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A toy model mimicking cage effect, structural fluctuations, and kinetic constraints in supercooled liquids

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In this work, we implement new toy models coined to reproduce the cage effect with variants including structural fluctuations and different kinetic constraints. We introduce structural fluctuations in the models from a distribution of the cages opening probabilities and a kinetic constraint from a variation of that probability with the local number of molecules involved in the creation of the cage. We model separately the caging mean field experienced by each molecule, and the cooperative mechanism with the kinetic constraint condition. We find that strong dynamic heterogeneities are present in the models with kinetic constraints. We find that the heterogeneities do not depend on the cage escaping probabilities, while the heterogeneities increase sharply with the strengthening of the kinetic constraint conditions. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4901424]

I. INTRODUCTION

To shed some light into the physics of the glass transition, we need toy models sufficiently simple to understand the phenomena but sophisticated enough to contain the whole set of relevant physical mechanisms. Facilitated spin glasses are such models that have leaded in the past to a better understanding of the physics at work behind the glass-transition phenomena. However, models in between facilitated spin glasses and real liquids are still lacking. The cage effect, i.e., the hindrance of motion due to the presence of the first neighbors, is widely accepted as the short time microscopic mechanism underlying the physics of supercooled liquids. In this work, we thus propose models based on the cage effect and kinetic constraint induced cooperative mechanisms. Our toy models consist in molecules moving inside a maze with doors that open and close randomly. We then add different kinetic constraints that open or close the doors of the cage depending on the number or behavior of molecules in the surrounding cages. The maze reproduces the caging mean field experienced by each molecule, while the kinetic constraint reproduces the cooperativity of motions, cooperativity due in real systems to the cages dependence in the molecules that constitute them. The doors surface is in these models the parameter that replaces, for the α relaxation, the temperature in real liquids. The underlying idea is that as the temperature decreases the easily accessible passages in the energy landscape decrease in size, an effect modelled here with a decreasing door surface, but in a more general picture the door surface is simply a parameter that sets in the model the probability to escape the cage after each collision. We observe with these simple models the appearance of most of the specific phenomena of the glass transition. We find that strong dynamic heterogeneities (DHs) are present in the models with kinetic constraints. We find that the heterogeneities do not depend on the cage escaping probabilities, while the heterogeneities increase sharply with the strengthening of the kinetic constraint conditions.

