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Universality behaviour in 'ideal' dynamical arrest transitions of a lattice glass model

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Abstract

Using dynamically available volume (DAV) as an order parameter, we study the ideal dynamical arrest for some simple lattice glass models. For these models the dynamically available volume is expressed as holes, or vacant sites into which particles can move. We find that on approach to the arrest the holes, which are the only mediators of transport, become increasingly rare. Near the arrest, dynamical quantities can be expanded in a series of hole density, in which the leading term is found to quadratic, as opposed to unfrustrated systems which have a linear dependence. Dynamical quantities for the models we have studied show universal behaviour when expressed in terms of the hole density. The dynamically available volume is shown to be a useful characterisation of the slow aging in lattice glasses. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many systems in nature pass from the liquid to a 'solid-like' but non-crystalline substance on changing some physically relevant parameter such as temperature, density, or more complex variables such as pH and ionic strength. Such processes are termed,

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variously, gellation, solidification, dynamical arrest, glassification, jamming, and the ergodic–non-ergodic transition. Furthermore, these phenomena are observed in systems as varied as simple atomic substances ('glassification') to particle and colloidal dispersions (aggregation, or particle-gellation) to polymers and proteins, and more exotic mixtures of these (gellation). We collectively label these 'dynamical arrest' phenomena thereby ensuring a lack of any prejudice in the physical processes leading to the arrest, and leaving open the possibility that they are all the same phenomenon, at some deeper, but yet to be understood manner [1].

Whatever the mechanism, the central observation is that the molecules, particles, or other objects in the system simply stop moving in a fairly reproducible, perhaps on closer inspection, completely reproducible manner. That they do stop moving does not imply that the system has crystallised, or that it has reached another equilibrium state in which the free energy is minimised. In fact, we shall typically direct our comments to those phenomena where the free energy is not minimised, whilst not absolutely excluding minimisation as an accompanying aspect of the 'transition'.

Phenomena of this type have been studied on an ad hoc basis within various branches of condensed matter science, and find many practical applications. In fact, if the reader would look around the current environment (including at him-, or her-self), it is likely that the vast majority of material substances fall within this category of arrest, rather than the typical states that minimise the free energy. However, a unifying framework, with simple concepts and clear underlying assumptions that can be derived, beginning from interactions leading to materials, has been difficult to find, despite the enormous advances made in the theory of spin-glasses, and latterly the structural glass transition [2–5].

The equilibrium phase transitions have been well-classified, leading to a high degree of universality in observations throughout nature. Thus, at the lowest level of classification we have the thermodynamical derivatives of the free energy of different orders. A discontinuity in the first-, second-order derivatives lead respectively to first-order (melting-freezing), second-order (critical point) phase-transitions [6]. These transitions, along with the 'infinite order derivative' phase-transitions (Kosterlitz-Thouless [7]) represent essentially all equilibrium phase-change behaviour known in condensed matter science, and their classification has been one of the key steps in developing the conceptual infrastructure of this part of science. Within these definitions there are further more detailed sub-classifications that have been of great importance [8]. Critical phenomena have been classified according to their critical exponents, these representing very large and universal groups of behaviour according to the type of order parameter in the system. The fluid-'solid' (three spatial dimensions) or fluid-hexatic-'crystal' (two spatial dimensions) phase-transitions have also been further classified. Firstly, we recognise that symmetries are broken differently; rotational and translational together in three dimensions, separately in two dimensions, leading to natural expectations about how the new state emerges, and acquires rigidity. Underlying all these classifications, and universal behaviour, is the observation that a useful description requires the use of an order parameter that makes primary or direct contact with the physical processes leading to the transformation. Also, an added simplification is that the resulting states are free-energy minima, so we have all of the long-tested machinery of Boltzmann statistics to rely upon in computing explicit properties of the system.

None of this intellectual framework, and little sense of organisation or cohesion has accompanied the study of the dynamical arrest through much of its history. In fact, until recently there seemed little reason to suppose that these different observations of solidification are in any way connected. Of course, from a deeper perspective this lack of unification of concept seems odd. Thus, it is certain that these solidification phenomena arise also from some embedded phenomena, or organisation of phase-space, based on the same Newtonian equations as do phase transitions. They are also macro-phenomena, so the simplifications in laws that govern the statistics of large numbers of interacting units (leading to thermodynamical simplicity), might be expected also to obtain here. It is therefore intuitively unsatisfactory that there be no unified means by which to understand them, given their common origin with the phase-transitions, and practically inconvenient that there be no obvious means by which to classify them.

