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The nature of the colloidal ‘glass’ transition

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The dynamically arrested state of matter is discussed in the context of athermal systems, such as the hard sphere colloidal arrest. We believe that the singular dynamical behaviour near arrest expressed, for example, in how the diffusion constant vanishes may be ‘universal’, in a sense to be discussed in the paper. Based on this we argue the merits of studying the problem with simple lattice models. This, by analogy with the the critical point of the Ising model, should lead us to clarify the questions, and begin the program of establishing the degree of universality to be expected. We deal only with ‘ideal’ athermal dynamical arrest transitions, such as those found for hard sphere systems. However, it is argued that dynamically available volume (DAV) is the relevant order parameter of the transition, and that universal mechanisms may be well expressed in terms of DAV. For simple lattice models we give examples of simple laws that emerge near the dynamical arrest, emphasising the idea of a near-ideal gas of ‘holes’, interacting to give the power law diffusion constant scaling near the arrest. We also seek to open the discussion of the possibility of an underlying weak coupling theory of the dynamical arrest transition, based on DAV.

A. Introduction

It has long been accepted that colloidal particles with ‘hard’ inter-particle interactions exhibit an interesting set of reproducible properties when in dense dispersion with a suitable solvent. Up to the volume fraction of 0.49 one observes a fluid, and beyond volume fraction 0.55 the equilibrium state is a crystal. Between these volume fractions the fluid and crystal co-exist in two-phase equilibrium. On approach to a packing fraction of 0.58 the system shows signs of ‘arresting’ for some period into a disordered solid-like state. If the details of the system are adjusted suitably, this state is sufficiently long lived that its time averaged properties may be characterised by a number of apparently quite constant physical measurements. Also, on approach to arrest, and as a function of packing fraction, one may determine that the single particle (sometimes called tracer particle) diffusion constant vanishes, consistent with a power law in the distance from the arrest volume fraction ($D = C|\Delta\rho|^{\alpha}$, where $\Delta\rho = \rho_c - \rho$ and ρ_c is the density of the dynamical arrest). Such behaviour is often associated with the term ‘ideal’ glass behaviour[1–3] to distinguish it from the more complex phenomenology observed in molecular glasses.[4,5] The single particle density

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correlation function, when plotted against the logarithm of time, develops a plateau-like behaviour reflecting the extended period that particles spend within the 'cage' provided (apparently) by neighbouring particles,[6] decaying finally as the cage time is exceeded.

The equilibrium phase-behaviour may be understood by simple entropic arguments, there being no energy scale in the system. For this purpose we may divide the motions into those taking place essentially within the cage, whether the system is a fluid or crystal, and more extended diffusive motions present only in the fluid. This leads to a natural division of entropy due to states explored by local, and more extended motion, and is an idea that can ultimately be made into a theory.[7] The fluid is then understood to have some entropy contribution from both the local and extended motion, the diffusional component becoming smaller as the the density increases, and the number of free diffusive pathways decreases. The perfect crystal, whilst it has no diffusive motion is more efficiently packed and has larger cage volume. It therefore possesses a higher entropy (due to its local motions) than a (random) fluid-like packing at the same density. This explains why the fluid is stable at lower, and crystal at higher density. At intermediate densities the system optimises its total entropy by separating into phases (fluid and crystal) that are respectively lower and higher than the mean density, the former gaining more diffusional motion, the latter yielding up that possibility in favour of better local packing and local entropy. This is the fundamental principle underlying the first-order phase transition of freezing–melting for a simple substance.

On the other hand, the fundamental status of non-equilibrium states such as 'glass', 'jammed', and random close packed (RCP) is far from secure. Thoughtful recent researchers[8] call into question the concept of a well defined RCP structure, and exclude an equilibrium glass transition for the hard sphere. The concept of a jamming transition, at a deeper level, is far from clear. It may simply be the finite shear shift of the 'glass' transition (dynamical arrest), analogous to the shift of any equilibrium transition under shear. The deeper definition of the glass transition (here considered a dynamical arrest, whilst reserving the possibility of a true equilibrium glass transition for some substances) is itself subject to debate, at least where structural glasses are concerned. There is reasonable evidence for a well-defined dynamical arrest transition for hard spheres from theory, simulation, and even experiment.[9] However, it is clear that this transition can only be defined practically speaking (for hard spheres) over a restricted time-window, and we here remark that a clear definition of the meaning of the dynamical arrest singularity has been lacking. We shall here propose such a definition, although we attempt to make that definition explicit only for a simple example of a lattice model.

Despite these fundamental questions, those who work with colloids are well aware of some practical manifestations of these phenomena. One of the useful roles of theory is to try to clarify, at least in principle, the questions. This is what we shall try to do for the dynamical arrest transition. Our discussion shall focus mainly on the 'ideal' arrest where the diffusion constant vanishes with a power law, though the remarks are more broadly applicable.[10] First we shall discuss the principles, then illustrate them with the study of a very simple lattice model that is believed to exhibit all the phenomena discussed above, but that is so simple that it can be fully elucidated by simulation, and theory.

