# Universality in Lattice Models of Dynamic Arrest: Introduction of an Order Parameter

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We introduce an order parameter for dynamical arrest. Dynamically available volume (unoccupied space that is available to the motion of particles) is expressed as holes for the simple lattice models we study. Near the arrest transition the system is dilute in holes, so we expand dynamical quantities in a series of hole density. Unlike the situation when presented in particle density, all cases of simple models that we examine have a quadratic dependence of the diffusion constant on hole density. This observation implies that in certain regimes ideal dynamical arrest transitions may possess a hitherto unnoticed degree of universality.

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It is commonly understood that in nature, many systems pass from the fluid to a "solidlike" but noncrystalline substance on changing some physically relevant parameter such as temperature, density, or more complex variables such as pH and ionic strength [1]. Such processes have been termed, variously, gellation [2,3], "solidification," dynamical arrest, glassification [4], jamming [5,6], and ergodic-to-nonergodic transition. So far these have typically been seen as somewhat unrelated processes, but there are some recent signs that they may be manifestations of the same phenomenon [1,3,5,6]. In this Letter we begin to explore the idea that, underlying the phenomenon of dynamical arrest, there may exist a broad set of unifying and in some regimes possibly even universal features that have not been appreciated until now. Here we will define a new order parameter for the dynamics, which we call dynamically available volume (DAV), and show that for some simple examples, apparently nonuniversal and complicated laws are considerably simplified when plotted against this quantity.

To test and refine these ideas we will need to examine some simple models that exhibit a form of "dynamical arrest" [7]. We shall give explicit results for the Biroli-Mezard (BM) [8,9] and Kob-Andersen (KA) [10] models. These models are representative of energy landscape pictures (BM), and so-called kinetic models (KA) that exhibit a regime of power law near-arrest.

The BM model 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 (LG) model, otherwise the model may be viewed as a minimalist description of the effects of geometrical packing frustration. We present results for the simple cubic lattice with, for example, 30% $A$-type particles with $c_A = 1$, and 70% $B$-type particles with $c_B = 3$, termed mixture $BM_{13}$. As reported in the original reference, for $\rho_c = 0.565$, we reach an arrest transition. We find the diffusion constants vanish as $D^i = C_i|\rho - \rho_c|^{\alpha_i}$ with exponents $\alpha_A = 4.0$ and $\alpha_B = 2.5$ the former being regarded as an effective exponent, since $A$ particles move so infrequently in this regime. We note that this particular mixture has a relatively short lifetime (during which it exhibits arrest) due to an underlying phase transition. Other BM mixtures we have explored are more suitable for further study, and exponents for some examples of 30/70 mixtures are given in the caption to Fig. 1(a). We note in passing that this model may also be understood in terms of the geometrical picture of dynamic arrest [11,12].

The extended model (EM) has precisely the same nearest-neighbor interactions as BM. However, the minority $A$-type particles have, in addition, next-nearest-neighbor exclusions between themselves. Interactions

