Relaxation properties in a lattice gas model with asymmetrical particles

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We study the relaxation process in a two-dimensional lattice gas model, where the interactions come from the excluded volume. In this model particles have three arms with an asymmetrical shape, which results in geometrical frustration that inhibits full packing. A dynamical crossover is found at the arm percolation of the particles, from a dynamical behavior characterized by a single step relaxation above the transition, to a two-step decay below it. Relaxation functions of the self-part of density fluctuations are well fitted by a stretched exponential form, with a $\beta$ exponent decreasing when the temperature is lowered until the percolation transition is reached, and constant below it. The structural arrest of the model seems to happen only at the maximum density of the model, where both the inverse diffusivity and the relaxation time of density fluctuations diverge with a power law. The dynamical non linear susceptibility, defined as the fluctuations of the self-overlap autocorrelation, exhibits a peak at some characteristic time, which seems to diverge at the maximum density as well.

I. INTRODUCTION

Most glassy systems such as structural glasses, ionic conductor, supercooled liquids, polymer, colloid, and spin glasses have similar complex dynamical behavior. As the temperature is lowered the relaxation times increase drastically, and the relaxation functions deviate strongly from a single exponential function at some temperature $T^*$ well above the dynamical transition. In the long time regime they can be well fitted by a stretched exponential or Kohlrausch-Williams-Watts function $f(t) = f_0 \exp\left[-(t/\tau)^\beta\right]$, with $0 < \beta \leq 1$.

There are two mechanism driving to non exponential relaxation. In disordered model like spin glasses, it is caused by the existence of unfrustrated ferromagnetic-type clusters of interactions, and therefore is a direct consequence of the quenched disorder. Another mechanism in frustrated systems is based on the percolation transition of the Kasteleyn-Fortuin and Coniglio-Klein cluster. In this approach disorder is not needed to obtain nonexponential relaxation.

In spin glasses there is a thermodynamic transition at a defined temperature $T_{SG}$, where the non linear susceptibility diverges. As $T_{SG}$ is approached, the static correlation length becomes larger. In glass forming liquids it seems that there is no sharp thermodynamic transition, and no diverging static length. However numerical studies have identified long lived dynamical structures which are characterized by a typical length and a typical relaxation time, which depend on temperature and density. In order to characterize this behavior a dynamical non-linear susceptibility was introduced by Donati et al., both for spin models and for structural glasses. They have found that the dynamical susceptibility exhibits a maximum at some characteristic time which diverges as the dynamical transition temperature is approached from above. Also in the annealed version of the frustrated Ising lattice gas model a similar behavior has been found, while in the quenched version the dynamical susceptibility is always increasing, due to the presence of the thermodynamic transition.

The understanding of the macroscopic process of relaxation in structural glasses, starting from the microscopic motion of the particles, has been boarded using different microscopic models, as for example the hard square model, the kinetically constrained models, and the frustrated Ising lattice gas (FILG) model. These models have reproduced some aspects of the glassy phenomenology, and recently the FILG model has been studied in its quenched and annealed version with kinetic constraints. The results found in the annealed version seems to be close to the experimental ones. In this paper we consider a two-dimensional geometrical model, which contains as main ingredients only geometrical frustration without quenched disorder and without kinetic constraints, as quenched disorder is not appropriate to study structural glasses and kinetic constraints are somehow artificial. Similar models have already been proposed and applied to study granular material.

In Sec. II we present the model and in Sec. III we study its percolation properties. In Sec. IV we show the dynamical results, and finally in Sec. V we present our conclusions.
II. THE MODEL

In this paper we introduce a model which can be considered as an illustration of the concept of frustration arising as a packing problem. In systems without underlying crystalline order, frustration is typically generated by the geometrical shape of the molecules, which prevents the formation of close-packed configurations at low temperature or high density; for systems with underlying crystalline order, frustration arises when the local arrangement of molecules kinetically prevents all the molecules from reaching the crystalline state.