II. CALCULATION

Our simplest model (model (a)) consists in molecular dynamics simulations of molecules located inside a cubic simulation box of size \((L \times L \times L)\) with periodic limit conditions and a substructure mimicking the cage effect (i.e., the confinement by other molecules). To create the substructure we divide the simulation box in \((n \times n \times n)\) smaller cubic boxes \((L/\text{rand})\) wide each, then in the center of each small box wall we manage a squared shape door that may be opened or closed. We call \(S\) the surface of the door. Figure 1 shows a schematic picture of the model. In this work, we use the parameters \(L = 70–140\ \text{Å}\) and \(n = 5–10\). The particular values of \(L\) that we use here for the cages are larger than the typical cage sizes in real liquids. However, the motions being ballistic inside the cage, the only physical effect of that large size is to increase the time between two collisions with the walls, a time that has thus to be rescaled if compared to real liquids simulations. We implement that model with 10–1250 molecules. The small boxes do have reflecting limit conditions so that a molecule will bounce elastically inside the box until it (i.e., its center of mass) finds an opened door in its trajectory. The doors are set opened or closed with a random number generator for a period \(\tau_{\text{rand}} = 100\ \text{ps}\). Velocities are initialized at random following a Maxwell-Boltzman distribution at the temperature \(T = 300\ \text{K}\). Note that the doors mean surface acts in the model as an effective temperature \(T_{\text{eff}}\) that controls the α relaxation process, while the real temperature \(T\) defined from the mean velocities of the particles controls the short time ballistic behavior of the particles. We chose rigid molecules constituted of two atoms \((i = 1, 2)\), and interacting with the Lennard-Jones potential \(V_{ij} = 4\epsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6})\) with the parameters: \(\epsilon_{11} = \epsilon_{12} = 0.5\ \text{kJ/mol}, \epsilon_{22} = 0.4\ \text{kJ/mol}, \sigma_{11} = \sigma_{12} = 3.45\ \text{Å}, \) and \(\sigma_{22} = 3.28\ \text{Å}\). We use the mass of Argon for each atom.
of the molecule that we rigidly bonded fixing the interatomic distance to $d = 1.73$ Å. We include these interactions to increase randomness and eliminate possible trapping in closed trajectories inside the boxes. At the temperature of study ($T = 300$ K) the corresponding liquid is above its melting temperature, insuring that the observed effects in the model are due to the cages only. We however found that removing totally the interaction has in most cases only small effects and as a result, various other interactions or molecules can be used. We study several variants of model (a). In a first variant (model (b)), we introduce the following kinetic constraint: The door is opened or closed depending on the total number $N = n_1 + n_2$ of molecules in the two boxes (boxes (1) and (2)) between which the door is opened. Below a threshold number $2K$ of molecules (i.e., when $N < 2K$), the door is opened and otherwise the door is closed. Our purpose here is to take into account the kinetic constraint induced by local density fluctuations in real liquids. As the cage is constituted in real liquids by the surrounding molecules, the probability to escape the cage must increase when the number of surrounding molecules decreases. In a second variant (model (b')), coined to reproduce facilitation mechanisms we introduce a kinetic constraint based on the mobility of nearby molecules. In that variant each door is opened or closed depending on the number of molecules that crossed the doors of the nearby cage during a time lapse $\Delta \tau$ (we chose $\Delta \tau = 10$ ps and a threshold of 4 molecules). To simplify the interpretation, we remove the intermolecular interactions in the models with kinetic constraints. In a third variant (model (c)), the size $l$ of the doors is distributed at random using a constant probability distribution centred on $l$ and $2l$ wide. We modify the distribution of the doors surface each $\tau_{\text{rand}}$ so that a molecule cannot be trapped indefinitely inside a closed cage, and a molecule finds a completely new environment after going through the simulation box. Variant (c) leads to a continuous distribution of environments that results randomly to soft zones (large doors or most doors opened) and hard zones (small doors or most doors closed). We use that variant to model the local structure fluctuations. Note that in our models structural fluctuations can be separated from density fluctuations, two effects that are clearly directly related in real liquids. Similarly in our models, the cage escaping probability can be separated from the kinetic constraints, while these physical mechanisms are also directly related in real liquids.