Let us begin by remarking that a superficial understanding of the dynamical arrest of the hard sphere system can be acquired by extending our discussion of entropy. Thus near the volume fraction 0.58, the diffusive pathways become rare. Then, if the system is prepared with fluid-like order, whilst it may be able to explore a 'reasonable' sample of its phase space, many fluctuations may be inaccessible over the duration of the experiment. Should these relatively inaccessible fluctuations include those that are irreversible (particularly those involving critical nuclei leading to crystal nucleation), the system will appear to have relatively 'equilibrium-like' properties over the experimental period. One may then determine that the diffusion constant vanishes (dynamical arrest) with the power-law dynamical singularity, for an 'ideal' transition. We remark that the preceding discussion is describing, in words, a conceptual framework satisfying the fluctuation–dissipation theorem of type two (FDT2),[3,11] which is the simplest scenario within which one may clearly define the dynamical arrest transition. This is an important point that is currently being missed in parts of the theoretical, simulation, and experimental literature. Research carried out in this field must fit within some overall conceptual framework, or one observes many different phenomena, mixed together in a manner that is interesting, but not yet quantitatively interpretable. The assumption of FDT2 is implicit, if not always so stated, in such theories as the ideal ('equilibrium') mode-coupling theory, and most other discussions of the arrest.

Much effort is made in simulations and experiments in glasses to prevent aging, or other non-equilibrium phenomena. Indeed experiments on colloidal arrest transitions often involve some attempt to suppress the nucleation rate by use of polydispersity, or an 'impurity' in the majority system, thereby partially achieving the FDT2 condition. Theories beyond FDT2[12–14] have been discussed in the literature, but so far limited progress has been made in their detailed application, so for all practical purposes current research has as its rigorous underpinning FDT2. None of these comments diminish the importance and interesting aging behaviour when FDT2 is relaxed, and when nucleation and growth kinetics occur on a comparable time-scale to the arrest. On the contrary these issues are of considerable scientific and practical interest. However it is yet early in these researches, and a deep theoretical and experimental understanding of this simplest model 'equilibrium' (FDT2) arrest transition, with its accompanying singularity, believed to be universal, would provide the field with many insights as to how the more general questions may be addressed. It is therefore important to identify the purpose of one's study. Either we are interested in accessing the dynamical singularity leading to the loss of ergodicity in the system (dynamical arrest), in which case every effort should be made to prevent violation of FDT2. Alternatively we may be interested in understanding the true system of particles, with all its interwoven phenomena of aging, crystallisation, or micro-phase separation in mixtures. Both endeavours are important, but they should not be confused. Here, by introducing a simple model that exhibits all these properties, we shall attempt to show how these strands of thinking inter-relate.

Finally, we note that our desire here is to make contact with the most simple examples of dynamical arrest in dense colloidal systems as 'models'. In fact, the competition between crystallisation and other non-equilibrium phenomena is much less severe, often irrelevant, in more common soft matter and colloidal systems[15] (*e.g.* gellation) where, on all reasonable time-scales the system is truly arrested. For those who seek an analogue of the 'Ising model' relevant to the dynamical arrest singularity the hard sphere system must still be of considerable interest.

B. Canonical definition of dynamical-arrest

We define the particle density *via*,

$$\rho(r) = \sum_{n=1}^{N} \delta(r - r_n(t)) \tag{1}$$

and thereby the Fourier transform components,

$$\rho_k = \sum_{n=1}^{N} \mathrm{e}^{ik\cdot r_n(t)} \tag{2}$$

The condition of FDT2 may be expressed in a form suitable for making direct connection to MCT,[3]

$$\left\langle |\dot{\rho}_k|^2 \right\rangle = \frac{\langle \eta_{-k}(t)\eta_k(t')\rangle}{\gamma(t - t')} \tag{3}$$

where $\gamma(t)$ is the memory kernel and $\eta_{-\boldsymbol{k}}(t)$ is the random noise, and

$$\frac{\left\langle |\dot{\rho}_k|^2 \right\rangle}{\left\langle |\rho_k|^2 \right\rangle} = \frac{k^2}{\beta m S(k)} \tag{4}$$

Thus, the random noise driving the density variables is time-translation-invariant and related to the averages of the density variables. These conditions essentially amount to the fact that there be no irreversible fluctuations or time-translation invariant phenomena. The temperature factor comes from averaging over the velocities on the left side of eqn. 4, and given that velocities typically equilibrate much more rapidly than configurations, this is usually a satisfactory approximation in many experimental systems, even near the arrest. However, time-dependent variations in the configuration (reflected in the time-dependence of $S(k)$), are slower and may compete with arrest.

Therefore, it is sufficient that there be some time-independent definition of temperature, and that the structure factor be relatively fixed for the duration of any time averages taken in the dynamical ensemble for this manifestation of FDT2 to be satisfied. Whilst this provides us with a definition of the ensemble over which averages must be taken, and experimental criteria by which this may be evaluated, it is also possible to try to create an appropriate simulation ensemble. The most direct method is to fix the structure factor, or significant parts of it, and require that the mean square of the instantaneous density variables, $|\rho_{\boldsymbol{k}}|^2$ has limited variation, and no overall drift. To enforce this is a significant but feasible task,[16] leading essentially to an added N-body potential. Other recent approaches have involved some modification of the potential to restrict the changes in the structure factor.[17] However, bearing in mind that we may seek only to find the singular dynamical behaviour, such as the vanishing of the diffusion constant (a rather universal type of behaviour) enforcing so much of the microscopic detail may not be necessary. Let us instead try to find the minimal level at which FDT2 must be maintained, at least for athermal systems.

