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Stretched exponential relaxation on the hypercube and the glass transition

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Abstract. We study random walks on the dilute hypercube using an exact enumeration Master equation technique, which is much more efficient than Monte Carlo methods for this problem. For each dilution p the form of the relaxation of the memory function $q(t)$ can be accurately parametrized by a stretched exponential $q(t) = \exp(-(t/\tau)^{\beta})$ over several orders of magnitude in $q(t)$. As the critical dilution for percolation p_c is approached, the time constant $\tau(p)$ tends to diverge and the stretching exponent $\beta(p)$ drops towards 1/3. As the same pattern of relaxation is observed in a wide class of glass formers, the fractal like morphology of the giant cluster in the dilute hypercube appears to be a good representation of the coarse grained phase space in these systems. For these glass formers the glass transition may be pictured as a percolation transition in phase space.

PACS. 61.43.-j Disordered solids – 61.43.Fs Glasses – 64.60.Ht Dynamic critical phenomena

Complex systems generally show strongly non-exponential dynamics. In 1854 R. Kohlrausch used a phenomenological expression $q(t) = C\exp(-(t/\tau)^{\beta})$ to parametrize polarization decay data in Leiden jars [1]. Rediscovered more than a century later, again in the context of dielectric relaxation [2], this "stretched exponential" or KWW expression has become ubiquitous in phenomenological analyses of relaxation data, experimental or numerical [3,4]. There has always been a sceptical school of thought which considers that in the context of real glasses the stretched exponential expression is nothing more than a convenient fitting function of no fundamental significance. Thus it has often been assumed that the KWW form is due to a sum over individual elements (atoms, spins, ...) each relaxing independently and exponentially with an appropriate relaxation time distribution. Analytical arguments have been given as to why certain model systems show KWW relaxation [5,6]; for instance in trap models which have been studied intensively [3,6,7] individual non-interacting walkers fall into random traps, giving stretched exponential decay of the number of surviving walkers in the appropriate limits. The connection between these models and the physical situation for relaxation in strongly interacting systems such as glasses or spin glasses where elements are all intimately interconnected is not at all obvious, and in addition the models do not give predictions concerning the temperature dependence of the time scale or of the stretching parameter β.

An alternative mechanism for KWW relaxation can be provided by a closed space fractal like topology approach. A random walk in a normal Euclidean flat space leads to the standard diffusion equation $\langle r^2(t)\rangle \propto t$ in any dimension. For random walks on a critical percolation cluster inscribed in a Euclidean space, which is a fractal, diffusion is sub-linear: $\langle r^2\rangle \propto t^{\beta}$, with β values smaller than 1 which have been estimated numerically in each dimension and which become exactly equal to 1/3 at and above the upper critical dimension $d = 6$ [8]. A random walk on a circular loop, which is a closed space, gives a pure exponential decay of the average autocorrelation function, $\langle\cos(\theta(t))\rangle \propto \exp(-t/\tau)$ where $\theta(t)$ is the angle between the vector corresponding to the initial position of the walker at time zero and the vector corresponding to the position at time t. It was conjectured [9] that for purely geometrical reasons, for random walks on percolation clusters inscribed in closed sphere-like spaces the analogue to the sub-linear diffusion would be the *stretched* exponential. In particular for the dilute hypercube in high dimension which has sphere-like topology, random walks on the percolation cluster would lead to stretched exponential relaxation with a limiting value of $\beta = 1/3$ at percolation in the infinite dimension limit.

Here we use an exact enumeration Master equation method which provides numerical results of high precision

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for this problem at high dimension. We find that the KWW functional form accurately fits data extending over a very wide range of $q(t)$ values (from about 0.5 to 10^{-5}), and that the effective β tends to 1/3 as the fraction of occupied sites p tends to the percolation value, as predicted. The accuracy of the agreement between the data and the stretched exponential fits at moderate and long times appear to be limited only by the dimension of the system studied which is high but not infinite, and by the number of realizations which were sampled. These results indicate to much higher precision than before that the stretched exponential is not merely an arbitrary empirical fitting function; we conjecture that it is exact for this geometry in the limit of N going to infinity and p going to p_c.

