Lattice glass model with no tendency to crystallize

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We study a lattice model with two-body interactions that reproduces in three dimensions many features of structural glasses, such as cage effect and vanishing diffusivity. While having a crystalline state at low temperatures, it does not crystallize when quenched, even at the slowest cooling rate used, which makes it suitable to study the glass transition. We study the model on the Bethe lattice as well, and find a scenario typical of *p*-spin models, as in the Biroli-Mézard model.

The glass transition is a phenomenon that is observed when a liquid is cooled well below its melting temperature, avoiding the crystallization of the system [1,2]. The motion of the molecules is slowed down more and more by lowering the temperature, until at some point it becomes so slow that the liquid appears as a disordered solid, with the molecules vibrating around some equilibrium positions, but not diffusing anymore. Two fundamental approaches have been put forward in the study of this phenomenon, from the point of view of dynamics [3] and thermodynamics [4]. A further insight into the understanding of the glass transition was achieved through the study of the *p*-spin glass [5], a mean field model with *p*-body interactions and quenched disorder, which reproduces many features of glass forming liquids. More recently, Biroli and Mézard have introduced a very interesting lattice glass model [6], where occupation variables interact via *p*-body potentials. The mean field solution on the Bethe lattice shows a scenario identical to *p*-spin models, and three-dimensional numerical simulations show a behavior typical of glass forming liquids. In order to reduce the tendency to crystallize, the authors considered a mixture of two types of particles. Further study of the model was done in Ref. [7]. Another model with *p*-body interactions and without quenched disorder, which shows a similar behavior, was studied in Ref. [8].

In this paper, we study a simple lattice gas model with only two-body interactions. The model reproduces in mean field again the scenario typical of *p*-spin models, and three-dimensional numerical simulations show the same behavior typical of glass forming liquids, including cage effect and two-step relaxation. Moreover, while having a crystalline phase at low temperatures, the model does not crystallize when cooled, even in the pure case (only one type of particles) and at extremely low cooling rates. This makes the model more suitable to study the glass transition, and allows to obtain very clear results.

The model is defined as follows. We partition the space in regular cells, such that not more than one particle can have its center of mass inside the cell. The position and orientation of the particle inside the cell are represented by a coarse grained discrete internal degree of freedom, which can assume a finite number q of states, and the interaction between nearest neighbor particles depends explicitly on their position inside the cell. The model is therefore described by the following Hamiltonian:

$$\mathcal{H} = \sum_{\langle ij \rangle} n_i n_j \phi_{ij}(\sigma_i, \sigma_j) - \mu \sum_i n_i, \qquad (1)$$

where $n_i = 0,1$ represents whether the ith cell is occupied by a particle or not, $\sigma_i = 1,...,q$ represents the internal position of the particle, and $\phi_{ij}(\sigma_i, \sigma_j)$ is the interaction energy between two particles in cells i and j with internal positions σ_i and σ_j.

It is clear that, by choosing a sufficiently large number q of internal positions, and an opportune interaction matrix $\phi_{ij}(\sigma_i, \sigma_j)$, one can approximate as closely as desired any model defined in the continuum, for example, a Lennard-Jones liquid. On the other hand, it is plausible that a few number of internal states may be enough to catch the fundamental characteristics of dynamics and thermodynamics of glass forming liquids.

Here, we study a particularly simple realization of model (1). In two dimensions, we partition the space in square cells, and subdivide each cell into four internal positions. When a cell is occupied by a particle in a given position, a hard-core repulsion forbids the presence of another particle in some of the internal positions of the neighboring cells (see Fig. 1). Therefore in this case $q = 4$, and the interaction $\phi_{ij}(\sigma_i, \sigma_j)$ is zero if the positions σ_i and σ_j are "compatible," infinite otherwise. The extension to three dimensions is straightforward. In that case one partitions the space in cubic cells, and
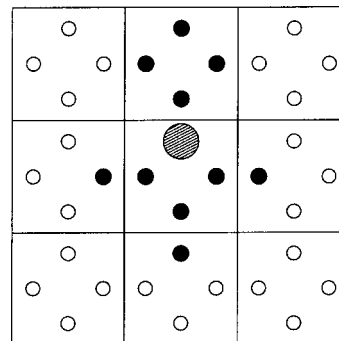