Later when we study the simple lattice glass model we shall conclude that it is 'dynamically available volume' (DAV) or 'holes', regions of space into which particles may move that determines the singular behaviour of the diffusion constant. In the fluid phase, on approach to dynamical arrest, DAV fluctuates, but its average is fixed over long time periods. Where the crystal is the equilibrium structure, but the fluid phase near dynamical arrest is stable for long periods, this available volume (implicit also within the structure factor) is relatively constant at early times. Thus, during the first part of the simulations of the simplest athermal lattice model (10^3 Monte Carlo Sweeps — MCS) the hole density is relatively unchanged, but then considerably increases, as the system finds its (more favourable) crystal. In fact, it is the increase of DAV that one may consider as an order parameter for transition to the crystalline equilibrium state, and we have been able to show that interesting laws for crystallisation emerge from this.[10] At a deeper level one can show that it is possible to constrain DAV to remain fixed, thereby ensuring the relevant part of FDT2 is maintained during calculations of the arrest.[18] This then, is the minimalist definition of the dynamical arrest. The singularity has the holes (in the lattice model) as the underlying order parameter. Ensembles must be created with fixed hole density to yield a well-defined dynamical arrest singularity.[10] For the moment we simply show that, by averaging over short trajectories in which the DAV is quite fixed, one can define true ideal dynamical arrest in a natural manner.

In summation, then, we have outlined the context in which a dynamical arrest (ergodic to non-ergodic) transition may be clearly defined. Now it will be helpful to study an explicit example of an athermal dynamical arrest, to see these ideas at work in practice.

It is worth remarking that arrest may be achieved in other ways, involving, for example, external fields. Indeed, in the absence of such methods as perfect density matching between particle and solvent a weak gravitational field is always present. Application of such a field may lead the system to 'jam' at densities lower than the equilibrium dynamical arrest. The interrelation between jamming and glassification is not understood fully, and is currently the source of some confusion between different communities, especially since colloidal scientists sometimes work with particles that are somewhat larger than one micron, and lessening influence of fluctuations means that one is crossing over to the granular material limit. In the current context jamming is probably related to the presence of 'blocked' states on the landscape, at densities that are somewhat lower than the dynamical arrest, but which can support shear in a particular direction.[19] In this sense well-defined jamming may simply be the finite stress equivalent of the glass (dynamical arrest) transition, with an appropriate shift of the parameters that one finds in all phase transitions under shear.

C. Calculations of the dynamical arrest transition of athermal systems

All of these questions may be explored in systems of hard colloidal particles, or by simulation of hard spheres. Preparation of the latter is possible at high densities by, for example, annealing of the systems from smaller particle size, but this is a costly and very laborious process, albeit apparently quite successful.[8,20] One possible alternative is the use of lattice models. This approach, valid when there are universal or generic features to be elucidated, ultimately contributed greatly to our understanding of the liquid–gas critical point,[21] soft matter systems such as microemulsions,[22] and many other complex systems. So, building on insights due to Biroli and Mezard,[23,24] we seek to

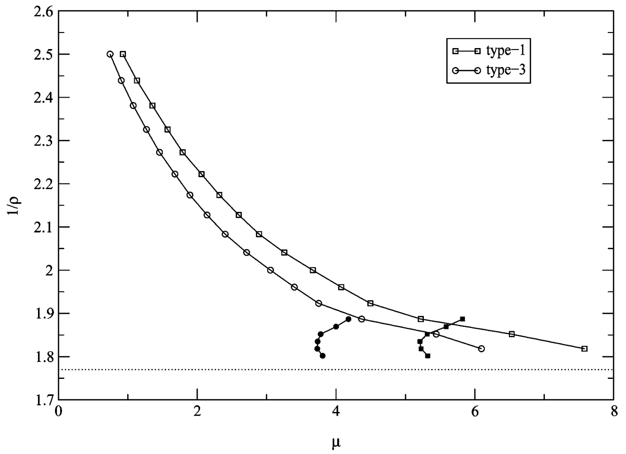

Fig. 1 Chemical potential against density for $c = 1$ and $c = 3$ type particles (open points are for 10^3 MCS). The chemical potential is defined as $\mu = \log(\rho/p)$ where ρ is the particle density and p is the fraction of sites where it is possible to insert a particle. The system slowly begins to crystallise with time, and the chemical potential decreases. This commences where the smoothly decaying fluid branch splits. A new branch develops for the crystal (solid points, 10^5 MCS) at $\rho = 0.51$ and the disordered fluid branch (albeit not at true equilibrium) continues. The dashed line represents the density at which we observe dynamical arrest $\rho = 0.565$.

represent the main features of geometrical frustration involved in packing hard spherical particles in three spatial dimensions. The program, whilst far from complete, seems promising, and we here report on some of the findings that emerged from the Biroli–Mezard limit, as well as a new model.[25]

On a simple cubic lattice, we define particles of type i to have a number of neighbours less than or equal to a prescribed number, c_i. If c_i is equal to the co-ordination number of the lattice, we have a lattice gas model, otherwise the model may be viewed as providing a minimalist description of the effects of geometrical packing frustration. We then permit particles to move stochastically only into those sites where no violation of these rules would occur. We focus on the mixture as studied by the original authors (70% particles with $c = 3$, and 30% with $c = 1$). The simplicity of the model enables us to construct a move table so that, remarkably, the simulation is faster near arrest than for less dense systems.

