# Lattice Glass Models

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Motivated by the concept of geometrical frustration, we introduce a class of statistical mechanics lattice models for the glass transition. Monte Carlo simulations in three dimensions show that they display a dynamical glass transition which is very similar to that observed in other off-lattice systems and which does not depend on a specific dynamical rule. A mean-field study shows the existence of a discontinuous glass transition, in agreement with the numerical observations.

Understanding the glass transition, and the glass phase, is one of the present major challenges in condensed matter physics. The experimental glass transition is related to a dramatic dynamical slowing down in which the structural relaxation time changes 14 orders of magnitudes in a relatively small window of temperatures. As a matter of fact, the glass transition temperature $T_g$ is empirically defined as that where the structural relaxation time becomes of the order of an hour. In the last 50 years there have been many efforts to try to understand whether this phenomenon is just a dramatic crossover, related to a pure dynamical transition, or the signature of a true thermodynamic glass transition, called the "ideal glass transition," which would take place at temperature $T_K$ below $T_g$ but which is kinetically avoided [1]. The possibility of this last scenario in fragile glasses is supported by the closeness of the Vogel-Fulcher temperature (where the extrapolated relaxation time has a divergence) and of the Kauzmann temperature (where the extrapolated excess entropy of the supercooled liquid vanishes) [2], and has been widely explored theoretically [1,3–7]. The analogy with mean-field discontinuous spin glasses [6] has recently given a new boost to this line of research [7]. These models can be solved analytically and display striking similarities with the experimental fragile glasses. However, they predict (because of their mean-field character) a dynamic freezing transition at a temperature $T_c > T_g$, equal to the mode coupling transition temperature, where real systems still have a finite relaxation time. This difference is generally attributed to the existence in finite dimensions of activated processes which would transform the "mean-field" dynamical transition into a crossover in such a way that the relaxation time increases very fast in the temperature region $T_K < T < T_c$ and eventually diverges at $T_K$.

In this paper we introduce new lattice models of glasses. We study them numerically in three dimensions, and show that (1) they display a dynamic glass transition similar to the one seen in the simulation of glass formers like binary Lennard-Jones [8], and (2) their mean-field solution, obtained using the Bethe approximation, predicts the same physical scenario found for mean-field discontinuous spin glasses (in particular, a dynamic freezing transition preceding the ideal glass transition).

Our lattice glass models are defined as follows. On each node of the lattice (e.g., a cubic lattice), there can be a 0 or 1 particle, but these occupations are restricted by a hard "density constraint": a particle cannot have more than $\ell$ among its six neighboring sites occupied. One possible interpretation of this model is a coarse grained version of a usual (off-lattice) hard sphere system taking into account the effect of geometric frustration [9]. One site of our lattice is then characterizing the density of spheres in a local cell of space, of volume of the order of an icosahedron built with the original spheres. The presence of a "particle" in our model means that the local arrangement of spheres in this cell is very dense, as happens when icosahedral order sets in. The absence of the particle corresponds to a less dense arrangement of spheres. Geometric frustration means that it is not possible to fit together the high density icosahedral structures to fill the space: this is taken into account by the density constraint.

Notice the important difference with the Kob-Andersen model [4,10]. In that case the jamming is forced by a dynamical rule: a particle which violates the density constraint is blocked. In our case, the model is defined thermodynamically: configurations violating the density constraint are forbidden. The thermodynamics definition has two advantages which were absent in previous lattice models [4,5]: (1) The existence of a dynamical phase transition, and the value of the density at which it takes place, do not depend on the type of *local* dynamics which is used, e.g., whether particles just hop on the lattice or whether they are exchanged grand canonically with a reservoir. (2) One can perform some analytic studies of the thermodynamics, relate them to the dynamical observations, and address key issues like the possible existence of an ideal glass transition.

