. Huerta, Yu. Duda, O. Pizio, D. Wasan, *Mol. Phys.* 96 (1999) 795.
- [11] M.E.J. Newman, G.T. Barkema, *Monte Carlo Methods in Statistical Physics*, Oxford University, 1999.