An example of glass-former that has difficulty in achieving crystalline order is the ortho-terphenyl, whose molecule is made of three rings. This system can be loosely modeled with a simple lattice model, in which “T” shaped objects occupy the vertices of a square lattice with one of four possible orientations. Assuming that the arms cannot overlap due to excluded volume, we see that only for some relative orientations two particles can occupy nearest-neighbor vertices. Consequently, depending on the local arrangement of particles, there are sites on the lattice that cannot be occupied (see Fig. 1). This type of “packing” frustration thus induces defects or holes in the system. This model resembles the hard-square lattice gas model \[13\] which can be seen as “+” shaped objects on the vertices of a square lattice with excluded volume interaction. A very important difference between these two models is the internal degree of freedom due to the particle shape which is absent in the latter.

We consider a two dimensional square lattice and impose periodic boundary conditions. In our system the maximum of density is \(\rho_{\text{max}} = 2/3\) at which all possible bonds are occupied by an arm. A configuration of density \(\rho_{\text{max}}\) is a ground state of the system, corresponding to chemical potential \(\mu \to \infty\) or temperature \(T \to 0\). It can be obtained for any size constructing larger systems from smaller ones with \(\rho_{\text{max}}\) and appropriated boundary conditions. In this way one can build an extensive number of different ground states that lack spatial order.

We have simulated the diffusion and rotation dynamics of this model by Monte Carlo methods. The dynamics of the particles is given by the following algorithm: i) Pick up a particle at random; ii) Pick up a site at random between the four nearest neighbor ones; iii) Choose randomly an orientation of the particle; iv) If it does not cause the overlapping of two arms, move the particle in the given site with the given orientation; v) If the diffusion movement is not possible, choose a random orientation and try to rotate the particle to this new orientation; vii) Advance the clock by \(1/N_s\), where \(N_s\) is the number of sites, and go to i).

Studying the dynamics by Monte Carlo simulations, the finite size effects are larger when we are near to \(\rho_{\text{max}}\), because the particles can be enclosed in cages, and the diffusion is blocked. In lattices of finite size, cages may be indefinitely stable. This has also been observed in the hard-square lattice gas model \[13\] where at the maximum of density the particles are on the diagonals, but in lattices of finite size cages of particles indefinitely stable are formed at lower densities.

III. PERCOLATION TRANSITION

In order to investigate whether the percolation transition has effects on the dynamics, in this section we analyze the percolation properties of the model, and relate the percolation density with a change in the dynamical properties of the model. The particles have three arms, and there are two bonds per site on the lattice, so the density of bonds occupied by an arm is given by \(\sigma = 3\rho/2\), where \(\rho\) is the density of particles. Therefore, if the correlations of the arms were not important, the arm percolation would occur at the density \(\sigma_c = 1/2\), corresponding to \(\rho_c = 1/3\). Nevertheless we expect some correlation effects.

We have simulated our system for various lattice sizes around the percolation density in order to determine \(\rho_c\). For each density we have reached equilibrium and then, taking \(10^3\) steps, we have evaluated the probability of existence of a spanning cluster \(P\) and the mean cluster size \(S = \sum s^2 n_s\), where \(n_s\) is the density of finite clusters of size \(s\).

Around the percolation density the averaged quantities \(P(\rho)\) and \(S(\rho)\), for different values of the lattice size \(L\), should obey to the finite size scaling \[18\]

\[
P(\rho) = F_P \left[ L^{1/\nu}(\rho - \rho_c) \right] \tag{1}
\]

\[
S(\rho) = L^{\gamma/\nu} F_S \left[ L^{1/\nu}(\rho - \rho_c) \right] \tag{2}
\]

where \(\gamma\) and \(\nu\) are then critical exponents, and \(F_P(x)\) and \(F_S(x)\) are universal functions of an adimensional quantity \(x\). Fig. 2 shows the finite size scaling of \(P\) and \(S\). We have selected the values of the exponent corresponding to the two-dimensional site-bond percolation universality class \[18\], that is \(\nu = 4/3\) and \(\gamma = 43/18\) and we have found \(\rho_c = 0.315 \pm 0.003\). The critical density can also be determined from \(P(\rho)\) as the density at which curves corresponding to different sizes cross. From the inset of Fig. 2(a) we see that \(\rho_c\) is between 0.315 and 0.32, so that the arm correlations and the thermal process decrease the critical density with respect to the random bond problem.