A generic explanation follows for the stretched exponential form of relaxation observed as the glass transition is approached in real glassy systems, if it is hypothesised that in such systems, just above the glass transition the "rough landscape" topology of phase space is the closed space analogue of a fractal. (Fractals can be defined precisely in Euclidean space; in real situations, structures are generally only fractal over a limited range of length scales. For want of a better expression, we will use the term "fractal-like" for the analogous structures with complex topology in closed spaces, in particular close to the percolation transition in the hypercube.)

Imagine a hypercube in high dimension N with a fraction p of its sites occupied at random. Clusters are defined as sets of occupied sites having one or more occupied sites as neighbors. It has been proved rigorously [10] that there is a critical "percolation" concentration p_c given by

$$p_c = \sigma + \frac{3}{2}\sigma^2 + \frac{15}{14}\sigma^3 + \ldots \tag{1}$$

where $\sigma = 1/(N-1)$. For $p > p_c$ there exists a giant spanning cluster while for $p < p_c$ there exist only small clusters with less than N elements.

Now consider the relaxation due to random walks on the giant cluster of sites, a strictly mathematical problem which apparently has not been solved analytically. For a given realization of the partially occupied hypercube with $p > p_c$ we can define a random walk among sites on the giant cluster. The walker starts at any such site i_0. A site j near neighbor to i_0 is drawn at random. If j is on the giant cluster (and so "allowed") the walker moves to j. Otherwise the draw is repeated until an allowed site is found. Each draw, successful or not, is considered one time step. The procedure is iterated.

We identify the distance H_{ik} between sites i and k on the hypercube with the Hamming distance, which is just the minimal number of moves needed to go from i to k on the full hypercube. The value of the normalized memory function $q_n(t)$ after time t for a given walk n starting from i_O and arriving at k_n after time t can be defined by $(N - 2H_{ik_n(t)})/N$. The definition is identical to that of the autocorrelation function relaxation for the N Ising spins. The value averaged over many walks will go to zero at long t.

Relaxation in the dilute hypercube has already been studied numerically by Monte Carlo techniques [11,12]. In the brute force Monte Carlo approach taking a mean over independent walks, the statistical noise becomes important at long t, limiting accuracy [12]. The exact enumeration considers a Master equation to study the time evolution of the entire probability distribution for the walker after t steps, $\boldsymbol{\rho}(t)$, which we will call the state vector. Each vertex of the hypercube is associated to an integer $0 \le i \le 2^N - 1$. At $t = 0$ the walker is localized on a single summit i_0 on the hypercube; the probability distribution then diffuses over the system at each time step following the equation:

$$\rho_i(t) = \rho_i(t-1) + \sum_j \left[\rho_i(t-1)W(j \to i) - \rho_j(t-1)W(i \to j)\right] \tag{2}$$

where $W(i \to j)$ represents the transition probability that is given by:

$$W(i \to j) = \begin{cases} \dfrac{1}{N} & \text{if } i \text{ and } j \text{ are allowed first neighbours} \\ 0 & \text{otherwise.} \end{cases} \tag{3}$$

Equation (2) can be rephrased as:

$$\boldsymbol{\rho}(t) = F\boldsymbol{\rho}(t-1) \tag{4}$$

where F is a linear evolution operator. Our numerical algorithm catalogues all sites on the giant cluster for each particular realization of the hypercube, and then equation (2) is iterated for one particular starting point. Close to p_c where time scales are long and there are fewer sites, it is more efficient to diagonalize the evolution operator F.

By explicitly solving the master equation we obtain an exact result (to within numerical rounding errors) for each combination of one realization of the hypercube occupation, and one given starting point on the giant cluster. There is no statistical "noise" for a given run, and by averaging over a moderate number of independent samples and starting points a mean $q(t)$ curve can be obtained, lying very close to the infinite ensemble average even to long times.

In practice, calculations were done on dimension $N = 16$ for values of p from 0.5 to 0.073 (which is close to p_c). At least 100 samples were used at each p. N must be large; the present value was limited by computer memory considerations. The present data give $q(t)$ values which have errors of about 10^{-5} while the Monte Carlo data with similar computer effort had limiting errors of about 10^{-2}. (The Monte Carlo data in [12] were taken at dimension $N = 24$ rather than 16.)