### III. RESULTS AND DISCUSSION

Figure 2 shows for model (a) the self Van Hove correlation function $G_s(r, t)$ that represents the probability for a molecule to be after a time lapse $t$, at a distance $r$ from its initial position, while the upper inset in Figure 2 shows the mean square displacement together with the non-Gaussian parameter $\alpha_2(t) = \frac{\langle r^2(t) \rangle}{\langle r^2(0) \rangle} - 1$ that measures the deviation of the Van Hove from the Gaussian shape predicted by Brownian motion. The inset shows that $\alpha_2(t)$ is maximum on a characteristic time $t^*$ located at the plateau ending of $\langle r^2(t) \rangle$, a result in amazing agreement with real supercooled liquids behavior. Interestingly, the Van Hove correlation functions in Figure 2 also display a tail similar to the tails observed in supercooled liquids where they are considered as fingerprints of the dynamic heterogeneities. The tail is due in our model to the contribution of the molecules that find the way out the cage through the doors. The tail is thus induced by the cage escaping process, a result that explains the $\alpha_2(t)$ location at the end of the plateau of $\langle r^2(t) \rangle$. In our model the tails are...
more abrupt than in real liquids, and the tail continue to increase with time well beyond what is seen in real liquids. The main reason for this behavior is that our cages are fixed, while in real liquids they are submitted to the diffusive motions of the molecules that constitute them. An amelioration of that point will constitute an interesting improvement of our models, that could, for example, lead to the understanding of the universal ≈5% most mobile molecules optimal proportion for the dynamic heterogeneity appearance in real liquids8–10 (i.e., the universality of the maximum surface of the Van Hove tail). The presence of a tail in the Van Hove correlation function suggests that model (a) spontaneously creates dynamic heterogeneities. However, these heterogeneities are relatively weak and for \( S \ll 36 \, \text{Å}^2 \) (a value of \( S \) that in our model do have some similarities with the melting temperature in real liquids), the heterogeneities do not evolve with the doors surface, while in real glass formers the DHs increase when the temperature decreases. Indeed investigating the non-Gaussian parameter \( \chi_4(t) \) evolution with \( S \), we find that \( \chi_4(t) \) is shifted to larger times when \( S \) decreases but otherwise is roughly constant. For the model with 50% opened doors, for example, we find \( \chi_4(r^+) = 0.30 \pm 0.01 \), while \( r^+ \) increased from 0.28 ns for \( S = 4 \, \text{Å}^2 \) to 298 ns for \( S = 0.04 \, \text{Å}^2 \). To confirm the DHs evolution with \( S \) that we observe with \( \alpha_2 \) we show, in the inset at the bottom of Figure 2, the dynamic susceptibility \( \chi_4 \) evolution with the door surface \( S \). We define the susceptibility as: \[ \chi_4(a, t) = \sum_{r} \left( \langle \Delta a^4(t) \rangle \right) \] where \( \Delta a^4(t) = \sum_{r} \left( \langle a(t) - \langle a \rangle \rangle^4 \right) \) is the volume of the simulation box, \( N \) is the number of molecules, and \( \Delta = (k_B T)^{-1} \). The symbol \( w_r \) stands for a discrete mobility window function, \( w_r(t) \), taking the values \( w_r(r) = 1 \) for \( r > a \) and zero otherwise. We chose in this work \( a = 14 \, \text{Å} \) that is the size of the cage in our model, a value that insures us that we are probing diffusive motions fluctuations. The inset of Figure 2 shows the same behavior, i.e., roughly constant and shifted in times, for the dynamic susceptibility than for the non-Gaussian parameter, a result that confirms that the DHs stay constant in these models.

A limitation of model (a) for the facilitation mechanism is the absence of connections between the number of molecules in a cage and the doors opening. The molecules motion outside the cage will then not trigger the motions of other molecules in that model. As discussed before we include now that kinetic constraint mechanism in model (b). Our constraint consists in opening the door only if the sum of the number of molecules in the two boxes connected by that door is below a threshold value \( 2K \). The inset of Figure 2 shows that the DHs are much larger in model (b), which includes explicit kinetic constraints mechanisms than in model (a). Figure 2 also shows that as in model (a), the DHs do not increase with \( 1/S \) in model (b). Note that we found for smaller values of the parameter \( a \) an increase of the susceptibility with \( 1/S \). Finally, model (b') that includes a kinetic constraint based on the mobility in nearby cages displays a small increase of the susceptibility with \( 1/S \). Our results thus show that the DHs do not evolve strongly with \( S \) in our different models. We will now study their evolution with the kinetic constraint. In Figure 3, we show the evolution of the dynamic susceptibility \( \chi_4 \) and non-Gaussian parameter \( \alpha_2 \) in model (b) when we modify the threshold \( K \) of our kinetic constraint. Figure 3 shows that when the kinetic constraint is made stronger (i.e., when \( K \) decreases) the dynamic susceptibility \( \chi_4 \) and the NGP \( \alpha_2 \) increase, showing that the dynamic heterogeneities increase with the constraint, while the characteristic times \( t^* \) and \( t^+ \), defined as \( \alpha_2(t^*) = \max(\alpha_2(t)) \) and \( \chi_4(t^*) = \max(\chi_4(t)) \), increase slightly. As a result the phenomenology of the glass-transition is reproduced with our model if an increase of the kinetic constraint is associated with the decrease of the probability \( p \) to escape the cage (i.e., a decrease of the door surface). That picture is correct, for example, if the kinetic constraint (here a condition in the very local density) is one of the origins of the cage escape process. In that picture as the temperature decreases the energy required to open the cage is less often encountered in thermal fluctuations and the conditions on density fluctuations become thus more stringent.