We have run some numerical simulations of the lattice glass models using two algorithms. The first one (CA) is a simple Monte Carlo simulation at fixed density in the

canonical ensemble, where a randomly chosen particle can hop to a neighboring site if the density constraint is satisfied. In order to find an acceptable initial configuration, we prepare the system through an annealing procedure, in which the constraint is soft: a particle with $r$ neighbors has an energy $E = (r - \ell)\theta(r - \ell)$ ($\theta$ is Heaviside's step function), and we simulate the system with a Metropolis algorithm at decreasing values of the temperature $T$. When a zero energy configuration is found, we turn to the hard density-constraint case (i.e., $T = 0$) and start our canonical run. At equilibrium, the chemical potential is measured from $\mu = \ln(\rho/p)$, where $p$ is the fraction of sites in which it is possible to add a new particle and $\rho$ is the density. The second type of simulation (GCA) uses the grand canonical ensemble. We have a reservoir with chemical potential $\mu$ which is coupled to each lattice site and can create or destroy particles.

As expected, the GCA simulation reaches the equilibrium faster. The obtained results look qualitatively very similar to the ones in Lennard-Jones systems [8]. For a one component fluid, we find for all $\ell \geq 1$ that upon increasing $\mu$ the system has a first order phase transition towards a crystal, identified by a discontinuity of the density, and the presence of Bragg peaks in the diffraction pattern. In order to study the glass transition, we have considered lattice glass binary mixtures, for which the tendency to crystallization is reduced. In these mixtures, one obtains a reproducible "supercooled liquid" which exhibits, when the density increases, a dynamical glass transition. We present the results obtained for a mixture containing 30% of particles $A$ with density constraint $\ell_A = 1$, and 70% of particles $B$ with density constraint $\ell_B = 3$ (called $m_{13}$ mixture in the following). Figure 1 shows the density as a function of the chemical potential, measured in the two algorithms. One sees a clear saturation which takes place at a density $\rho_c \simeq 0.565$: none of these two local algorithms can reach a density higher than $\rho_c$. The inset of Fig. 1 shows the diffusion coefficient $D_A$ ($D_B$) of the particles measured in the CA simulation. Their decrease with increasing $\rho$ is well fitted by a function vanishing at $\rho_c$ with a power law:

$$D_{A,B}(\rho) \simeq C_{A,B}(\rho_c - \rho)^{\alpha_{A,B}}\theta(\rho_c - \rho) \qquad (1)$$

with exponents of order $\alpha_A \sim 4.2$ and $\alpha_B \sim 2.3$.

This vanishing is generally taken as the numerical signature of the dynamical phase transition [11,12]. When the chemical potential is quenched above the critical value (corresponding to the dynamical transition) the system remains out of equilibrium and has an aging behavior which we have seen measuring the two time correlations of occupation numbers of a site. On the contrary, if we increase the chemical potential very slowly, we can observe the transition to a crystalline phase even in this case of mixtures as shown in Fig. 1. It is quite possible that the $m_{13}$ mixture will eventually phase separate on very large times, but we have not seen any such effect on the time
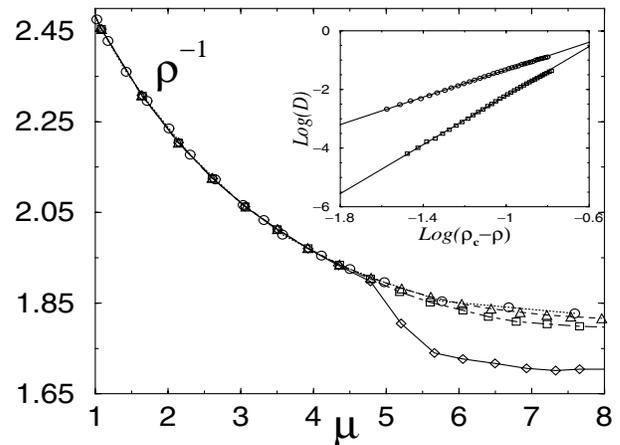
FIG. 1. The inverse of the density is plotted versus the chemical potential of the $A$ particles for the mixture $m_{13}$ on a 3D cubic lattice of size $15^3$. Circles are obtained from the canonical simulation CA with $10^3$ Monte Carlo steps per particle (MCSP). Triangles, squares, and diamonds are obtained from the GCA with, respectively, $10^3$, $3 \times 10^3$, $10^5$ MCSP at a fixed increasing rate of the chemical potential between $\mu = 0$ and $\mu = 8$. In the last case, the transition to the crystalline state is clearly visible. Inset: The diffusion coefficient for the two types of particles, in the CA simulation of the same mixture, is plotted in log-log scale versus $\rho_c - \rho$, showing the dynamical transition at $\rho = \rho_c$.