We expect three relaxation regimes *a priori*. First, at short times $q(t)$ must behave as $1 - \alpha t$ where α is the probability that a step will be made at a given attempt. Short time decay will thus be $\exp(-\alpha t)$; this corresponds to the fine-grained structure. Secondly, there will be the onset of the slow relaxation regime which interests us and which should extend over a wide range of times as the system explores the labyrinthine geometry of the

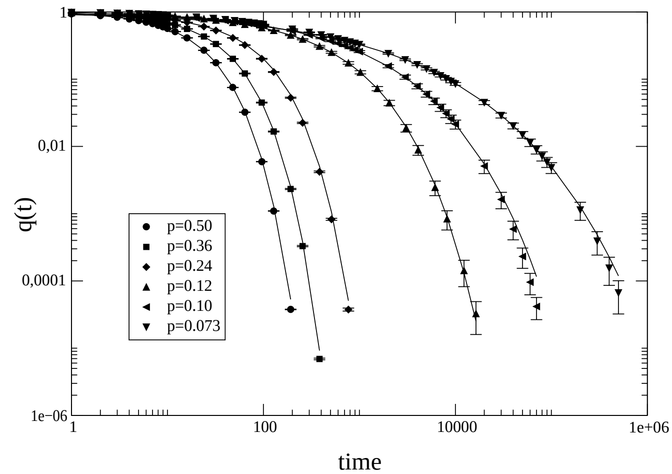

Fig. 1. Decay of the autocorrelation function $q(t)$ on a log-log plot for different values of p, as listed in the inset. The solid lines correspond to stretched exponential fits, with $\beta(p)$ and $\tau(p)$ as indicated in Figure 4. The error bars correspond to an estimate of the uncertainty of the points due to limited sampling.

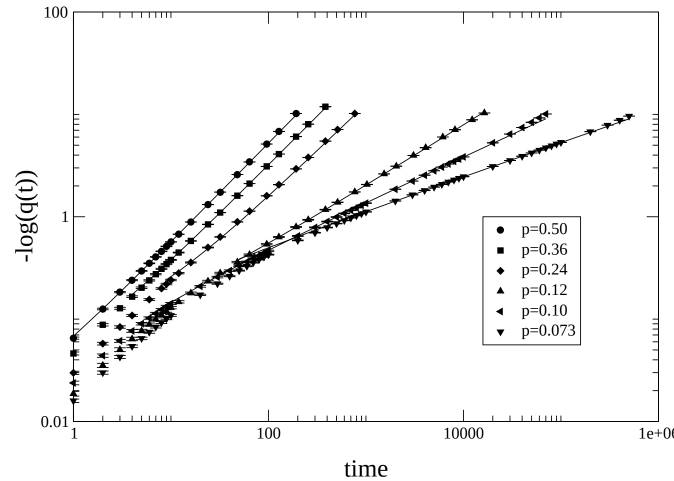

Fig. 2. A more stringent test of the stretched exponential behavior of $q(t)$ is the $\log[-\log(q(t))]$ against log t plot. The different values of p are listed in the inset. The solid lines correspond to a stretched exponential fit, with β and τ as indicated in Figure 4. The fitted curves are not linear due to the constant C.

giant cluster. Finally, for very long t finite size effects will set in (the number of sites is finite for finite N) and an ultimate crossover to another exponential regime will occur.

The numerical data obtained together with the stretched exponential fits are shown as $\log q(t)$ against $\log(t)$ in Figure 1. The normalization parameter C is always close to 1 and was included to guarantee better fits at intermediate times. It can be seen immediately that the fits are of excellent quality.

There are various methods of exhibiting this sort of data in order to make stringent tests of the functional form of $q(t)$. For example, Figure 2 shows $\log[-\log q(t)]$ against $\log(t)$. In this plot perfect pure or stretched exponentials with $C = 1$ should be straight lines at long t, with the pure exponential having slope one. For C not strictly 1 the fitting curve bends slightly at short p. The data show that over a very wide intermediate time regime, at each p the functional form of $q(t)$ is indistinguishable from a stretched exponential with a β value which decreases as p decreases. As we expect, deviations occur at short times for all values of p, and small deviations can begin to be observed at long times for small values of p where the longest times scales for the relaxation occur. We show in Figure 3 data for different dimensions, $N = 12, 14$, to compare with $N = 16$. At each value of N the data correspond to $p = p_c$ where p_c is the appropriate critical concentration (which changes with N). It can be seen that the larger N the later the $q(t)$ curve deviates from the limiting Kohlrausch straight line, demonstrating that the long time curvature is a finite size effect. If calculations could be carried out for much larger N the ultimate deviation from the Kohlrausch regime would only appear at extremely long times and extremely small $q(t)$.