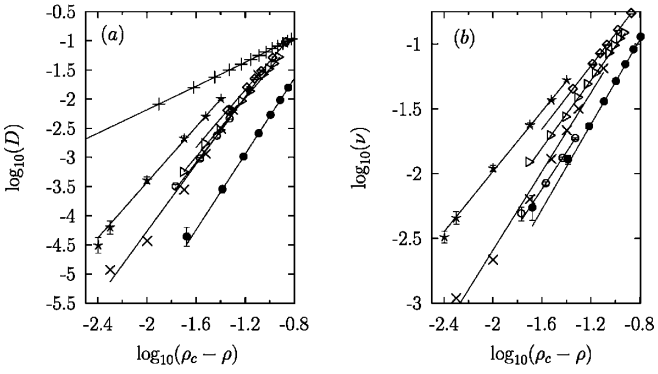


FIG. 1. (a) Log (majority particle) diffusion constants vs log density difference for $BM_{13}$ ($\diamond$) $\alpha = 2.46 \pm 0.02$, $BM_{35}$ ($\circ$) $\alpha = 2.75 \pm 0.09$, $EM_{13}$ ($\star$) $\alpha = 2.38 \pm 0.06$, KA ($\bullet$) $\alpha = 3.25 \pm 0.03$, $BM_{65}$ ($\times$) $\alpha = 2.88$, $BM_{14}$ ($\triangleright$) $\alpha = 2.51$, and LG ($+$). (b) Log (majority) hole density vs log density difference for the same models. $BM_{13}$ $\beta = 1.22 \pm 0.01$, $BM_{35}$ $\beta = 1.43 \pm 0.04$, $EM_{13}$ $\beta = 1.17 \pm 0.03$, KA $\beta = 1.64 \pm 0.02$, $BM_{65}$ $\beta = 1.52$, $BM_{14}$ $\beta = 1.31$.

  

between $B$-type particles, and between $A$ and $B$-type particles are unchanged for the EM model.

The particular case of the Kob-Andersen (KA) kinetic model we study here [10] has been reported to exhibit an ideal arrest at the density $\rho_c = 0.881$, and exponent $\alpha = 3.2$.

From the point of view of simulation, the simplicity of these models enables us to construct a move table so that the simulation becomes faster near the transition, than away from it. We select moves from the table, and scale time appropriately so that the meaning of the Monte Carlo time step (MCS) is consistent with all earlier work. Error bars are converged with respect to new initial conditions, but apparent arrest is determined by extrapolation from that regime where power-law exponents are extrapolated to zero. We have marked errors for system sizes of $L = 30$ (there being $L^3$ sites on the lattice). However, we have considered smaller numbers of results for $L = 20$, $L = 40$ to ensure that a reasonable assessment has been made of the real errors involved. For the KA model, we have noted that initial conditions are often chosen to be blocked states, the number of these growing at higher density, and reducing as system sizes increase. We remove those trajectories that produce negligible diffusion constant, since these should vanish in the large system size limit. Errors for the exponents are given in the caption to Fig. 1.

We now propose the concept of DAV as a suitable order parameter for dynamical arrest. We note that an important feature of our definition of DAV is that the accessible volume is defined in relation to the dynamics studied. In the case of collective particle dynamics [11], as naturally incorporated in molecular dynamics, the definition of DAV will be different from single particle dynamics, so we discuss only the latter here.

In the lattice models, with single step dynamics, DAV may be expressed in terms of ''holes,'' empty sites into which a neighboring particle can move. Those empty sites that are not accessible by one step of dynamics we continue to label vacancies. We emphasize that, though the definition of a hole is the same for all models, the particle arrangements constituting a hole are completely different for each model studied. This renders the observation of ''universality'' reported here even more surprising.

Holes may be created and destroyed by movements of particles on the lattice, a common occurrence being a particle movement that unblocks a vacancy and renders it a hole, or the reverse. It may be shown that the distribution of holes is a steady state of the system, and by finite size scaling and simulation for large system sizes we find they behave as a grand ensemble [11].

Particles near the arrest transition run out of spaces into which they are free to move, though there are many vacancies. Therefore holes are rare (dilute) in the vicinity of the arrest transition. We find a vanishingly small arrest density of holes for the BM and EM models, but in the KA model it is worth noting that a small but measurable number of isolated holes remains at the arrest density, and their density at arrest is subtracted to obtain the order parameter of arrest [13]. We may fit all hole densities in the different models to a power law, $\nu = H|\rho - \rho_c|^\beta$ each with different exponents, as we approach arrest [Fig. 1(b)]. The hole density exponents, like those of diffusion constants with particle density, are nonuniversal, varying between models, and even for different parameters of the same model (see Fig. 1).

We can now replot the data for the vanishing of the diffusion constant in terms of the hole density. Thus, combining data from Fig. 1 to eliminate the particle density, we find that all of the models and concentrations within different models may be fitted to the law,

$$D = \gamma|\nu|^2, \tag{1}$$

where $\gamma$ is a nonuniversal effective rate constant. This conclusion, indicating that the ideal-arrest transitions of all of these apparently different models are essentially the same phenomenon and have universal exponents, is the central result of the present Letter.