scales of our simulations. Whether there exist mixtures where the true equilibrium state at large $\mu$ is a glass, with a thermodynamic phase transition from the liquid to this glass, is under current study [13]. Let us finally note that the existence of a metastable glassy phase does not depend on the type of *local* dynamics we use (GCA or CA), only the time to nucleate the crystal (contrary to the Kob-Andersen model).

We now present a mean field theory of the finite dimensional lattice glass models. We focus on the Bethe lattice version of these models [14], whose underlying lattice structure is a random graph with fixed connectivity: every vertex has exactly $k + 1$ neighbors, but the graph is otherwise random (to study the three dimensional case one takes $k = 5$). Locally (on finite length scales), such a graph has the structure of a Cayley tree with a fixed branching ratio, but it also has loops of typical size $\ln N$. The presence of these loops is crucial to induce the geometric frustration, but the local tree structure allows for an analytic solution of the model. For the sake of clarity, we shall describe this solution in the simple case where there is only one type of particle, with a density constraint given by the integer $\ell$; we have extended these computations to mixtures [15], and we shall present the results for the $m_{13}$ mixture.

Since the underlying lattice structure is locally treelike, one can write iterative equations on the local probability measure. More precisely, let us analyze one branch of the tree ending on site $i$. We denote by $j \in \{1, \ldots, k\}$ all the neighbors of $i$. We call $Z_0^{(i)}$ the partition function of this branch, restricted to configurations where site $i$ is empty, and $Z_{1,p}^{(i)}$ the partition function restricted to configurations

where site $i$ is occupied and has $p$ neighbors occupied. Defining $S_q^{(i)} \equiv \sum_{p=0}^{q} Z_{1,p}^{(i)}$, we find the recursion relations

$$Z_0^{(i)} = \prod_{j=1}^{k} (Z_0^{(j)} + S_\ell^{(j)}),$$

$$Z_{1,p}^{(i)} = e^\mu \sum_{1 \le j_1 < \ldots < j_p \le k} S_{\ell-1}^{(j_1)} \ldots S_{\ell-1}^{(j_p)} \prod_{m \notin \{j_1, \ldots, j_p\}} Z_0^{(m)}.$$
$$(2)$$

It is convenient to introduce on any site $m$ the local fields $h_m = \ln(S_\ell^{(m)}/Z_0^{(m)})$ and $a_m = \ln(S_{\ell-1}^{(m)}/Z_0^{(m)}) - h_m$, in terms of which the iteration reads

$$e^{h_i} = e^\mu \left( \prod_{j=1}^{k} \frac{1}{1 + e^{h_j}} \right) \sigma_\ell, \qquad e^{a_i} = \frac{\sigma_{\ell-1}}{\sigma_\ell}, \quad (3)$$

where

$$\sigma_q = \sum_{p=0}^{q} \left[ \sum_{1 \le j_1 < \ldots < j_p \le k} e^{h_{j_1} + a_{j_1} + \cdots + h_{j_p} + a_{j_p}} \right] \quad (4)$$

and the sum over $j_1 < \cdots < j_p$ is defined to take the value 1 when $p$ is 0.