Indeed, this feeling of dissatisfaction has expressed itself in, until now, unsuccessful attempts to find hidden symmetries that are broken in 'glassification' [9], rather than the explicit space symmetries broken in the typical phase transitions. It may be remarked that our expectation of finding some simple hidden symmetry that is broken may be baseless, since in fact these phenomena we discuss are dynamical arrests, rather than the infinitely long-lived 'phases' previously understood. Might it be, therefore, that the symmetry of Newtonian equations that is really broken is time-translational-invariance; that these are long-lived, but ultimately decaying states to some more ordered equilibrium phase. And, as a result, there is no real basis for our desires to have a physical 'order-parameter' description, and all the familiar simplifying regularity of the condensed phase. It may be, that time-translation-invariance (TTI) breaking of this type can occur and lead to no particular 'order' or, worse still, no particular rationale. In some sense, whether expressed explicitly or not, it is this rather ill-framed doubt that has been the dominant intuition in the science of this aspect of the condensed phase for many years. Some more positive views and achievements have emerged from the theory of spin-glasses, where time-translational-invariance breaking has been confronted in a very general manner using the theory of replicas, and the accompanying replica symmetry breaking, essentially the expression of the loss of time-translational-invariance in various prescribed manners according to the RSB prescription [4]. The symmetry broken replicas indicate how important successive configurations (in time) become trapped and ergodicity lost. Despite, or perhaps because of, the great beauty and generality of these concepts, valid for spin-glasses and structural glasses, the dynamical arrest still lacks a synthesis that is directly related to the physics of solidification, and some appropriate classification scheme.

It may be that the lack of success in determining broken symmetries and related order parameter changes, has led to the overly negative opinion that, indeed, there is no rational basis for unification of the science of emergent rigidity in the vicinity of dynamical arrest. That is, we know it is possible in very general terms to parameterise the loss of time-translational-invariance by the breaking of replica symmetry (RSB) analysis of the non-ergodic parameter. However, this is a very general prescription that deals with how TTI is lost. Of course, we may still hope that on approach to arrest, it is possible to find a deeper level of universality in physical properties. This is a profound question that we are not yet in a position to answer in a very general manner. Rather our view is that by the study of simple examples, to be viewed almost as 'toy models' of the phenomena, we might be able to refine the questions somewhat, and draw some more limited conclusions on which we can rely. That this strategy might lead to conclusions for the more general situation of dynamical arrest is therefore an aspiration, though if the processes leading to emergence of solid-like structures are generic, then it may well be a legitimate aspiration.

We have outlined this perspective in some detail because the whole approach we shall adopt is framed to make logical connection to these concepts. We study simple models, with generic processes of dynamical arrest where simulations, and theory are both feasible at a high level. We cannot therefore claim to have understood the dynamical arrest of any particular substance, and such models have really deep value only if there are generic, perhaps 'universal' phenomena to be understood.

In this paper, we will present some findings, based on simulation, but to be later supported by theory, for a few very simple lattice models. The aim of our paper will be to analyse these findings for different regimes of the lattice description, and on this basis, propose a general view of the (ideal) dynamical arrest, and a perspective for arrest in its largest sense. In particular, we shall propose that, at least for the so-called ideal transitions, there may be a very few clearly defined generic mechanisms by which ergodicity is lost, and by which solidification emerges. Indeed, we will propose that there may be a natural order parameter description of dynamical arrest ('dynamically available volume'), and that this has a simple expression for ideal-lattice defined arrests.

A question naturally emerges as to what the 'ideal' arrest means. This phrase has arisen in the context of simplified treatments of the glass transition, or in real transitions of simple systems. In essence it has become used where the characteristic relaxation time is a power law in the density-(or temperature-) difference from the arrest point. It is often felt to be inextricably linked to the mode-coupling-theory [10,11] of arrest, and this link seems correct for a number of specific cases [4,12–14]. In general it seems likely that the ideal dynamical arrest is a sort of mean-field solution to general dynamical arrest phenomenon (where fluctuations or 'hopping' is also involved. It appears that many systems (especially colloidal ones) fall within this ideal or mean field limit, explaining the success of that theory [15,16].

2. The concept of dynamically accessible volume as an order parameter

One of the advantages of working with lattice models is that they are so simple that concepts that are more generally defined can be quite simply realised within them. This is especially helpful when a number of closely related ideas are of interest, and one must validate one of them, requiring a reasonable level of precision from simulations.

We wish to introduce a concept of dynamically accessible volume (DAV), a quantity that we expect to govern the dynamics of a dense system. However, this volume will not be the same as, for example, the voids used to calculate the chemical potential by the insertion method, and if we use the wrong definition of 'free volume' it is found that no useful order parameter emerges. We define dynamically accessible volume as follows. Imagine a group of particles that is about to move under some prescribed dynamics. We may determine the total volume of phase-space available to those particles, subject to all others in the system being fixed. For an athermal system this construction is sufficient to define the quantum of phase space available to the group of particles under consideration, the more general (finite-energy) case requiring only modest modifications [17]. The ensemble of such packages of phase-space volume, conceived as distributions of sizes and shapes, represents a stationary distribution for systems 'at equilibrium' in the sense that the fluctuation dissipation theorem is satisfied (FDT2), an issue to be discussed in detail below. The distribution, and thermodynamic averages may be taken with respect to it. Should we find the typical or average size of DAV to be representative of the ensemble, it is natural to approximate the distribution using this quantum of accessible volume. These definitions can be explained, and elementary implications explored by treatment of a simple example.

