Finite-energy extension of a lattice glass model

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We extend a previously studied lattice model of particles with infinite repulsions to the case of finite-energy interactions. The phase diagram is studied using grand canonical Monte Carlo simulation. Simulations of dynamical phenomena are made using the canonical ensemble. We find interesting order-disorder transitions in the equilibrium phase diagram and identify several anomalous regimes of diffusivity. These phenomena may be relevant to the case of strong orientational bonding near freezing.

Dynamical arrest [1–6] is a ubiquitous phenomenon in nature, with many manifestations. Well-known examples include conventional glasses [7–9], but in modern condensed-matter studies the range of systems where the issues have become relevant is remarkable. Thus, dynamical arrest is now believed to be a useful description for gellation [10–15], "solidification", glassification [7,8,16,17], jamming [18–20], and the ergodic-to-non-ergodic transition. Recent work tends to indicate that scientists increasingly see these phenomena as manifestations of a single underlying set of principles [12,18,20–22].

Numerous attempts have been made to study simple models to develop ideas of dynamical arrest [9,23–31]. Two approaches have been prominent in recent years, exemplified by the Kob-Andersen kinetically constrained models [32,33] and Hamiltonian-type models such as that introduced by Biroli and Mézard (BM). This model, introduced in Ref. [3], permits particles of any given type i to have a number of neighbors less than or equal to a prescribed number, c_i. If c_i is equal to the coordination number of the lattice, we have a lattice-gas model; elsewhere the model is believed to be an attempt to represent packing constraints [1,3,34]. The relationship between these two different kinetic models has never been fully explored, although there has been a tendency to conclude that they are quite similar in spirit.

In this paper we extend the concept of a Hamiltonian model to include "soft" repulsions, rather than simply hard constraints. Thus, we now stipulate that c_i neighbors of a given type have zero energy and additional particles have a repulsive energy $\epsilon(i)$ (in our case chosen to be V_0). Clearly, as we pass to the limit of infinite repulsions we expect to recover the original BM model. In what will follow the reader may assume that this is indeed the case, although that limit is not explicitly shown. Here we focus on this generalization and in particular two of its applications. First, it gives additional insights into the mechanisms involved in the dynamical arrest of such models, and second, such models may be applicable to systems with oriented bonding effects.

In the work discussed below, we have calculated phase diagrams using the grand canonical Monte Carlo method. The initial configurations of these models are obtained by slowly annealing in the repulsions from a random lattice-gas configuration. Since we form crystals for a large portion of the phase diagram, such annealing procedures may some-times have to be optimized over long periods of time. Phase-transition curves are typically determined from system sizes of $L=12$, although in some cases larger sizes have been used to study particular transitions. After annealing, equilibration times of $\tau=2000$ Monte Carlo sweeps (MCS) and averaging times of 100 000 MCS have been used. Again, some specific areas of the phase diagram have been studied with averaging times of several millions sweeps.

The dynamical studies, from which we calculate the mean-squared distance traveled ($\langle r^2 \rangle$) and consequently the single-particle diffusion constant (D), are based on a single-step canonical Monte Carlo approach. In this method, random movements are proposed and the conventional Metropolis procedure is used to choose successful moves. We have checked that both the known lattice gas [35] and BM limits are faithfully reproduced.

In Fig. 1 we present results for the simplest single component system ($c=3$) model. The phase diagram for this system is quite striking. A "crystalline" region is bounded by first-order transitions on the low-density side by the gas and on the high-density side by the fluid. Apart from the special density $\rho=\frac{2}{3}$ where the crystal is perfectly packed, the crystalline state contains many defects, and with the present level of simulation and theory it is not possible to establish that it possesses true long-ranged order. Hence we have referred to this state as "crystal." The first-order phase-transition curves from gas and fluid to the crystal terminate at high temperature with a regime in which the crystal passes to the fluid. The restricted resolution of simulation prohibits us from deciding if this is a short curve of weak first-order phase transitions, or a single point of second-order (critical) transitions. We consider, on quite general grounds, that either is possible. In the inset to Fig. 1 we show the heat capacity as one crosses (by lowering temperature) the transition near the "critical" region ($\beta\mu=6.0$). The density difference between gas or fluid appears to be nearly continuous, as illustrated in the two-phase regions of the phase diagram. If indeed the transition were to be continuous, the topology of the phase diagram and form of the heat capacity suggest that it would be a λ-like transition [36].