From these fields, one can obtain [15] the grand canonical potential $A = -\log(Z)$ as a sum of sites and links contribution [14,16]: $A = -k \sum_i A_i^{(1)} + \sum_{\langle i,i' \rangle} A_{i,i'}^{(2)}$. The contribution from the bond $\langle i, i' \rangle$ is given by the local fields obtained from the two branches arriving on $i$ (in absence of $i'$) and on $i'$ (in absence of $i$) as

$$\exp(-A_{i,i'}^{(2)}) = 1 + e^{h_i} + e^{h_{i'}} + e^{h_i + a_i + h_{i'} + a_{i'}}. \quad (5)$$

The contribution from site $i$ reads

$$\exp(-A_i^{(1)}) = 1 + e^{H_i}, \quad (6)$$

where $H_i$ is the total field on site $i$, given by formula (3) where $k$ is changed to $k + 1$. The shift in grand potential when merging the $k$ branches ending at points $j = 1, \ldots, k$ onto the node $i$ is given by

$$\exp(-A_i') = 1 + e^{h_i}. \quad (7)$$

Starting from the previous equations, we find at low density a liquid phase characterized by a homogeneous solution $h_i = h, a_i = a$, where $h, a$ verify two simple self-consistent equations. Given this solution one can easily obtain all the thermodynamic quantities, and in particular the density $\rho$ and the entropy per lattice site $S = A - \rho \mu$. For every $k \ge 2$ and $\ell \le k$ (and for generic mixtures), the entropy becomes negative when the chemical potential $\mu$ becomes larger than a certain critical value $\mu_{s=0}$. Therefore a thermodynamic phase transition takes place at a chemical potential $\mu \le \mu_{s=0}$, as shown in Fig. 2.

To gain some further insight to the thermodynamic transition we study the stability of the liquid phase; i.e., we analyze all the generalized susceptibilities:

$$\Xi_p = \frac{1}{N} \sum_{i,j} \overline{\langle n_i n_j \rangle_c^p} = \sum_d k^d (G_d)^p, \quad (8)$$

where $n_i \in \{0, 1\}$ is the occupation number of site $i$ and $\langle n_i n_j \rangle_c = G_d$ denotes the connected correlation function
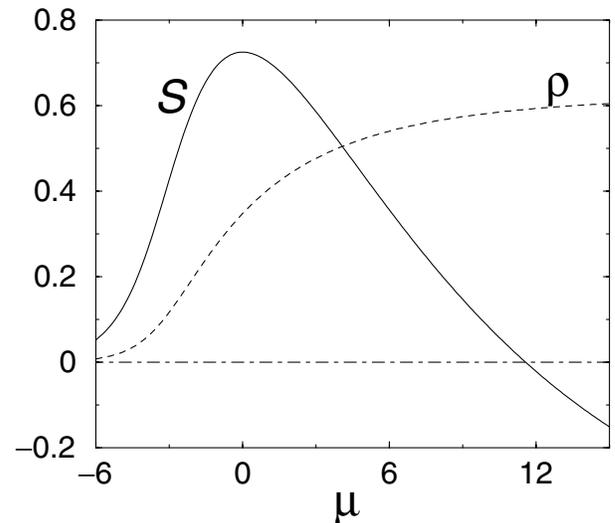


FIG. 2. The entropy per site (continuous line) and the total density (dashed line) predicted by the liquid solution are plotted as a function of the chemical potential of the $A$ particles for the mixture $m_{13}$ on a $k = 5$ Bethe lattice.

between points $i$ and $j$ at a distance $d$. Since there is only one finite path (with probability one) connecting two points at a finite distance $d$, the computation of $G_d$ (and therefore the stability analysis) can be reduced to a one-dimensional problem which can be solved by transfer matrix technique [15]. The divergence of $\Xi_1$ signals an instability toward a cyclic solution of the iteration equations [15], which corresponds to the crystal as found for $l = 0$ by Runnels [17]. Here we focus on the next instability related to the divergence of the "glass susceptibility" $\Xi_2$. Depending on the value of $k, l$ (and the type of mixture), we can encounter two types of situations. The first one is when the glass susceptibility remains always finite (this is found for $k = 1, 2, 3$ and every $l > 0$) the glass transition is then discontinuous. Instead, when the susceptibility $\Xi_2$ diverges at $\mu = \mu_2$, either there is a continuous glass phase transition at $\mu = \mu_2$ (this is found for $\ell = 0$, which is nothing but the vertex covering model studied in [18]) or a discontinuous phase transition (without any divergence of $\Xi_2$) takes place at $\mu_c < \mu_2$. This happens for sure whenever $\mu_{s=0} < \mu_2$ (this is found, e.g., in the $k = 5, l = 3$ case). The discontinuous transition case, on which we focus in the following, is the one relevant for glasses, contrary to the continuous transition which is typical of spin glasses [7].