Thus, in Fig. 2(a), as has been traditional for the ideal lattice gas [14] we divide the diffusion constant by the hole density and present data from different models. This quantity has an interesting physical interpretation since, apart from a constant, it is the ''correlation factor'' $f(\nu)$. Of those particles that can move on the lattice, $f(\nu)$ represents the fraction that leads to diffusion. The linear law exhibited in Fig. 2 implies a quadratic dependence for the diffusion constant, the different slopes reflecting the nonuniversal dependence on $\gamma$.

Replotting these results by removing the dependence on $\gamma$ ($D/\gamma\nu$ vs $\nu$) reveals that there is a remarkable degree of universality. Instead of presenting this result, we replot the data in the form $\log(D/\gamma)$ vs $\log(\nu)$ [Fig. 2(b), and $\gamma$ has been fitted from the results of Fig. 2(a)]. This provides the reader with information from a different scale than Fig. 2(a). All examples of these models we have examined obey this quadratic law. In the future it would be of

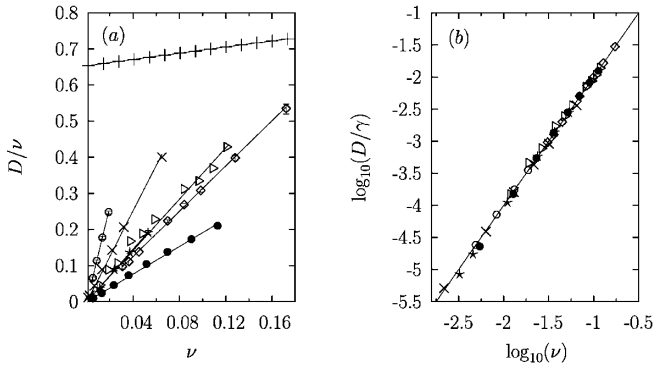


FIG. 2. Universal scaling plot (symbols same as Fig. 1). In (b) the solid line has a slope of 2.0.

considerable interest to make this type of plot for all models known to exhibit ideal dynamical arrest, as well as for continuum simulations.

Now, if holes are the only means of transport in a dense system, we expect to be able to represent the diffusion constant in terms of them (we shall present information only for the majority particle holes, but we have studied minority particles and obtained comparable results). The simplest possible idea [14,15] would be to assume that each hole contributes in an independent and equal manner to the bare diffusion constant (that neglects interactions between, and trapping of, holes). This leads to $D_0 = \gamma_0 \nu$ where $\gamma_0$ is the (bare) rate constant for a particle moving to a neighboring site if it is free to do so. For the ideal lattice gas it has been recognized that when a particle moves into a hole, the hole that is emitted from the particle site is either filled by a new particle (in which case the move contributes to diffusion) or the particle (and therefore hole) returns to its original site. This type of oscillation that fails to lead to net particle motion has in the past been accounted for by the correlation factor, $f(\nu)$, that is unity for isolated particles, and smaller than unity for all higher concentrations reflecting the blocking effects of the other particles. In the very dilute lattice gas limit, holes do not interact, and the true diffusion constant is given by $0.65D_0$ (simple cubic) representing the fraction of possible moves leading to diffusion. In general, the independent-hole diffusion constant may be corrected by a factor $f$, representing the effects of these oscillations and, at higher density, multiple hole effects,

$$D = \gamma \nu f(\nu). \tag{2}$$

For the lattice gas this equation can be expanded around small concentrations of the carriers of transport (the holes). We might expect that this virial-type expansion would also be true for the lattice glass if the hole concentration is sufficiently small, and the vacancy concentration sufficiently large so as to ensure that only hole density is relevant. We may thus propose the expansion,

$$D = \gamma_1 \nu + \gamma_2 \nu^2 + \gamma_3 \nu^3 + \cdots \tag{3}$$

for low hole concentrations (where transport vanishes) including at ideal arrest. The essential difference in the lattice glass is that isolated holes become immobilized due to the packing or kinetic rules of the glass model. This means that the first term in the series vanishes ($\gamma_1 \to 0$), and the leading term then becomes quadratic. This would imply that $f$ vanishes in the limit of low hole concentrations, there being vanishing numbers of moves into holes that subsequently lead to diffusion. This expectation is borne out in Fig. 2(a), which is essentially a plot of $f$.