The equilibrium phase diagram may be represented in terms of the chemical potential μ as a function of density, as in Fig. 1. The dynamical arrest transition is located as described below, and marked on the phase diagram. We may determine the diffusion constant using the mean squared distance travelled by particles. However, as reported in previous studies, we observe that the system begins to 'age' towards a crystal (the lamellar crystal structure is shown in Fig. 2) for densities beyond 0.51. Even there, for time-scales less than about 10^3 MCS, aging is not significant, and we may still obtain an effective diffusion constant. This aging behaviour is seen in Fig. 3 where the diffusion constants for both types of particles in the simple model are shown for shorter and longer simulation times. This behaviour is precisely what one would find in simulations of the hard sphere system, where arrest occurs at a volume fraction of 0.58, well beyond that value of 0.49 where the system begins to violate FDT2 as it phase separates. The extrapolated values of the diffusion constant are well-fitted by a power law

$$D_i = C_i|\Delta\rho|^{\alpha_i} \tag{5}$$

with exponent $\alpha = 2.5$ for type-3 particles. Such a law is usually associated with the 'ideal' singularity of dynamical arrest, which appears to be appropriate for the hard sphere fluid.

Given the limited simulation time-scale (10^3 MCS) before aging sets in, we have investigated other models with the aim of avoiding the crystal (Fig. 2). We have simulated an extended model using the same ratio of type-1 to type-3 particles as in the conventional model, but we impose an extra constraint on the impurity particles (type-1) which prevents them from occupying the positions they would have in the lamellar crystal. The extended model has a similar phase diagram to

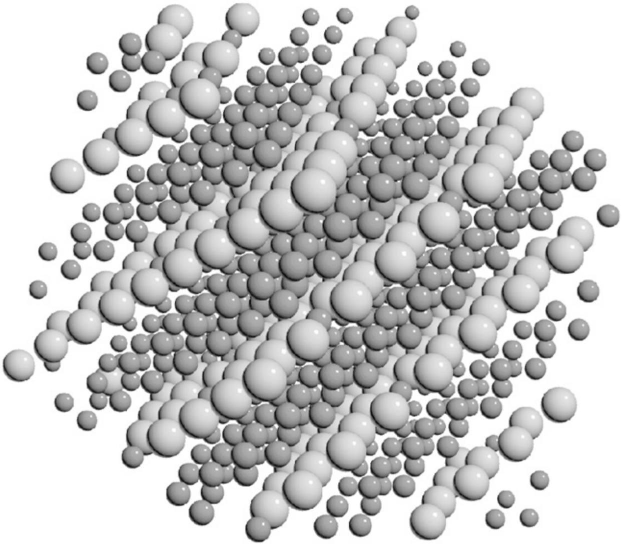

Fig. 2 The equilibrium crystalline phase is lamellar—alternate layers of larger particles (type-1) and smaller particles (type-3), separated by layers of spaces.

the conventional model but the additional constraint has the desired effect of preventing the crystal forming on significantly longer time-scales.

D. The nature of the landscape in the vicinity dynamical arrest

A fruitful viewpoint of the arrest transition has arisen in studies of the mean field theory of the *p*-spin model,[26–28] and previous simulations.[29] The essential idea is that dynamics should be a reflection of the landscape in the vicinity of the arrest. To study this we have located the 'blocked

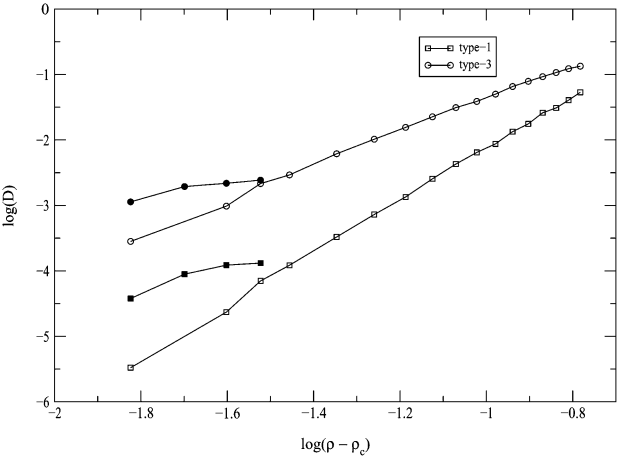

Fig. 3 Log–log plot of the diffusion constant *vs.* distance from the ideal arrest density. Note that, prior to equilibrium phase-separation, the diffusion constant is a true long-time limit. In that regime where equilibrium is no longer the fluid, phase-separation begins to play a significant role beyond 10^3 MCS. There we draw two branches to the diffusion constant, one calculated for time-scales of 10^3 and less, the other calculated for time-scales of 10^5 MCS.