The high-density glassy phase can be analyzed in the Bethe approximation, taking into account the existence of many different local minima of the Thouless-Anderson-Palmer free energy (called pure states in the following; see [19]). In this case the fields $h_i$ and $a_i$ fluctuate not only from site to site but also from pure state to pure state. One defines for each site a probability distribution $R_i(h, a)$ that the fields $h_i, a_i$ equal $h, a$ for a randomly chosen pure state. In our case we have verified that $R_i$ does not fluctuate from site to site, and the analysis of the high-density glassy

phase reduces to obtaining a single function $R(h, a)$. Using the cavity or the replica method [15] we find that this function satisfies the self-consistent equation

$$\frac{\mathcal{N} R(h, a)}{(1 + e^h)^{-m}} = \int \prod_{j=1}^{k} [dh_j \, da_j \, R(h_j, a_j)]$$
$$\times \delta(h - h_i) \delta(a - a_i), \qquad (9)$$

where $\mathcal{N}$ is a normalization constant, $h_i, a_i$ are the local fields on site $i$ obtained when merging the $k$ branches that carry the fields $\{h_j, a_j\}$ [see Eq. (3)], and $m$ is a Lagrange multiplier which fixes the value of the free energy density of the pure states giving rise to $R(h, a)$ [20]. We have solved this equation numerically using the algorithm of [14]. For some choices of $k$ and $\ell$, we find a scenario identical to the one of discontinuous spin glasses, with two transitions: (1) a dynamical transition at $\mu_d, \rho_d$, and (2) an equilibrium glass transition, due to an entropy crisis à la Kauzmann, at a certain density $\rho_{eq} > \rho_d$ and chemical potential $\mu_{eq} > \mu_d$. Precisely, when we increase $\mu$ starting from the liquid phase [where $R_{liq}(h, a) = \delta(h_{liq} - h)\delta(a_{liq} - a)$], we first encounter at $\mu = \mu_d$ a nontrivial solution $R_{glass}^{m=1}(h, a)$ of (9) which appears discontinuously, signaling the existence of many pure states. The static (equilibrium) transition appears at a higher chemical potential when these new solutions dominate the thermodynamics [7,20]. For the $m_{13}$ mixture on a $k = 5$ lattice, we find $\rho_d \simeq 0.58$, which is surprisingly close to the 3D value. The discontinuous character of the transition is assured by the fact that the difference $q_1 - q_0$ is finite and positive at the transition, where the overlaps $q_0$ and $q_1$ are defined as usual [19]: $q_0 = (1/N)\sum_i \langle n_i \rangle_\alpha \langle n_i \rangle_\beta / N$ and $q_1 = (1/N)\sum_i \langle n_i \rangle_\alpha^2 / N$ and the indices $\alpha, \beta$ denote two pure states randomly chosen according to their Boltzmann weights. Moreover we have checked, by running a CA simulation on the Bethe lattice [15], that the dynamical transition takes place at the density where the diffusion coefficients vanish. A detailed study of the thermodynamics of the lattice glass models, and of their equilibrium transition, will be presented elsewhere [13].

In this Letter we have introduced a new class of lattice models of glasses. Their 3D numerical simulations display a phenomenology very similar to the one of the Lennard-Jones systems, whereas their solution in the Bethe approximation exhibits a discontinuous glass transition. These models allow one to bridge the gap between the phenomenology of fragile glasses and their disordered spin glass analogs. They should allow one to study key issues like the existence or not of a true thermodynamic phase transition, and the finite dimensional counterpart of the mean-field dynamical transition, because (1) they are among the simplest systems to exhibit a glass transition in 3D, (2) this transition is not linked to a specific dynamical rule, but it is present in any local dynamics, (3) contrary to off-lattice models, they can be solved in the Bethe approximation (i.e., in the limit of infinite dimension), and (4) within such an approximation scheme they present a discontinuous spin glass transition.

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