IV. DYNAMICAL RESULTS

We wish now to define a self-overlap parameter, in order to measure the autocorrelation of the model. Different definitions of \(q\) can be used, and the form of the
relaxation functions is different for different overlap parameters. Here we define a self-overlap parameter which takes into account the orientation of the particle, rather that its position. The orientation of the particle is defined by the discrete values of the angle, $\phi_i = 0, \pi/2, \pi$, or $3\pi/2$, and we define the self-overlap
\[ q(t) = \frac{1}{N} \sum_i n_i(t') n_i(t' + t) \cos[\phi_i(t' + t) - \phi_i(t')] \tag{3} \]

where $n_i(t) = 0, 1$ is the occupation number of site $i$ at time $t$, $\phi_i(t)$ is the orientation of the particle on site $i$ at time $t$, and $N$ is the number of sites. This parameter is a generalization of the self-overlap defined in Ref. [2], where the orientation $\phi_i$ plays the role of the spin variables. When all particles are frozen then $q = 1$. The associated dynamical nonlinear susceptibility $\chi(t)$ is given by
\[ \chi(t) = N \langle (q(t)^2) - \langle q(t) \rangle^2 \rangle, \tag{4} \]

where the average $\langle \cdots \rangle$ is done on the reference time $t'$.

In Fig. 3, we show the relaxation function of the self-overlap parameter, for a system of size $64^2$ and densities between $\rho = 0.2$ and 0.66. Each curve is obtained averaging over a time interval for $t'$ of $10^4 - 10^8$ Monte Carlo steps, depending on the density. For high and intermediate densities we observe a two-step relaxation functions, which gives evidence of two well separate time scales in the system. The first short time decay of the relaxation functions is due to the rotations of the particles in a frozen environment, which appears as quenched on this time scale, while the second decay is due to the evolution of the environment and final relaxation to equilibrium.

For very low densities $\rho \leq 0.1$ the relaxation function is well fitted by an exponential form. From $\rho \approx 0.1$ to $\rho \approx 0.32$ we can fit the relaxation function by a stretched exponential form, with the exponent $\beta$ decreasing slowly until $\beta \approx 0.9$ at $\rho \approx 0.32$. For higher values of densities it is impossible to fit the relaxation function with a single form over the whole time interval. As we have seen, $\rho \approx 0.32$ corresponds to arm percolation. This suggests that the percolation transition induces a crossover in the dynamics, from a single relaxation regime to two temporal scales for the relaxation of the particles. At densities higher than $\rho \approx 0.32$, the long time tail of the relaxation functions is well fitted by a stretched exponential form, where the exponent $\beta$ depends very weakly from the density (it is constant within the errors) and ranges between $\beta = 0.64$ and $\beta = 0.71$. We show in Fig. 4 the time-density superposition of the relaxation function $\langle q(t) \rangle$, for densities between $\rho = 0.62$ and $\rho = 0.66$. Also shown as a dashed line is a fit with a stretched exponential function.

In Fig. 5 we show the intermediate time behavior of the self-overlap relaxation functions, for densities $\rho = 0.62, 0.64$ and 0.65. We have tried to fit them with the simplified form of the function predicted by the MCT,
\[ \langle q(t) \rangle = f + At^{-a} - Bt^b \tag{5} \]

where the fitting parameters are $f$, $A$, $B$ and $\lambda$, and $a$ and $b$ are related to $\lambda$ by the transcendental equation
\[ \frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)} = \lambda. \tag{6} \]

The values of $\lambda$ given from the fits are constant within the errors, with a mean value $\lambda = 0.785 \pm 0.005$, which correspond to exponents $a = 0.285 \pm 0.005$ and $b = 0.50 \pm 0.01$.