We illustrate with a snapshot in Figure 4 the appearance of the dynamical heterogeneities in model (b). The heterogeneities arise mainly in model (b) due to density fluctuations. In zones of smaller density the model increases the probability to escape the cage, i.e., to be mobiles. As a result there is an aggregation of mobile molecules in the low density zones, and similarly an aggregation of non-mobile molecules in the zones of larger density. The reason for the appearance of the heterogeneities in the second constrained model (model (b')) is more direct as the constraint of that model increases the probability to escape the cages around mobile molecules, a constraint that clearly implies the aggregation of mobile molecules.

We also test the effect of structural fluctuations in model (c) which is obtained from model (a) by replacing the fixed...
door surfaces with randomly chosen surfaces for each door. Including that fluctuations results in an increase of the DHs, however much slighter than the increase observed when we introduced the kinetic constraints. Again the DHs do not increase within that model when the mean door surface decreases. The diffusion is also slightly modified in that model as shown in Figure 5 that displays the evolution of the diffusion coefficient $D$ with the doors mean surface $S$ (for the two densities investigated and various models). The green dashed line in the figure results from the assumption that for each collision with a wall the probability $p$ to escape the cage is the ratio of the door to the wall surfaces $p = S/S_0$, leading to $D = (S/S_0)(1/6t_0)$, where $t_0$ is the time between two collisions, i.e., the time to cross the box ballistically. Figure 5 shows that for large doors, the diffusion coefficient follows the probabilistic law described above, then deviates from that law when $S$ becomes to be small tending to a law of the form $D = \alpha(S/S_0)^{1.5}$ where $\alpha$ is a constant. We interpret that deviation as arising from percolation phenomena in our maze that are not included in the simple linear probabilistic law. Interestingly that deviation is reminiscent of the non-Arrhenius behavior with temperature of fragile glass-formers. Indeed, relating the probability $p$ to escape the cage to an activation energy $p = (S/S_0) \sim e^{-E_o/\tau_0 T}$ (in the picture of an energy barrier to overpass to open the cage) the deviation of Figure 5 from the linear law leads to a non-Arrhenius behavior of the diffusion with temperature, the activation energy increasing by a factor 1.5. Figure 5 also shows very similar diffusive comportment for the various models. That result suggests that if diffusion depends strongly on the cage opening probability (i.e., here on the mean door surface), it depends more weakly on structural fluctuations (i.e., fluctuations of the door surfaces), a result reminiscent of the recent finding that similar potentials with different attractive parts (thus different cage breaking probabilities) lead to different diffusive comportment while structures are similar.

We show in Figure 6 the mean square displacements $(\langle r^2(t) \rangle)$ plotted for model (a), the different variants leading to qualitatively similar results. We observe the three characteristic time scales of supercooled liquids, namely, the ballistic time scale, then the plateau due to the trapping of the molecule inside the cage and the diffusive time scale when the molecule finally escapes the cage. As the doors surfaces

![Figure 4](image_url) **FIG. 4.** Snapshot with molecules mobility displayed as different colours in model (b). $S = 1.0 \text{ Å}^2$ and $K = 2.5$. Blue (or dark grey): molecules are non-mobiles (i.e., they did not escape their cages); Red (or light grey): mobile molecules. The characteristic time used here for the mobility calculation is $t = t^* = 2$ ns (i.e., a molecule is considered mobile in the snapshot if it escaped its cage during the last 2 ns).

![Figure 5](image_url) **FIG. 5.** Diffusion coefficient $D$ versus doors average surfaces $S$ for various models. $D$ is here corrected from the percentage of doors opened. The dashed line is the simple law $D = (S/S_0)(1/6t_0)$ that results from the assumption that the probability to escape the cage is proportional to the surface of the door $S$ divided by the surface of the wall $S_0$, where $t_0$ is the time necessary to cross ballistically the cage at the temperature of study. There is 1050 molecules in the maze otherwise it is specified. The models are as follows: Solid (red) circles: the 6 doors are opened for every boxes. Open (blue) triangles (1050 molecules in the maze) and open (pink) inverted triangles (10 molecules only): We chose randomly 50% of the doors to be closed (hence some boxes may be totally opened or totally closed, but that random choice is reinitialized periodically each 100 ps time lapse). Open (green) circles: 20% of the doors are opened randomly. Solid (blue) triangles: We use a continuous random distribution of surfaces for the doors.