For stochastic single particle motion on a lattice model, dynamically accessible volume at high density consists of those vacancies in the system that are accessible in a single move of the dynamics. Such objects are termed 'holes', and their number fluctuating around the average is termed the hole density. We emphasise that the hole is an elementary, but crucial, extension of the concept of a vacancy. The fact that DAV naturally occurs on a lattice in fixed packages, and the fact that we work in the dense lattice limit implies that only single quanta of DAV are found, rather than double holes, triples and so forth. This makes their use very simple indeed.

To sum up. On a lattice undergoing single particle dynamics, a hole is defined as a vacancy into which at least one of its surrounding particles can move. For simple cases such as the lattice gas model, vacancies and holes are equivalent. However, when packing rules are introduced, not every part of unfilled space is dynamically available, and holes are then defined as accessible according to the dynamical rules associated to the lattice model. In the next section we define such models.

3. The models

To provide an example we introduce a set of lattice models where these ideas can be worked out in detail [18–21]. Ideas underlying those we discuss began with the lattice glass model that has recently been developed by Biroli and Mezard [22]. Our studies of this model have encouraged us to believe that the basic direction is very promising. However, in working out the detail, it has been found that the time-scale over which one can see glassy behaviour is modest, and consequently that some quantitative calculations of the approach to dynamical arrest, and glassification are not possible, or are possible with limited precision. This has lead us to generalise the interactions somewhat.

We define the model as follows. Begin by dividing space up into cubes of side a, the microscopic length. We believe that this length represents a convenient measure of the frustration length of the system [23,24]. To the centre of each such cube we may associate a 'particle' of type *i*. Between like particles we define interactions e_i with

 c_i nearest neighbours, e_{i+1} between particles c_{i+1} that are diagonal neighbours, and so forth. Between particles of different types we define energies e_{ij} between nearest neighbours, e_{ij+1} between next (diagonal) neighbours, and so forth.

In practice it will as yet be necessary to study only the much more restricted models where there are two types of particle, a majority and minority system with nearest neighbour interactions between one type, and nearest neighbour and more extended interactions between the other. Between different particles we will require only interaction between nearest neighbours. However, it would appear that the full range of interactions between particles up to diagonal neighbours is required to capture the richness of repulsive and attractive particles in very dense systems [25]. Note that by taking the limit of infinite energy for the nearest-neighbour model we arrive back at the Biroli–Mezard model BM_{13} (30% 1-particles and 70% 3-particles). By allowing for additional interactions between diagonal neighbours for the minority particles, and leaving all other interactions as for the Biroli–Mezard case we arrive to what shall here be called the extended model EM_{13} .

We then define a local single-particle stochastic dynamics in which sites, and directions for proposed moves, are chosen randomly, and then moved according to the normal Monte-Carlo algorithm. In the athermal case in which the energies have all been taken to zero, we simply execute the move if it leads to no violation of the packing rules in which particles of type *i* have no more than c_i nearest neighbours of type *i*, no more than c_{i+1} second nearest neighbours of type i + 1 and so forth.

4. The move table

In principle, simulations become increasingly lengthy near the dynamical arrest transition. Thus, the vast majority of proposed moves lead to unfavourable energies, or in the athermal model, to illegal configurations. This is, of course, the reason for the arrest transition. However, from a practical point of view, this is an unsatisfactory situation since not only are the simulations more costly in time, but ultimately the sampling becomes so inefficient as to be misleading. This is particularly true of continuum calculations where both Monte-Carlo calculations become very slow, and Molecular Dynamics (crucial to dynamical properties) may become of limited value in the vicinity of the 'ideal' arrest transition, meaning that the true singularity is difficult to evaluate. These issues represent the main challenge facing those who simulate realistic models of particles undergoing dynamical arrest, and are the reason that it is difficult to evaluate general questions using detailed models.

The situation is, of course, greatly improved for lattice models because of the simplicity of the interactions, and the regularity of the data structures. However, the fundamental limitations remain in that typically much less than 1% of the proposed moves is acceptable in that limit where we may hope for true dynamical arrest laws.

To remedy this limitation we have defined the model as a selection of moves from a table. At the beginning of the calculation it is straightforward to scan through the lattice to determine those moves that lead to legitimate states of the model. Subsequent moves affect the status of only a few particles, and the cost in updating the table is therefore minimal. Moves, and times, are selected from the table, each such move being successful by definition. The only computational overheads are associated with performing the moves and the management of the move table.

Although at first site it seems counterintuitive, it is clear that on approach to the dynamical arrest transition there are fewer, in fact vanishingly small numbers of legitimate moves, and the overall table overheads become much smaller. Therefore, our approach, whilst less efficient than the standard method at low concentrations becomes remarkably rapid near the transition. In fact, as we shall show, this apparently quite technical innovation should not come as much of a surprise, for the natural way in which to view the dynamical transition turns out to be terms of a dilute gas of 'holes', defined as vacancies on the lattice into which at least one particle can move. In essence then, we have transformed the approach to dynamical arrest to a simulation of relatively few holes on a cubic lattice. Typical times-scales for simulation in the results that we report are 10^6 MCS (L = 20). However there is no particular limitation in accessing time-scales of 10^8 MCS near the arrest using a personal computer. Continuum simulations equivalent to this are not yet feasible even with the largest super-computers.