In Fig. 5, we show the dynamical non linear susceptibility for some values of the density. The maximum in the susceptibility $\chi(t^*)$ and the time of the maximum $t^*$ seem to diverge together when the density grows. This has also been found previously in other models as p-spin, Lennard-Jones binary mixture [10], and in the annealed version of the frustrated Ising lattice gas model [12]. In our model we obtain that the maximum of $\chi(t^*)$ can be fitted by the power law $\chi(t^*) \propto (\rho_{\text{max}} - \rho)^{\alpha}$. Here we have $\rho_{\text{max}} = 0.664 \pm 0.002$ and $\alpha = 0.71 \pm 0.02$. The equilibrium value is $\chi(t \to \infty) = \rho^2/2$ for low densities and $\chi(t \to \infty) = 1/2$ for the higher ones.

The density-density autocorrelation function and its dependence with the time is an important property which characterizes the glassy behavior. We have studied the self-part of the autocorrelation function of the density fluctuations defined as
\[ F_k^\rho(t) = \frac{1}{N} \langle \sum_i e^{i \mathbf{k} \cdot (\mathbf{r}_i(t' + t) - \mathbf{r}_i(t'))} \rangle, \tag{7} \]

where $\mathbf{r}_i(t)$ is the position of the $i$th particle in units of the lattice constant. The wave vector can take the values $\mathbf{k} = (2\pi/L)\mathbf{n}$, where $\mathbf{n}$ has integer components $n_x$ and $n_y$ ranging from 0 to $L/2$.

Fig. 6 shows $F_k^\rho(t)$ corresponding to $k_x = \pi$ and $k_y = 0$ for different densities. For all densities the whole time interval of the autocorrelation function can be fitted by a stretched exponential function, $f(t) = \exp[-(t/\tau)^\beta]$, where the exponent $\beta$ depends on the density. In Fig. 6, we show $\beta$ as a function of the density. We can see that the exponent $\beta$ decreases with the density until a density near $\rho \approx 0.32$ is reached. From this density the exponent becomes constant $\beta \approx 0.82$ (within of the error bars). At densities near to $\rho_{\text{max}}$ the finite size effects become important and $\beta$ deviates from the constant value. As in the $\alpha$-relaxation of the self-overlap parameter, the effect of the percolation on the relaxation of $F_k^\rho(t)$ is to leave $\beta$ constant, but now there is not two step relaxation process.

If we look at the relaxation of the position of particles there is no vibration relaxation, the relaxation begins
when frozen domains evolve. Instead the relaxation of the orientation of the particles has a relaxation process where it is possible the vibration of the rotational degree of freedom. Nevertheless after the arm percolation the position and orientation relaxation in the $\alpha$-relaxation have a stretched exponential form with the exponent $\beta$ constant (within the errors) although with different value each other.

The relaxation time $\tau$ is obtained from the fitting of $F_k^0(t)$ with a stretched exponential function, and can be fitted by a power law $\tau \propto (\rho_{\text{max}} - \rho)^{-\gamma}$, with $\gamma = 2.70 \pm 0.02$ and $\rho_{\text{max}} = 0.666 \pm 0.003$ (see Fig. 9). Note that the value of $\gamma$ coincides within the errors with the one deduced by the exponents $a$ and $b$ given by the fit of Fig. 5, using the relation predicted by Mode-Coupling Theory

$$\gamma = \frac{1}{2a} + \frac{1}{2b},$$

which gives $\gamma = 2.74 \pm 0.03$.

We have calculated the diffusion coefficient from the mean-square displacement $\langle \Delta r(t)^2 \rangle$ at very long times. The values obtained for $D$ are well fitted by a power law near of $\rho_{\text{max}}$, $D \propto (\rho_{\text{max}} - \rho)^{-\gamma}$ with $\gamma = 2.70 \pm 0.02$ and $\rho_{\text{max}} = 0.666 \pm 0.003$ (see the inset of Fig. 9). The power law agrees with the law found in some lattice gas models (the kinetically constrained model [14]) but it is different of the law found in the hard-square lattice gas model [3]. This singular behavior of $D$ is in accordance with the prediction of MCT. Form the behavior of $D$ and $\tau$ we arrive to $D^{-1} \propto \tau$ and so to the Stokes-Einstein relation $D^{-1} \propto \eta$ (due to $\tau \propto \eta$).