states' of the model, defined as those arrangements of particles on the lattice that are stationary with respect to the stochastic single particle dynamics we have applied to the model in calculating the diffusion constant. To locate these states is not trivial, but it can be accomplished in the following manner. We prepare random configurations of particles on the lattice. A cost or energy function is composed of a penalty for i-type particles with more than c_i neighbours, and a separate penalty for 'holes', defined as vacancies into which particles can move. The energy cost for states with the wrong number of neighbouring particles ('violations') has an associated temperature that can be annealed to create states that satisfy the packing constraints (legal states). The penalty for holes has an associated 'chemical potential' that can be annealed to produce arrangements of particles on the lattice that possess no further holes; that is, blocked states. We adjust the annealing schedule of the temperature, and chemical potential separately, and sample using a Kawasaki-type algorithm in which different particle types are swapped and particles are swapped with vacancies if this causes no packing violation. By this method we can create blocked states at all densities above and below the dynamical arrest. These blocked states are of considerable general interest. They contain information on the topographical nature of the landscape for the typical densities at which they were formed. We have studied an ensemble of these blocked states as follows.[24,30] Each particle on the lattice is moved to a randomly chosen diagonal neighbour, the next largest distance for moves on the lattice, all nearest neighbouring moves being forbidden by definition.Such perturbations are made, irrespective of whether they generate a localised illegality or not. The dynamics is then applied many times to this perturbed state, with the supplementary condition that we move only towards a higher degree of legality. Illegalities are found to vanish very quickly, and play no substantial role in the picture. By this method, we can determine all those sites (elsewhere called 'directions' in phase space) that are stable, and unstable. Thus, it is found that the perturbation of some sites has little effect, the configuration evolving quite quickly back to close to its original state, whether measured *via* the overlap between original and subsequent states $q(t) = N^{-1}\sum_i n_i(t)n_i(0)$, or the mean-squared distances $\Delta r^2(t) = N^{-1}\sum_i [r_i(t) - r_i(0)]^2$.

A typical scatter plot of this behaviour is presented in Fig. 4, indicating clearly that most particle perturbations lead to two qualitatively different types of behaviour; stable or unstable. The number of perturbations that lead to unstable behaviour has been taken to be representative of the number of unstable directions K_f in the underlying landscape, and is plotted as a function of density in Fig. 5.

As expected, this number of unstable directions tends to zero as we approach the dynamical arrest, and has been interpreted as the geometrical signature of the transition. However there is another, more direct interpretation. Thus, we exhibit a typical configuration of particles near the dynamical arrest (Fig. 6), in which we show those particles that lead to unstable behaviour when removed.

These particles are seen to constitute an extended network, running through the whole configuration. They may be viewed as the 'load-bearing' particles, being part of the system of particles that support the structure. Removal of one of them, as we have shown, means that the whole arrangement of particles becomes unstable with respect to thermal fluctuations, or local flexing of the structure. In fact, this suggests a simple relation between the 'stress networks' discussed in other parts of the literature[31,32] and the natural definition of the ideal dynamical arrest.[18]

E. The canonical means of transport near the ideal arrest transition of hard particles; towards a weak coupling theory of the glass transition

Holes, by our definition, provide the only means by which particles can move in a highly constrained system such as that of the frustrated lattice glass model. This observation leads to a natural conception of dynamically available volume (DAV), regions of space into which particles can move with the prescribed dynamics. In some cases, hard spheres being a possible example, we may expect this volume to be distributed as relatively discrete packages, and this is precisely true of the lattice model. It is worth emphasising that DAV, whilst relevant to dynamics, has a definition based on equilibrium averages. This is a key step, involving non-trivial connections between dynamics and statics that seems to be deeply embedded in the story of the glass transition, though it has been difficult to give it clear expression as a theory.[33] The degree to which this connection can be

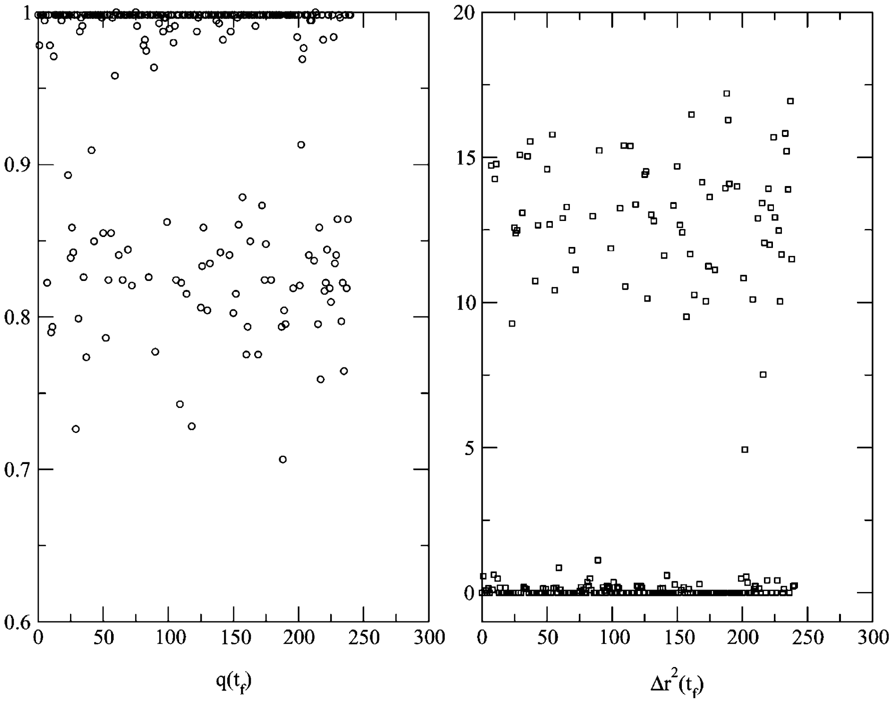

Fig. 4 Distribution of final overlap $q(t)$ (left panel) and mean square displacement Δr^2 after unblocking attempts. The states that remain blocked have overlap with respect to the initial blocked state of $q(t_f) \sim 1$ and mean square displacement $\Delta r^2(t_f) \sim 0$, where the final time $t_f = 10^5$ MCS.