Besides this definition of the dynamics associated with the model, we also comment that the model's phase space may be explored by a number of sampling Monte-Carlo techniques. We have used a Kawasaki algorithm in which different particles are swapped, and particles are swapped with vacancies providing this does not lead to any violation. However, the Kawasaki method is a much more efficient way of exploring the phase space, and this is the method we use to 'equilibrate' the systems.

We may conclude, therefore, that whilst we have yielded up much of the detail associated with continuum simulations in favour of a more schematic representation, we have gained access to a level of sampling not normally explored on approach to the glass transition. This exchange is a sensible one, providing the essential features of the interactions leading to characteristic landscapes are captured in the model. The degree to which this is deeply true has not yet been established, but progress is being made.

5. Survey of dynamical arrest

The nature of the dynamical arrest transition for the Biroli–Mezard model has been discussed in the literature, so we will recount only the outline here. The BM_{13} mixture of 70% percent 3-particles and 30% 1-particles has been studied in some detail. As we increase the total volume fraction the diffusion constant, as determined from the mean-squared distances travelled begins to decrease towards dynamical arrest. However, at a total density of 0.51 the system undergoes a phase separation to a fluid in equilibrium with a lamellar crystalline phase. The dynamical arrest is pre-empted by the equilibrium phase transition, and irreversible fluctuations begin to dominate the system. This point is illustrated Fig. 1 where we plot the diffusion constants for 3-particles for two distinct models, the original *BM* limit, and new extended model *EM* in which extended interactions are defined between the minority 1-particles. In both cases, we



Fig. 1. Log Diffusion constants against log density difference from the arrest. For the two models, *BM* (\diamond) and *EM* (\diamond), we show diffusion constants calculated after 10⁴ MCS. We also do the same diffusion calculation after performing 10⁵ Kawasaki MCS which are shown for the two models, *BM* (\star) and *EM* (\times). From the best fit lines to the data $D \propto \Delta \rho^{\alpha}$ we find that $\alpha_{BM} = 2.38$ and $\alpha_{EM} = 2.50$.

present data for the $\frac{70}{30}$ mixture, and the diffusion constants have been determined from the mean-squared distances. Up to the equilibrium phase transition only one data set is defined for the diffusion constant, as might be expected. Beyond, where non-equilibrium effects begin to predominate, the diffusion constants begin to drift slowly. In the case of the *BM* limit this drift is moderately large, and beyond the branch point in Fig. 1, the diffusion constant data are plotted for two time-scales (see caption). The *EM*₁₃ has been selected to avoid such problems, and the diffusion constants are almost insensitive to slow changes up the transition at $\rho = 0.495$.

6. Transport near the ideal arrest transition of hard particles

Here we begin by making the simplifying assumption that 'holes', defined as vacancies into which at least one neighbouring particle can move, have a density that is on average fixed over the duration of the observation to be described. This is true for the BM and EM for densities up to the 'branch' point of the diffusion constant curves (Fig. 1).

We begin by emphasising the point that holes, by definition, provide the only means by which particles can move in a highly constrained system such as that of the frustrated lattice model. It is clear that, for the simpler case of the lattice gas model (c = 6) in which there is no frustration, every empty site (vacancy) can be used by the surrounding particles. Thus, in the vicinity of a vacancy on a simple cubic lattice, any of six particles can move into that vacancy, leading to particle motion and, providing the particle does not move backward again, a contribution to nett diffusive motion results.

This is clearly not so for the frustrated models (c < 6) where the packing rules can render vacancies inaccessible to their surrounding particles.

The rules that define a hole in such models are unambiguous, being easily represented on a computer or as a multi-particle correlation function. It may be remarked that the hole operator is a product of equal-time particle density operators, and as a consequence averages of products of this operator at equal times are equilibrium properties of the model. Simply put, quantities such as the hole density are thermodynamic quantities, even though we will later show that they tell us quite a lot about the dynamics and non-equilibrium phenomena of the lattice model. This is an important question of principle that later implies many interesting results so it is worth dwelling on its meaning.

We observe that, despite being an equilibrium quantity, the hole density represents a good order parameter for the dynamical arrest transition. Hole density vanishes as we approach dynamical arrest, though it is also in principle possible for a small residue of immobilised holes to remain at arrest. The true order parameter would then be the difference between the hole density and this small residue. However, for the cases we have studied so far there is no evidence of a finite and measurable number of holes in the (extrapolated) limit where the diffusion constant vanishes. In fact, the diffusion constant and hole density for both the *BM* and *EM* can be well-fitted by a power law on approach to arrest,

$$D = A_i \left| \rho - \rho_c \right|^{\alpha_i},\tag{1}$$

$$v = B_i \left| \rho - \rho_c \right|^{\beta_i}.$$
 (2)

For the athermal case we may construct a Landau-type theory of the transition based on the entropy, with the order parameter being hole density. Assuming there is an analytic series connecting entropy and hole density we write the series,

$$S - \mu v = \frac{a_2}{2} v^2 + \frac{a_3}{3} v^3 + \cdots,$$
(3)

where the conservation of hole density is expressed by the chemical potential μ . Minimising the entropy we obtain,

$$\mu = a_2 v + a_3 v^2 + \cdots, \tag{4}$$

where the coefficients a_n are functions of the particle density that are at present unknown. The solution of Eq. (4) near arrest is equivalent to the results in Eq. (2).