V. CONCLUSIONS

We have proposed a two-dimensional geometrical model, based on the concept of geometrical frustration which is generated by the particle shape. This model has neither quenched disorder nor kinetic constraints. Percolation in the model has been studied, and it has been found that at the critical density of arm percolation the model shows a dynamical crossover, characterized by the onset of a two step relaxation in the orientational relaxation of the particles. Below the transition, the long time regime of orientational and positional relaxation functions can be fitted by a stretched exponential with an exponent $\beta$ constant within the errors. The dynamical results have been compared with the prediction of the MCT, finding good agreement. A self-overlap parameter has been defined which takes into account the orientation of particles, and the corresponding dynamical non linear susceptibility has been studied. It has been found that this dynamical susceptibility shows a peak at some characteristic time, which gives evidence of long lived dynamical structures with a growing length and relaxation time, as found in some molecular dynamics simulations.

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FIG. 1. Schematic picture of one particular configuration in a system size of $4^2$ and density $\rho = 9/16$.

FIG. 2. Finite size scaling of (a) $P(\rho)$ and (b) $S(\rho)$ for lattice sizes $L = 40, 50, 60, 70, 80, 90, 100, 110, \text{ and } 120$. Inset: (a) $P(\rho)$ and (b) $S(\rho)$ for the same sizes.
FIG. 3. Relaxation functions for the self-overlap for system size $64^2$ and densities $\rho = 0.2, 0.3, 0.4, 0.5, 0.55, 0.6, 0.62, 0.63, 0.64, 0.65, 0.655, 0.657$, and 0.66.

FIG. 4. Time-density superposition principle for the relaxation function of the self-overlap, for densities $\rho = 0.62, 0.63, 0.64, 0.65, 0.655, 0.657$, and 0.66. The dashed line is a fitting function corresponding to a stretched exponential form with exponent $\beta = 0.71$.

FIG. 5. Fit of the intermediate time regime of the relaxation functions of the self-overlap, for densities $\rho = 0.62, 0.64$ and 0.65. The fitting function is $f + At^{-a} - Bt^b$ (dotted line), where the fitting parameters are $f$, $A$, $B$, and $\lambda$, and $a$ and $b$ are given by the relation (6).

FIG. 6. Dynamical susceptibility for $L = 64$ and densities $\rho = 0.6, 0.62, 0.63, 0.64, 0.65, 0.655, 0.657$, and 0.66. Inset: the maximum $\chi(t^*)$ as a function of density. The fitting function is a power law $\chi(t^*) = 0.12(0.664 - \rho)^{-0.7}$.

FIG. 7. Relaxation functions for the self-part of the density-density autocorrelation function for $k_x = \pi$ and $k_y = 0$ and the same system size and densities of Fig. 2. Dotted lines are fitting functions corresponding to stretched exponential functions.
FIG. 8. Parameter $\beta$ as a function of the density, obtained by fitting $F_{k}(t)$ for $k_x = \pi$ and $k_y = 0$ with the function $f(t) = \exp\left(-\left(t/\tau\right)^{\beta}\right)$. The densities represented are $\rho = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.33, 0.35, 0.37, 0.4, 0.45, 0.5, 0.55, 0.6, 0.63, 0.64, 0.65, 0.655,$ and 0.66. The solid line corresponds to $\beta = 0.82$.

FIG. 9. The relaxation time $\tau_\alpha$ as a function of density $\rho$. Solid circles: relaxation times obtained from the fit in Fig. 7. Asterisks: relaxation times obtained from the fit in Fig. 4. The solid lines are power law functions $\tau_\alpha = a(0.666 - \rho)^{-2.7}$, with $a = 0.115$ in the former case and $a = 0.04$ in the latter. Inset: the diffusion constant $D$ as function of density $\rho$. The fitting function is a power law $D = 8(0.666 - \rho)^{2.7}$. 