FIG. 1. The model in two dimensions: the space is partitioned in square cells, and each cell can be occupied by at most one particle in one of four positions (little circles). A particle in a given position (big shaded circle) forbids the presence of another particle in the positions colored in black.
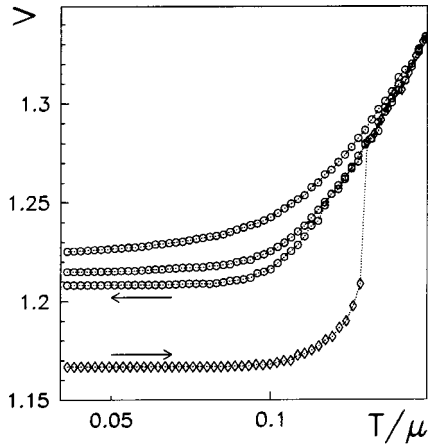
FIG. 2. Specific volume (inverse density) as a function of the temperature, for a three-dimensional system of size 28^3. Circles: the system is cooled starting from high temperature, for cooling rates (from top to bottom) $\dot{T}/T = -10^{-4}$, -10^{-5}, -10^{-7}. Diamonds: the system is heated starting from the crystalline ground state, with heating rate $\dot{T}/T = 10^{-7}$.

considers six internal positions instead of four. For every spatial dimension d, the model has a crystalline ground state with density $2d/(2d+1)$, on lattices with sides multiples of $2d+1$ lattice spacings. For example, on a cubic lattice with periodic boundary conditions it can be found as follows. Consider the cell with coordinates (x, y, z), and evaluate the number $a = (x + 2y + 3z \mod 7)$: if $a = 0$, leave the cell empty; if $a = 1, 2, 3$ put a particle in the negative x, y, or z direction, respectively; if $a = 4, 5, 6$ put a particle in the positive z, y, or x direction, respectively.

We have simulated the model in three dimensions, by means of grand-canonical and canonical dynamics. A compression experiment on a system of size 28^3 is shown in Fig. 2. A simple Monte Carlo grand-canonical (variable density) dynamics is performed, and temperature is slowly decreased, starting from some high value. The results are shown as open circles in Fig. 2, for various cooling rates. The final high-density state is strongly dependent on the cooling rate, as observed in glass forming liquids. On the other hand, no tendency to crystallization is observed: even at the slowest cooling rate ($\dot{T}/T = -10^{-7}$) no transition to the crystalline state was observed. We have also computed the density in the crystalline state, starting from the ground state at very low

temperature, and heating up slowly (diamonds in Fig. 2). This ordered state becomes unstable at $T \simeq 0.150 \mu$, where the system falls into the liquid phase.

After having equilibrated the system at a certain density in the liquid phase, we have switched to a canonical (fixed density) dynamics. These simulations are performed on lattices of size 15^3. The mean square displacement $\langle r^2(t) \rangle$ of the particles is show in Fig. 3(a). This is defined taking into account also the position of the particle inside the cell, giving to each internal position a shift $\frac{1}{4}$ of a lattice spacing with respect to the center of the cell. In Fig. 3(b) instead we plot the self-overlap, defined as

$$\langle q(t) \rangle = \frac{1}{N} \sum_i \langle n_i(t) n_i(0) \boldsymbol{\sigma}_i(t) \cdot \boldsymbol{\sigma}_i(0) \rangle, \qquad (2)$$

where $\boldsymbol{\sigma}_i(t)$ are unit length vectors, pointing in one of the six coordinate directions, representing the position of the particle inside the cell, and N is the number of particles. As it happens in glass forming liquids, at high density a *plateau* develops both in the mean square displacement and in the self-overlap. This is the signature of the so called "cage effect." Particles are trapped in cages formed by neighboring particles, and vibrate rapidly around some equilibrium position, giving rise to the first decay in correlation functions. Only after a long time they manage to escape from their cages, giving rise to the second final decay to equilibrium. While the time of the first step remains finite, the time of the slow relaxation diverges when the glass transition is approached. Figure 4(a) shows the diffusivity as a function of $\rho - \rho_c$, with $\rho_c = 0.844$. It can be fitted by a power law, with an exponent $\gamma = 3.45$. Figure 4(b) shows the dynamical susceptibility $\chi(t) = N[\langle q(t)^2 \rangle - \langle q(t) \rangle^2]$, which shows a behavior typical of p-spin models, and observed also in a Lennard-Jones binary mixture [9], with a peak at finite time that grows when approaching the glass transition, signaling the presence of dynamical heterogeneities.