Now we turn to the application of dynamically accessible volume (DAV) as the order parameter for dynamical processes. Since transport properties are controlled by (a decreasing) hole density in the limit of arrest, it is reasonable to propose, say, that the vanishing of the diffusion constant may be expanded in a low order series in terms of the (vanishing) hole density. Thus,

$$D = \gamma_1 v + \gamma_2 v^2 + \gamma_3 v^3 + \cdots .$$
⁽⁵⁾



Fig. 2. The quantity D/v as a function of hole density v for different models: BM_{13} (\diamond), BM_{35} (\bigstar), BM_{65} (\bigstar) and EM_{13} (\diamond). For comparison we have shown the case of the lattice gas (+) along with the Tahir-Kheli result (solid line) for f(v) [26].

We know, that the lattice gas diffusion constant vanishes linearly in the limit of vanishing hole (vacancy) density [26–28],

$$D^{c=6}(v \to 0) \approx \gamma_1 v \,. \tag{6}$$

For the lattice glass models we may plot the diffusion constant data against the hole density (Figs. 2 and 3. Remarkably, the data appear to collapse onto the very simple law,

$$D^{c<6}(v \to 0) \approx \gamma_2 v^2 \tag{7}$$

a result that is obeyed for a remarkably large range of particle densities and different mixtures.

Evidently, as c becomes less than the co-ordination number of the lattice, the degree of frustration increases, the loss of transport occurs as a dynamical arrest, rather than a simple lack of vacancies and a new mechanism obtains. This is the origin of the novel diffusion constant scaling with hole density. Therefore, we seek to explore this issue in a little more depth.

7. Realization of the Adam–Gibbs relationship

The forgoing discussion must be considered to involve some fundamental assumptions, since it leads to some fundamental conclusions. The steps taken so far imply that



Fig. 3. $D/\gamma_2 v$ against v for different models (symbols as in Fig. 2). The straight line has a slope of 1.0.

there must be a relationship between diffusion constant and entropy. Such a relation is by no means built into the fundamental laws lying at the foundations of dynamics and statistical mechanics. It arises by virtue of two assumptions.

Firstly, the definition of holes ensures their role as the mediators of motion and, implicitly, their status as order parameter for dynamical arrest. This is not guaranteed in a trivial manner, and most other definitions of 'free volume', leads to no meaningful relationship to the motion.

Secondly, despite their relevance to dynamics, the fact that holes are defined as equilibrium averages makes it possible to define a constrained average in which the entropy is calculated for fixed hole density,

$$S(v) = k_b \ln W(v, \rho) .$$
(8)

This implies that the number of micro-states of the system must be calculated for fixed hole density, and particle density. This can be carried out explicitly [17], but here we emphasise the conceptual elements in our presentation. In Eq. (3) we assumed that *S* can be expanded in an analytic series of the hole density, an assumption that is correct for our current presentation, but which is not in general guaranteed, and which is, we believe, not true for the general (non-ideal) case [29]. Thus, the entropy vanishes as the hole density vanishes, and arrest implies very low hole density, so there are valid reasons to attempt a hole density expansion. If we assume no thermodynamic singularity then derivatives of the entropy in terms of hole density must vanish in the limit of zero hole density, and the series thereby possess no regular singularity. It is therefore either a simple Taylor series in hole density, or at most an essential singularity that is sufficiently weak that its derivatives all vanish at zero hole density.

These possibilities constitute what may be the generic, and perhaps even universal, classes of arrest.

In fact, for the following observations on the Adams–Gibbs relationship [30] we require only the weaker condition that the entropy-hole density relation be invertible, and we immediately obtain a direct, in principle exact, relation between transport properties, such as diffusion constant, and entropy.

The ingredients are therefore relatively simple, to obtain such a relation as that found by Adams and Gibbs, though it has been difficult to find an explicit realization of the ideas until now. Holes, and their extension to the most general continuum case (dynamically accessible volume) appears to represent such a realization.

8. Phenomenological description of the scaling with diffusion constant with hole density

By definition all transport in lattice models of the type we discuss occurs only by 'holes'. For the lattice gas, in the limit of vanishing hole (there equivalent to a vacancy) concentration all transport occurs by a particle moving into a neighbouring hole. If these vacancies are uniformly spread throughout the lattice it is natural to suppose that the diffusion constant should depend linearly on the rates with which particles move into the vacancy, γ_0 , and the concentration of holes, v [31,32],

$$D_0 = \gamma_0 v \,. \tag{9}$$

This has, within the solid state physics literature, been named the mean-field approximation. We shall avoid that language here as it could lead to confusion in the arena in which we work.