![Figure 6](image_url) **FIG. 6.** Mean square displacements $(\langle r^2(t) \rangle)$ for various average door surfaces $S$ with model (a). We have used model (a) to obtain these curves but the different variants lead to qualitatively similar results. From bottom to top $S = 0.04, 0.16, 0.36, 1., 1.44, 1.96, 2.56, 3.24, 4.0, 9.0$, and $36 \text{ Å}^2$. The average surface of the door is the parameter that represents the temperature in the model. (Inset) Same curve and axis but for $N = 10$ molecules and $S = 0.36 \text{ Å}^2$. The oscillations that are washed out for larger numbers of molecules are here clearly visible.
decrease the plateau increases leading to a decrease of the diffusion coefficient. The ballistic part of the MSD is here entirely defined by the temperature $T$ ($\langle r^2(t) \rangle = 3k_B T r^2/m$), while the plateau and diffusive part depend on the door surfaces only. When small numbers of molecules are considered, we observe oscillations in the MSD in the approach of the plateau time scale (see Fig. 6 inset). These oscillations arise here due to the bouncing of molecules on the cages walls and are also present in simulations of real glass-formers where they are most often related to the Boson peak unsolved phenomenon. For the larger doors used in the figure ($S = 36 \text{ Å}^2$), the plateau disappears, reproducing the behavior of liquids above their melting temperature.

Coming back to the Van Hove correlation functions that we already studied in Figure 2 but only for the intermediate timescale and for model (a), we show in Figure 7(a) that for short timescales and long timescales the Van Hove functions are Gaussians in our model as in real liquids. For short timescales that behavior results from a pure ballistic motion inside the cages, while for long timescales it results from the pure diffusive motion that we reach in the long time limit (as seen in Figure 6). In Figure 7(b), we show that models (b) and (b') display quite similar Van Hove functions than model (a). A more detailed analysis however reveals that the tail of the Van Hove is more pronounced in the models with kinetic constraints (i.e., models (b) and (b')) than in model (a). These results confirm that the diffusive motions are mainly controlled in the models by the probability to escape the cage, that is represented by the surface of the doors, while the DHs are controlled by the kinetic constraints. Note however that in real liquids these two mechanisms are directly related as both are induced by the cage effect. It is surprising anyway that the heterogeneities are not directly controlled by the parameter $S$ that represents the temperature (for the $\alpha$ relaxation) in our models. A reason for that behavior is that as the cages location and doors surface are fixed, a decrease of the door surface only modifies the probability to escape the cage for a molecule. As a result the same physical mechanisms appear in both cases, only being shifted in time when the door is smaller. The time-temperature superposition principle thus holds too well. An interesting development will be to take into account the cage evolution in the models, in a way consistent with previous studies, and work is in progress in that direction.

IV. CONCLUSION

To summarize, we have implemented toy models, situated in between constrained spin glasses and real liquids, and intended to serve as paradigms for studying the glass-transition physical mechanisms. Our simplest model based on the cage effect, reproduces most of the features of the dynamics of supercooled liquids, namely, the plateau and small oscillations in the density correlation functions, the three different time scales (ballistic, plateau, and diffusive), the non-Gaussian behavior of the Van Hove correlation function with a maximum of the non-Gaussian parameter localized in time around the plateau regime ending, and the appearance of a tail in the self-Van Hove correlation function. We also observe a door surface equivalent to the melting temperature, and the appearance of the cooperative effects called dynamic heterogeneities. But in that model the dynamic heterogeneities do not increase with the relaxation time (i.e., the decrease of the probability to escape the cage) and when we include structural fluctuations in the model, these results do not change drastically. However, dynamic heterogeneities increase significantly when we include kinetic constraints inside the model. Thus our results suggest that the increase of the DHs when the temperature decreases is due to the hardening of kinetic constraints as opposed to a structural fluctuation origin.

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