For large N and as p approaches p_c the time scale τ tends to diverge and the stretching exponent β tends to

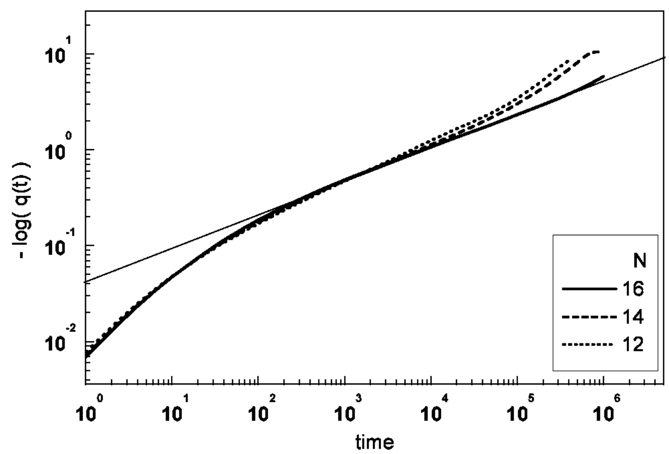

Fig. 3. Plot of $\log[-\log(q(t))]$ against $\log t$ at the critical concentration $p = p_c$ for three different hypercube sizes: $N = 12, 14$ and 16. The curves corresponding to smaller samples deviate from the stretched behavior (thin straight line) at smaller times than the curve for the largest size.

near 1/3. This limiting behaviour is consistent with the prediction quoted above, where the stretched exponential behaviour and the exponent 1/3 are linked to a fractal like topology for the closed space percolation cluster. The fact that accurate stretched exponential behaviour (with $\beta > 1/3$) is still observed numerically over long time ranges at p values higher than p_c is *a priori* unexpected. In standard Euclidean spaces only *local* fractal behaviour occurs once p is above the critical value. However it must be remembered that we are dealing with very high dimensions where geometry becomes unconventional – for instance, percolation fractals become self transparent. Already in the Euclidean case, it would be of interest to study the high dimensional regime further.

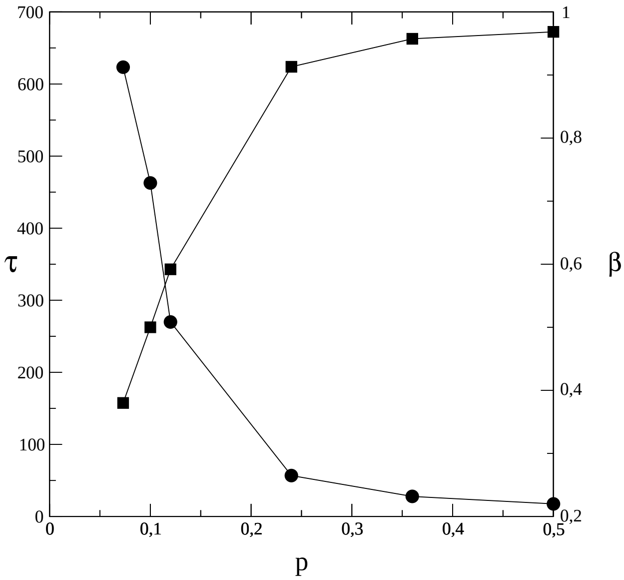

Fig. 4. Relaxation time $\tau(p)$ (circles) and stretched exponential exponent $\beta(p)$ (squares) against p. As $p \to p_c$, τ diverges while $\beta(p)$ approaches 1/3.