Whatever the terminology, it is clear that after this first movement of a particle into the hole, the concept of a uniform distribution of holes contributing equally to transport breaks down. Thus, of the particles that are now nearest-neighbours of the new hole, one is the particle that moved to create the new hole, and if we assume that the next set of particle movements into the new holes contributes in an equal manner to the preceding step, this leads to an overestimation of the diffusion constant. If the particle, which in the last step moved to create the hole, should now move backwards then, despite the fact that the hole has moved twice, no contribution to the diffusion processes has occurred. Also, at higher hole density, holes may merge and compete for particles, thereby complicating the simple results of Eq. (7). These effects have been described by a correlation factor, f(v), that describes the reduction of the diffusion constant leading to [33],

$$D = \gamma v f(v) . \tag{10}$$

This over-counting effect is quite simple at low density since the miscounted particle moves backwards into the hole it created only if the hole remains at this site for long enough. It will move away if one of the other neighbouring particles moves into this site. Thus, the correlation factor, in the dilute limit is a result of competition between the rate of the particles return, and forward motion of the hole [34]. Thus,

$$f(v \to 0) \approx \frac{k_v}{k_v + 2\gamma} \,. \tag{11}$$

Furthermore, in the dilute limit the hole vanishes if another particle moves into it. This quantity is independent of hole concentration since all but one particle surrounding the hole has contributed some probability to move into it, causing the hole to move away. That is, in the dense limit, nearly all neighbouring sites are filled with particles, and the overall concentration of the system now makes no difference to the escape processes. The rate is given by $k_v(v \rightarrow 0) = \gamma G$, where G is a geometrical factor. Thus, in the limit of small hole concentrations, the correlation factor, f(v), becomes a constant, and the diffusion constant vanishes linearly. Here, there is no dynamical arrest in any meaningful sense.

This whole scheme of thought is greatly modified if we consider the geometrical constraints (c < 6). Then the definition of holes becomes non-trivial, and the hole density must be calculated via equilibrium statistical mechanical methods, either analytically as outlined in Eq. (3), or by simulation. However, in addition to the mechanism by which particles move in highly frustrated systems is different, and we must therefore also revise the link between hole density and diffusion constant.

Near the dynamical arrest our description begins as before. Particles move into neighbouring holes, and the diffusion constant is written linearly in the hole density (itself calculated from equilibrium statistical mechanics), with a correlation factor f'(v).

$$D = \gamma v f'(v) . \tag{12}$$

However, the nature of f'(v) is now quite different, though it may be represented in the same manner as for f(v) above in Eq. (11). Rather than (as for the lattice gas), reflecting simply the equal probability of a particle to move backwards into the site it has just vacated we now find that, typically, there is no choice but to move backwards. This is because other neighbouring particles, besides the one that has just moved to create the new hole, when they attempt to move into the hole lead to a violation of the constraints. Of course, this is a rather extreme example, but it is true that the hole is typically highly immobilised and spends much of its time oscillating around a central location. This means that the hole escape rate must be become small (in fact vanishing) near the arrest. If we write Eq. (11),

$$f'(v) \approx \frac{k_v}{2\gamma},$$
 (13)

we need only to approximate the leading behaviour of the hole escape rate in the vicinity of arrest, k_v . We may suppose, and then check from the simulations that, there appears to be no limiting density independent escape rate for holes in the limit of low concentration so that $k_v \rightarrow 0$ for $v \rightarrow 0$. We may then propose that k_v may be expanded

(see Fig. 2 where we plot a quantity proportional to k_v),

$$k_{\nu} \approx \gamma' \nu + \cdots \tag{14}$$

and therefore,

$$D(v \to 0) \approx C v^2 \,. \tag{15}$$

These observations may be presented in a few different ways. As we have remarked above, closer examination of the simulations lead us to conclude that when a particle moves to liberate a hole, it is typical that all other surrounding particles (except the particle that moved to create it) are forbidden to occupy that new hole, unless it can become unblocked. This unblocking may occur only if some of the particles up to say, two linear lattice spacings distant move, unblocking the hole under question. The main point to be drawn here is that the escape rate for a hole is dependent on the concentration of surrounding holes. This is a remarkable distinction to the lattice gas, and may be viewed as typical of the frustration limit implied by ideal dynamical arrest.

In essence, then, the dependence of the diffusion constant on the square of the particle density results from the collision of a pair of holes. The transport properties near dynamical arrest are expected to be very simple when written in terms of the canonical order parameter that underlies them. They reflect the simple processes that lead to the remaining relaxation present in an almost blocked system.

9. Towards universality for ideal dynamical arrest transitions in the lattice glass models?

Now we come to the crux of the matter. Suppose it is generally true that we can expand the diffusion constant (or other transport properties) for the ideal transition in terms of powers of the hole density,

$$D = \gamma_1 v + \gamma_2 v^2 + \gamma_3 v^3 + \cdots$$
 (16)

We now know that if γ_1 remains finite at arrest, as with the lattice gas, we have a rather simple arrest in which vacancies are exhausted. Now we consider the possibility that γ_1 vanishes due to single-hole localisation. In the absence of any other effects, single isolated holes are trapped by the frustration effect. However, if γ_2 is finite then we have a dynamical arrest of 'glassy' type in which pairs of holes collide to produce the residual dynamical relaxation on approach to the transition. It is also possible, in even more highly frustrated cases, that two-hole processes are ineffective, and three-hole collisions are required to provide unblocking. Thus, we propose that critical indices (by analogy with critical phenomena), may be universal,

$$D = \gamma_{\alpha} v^{\alpha} , \qquad (17)$$

where α is the critical exponent of dynamical arrest, and may be expected within this ideal-glass scenario to be integer-valued. Notably, it also is expected (and so far our studies are in agreement with this expectation) that these exponents depend only on the presence of geometrical frustration. Each of these integers represents a universality class for the (ideal-type) arrest.