The apex of the envelope of phase transitions appears to occur precisely at that density at which the crystal is perfectly packed ($\rho=\frac{2}{3}$). At higher or lower density (and temperatures lower than this apex) the crystal has either an ex-
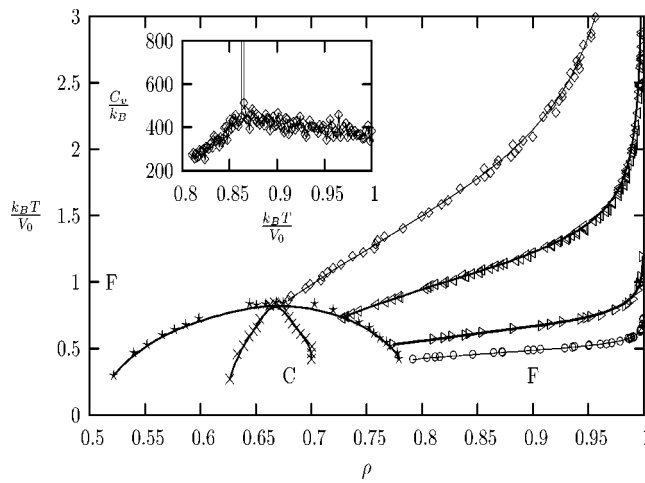
FIG. 1. The phase diagram of the $c=3$ system. The points marked $\times$ bound the single-phase "crystalline" region C. The points marked $\star$ bound the two-phase coexistence regions on either side of C. The region between C and F is therefore a coexistence region and is determined from the discontinuities in the density for each constant chemical potential. However, the apex of the crystalline phase (that is its high-temperature limit) appears to lie on the line of fixed density $\left(\rho=\frac{2}{3}\right)$ at which the crystal is perfectly packed. The nature of the transition there is uncertain. To the left of this line, the crystal [see Fig. 2(a)] has an excess of vacancy defects and is in two-phase coexistence with a low-density isotropic fluid. To the right of the line $\rho=\frac{2}{3}$, the crystal [see Fig. 2(b)] has excess particle defects and is in coexistence with a high-density isotropic fluid. The points marked $\diamondsuit$, $\triangleleft$, $\triangleright$, $\bigcirc$ show lines of constant chemical potential, $\beta\mu=6.0, 9.0, 15.0, 20.0$, respectively. Inset: C_v/k_B vs $k_B T/V_0$ for constant $\beta\mu=6.0$.

cess or deficit of particles leading to vacancies. This point is illustrated in Fig. 2. The low-density crystal [2(a)] has extra vacancies in the particle-filled layers, whereas the high-density crystal [2(b)] has extra particles in the "empty" layers. The defect density therefore vanishes on approach to this special point, at density $\rho=\frac{2}{3}$. Furthermore, at this highest temperature the (free) energetic cost of these defects is vanishing. It is therefore unclear whether the true order parameter of the transition is the Fourier transform of the periodic density of the crystal (as would be usual [37,38]) or the defect density. This is connected to the uncertainty in the nature of that transition.

The equilibrium phase diagram is reminiscent of many structured fluids composed of molecules that have strong directional bonding in the solid. The "bonds" (in this case the repulsive energy between three of the neighbors may be considered an effective attraction between the others) are of finite energy, so that at low density or high temperature we have a fluid, the crystal forming only when the effective bond energy becomes sufficiently relevant. As the packing density increases yet further, the bonds are broken and the crystal remelts to form a fluid. In this sense the model is an interesting simple example where ideas related to such systems may be worked out.

We now study dynamical slowing across the phase diagram. For infinite repulsions there is a transient slowing [1,3,34] that for some conditions or mixtures appears to be a
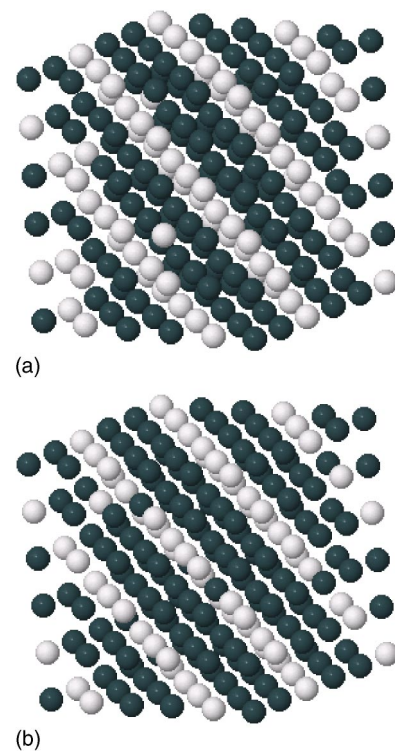