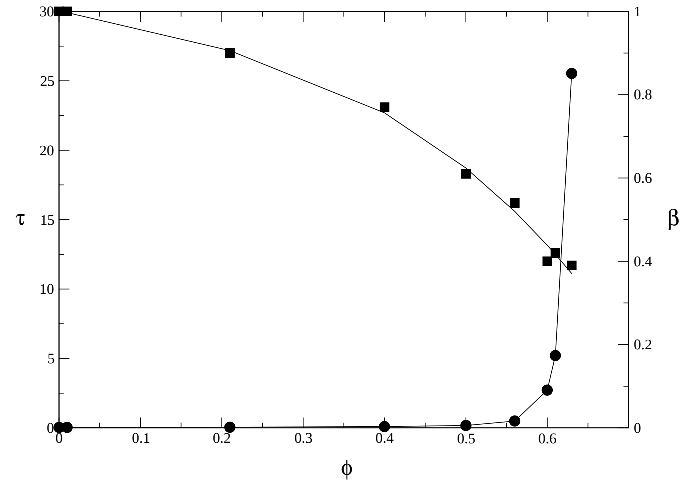

Fig. 5. Experimental data from light scattering measurements on a polystyrene colloid, taken from Bartsch *et al.* (Ref. [18]). In the publication the relaxation curves were parametrized using the KWW form. The relaxation was measured as a function of the colloid volume fraction ϕ. The critical value ϕ_c where a gel forms is about 0.69.

The Kohlrausch behaviour for p above p_c could be an intermediate regime rather than the true asymptotic regime. The numerics show that if this is the case, the intermediate regime extends over a wide range in t.

Recent numerical results for random walks on percolation clusters inscribed on hyperspheres of dimension 3 to 8 give accurate confirmation of stretched exponential decay behaviour at the critical percolation concentration with the stretching exponent equal to the Euclidean sublinear percolation cluster random walk exponent for each dimension [13]. Taken together with the present results close to the critical concentration for percolation p_c, it can be concluded that random walks on a critical percolation cluster inscribed in a space of spherical topology indeed give precisely stretched exponential decays.

The initial motivation of this work was to try to provide a generic explanation for the ubiquitous observation of stretched exponentials in experimental and numerical relaxation data. We can compare heuristically the model data with examples of numerical and experimental relaxation results in complex systems above the glass transition. The autocorrelation function relaxation in the 3d bimodal Ising spin glasses has been studied numerically to high precision [15]. The long time relaxation function above the ordering temperature is of stretched exponential form with an exponent β which tends to 1/3 within numerical accuracy at the temperature at which the times scale τ diverges. Relaxation in other spin glasses are of the same limiting form, independently of space dimension or of the type of spin-spin interaction [16]. Spin glasses and fully frustrated models return to simple exponential relaxation behaviour above the Coniglio-Klein (or Kastelyn-Fortuin) temperature which is well above the ordering temperature [17]. This pattern of behaviour is not restricted to spin glasses. For instance the relaxation of a colloid glass former [18], a system having an entirely different microscopic mechanism for glassyness, again shows stretched exponential decay with β tending to 1/3 as τ diverges with concentration because of steric hindrance, and a pure exponential decay at small concentrations, as shown in Figure 5. A large number of polymer glass formers also show a similar characteristic relaxation pattern [19].

What could the logical connection be between the dilute hypercube random walk and relaxation in glasses? The ensemble of all possible configurations of a thermodynamic system form a high dimensional closed space. The *available* phase space at temperature T can be considered at the microcanonical level as the set of configurations having the appropriate energy for that temperature, $E(T)$. This available phase space becomes sparser as T decreases. Phase transitions correspond to discrete qualitative changes in the topology of the microcanonical phase space with temperature [20]; thus at a standard ferromagnetic second order transition T_c the phase space splits into two. Also quite generally, relaxation is just the consequence of the random walk of the configuration point of the whole system in the available phase space, and its form is necessarily a reflection of the morphology of this phase space. Explicitly the N dimension hypercube is exactly the total phase space of an N spin Ising model; the spin by spin relaxation of a coupled N spin Ising system can be mapped directly onto a random walk of the configuration point on the thermodynamically available sites of the N dimension hypercube [15]. For systems with more complicated total phase spaces than the hypercube, the same argument applies *mutatis mutandi*.

In all relaxation models including the present one the shape of the decay can be related formally to a particular distribution of relaxation times of independent modes of the system. The present model is not in the class of models with single spins relaxing independently and exponentially at different rates, and the initial site is not a privileged configuration. All the relaxations of the single spins are coupled together implicitly through the complex "rough landscape" topology of the giant cluster.