prescribed in practice depends on the nature of the dynamics. Local dynamics, in which one particle moves at a time, with the others being held fixed, should lead to a relatively straightforward definition of DAV. On a lattice, the definitions are easily constructed, and we can make progress. But, even on the lattice, one needs multiple density correlation functions to determine the number

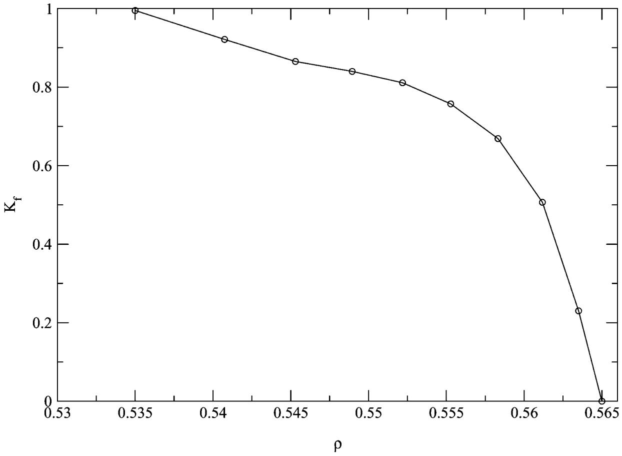

Fig. 5 Fraction of free directions, defined as the ratio of the number of free to total number of directions as a function of density.

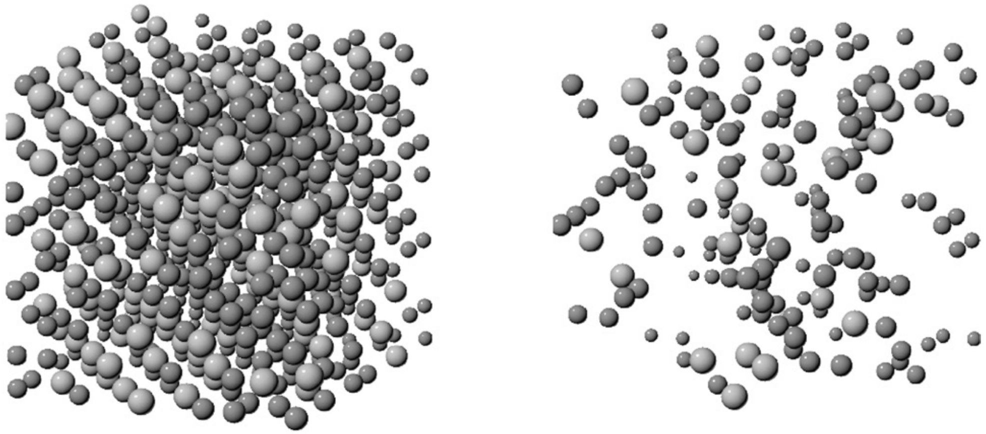

Fig. 6 The left panel shows a blocked state at $\rho = 0.5575$. The particles which lead to unblocking after perturbation are shown on the right.

of holes, and DAV should therefore not be confused with other concepts of 'available volume'. Here our main point is the observation that, indeed, DAV is a thermodynamic quantity. As an example, we calculate the number of holes by an efficient Monte Carlo (Kawasaki) procedure, and compare it to the time-averaged hole-number, calculated from dynamical trajectories. These results are generated for the extended model, there being a much larger window of averaging available there. The same results may be obtained for the original model, albeit with reduced statistics.

In Fig. 7 we show results from equilibrium sampling and the dynamics simulation, deviations arising only beyond the density where FDT2 breaks down, and non-equilibrium effects begin to play a role. We also find that the hole density ν appears to vanish on approach to the dynamical arrest, as determined by the vanishing of the diffusion constant D. Therefore, the hole density ν, despite being an equilibrium quantity, represents a good order parameter for the dynamical arrest transition.

It is natural that all transport properties be a function of DAV. The DAV (here expressed as holes on the lattice) must vanish in the limit of the arrest ($\nu \rightarrow 0$), as must the diffusion constant.

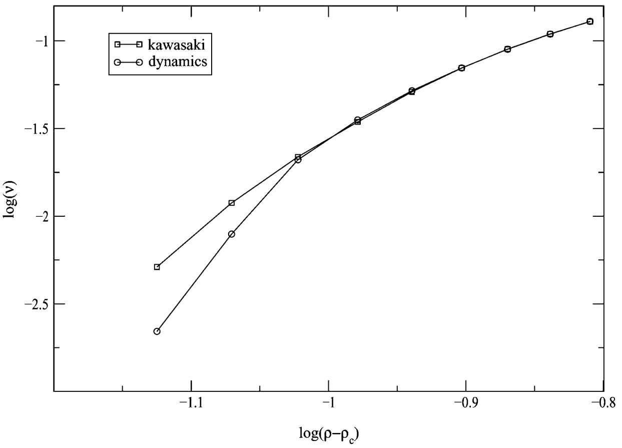

Fig. 7 The calculation of hole density ν in the extended model, the holes being defined as sites into which at least one particle can move. The (□) points are calculated using the equilibrium sampling techniques, whereas the (○) are calculated by counting holes arising directly from the dynamics.