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We provide examples of this type of thinking by considering the asymptotic behaviour of the diffusion constant in Eq. (7). That is, we define the reduced correlation factor by dividing the diffusion constant by the hole density, and then removing the dependence on the rate constant γ_2 . In the first step we would expect all correlation factors to reduce to a linear behaviour, with different slopes near arrest (2). Indeed this is found to be true for those case of frustrated lattice modes that we have explored. By fitting these data to a straight line we may determine the slopes, and thereby the rate constants γ_2 . One expects therefore,

$$\frac{D}{\gamma_2 \nu} = \nu \tag{18}$$

and, so presented, the data would fall on a straight line with slope unity. In Fig. 3 we present data from a range of lattice glass models which have been treated in this manner. A straight line with slope of unity has been drawn for comparison. This figure contains the same information as that in Fig. 2. However, with the removal of the microscopic constants, we expect a universal plot of a straight line, so the scatter about that plot is a direct measure of the scatter about proposed universality.

In fact, there is reasonable agreement with our expectations based on these ideas of 'universality'; apparently only two types of behaviour (linear and quadratic diffusion) arising from the lattice gas and glass models. Simulation, even of a simple model, is intrinsically limited in the strength of the statements that can be made. However the results of figure point towards the possibility of 'generic behaviour', and possibly even universality classes based on simple hole processes.

One should note carefully the distinction between exponents defined with respect to hole density and particle density. The exponents defined in relation to particle density are expected to be, and indeed are usually found to be, dependent on details of the system. They reflect details of the dynamics that are not easily classifiable. On the contrary, exponents defined in relation to the hole density represent canonical mechanisms of relaxation of arrest, in the simple case of ideal transitions representing hole collisions of various types. We have seen how different lattice glass models, yielding different exponents in relation to the particle density, nevertheless, fall onto a remarkably common curve when plotted in terms of the hole density (see Fig 4).

Another way of explaining this simplification that may appeal to some is to observe that the representation of the dynamical arrest in terms of hole densities sums up many perturbation diagrams [35] that are present when the dynamics is presented in terms of the particle density. Thus, representation of the dynamics in terms of particles rather than holes is inappropriate near the dynamical arrest transition. We have taken the first, albeit currently very limited step towards establishing a order-parameter space for dynamical arrest.

Another very important possible universality scenario outside of what has been discussed here does, however, exist. That is, in those cases where the series in Eqs. (3) and (5) do not converge (because of the behaviour of the coefficients) then, no matter how small the hole density the arrest cannot be represented by any simple integer power of hole density. There are physical phenomena that would lead to such a new variety of (non-ideal) universality, but the methods to treat them are somewhat advanced and



Fig. 4. The hole density v as a function of time for the BM_{13} (upper panel) and the EM_{13} model (lower panel). For the BM_{13} model we show v at particle density ρ 0.53 (\star), 0.54 (\times), 0.55 (*), 0.56 (+) and for the EM_{13} model at ρ 0.47 (\star), 0.475 (\times), 0.48 (*), 0.485 (+).

cannot be addressed within the present paper. This is, however, an important point since it transpires that universality may still be a useful concept. The details will be laid out elsewhere [17].

10. The breakdown of fluctuation dissipation theorem of type two; alternative scenarios

Study of this model has lead us to conclude that the system may violate FDT2, beyond a critical density by two distinct mechanisms. The first arises if we cross an equilibrium phase transition, the second if we pass through, for example, the ideal dynamical arrest transition.

We have discussed in some detail elsewhere [36] the observation that, for the *BM* limit of the lattice model, mixtures of particles of different type may undergo a transition from fluid to crystal at mesoscopic length-scales. There we have also remarked that one useful approach to a formal definition of the dynamical arrest transition is to enforce the fluctuation–dissipation of type two (FDT2) during the simulations, thereby creating an ensemble identical to the unconstrained one, but without the irreversible fluctuations that drive the system away from equilibrium.

Here we wish to discuss the possibility of using the holes, defined earlier, as a useful order parameter to determine how far one has drifted from the 'equilibrium' dynamical manifold (regions of the landscape) for which FDT2 is obeyed. Thus, the

hole density fluctuates, without any overall drift when FDT2 is obeyed, but begins to slowly increase as we drift towards the more stable crystal phase. Consider Fig. 4 where we have plotted hole density data (v vs. time) for a few rather long simulations, again for the BM_{13} and EM_{13} models. In each case we have plotted hole densities for a number of different particle densities, to illustrate the change as one crosses the phase-transition.