We have then studied the model on the Bethe lattice, namely a random lattice with fixed connectivity [6,12,13]. Each site of the lattice is subdivided into $k+1$ internal positions, and is connected to $k+1$ randomly chosen neighbors [see Fig. 5(a)]. For large number of sites N, the lattice is locally treelike, but has loops of length of the order of $\ln N$. Consider a "branch" ending on site i, that is, a graph in which site i has only k neighbors, and let $Z_0^{(i)}$, $Z_{ext}^{(i)}$, and $Z_{int}^{(i)}$
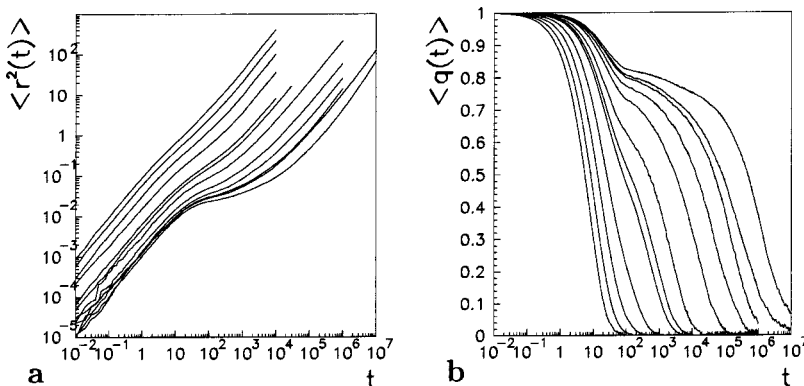

FIG. 3. (a) Mean square displacement $\langle r^2(r) \rangle$ and (b) self-overlap $\langle q(t) \rangle$ as a function of time, in a three-dimensional system of size 15^3, for densities $\rho = 0.55$, 0.6, 0.65, 0.7, 0.75, 0.76, 0.78, 0.8, 0.81, 0.815, 0.818, 0.821.
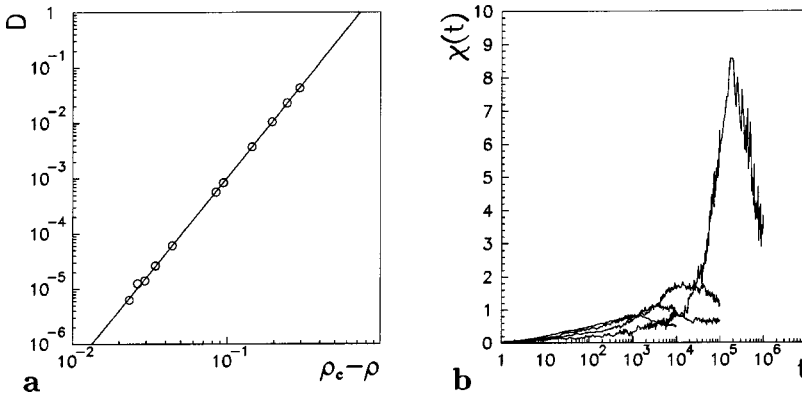
FIG. 4. (a) Diffusivity D as a function of $\rho_c - \rho$, with critical density $\rho_c = 0.844$. The fitting function is a power law $D = a|\rho - \rho_c|^\gamma$, with $\gamma = 3.45$. (b) Dynamical susceptibility $\chi(t)$ as a function of time, for densities $\rho = 0.76, 0.78, 0.8, 0.818$.