Thus, assuming that the diffusion constant is an analytic function of DAV, we expect a series of the form,

$$D = \gamma_1 \nu + \gamma_2 \nu^2 + \gamma_3 \nu^3 + \ldots \tag{6}$$

This expansion, which applies separately to type-1 and type-3 particles, amounts to a virial expansion of transport co-efficients in terms of the holes. Such expressions have implicitly been discussed previously in the literature, as for example the lattice gas model ($c = 6$), but not to our knowledge in the context of the glass transition. For the lattice gas ($c = 6$), vacancies and holes are trivially equivalent, and it has long been known that in the limit of a fully filled lattice the diffusion constant vanishes linearly,[34]

$$D^{(c=6)} \xrightarrow[\nu \to 0]{} \gamma_1 \nu \tag{7}$$

Now, by plotting the hole density against the diffusion constant Fig. 8, we see that eqn. (6) has only one term and the following intriguing law holds over the whole range of interesting densities,

$$D^{(c=3)} \xrightarrow[\nu \to 0]{} \gamma_2 \nu^2 \tag{8}$$

Evidently, as c becomes less than the co-ordination 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 we find the modified diffusion constant. It may be expected therefore that the range of 'ideal' transitions is very limited, there being near-universality of the laws. Thus, the weak frustration limit implies a vanishing of the diffusion constant linearly, whilst the high frustration limit implies this new quadratic law. It will be of considerable interest if off-lattice ideal athermal systems are found to behave in this manner.

It is worth noting that such 'universality', if it is indeed established in off-lattice systems, may easily have been missed in the past. The vanishing of the hole density as a power law on approach to the arrest contains all of the microscopic detail, and the exponent varies depending on detail. However, it is merely a thermodynamic quantity, and the link to the dynamics, expressed in the dependence of the diffusion constant with DAV may be expected to represent the fundamental universal dynamical arrest mechanism in question.

It is also of interest to ask why, in the case of the lattice glasses in the high frustration limit, the diffusion constant vanishes as the square of the hole density rather than linearly, as with the lattice gas in the nearly filled limit.

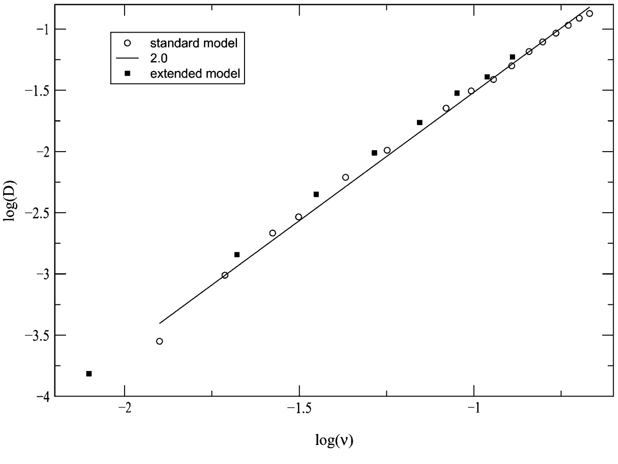

Fig. 8 Log–log plot of the hole density ν against the diffusion constant D. The best fit line to the standard model, (○) is found to have a slope of 2.0. The remarkable observation is that, even in the high frustration limit, arrest appears to occur as a universal law in hole density. The same law $D \propto \nu^2$ holds for the extended model (■).

Let us recount the underlying physics of the lattice gas.[34,35] In the limit of vanishing hole (vacancy) concentration all transport occurs by a particle moving into a neighbouring (vacancy) hole. Assuming a uniform distribution of holes, the probability of finding a hole as a neighbour is ν so that we may propose

$$D_0^{(c=6)} = \gamma\nu \tag{9}$$

where γ is the rate with which particles move into an empty site (hole) that is a neighbour. However, this assumes that every such move contributes to the transport, whereas after this movement there is, with enhanced probability, a hole at the site from which the particle just moved, and thereby an enhanced probability of moving backwards. This has been described by a correlation factor, $f(\nu)$, that describes the reduction of the diffusion constant from the simplest approximation. The outcome is

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

However, the particle can move backwards into the hole only if that hole remains there long enough, and therefore the rate of decay of the hole, k_ν, is an essential parameter in determining $f(\nu)$. In the limit of vanishing hole concentration the correlation factor is given by,[34]

$$f(\nu) \xrightarrow[\nu\to 0]{} \frac{k_\nu}{k_\nu + 2\gamma} \tag{11}$$

Furthermore, in the dilute limit of the lattice gas the hole vanishes if any neighbouring particle (except the particle that created it) moves into it, there being no restriction on such a movement. The rate of vanishing of the hole therefore involves only the neighbouring particles and is itself independent of any other holes, for low overall hole concentration. The rate of hole decay is given by,

$$k_\nu = \gamma G \tag{12}$$

where the geometrical factor $G = -(1 + 1/\langle\cos\theta\rangle)$ and for the simple cubic lattice $\langle\cos\theta\rangle = -0.20984170$. Therefore, it is a central observation that $f(\nu \to 0)$ tends to a constant depending on the lattice alone. Thus, the linear law for the diffusion constant is exact in the limit of very dilute holes. The 'uniform' approximation D_0 of eqn. (9) is therefore modified only by a multiplicative constant.