Near arrest then, the frustration leads many of the holes to be blocked for long periods of time, the only particle being able to move into them being the one that moved in the last step. Such particles therefore "rattle" between very few sites of the lattice leading to no effective diffusion. Proximity of another hole, perhaps created from the assumed abundant pool of vacancies, to the immobilized hole can relieve the frustration. Particles can then move into the formerly immobilized hole, and release it to continue a short diffusive pathway in a correlated motion with another suitable hole, or failing this, until it is once more immobilized or annihilated, or assisted by another vacancy-hole transformation. Such a mechanism would cause a leading order squared hole density for the diffusion constant, for it implies correlated two-hole motion.

We may give some substance to this argument in the following simple mean-field-type framework. We write the diffusion constant as in Eq. (2). Here $f(\nu)$ reflects the fraction of independent movements into holes (these represented by the factor $D_0 = \gamma_0 \nu$) that lead to true particle diffusion. Fewer of these lead to diffusion because the hole is typically a rattler. However, there may be a proximate hole (for example another rattler), into which one of the particles causing the first hole to be blocked can move, at least temporarily. To enforce self-consistency this correlated movement of a particle into a second hole (which now leads to an overall diffusive motion of the first particle) must be described by another factor proportional to the hole density. The competition between these successful forward and unsuccessful backward moves of the first particle is represented by the ratio $f = CD_0/\gamma_0$ ($C$ is a dimensionless number) [14,15] a dimensionless quantity that describes the fraction of moves that lead to diffusion. Therefore, we expect

$$D = \gamma_2 \nu^2, \tag{4}$$

where $\gamma_2 = C\gamma_0$ reflects the details of the two-hole process involved.

The argument given here is sufficiently simple and general that it is difficult to see how it could be violated providing the element of generalized "blocking" is present in the system, and providing that there are no subtle summations of many-hole processes that would cause a breakdown of the idea of a low hole density series. This latter possibility seems not likely in the excess-vacancy regime, but must be considered present in the more general case of dynamical arrest.

We may summarize the important new finding of this paper as follows. Holes are a quantitatively useful tool for lattice model arrests in the regime where they have been described by power laws in density. Apparent dynamical arrest in the ideal-arrest cases we have examined can be described using "dilute gas" virial-type approximations in terms of holes. Concretely, two remarkable features have emerged.

First, the leading approximation in the case of the frustrated limit is a dilute gas of pairwise interacting holes, suitably renormalized by $\gamma_2$ reflecting different

effective two-hole processes, and the particle processes that underlie them. This suggests, contrary to long-held expectations, that the ideal-glass transition possesses a weak-coupling limit due to the low density of the relevant interacting excitations. However, the models suggest a surprisingly subtle mechanism of two-hole correlations, that has not been reported in the literature previously.

Second, the development of an order parameter that makes direct contact with the underlying physics of the problem may unmask degrees of "universality" present in regimes of the models, and possibly elsewhere.

It is also worth remarking that there is a long tradition of "free-volume" descriptions in discussing transport in dense systems [16]. In many cases, where these ideas have had explicit expression, they have involved voids of empty space, and have emphasized the time required to create such voids as the rate-limiting step in transport. In some regimes that are depleted of "vacancies," we might indeed expect to emphasize the cost of producing sufficient void volume to permit holes to exist, and such ideas are indeed more naturally connected to thermodynamic quantities of the system such as chemical potential [17]. In general we believe it will be important to distinguish between volume that is accessible to the dynamics of the system at every time step, and void volume that is accessible from a thermodynamic point of view. Both may be expressed as equilibrium averages, but they are distinct, and lead to different concepts of dynamical laws.

The degree to which these ideas can be extended beyond the "ideal" regime on a lattice studied here is not yet clear, and is a subject of our current investigations.

We here emphasize the much simpler point that the search for an equilibrium order parameter that is directly tailored to the dynamics is worthwhile. We now have examples where the lack of such a device leads to common features being missed, opening the possibility that the paradigms for dynamical arrest may be fewer and more universal than has been hitherto understood. These directions of research are being actively pursued by simulation and theoretical developments by ourselves, and others.

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