As the spins are strongly interacting, it is essential not to confuse the relaxation *modes* with the individual elements (spins) which are relaxing. Thus for the present calculations the effective number of spins is small ($N = 16$) but the number of independent modes is much bigger: it is equal to the number of eigenstates of F, *i.e.* to $p2^N$, typically of the order of 10^4 modes for $N = 16$ (the value varies with p). The mode spectrum is discrete and by definition has upper and lower limits. As we have discussed above, for times less than the minimum characteristic time (highest mode frequency), relaxation will be exponential, and for times much longer than the (N and p dependent) maximum characteristic time (lowest mode frequency) there must again be a second exponential regime, the finite size limit discussed above. The short time regime can be seen on all the numerical curves, for $q(t)$ values above about 0.5; the beginning of the long time tendency to exponential decay is only visible for the lowest values of p where the number of modes is smaller and where the calculations have been taken to very long t.

We argue that the "rough landscape" of complex systems takes up a specific closed space fractal like form above the glass transition, and that the relaxation is a reflection of this topology. In a sense the present model expresses concretely the physical picture proposed by Palmer *et al.* [5] where the relaxation of each element depends on its instantaneous environment, but in contrast to [5] the mode relaxation time distribution is not injected "by hand" but emerges spontaneously as a necessary consequence of the fractal-like closed space topology of the giant cluster, with no adjustable parameters of any kind. It is important that the present approach not only leads naturally to the stretched exponential functional form, but it provides an explicit quantitative relation between the time scale and the stretching. As p drops towards p_c the time scale $\tau(p)$ gets progressively longer (a divergence at p_c in the very large N limit). Concomitantly $\beta(p)$ decreases from 1 at large p towards a limit of $1/3$ at p_c, (Fig. 4). Both effects reflect the increasing sparseness and complexity of the giant cluster with decreasing p. The limiting value of $1/3$ for β when τ diverges is a consequence of the "fractal like percolation cluster" topology of the sparse giant cluster [9].

The question may be raised as to whether the stretched exponential is the true limiting long time relaxation form in spin glasses. It has been stated that the long time relaxation should be dominated by large, compact, nonfrustrated, isolated clusters of spins for temperatures below the Griffiths transition [21–23], but no numerical evidence has ever been found for the onset of this regime [15,22,24]. The probability of encountering large unfrustrated clusters in samples of the sizes studied numerically can be estimated and is microscopically small; thus any cluster-dominated regime would correspond to tiny values of $q(t)$ in huge samples, and so is unattainable in practice for numerical or experimental studies.

A number of experimental studies [25–27] conclude that there is spatial heterogeneity in the relaxation of glasses. As is pointed out particularly clearly by Kirchner *et al.* [26], above the freezing temperature any such heterogeneity must be purely dynamic for systems with self induced disorder, such as supercooled liquids. Cugliandolo and Iguain [28] show that responses very similar to those of the experimental results can be generated from numerical studies of models with no spatial structure, so the interpretation of experiments in terms of spatial heterogenetity must in any case be treated with caution. In systems with quenched-in disorder such as spin glasses, simulations show that there is some spatial heterogeneity of relaxation times, but that the relaxations of individual spins are generally strongly non-exponential [29,30]. In the phase space approach, local relaxation rates are expected to be heterogeneous in the sense that at a given time some sites are relaxing faster than others; however the sites that are relaxing fast at one time may well be relaxing slowly at a later time so this heterogeneity is intrinsically dynamic. Even in the presence of some quenched in static inhomogeneity, heterogeneity can be expected to be mainly dynamic and the argument for an overall fractal phase space morphology leading to the stretched exponential global relaxation is not affected.

In conclusion, using a Master equation approach for random walks on the dilute hypercube, high precision results have been obtained compatible with the stretched exponential being the exact functional form for the autocorrelation function relaxation at the approach to the percolation concentration in the limit of infinitely high dimension. The stretched exponential decay is clearly related to the complex topology of the percolation cluster in closed space, which we have referred to as fractal like. The striking resemblance between the dilute hypercube relaxation pattern and the relaxation actually observed in numerical studies of spin glasses or in experiments on glasses above the freezing temperature strongly suggests that in the physical systems the phase space has an analogous structure in this temperature range. Thus, at short times (fine grained phase space) the relaxation will depend on the details of the physics of each system, but at moderate and long times (coarse grained phase space) these systems all appear to have the same specific percolation-fractal-like phase space topology with its characteristic relaxation signature, the precursor of a phase space percolation breakdown at the glass transition.

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