be the partition functions of the branch, restricted, respectively, to configurations where site i is empty, occupied on the "external" position, and occupied on one of the k "internal" positions [see Fig. 5(b)]. We define the "local fields" a_i and h_i acting on the site i by the relations $e^{\beta h_i} = Z_{\text{int}}^{(i)}/Z_0^{(i)}$, $e^{\beta a_i} = (Z_{\text{ext}}^{(i)} + Z_{\text{int}}^{(i)})/Z_0^{(i)}$. The branch can be seen as the result of the merging of the k branches ending on the neighbor sites $j = 1,...,k$, which leads to recursion relations for the local fields, and a free energy shift:

$$e^{\beta a_i} = e^{\beta \mu} \left(\prod_{j=1}^{k} \frac{1 + e^{\beta h_j}}{1 + e^{\beta a_j}} \right) \left(1 + \sum_{j=1}^{k} \frac{1}{1 + e^{\beta h_j}} \right), \quad (3a)$$

$$e^{\beta h_i} = e^{\mu\mu} \left(\prod_{j=1}^{k} \frac{1 + e^{\beta h_j}}{e^{\beta a_j}} \right) \left(\sum_{j=1}^{k} \frac{1}{1 + e^{\beta h_j}} \right), \quad (3b)$$

$$e^{-\beta \Delta F} = Z_0^{(i)} \Bigg/ \prod_{j=1}^{k} Z_0^{(j)} = \prod_{j=1}^{k} (1 + e^{\beta a_j}). \quad (3c)$$

To evaluate the total free energy, one has to consider also the free energy shifts when merging $k+1$ branches on a new site, and when merging two branches are given, respectively, by
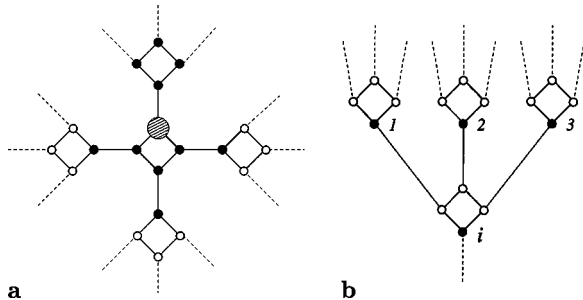
$$e^{-\beta \Delta F^{(1)}} = \prod_{j=1}^{k+1} (1 + e^{\beta a_j}) + e^{\beta \mu} \sum_{p=1}^{k+1} \prod_{j \neq p} (1 + e^{\beta h_j}), \quad (4a)$$

$$e^{-\beta \Delta F^{(2)}} = 1 + e^{\beta a_1} + e^{\beta a_2} + e^{\beta (h_1 + h_2)}. \quad (4b)$$

The replica symmetric solution of the problem corresponds to the case in which there is only one pure state, and the fields do not fluctuate from site to site. In this case, the total free energy is given by $F = \Delta F^{(1)} - (k+1)\Delta F^{(2)}/2$, from which one can find the specific volume and the entropy per site, which are shown as solid lines in Figs. 6 and 7 (in the case $k = 5$). As it happens in the model studied by Biroli and Mézard [6], the entropy becomes negative for temperatures below some threshold. A similar behavior is observed for every $k > 1$. One can also find a (replica symmetric) crystalline solution, where the fields do not fluctuate on the single site, but are different on different sites, and the merging of the branches is done preserving the crystalline structure. For $k = 5$, this solution appears below $T_{ms} = 0.1633\mu$, and becomes stable below the melting temperature $T_m = 0.1444\mu$. The corresponding volume and entropy are shown as dashed lines in Figs. 6 and 7.

We have then looked for a solution at the level of one-step replica symmetry breaking (RSB) [10–13]. In this case, many pure states exist, and the local fields fluctuate also on
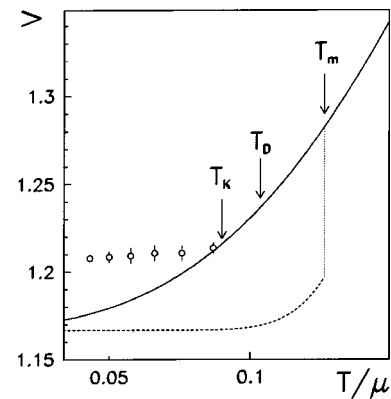

FIG. 5. (a) The model on the Bethe lattice (here with $k = 3$): each site is subdivided into $k+1$ positions (little circles), and connected to $k+1$ randomly chosen neighbors. A particle in a given position (big shaded circle) forbids the presence of another particle in the positions colored in black. (b) Merging of the branches $j = 1,...,k$ onto the site i: the "external" positions are those colored in black, the others are the "internal" ones.