The dependence of the diffusion constant on hole density is, however, quite different for a highly blocked lattice glass system. As before, we expect a particle to move into the hole, found with probability of the hole density, thereby liberating a hole behind it. However, due to the frustration on the lattice, itself increasing as the density approaches arrest, movement into the hole created by the first move may be forbidden to any of its surrounding particles, except for that particle that moved to create it. Again we may consider a correlation factor to reflect this tendency to move backwards.

$$D = \gamma\nu f'(\nu) \tag{13}$$

Since the hole is typically unable to move, except back to where it came from, k_ν, the rate of escape is very small, and we may approximate from eqn. (11),

$$f'(\nu) \approx \frac{k_\nu}{2\gamma} \tag{14}$$

We therefore need only to approximate the leading behaviour of the hole escape rate in the vicinity of arrest. We may suppose, and then check from the simulations, that because of the frustration, most holes become blocked to all but one particle near the transition. There appears to be no limiting density independent escape rate for holes in the limit of low concentration so that $k_\nu \to 0$ for $\nu \to 0$. We may then propose that k_ν may be expanded,

$$k_\nu \approx \alpha\nu + \beta\nu^2 + \dots \tag{15}$$

and therefore,

$$D \xrightarrow[\nu \to 0]{} C\nu^2. \tag{16}$$

The underlying mechanism leading to the conclusion that the hole escape rate vanishes linearly may be probed a little further, by examining the simulations in detail. Thus, we observe that when a particle moves to liberate a hole, it is typical that all other neighbouring particles are forbidden to occupy that hole, unless it can become unblocked by some independent mechanism. This unblocking may occur only if some of the particles up to say, 3 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 linearly dependent on the concentration of surrounding holes. By this self-consistent field type of argument we obtain the diffusion constant dependence on hole density squared in the highly blocked or frustrated limit.

In this case, we note that the concentration of holes for the lattice glass is not known *a priori*, unlike the lattice gas vacancies where it is simply $\nu = 1 - \rho$. As a simple equilibrium quantity (order parameter) its dependence on particle density would be given by some effective Landau theory (entropy for an athermal system) based on the hole density

$$S = -\mu\nu + \frac{a_2}{2}\nu^2 + \frac{a_3}{3}\nu^3 + \frac{a_4}{4}\nu^4 + \cdots \tag{17}$$

We should then minimise this function with respect to ν, and solve for ν. With knowledge of the dependence of the coefficients a_n on particle density ρ, we may obtain the hole density ν in terms of the particle density. This thermodynamic part of the calculation may be avoided if one simulates the equilibrium hole concentrations directly. For the case of 3-particles we find

$$\nu = 1.98|\rho - \rho_c|^{1.25} \tag{18}$$

for the original model, and

$$\nu = 3.37|\rho - \rho_c|^{1.34} \tag{19}$$

for the extended model.

There is, however, a philosophical point to be deduced here. Our simple theoretical considerations involve two equations; one for the entropy dependence on hole density, and the other the dependence of the diffusion constant on hole density. By eliminating the hole density between them, this leads directly to an explicit relation between the diffusion constant and the entropy arising because the hole density is finite, and the system is therefore still exploring different configurations. This is essentially the configurational entropy. It is remarkable, therefore that we see an explicit manifestation of the Adams–Gibbs relation emerging, based on the hole densities, albeit for an ideal transition. The way seems clear to extend these arguments to the general case.

Naturally, to what degree these arguments are borne out in detail for off-lattice athermal systems is as yet not known. Certainly they seem quite general enough not to be affected by details of the system, providing there is a good definition of 'holes' (more generally DAV) for such systems.

F. Conclusions

We have argued that the fundamental dynamical singularity can be isolated in a system as it nears loss of ergodicity by averaging the dynamics over the FDT2 ensemble. However, in athermal systems on a lattice we have isolated the essential excitations ('holes') that drive the dynamical arrest, and the underlying singularity.

This leads us to a natural choice of averaging ensembles that can be specifically created (fixed-ν ensemble), or approximated by adjusting the mixture to slow up non-FDT2 phenomena. We see these hole excitations as one expression of the general picture of dynamically available volume (DAV-defined in relation to a particular dynamics) DAV represents a partitioning of that part of space into which particles can move into suitable units or packets, whose statistics can be studied by equilibrium thermodynamics and statistical mechanics.

We show that in two lattice models, this approach leads to very simple laws in terms of DAV, that make explicit the connection between dynamics and entropy such as that outlined by Adams and Gibbs some time ago. These laws appear to be relatively universal, and simple.

We remark that much of what we do has the flavour of an underlying weak coupling theory that might ultimately be the basis of a new fundamental approach to study the 'glass' transition.[36]

Our results are derived mainly from the 'ideal' athermal arrest transition as manifested, for example, by hard sphere colloidal systems. However we believe they have broader relevance to the underlying questions and issues involved in understanding jamming, glassification, arrest and non-ergodicity. Validation of these ideas using off-lattice calculations, and for real colloidal systems now seems to be of some considerable interest.

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7 This simple idea is founded on the existence of 'inherent structures', or blocked states that dominate the landscape near arrest. The entropy may be calculated by a harmonic approximation within these states, and a sum over them, the latter an expression of 'Edwards Measure' (ref. 37 and 38).
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