The results for the BM limit are quite striking. Up until the phase transition the hole densities fluctuate around a fixed, time-dependent average, that is typical of the hole density in the disordered fluid. Beyond the density 0.51, we find that after a period (that itself depends on the quench into the crystal region) the hole density rises to a much higher value. Here the hole density is essentially being used as an order parameter for the dynamically slowed fluid to crystal transition.

In parenthesis we may remark that it is hardly surprising that the hole density should be a good order parameter for the transition. In fact, larger hole density implies that particles have a larger amount of dynamically accessible volume (DAV), or holes on the lattice), and this implies a higher entropy. This possibility to improve the packing is, in fact, the driving force for the transition to the crystal, and hole density is therefore also the natural order parameter.

Now, returning to the lower panel of Fig. 4, we see quite a different situation in which for much of the density range, and until very close to the dynamical arrest, the hole density fluctuates around its average value. It is true that, beyond 0.49, we do find very small slow drifts of hole density, but at that point the diffusion constant is already so small that the drift is negligible. We may remark also that, even using the Kawasaki algorithm, for the chosen parameters, the *EM* shows no visible signs of formation of ordered structures.

11. Conclusions

The conclusions to be drawn from our study fall into two broad classes of discussion. The first are deductions that can be drawn about the lattice glass models, both in terms of the nature of lattice glass dynamical arrest, and aging. The second class of comments are much broader propositions for continuum which are based on the lattice glass behaviour.

We have concluded firstly, that for at least the examples discussed, the concept of dynamically accessible volume (DAV) appears to be a useful order-parameter for the dynamical arrest. In fact, we now suppose that it is the primary object in such systems, parameterising directly the objects or excitations of the system that control arrest. In this sense, particle density is an inappropriate order parameter for the transition. The situation is thus subtle. There appears to be no generic rational behaviour of the transport coefficients in the vicinity of the arrest when written in terms of the particle density, even for the restricted class of ideal behaviour.

On the contrary, transport coefficients written in terms of the hole density immediately tend towards a few simple canonical behaviours. These may be the signatures of generic, perhaps universality, classes. If so, they reflect the dominance of low order hole processes, beginning with single hole dynamics in the low frustration (lattice-gas type) behaviour, with two-hole collisions dominating the more highly frustrated cases. Elementary arguments allow for one other type of arrest transition, not discussed here.

Recognising the value of holes as an order parameter for the dynamical arrest of the lattice model, we can also suppose that they represent a suitable variable in which to write the entropy of the highly restricted phase space of a nearly-arrested system in terms of the hole density. This is not an entirely trivial step. One should not mistake these 'holes' for the vacancies into which one can insert a particle, thereby evaluating the (particle) chemical potential. It is natural that entropy is a function of the (particle) chemical potential of the system, but this leads to no particular simplification for the arrest. Rather, we recall that we study those functions of the vacancies that are dynamically accessible to their neighbours, and indicate the possibility of movement. It is natural that such holes should also parameterise the number of micro-states of the system, and thereby the entropy, whilst phase-space still percolates, as it does until dynamical arrest. Assuming that the entropy-hole density relation is invertible, we can then write the transport coefficients in terms of the entropy. Dynamically accessible volume is therefore a bridging concept spanning thermodynamics, and dynamics. It is likely that 'holes' (or, more generally, DAV) therefore represent the basis of the Adam-Gibbs relationship. The equivalent relationship for the ideal arrest is trivial.

At this point we may remark that if our understanding of the situation is correct, the ideal-transitions, besides being simple powers of the hole density, are also weak-coupling transitions. That is, the transition may be written exactly in terms of the low-order expansion in holes. This may be exploited to develop an exact analytical theory of the lattice glass transition [35], and likely it can be further developed for continuum theory.

We turn to the conclusions we have been able to draw in relation to the 'aging' of the system. Here again we find that the slow aging of the system is well-represented by the hole density. We have not explored this issue in detail yet, but it may offer promise in understanding how microscopic theories of aging can be developed [37,38].

Now let us review these results for the potential application to continuum systems. We have not yet applied the approach to continuum systems, so strictly speaking we can only make statements about their possible relevance. However, we remark that the idea of dynamically accessible volume as an order parameter near arrest does not seem tied to the lattice in any way, although it is clearly much more readily applied to such situations. Also, the phenomena that arise on the lattice seem rather universal in character, and the arrest processes rather generic in mechanism. It would seem likely that the ideas should be applicable to the continuum system. If simplifications do emerge, then it may be possible to consider the (ideal) dynamical arrest phenomenon in a new light.

In this presentation, we have been able only to touch on some of the main features of the dynamical arrest transition. In particular, if we define order parameter spaces that make primary contact with the physical phenomena, such as dynamically accessible volume, we may expect a high degree of universality, predicated on a small number of mechanisms of arrest. It is clearly very early days in these and related investigations, and it is not yet possible to see if an elegant and compact formalism such as found for critical phenomena will result. However, there are encouraging signs that the emergence of generalised rigidity for gels, glasses, aggregates, and the many other seemingly unconnected arrested condensed states of matter may be essentially the same phenomena. There is the possibility that they are precisely the same phenomenon, being manifestations of a simple set of arrest behaviours, with relatively universal features.

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