FIG. 6. Specific volume (inverse density) as a function of the temperature, on the Bethe lattice with $k = 5$. Solid line replica symmetric liquid phase: broken line, crystalline phase; open circles, glassy phase in the one-step RSB approximation. Arrows mark the various temperatures cited in the text.
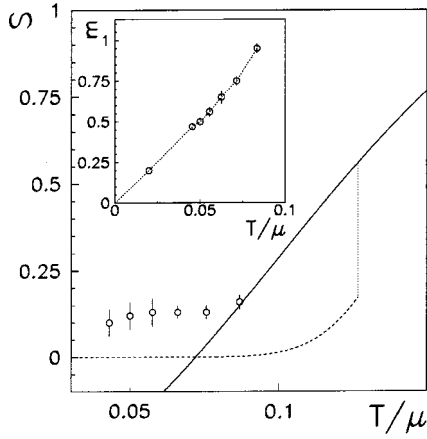
FIG. 7. The same as in Fig. 6, but for the entropy per site. Inset: parameter m as a function of the temperature. The line is a guide for the eye.

the single site. We work in the so called "factorized case," in which the probability distribution of the local fields $P(a_i, h_i)$ on the single site is the same on all the sites of the lattice. The self-consistency equation, when merging k branches on a site i, now reads

$$P(a,h) \propto \int \prod_{j=1}^{k} da_j dh_j P(a_j, h_j)$$

$$\times \delta(a - a_i) \delta(h - h_i) \exp(-\beta m \Delta F), \quad (5)$$

where a_i, h_i, and ΔF are functions of a_j and h_j via Eqs. (3), m is a real parameter, and the total free energy is

$$F = -\frac{1}{\beta m} \left\{ \ln \int \prod_{j=1}^{k+1} da_j dh_j P(a_j, h_j) e^{-\beta m \Delta F^{(1)}} \right.$$

$$\left. -\frac{k+1}{2} \ln \int \prod_{j=1}^{2} da_j dh_j P(a_j, h_j) e^{-\beta m \Delta F^{(2)}} \right\}. \quad (6)$$

One then has to maximize the free energy with respect to the parameter m, in the interval $0 \leq m \leq 1$.

At temperature $T=0$ the solution of Eq. (5) is easily found. Indeed, in that case the fields a_i and h_i can only have the finite set of values

$$a_i = (1-k)\mu, \ldots, 0, \mu,$$

$$h_i = \begin{cases} a_i & \text{if } a_i < \mu \\ 0, \mu & \text{if } a_i = \mu \end{cases}. \quad (7)$$

The distribution $P(a, h)$ is then a sum of $k+2$ δ functions, and the integral equation (5) gives rise to $k+2$ algebraic equations for the weights of the δ functions. One has to give a finite value to the parameter $\beta m \mu$, and maximize the free energy with respect to it. For $k=5$, the maximum is $F = -0.8265\mu$, for $\beta m \mu = 8.078$. At temperature $T>0$ the solution of Eq. (5) can be found iteratively. We discretized the distribution $P(a, h)$ over a domain of the plane (a, h), using a fine grid with spacings $da = dh = \mu/1024$, and starting from some initial distribution applied iteratively Eq. (5) until the procedure converged. Of course one must be careful that the chosen domain in the plane (a, h) covers all the support of $P(a, h)$. To locate the maximum of the free energy as a function of m, it is useful to evaluate explicitly the derivative dF/dm [12]. The results for the volume and entropy, and for the parameter m, are shown as open circles in Figs. 6 and 7, in the case $k=5$. The one-step RSB solution appears below $T_D \simeq 0.105\mu$, and becomes stable below $T_K \simeq 0.087\mu$, where $m=1$. Note that below T_K the configurational entropy vanishes, and therefore the residual entropy, at low temperatures in the one-step RSB solution, has to be interpreted as a "vibrational entropy," due to the "rattling" of the particles inside their cages. This vibrational entropy is absent in the crystalline state.

In conclusion, we have studied a lattice glass model with two-body interactions. On the Bethe lattice, it shows the same scenario of discontinuous spin glasses, and of other recently studied lattice models of glass. Moreover, it shows no tendency to crystallize when simulated in three dimensions with a simple Monte Carlo dynamics, which avoids the need to introduce a mixture, as in many models of glass.

Note added. Recently we learned about the work of Weight and Hartmann, who have studied a lattice glass model that shows a similar behavior [14].

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