FIG. 2. Samples of crystalline lattices at densities above and below the "critical" density $\left(\rho_c=\frac{2}{3}\right)$. The black spheres represent an occupied position on the lattice and the white ones represent a vacancy. (a) ($\rho=0.6424$) shows hole defects within the occupied layers. (b) ($\rho=0.6811$) shows particle defects within the vacant layers.

near-arrest transition. For the infinite repulsion case the onset of this phenomenon always lies within the crystal regime and therefore competes with crystallization. It is interesting to ask if there is any true arrest for finite energy or higher density. The answer we have obtained for this model is, at first sight, a little surprising. The transient phenomenon present at infinite repulsion is barely appreciable for any finite repulsion and in the higher-density remelted regime significant dynamical slowing (and indeed arrest) occurs only near the fully filled lattice limit in which the system is close packed. Thus, even at very low temperatures, where the repulsions become very large, providing the density is sufficiently high that the crystal melts, there is no arrest.

However, it is interesting that the diffusivity is nonmonotonic in density or temperature. We have studied the diffusion constants along a series of isochemical potential curves ($\beta\mu=6.0, 9.0, 15.0, 20.0$). These are given in Fig. 1 and the diffusion constants along these curves are given in Fig. 3. In each case the diffusion constant rises to a maximum as the temperature is lowered, decreasing for yet lower temperatures. In the equivalent density representation it is clear that there is a band of anomalously high diffusivity in the high-density fluid (remelted) regime of the phase diagram. The reasons for this are quite interesting and are related to the issue of defects in the crystalline state. They merit a short discussion.

At high density, as the fluid remelts there develops a small population of particles that cannot find a location where their
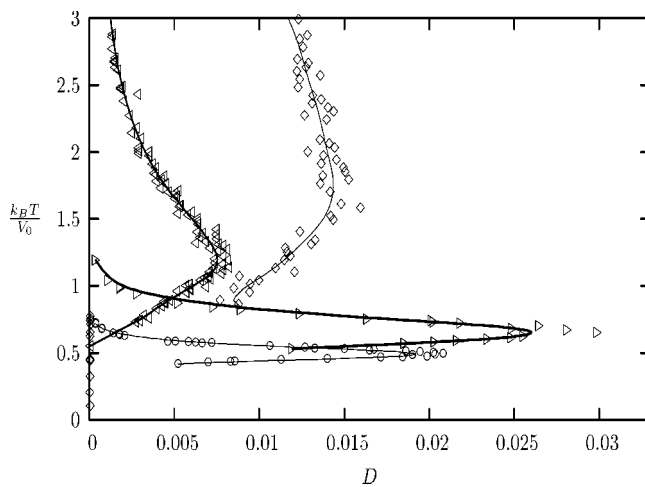
FIG. 3. Diffusion constant (D) vs temperature (k_BT/V_0) for a set of constant chemical potentials, $\beta\mu=6.0, 9.0, 15.0, 20.0$ marked $\diamond$, $\triangleleft$, $\triangleright$, $\bigcirc$, respectively. The peaks in the $\beta\mu=15, 20$ curves illustrate the anomalously high diffusion at high density and low temperature.

three-bond limit is satisfied. This is true even of the crystal, as noted earlier. Thus, in the fluid, the density exceeds that limit at which every bond number is satisfied. While it is true that these particles are unfavorable with respect to energy, they are equally unfavorable no matter where they are located in the system. They can therefore move with ease and become "superfast" diffusing particles. As the density in-

creases the number of such particles increases, conferring greater mobility to the system. At yet higher density the repulsive energy is overcome, the system becomes similar to the lattice gas, and the diffusion constant decreases due to the limited numbers of spaces into which particles can move. This phenomenon is sufficiently general that it may be expected to occur in the remelted regimes of structured fluids.

From a more general perspective we note that there is no significant dynamical arrest phenomenon in the dense fluid, with the diffusion constant vanishing only at the close-packed limit (lattice gas). We may conclude that the blocking effects that lead to the transient near-arrest phenomena in the infinite energy version of this model are strongly associated with the crystalline region itself. That is, when the forces are sufficient (and the density high enough) to destabilize the crystal, dynamical arrest becomes less, not more, likely.

In the future it may be important to explore more carefully the mechanisms of these Hamiltonian and kinetic arrest models to see if indeed there are more substantive differences that have hitherto not been recognized.

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