Diffusion in Glassy Systems

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Abstract

The transport properties of glass-forming systems have many features that are not found in normal liquids. Among them is a very strong sensitivity of the relaxation times upon a change in temperature and the presence of so-called dynamical heterogeneities. In this review we discuss these unusual properties and present the results of a simple lattice gas model that helps to understand the origin of these heterogeneities from the microscopic level. Furthermore we discuss a simple analytical model, the continuous time random walk, and show that it allows to describe some aspects of the relaxation dynamics of glass-forming systems on a semi-quantitative level.

Keywords: Glass transition; dynamical heterogeneities; slow relaxation; lattice gas; Stokes-Einstein relation; van Hove function; continuous time random walk

1 Introduction

Most elementary textbooks teach us that a liquid will crystallize if it is cooled below it melting temperature T_m. In reality it is found that many liquids can be supercooled, i.e. they do not transform into a crystal but continue to flow even at temperatures below T_m. Although from a thermodynamic point of view this state is only metastable, experiments show that there are quite a few liquids which can be kept for hours below T_m without crystallizing. For reasons that will be discussed below, these systems form easily a glass and are therefore called "good glass-formers". Since good glass-formers can be kept in the liquid state even at low temperatures, one can investigate their thermodynamic, structural, and dynamical properties. Almost hundred years of studies have taught us that the thermodynamic properties (density, compressibility, specific heat,...) of the vast majority of glass-formers are a very smooth function of temperature T. Also structural quantities (radial distribution function, static structure factor, ...) show only a mild $T-$dependence in that, e.g., the height of the first peak in the structure factor shows a variation of say 20-30% if the temperature is changed by a factor of two [1, 2, 3, 4]. (However, very recently evidence has been given that structural multi-point correlation functions, i.e. functions that go beyond the two point correlation that is encoded in the static structure factor, might show a relatively strong $T-$dependence [5].) Thus many researchers in the field believe that the thermodynamic and structural properties of supercooled liquids are qualitatively very similar to the one of the corresponding liquid at temperatures above T_m.
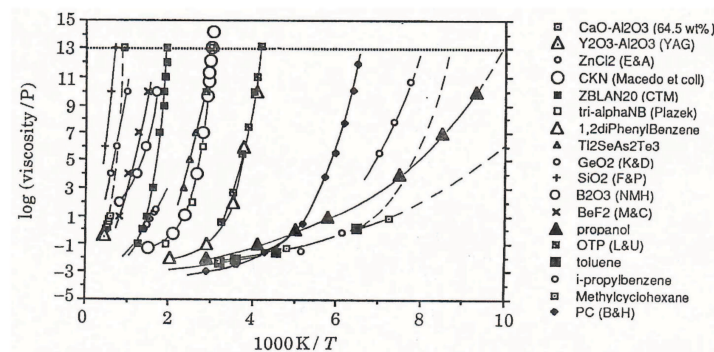

Figure 1: Logarithm of the viscosity η as a function of inverse temperature for various glass-formers. After Ref. [6].

The situation is very different if one considers *dynamic* quantities, such as the viscosity, the structural relaxation time, the diffusion constant, or electrical conductivity, since all these observables show an extremely strong $T-$dependence. As an example we show in Fig. 1 the viscosity η as a function of inverse temperature
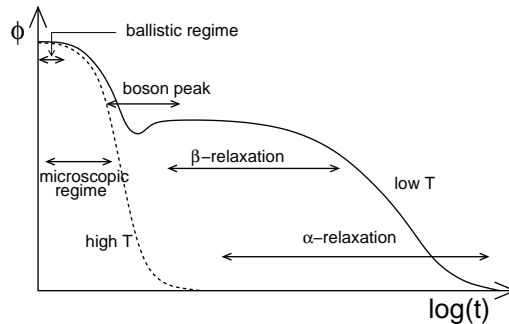
Figure 2: Schematic time dependence of a typical time correlation function of a glass-forming system at high temperatures (left curve) and low temperatures (right curve). After Ref. [7].

for a variety of glass-forming liquids. We see that a decrease of T by a factor of 2-3 leads to an increase of η by a factor of $10^{12} - 10^{15}$, i.e. in a temperature window in which the thermodynamic and structural properties of the glass-formers change by a factor of 2-3 the dynamics changes by many orders of magnitude. Note that for most glass-formers this dramatic change in the relaxation dynamics shows a noticeable deviation from an Arrhenius dependence (which would be a straight line in this representation), i.e. the strong slowing down cannot be rationalized in terms of a simple activated process, such as, e.g. the breaking of one or several bond(s) and the subsequent displacement of the atom. The microscopic mechanism that is responsible for this strong $T-$ dependence is currently still a matter of intensive research and many different approaches have been proposed to rationalize it [3, 7].

The strong $T-$dependence of the viscosity is not the only unusual feature of the dynamics of glass-forming liquids [8]. As an example we can consider the relaxation dynamics of a glassy liquid on the microscopic scale. This dynamics can, e.g., be characterized by the time correlation function $\phi(t) = \langle \delta A(t) \delta A(0) \rangle$, where $\delta A(t)$ is the fluctuation of an observable $A(t)$ at time t. (Below we will discuss concrete examples for such observables) [9]. In Fig. 2 we show the behavior of the time dependence of $\phi(t)$ for a typical glass-former. At all temperatures one finds that $\phi(t)$ shows at short times the so-called "ballistic" regime. In this time window the particles move just ballistically, if we assume that we have a Newtonian dynamics, and hence the correlator $\phi(t)$ shows a quadratic time dependence [1].

At high temperatures $\phi(t)$ shows at intermediate and long times just an exponential time dependence, with a relaxation time that depends on T. At low temperatures the $t-$dependence of $\phi(t)$ is more complex: At intermediate times the correlator shows a plateau, i.e. the correlation is basically independent of time, and only at very long times the correlator finally decays to zero. The reason for

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[1] This quadratic $t-$dependence is due to the time reversal invariance of the equations of motion. For a Brownian dynamics $\phi(t)$ is, at short t, linear in time.

the existence of this plateau is the so-called "cage-effect", i.e. the fact that in this time window most particles are temporarily trapped by their nearest neighbors that form some sort of a cage and thus confine the tagged particle to rattle around in this cage. Note that these caging particles are themselves also caged and hence in this time window most of the particles rattle just around inside their own cage. However, these cages are not completely tight and thus, after many attempts, the tagged particle has a reasonable probability to escape it, thus leading to the final decay of the correlation function. However, the details of this trapping as well as the escape from the cages are currently not very well known and thus are in the focus of interest of many studies. E.g. it has been found already long ago that at long times the shape of the correlator is no longer an exponential, but instead a so-called stretched exponential (also called a Kohlrausch-Williams-Watts function [10, 11]). The origin for this non-exponential dependence has puzzled researchers for many years since this $t-$dependence suggested the possibility that at low temperatures the liquid is relaxing in a heterogeneous manner [12], i.e. that there are "dynamical heterogeneities" (DH). By this one means that at any given time there are regions in space in which the particles relax quicker than average and other regions in which they relax slower. These DH appear and disappear for reasons that are not understood yet and also their size and shape are not really known. Already quite early experiments showed indirect evidence for the existence of these DH [13, 14] and later on computer simulations gave direct evidence for a heterogeneous dynamics [15, 16, 17, 18], results that were later confirmed directly in experiments on colloidal systems [19, 20]. Subsequently theory and experiments were proposed that allowed to determine in a relatively simple manner the size of the DH, although only if one made some assumptions on their shape [21, 22, 23].

From the above discussion it becomes clear that at present we have good evidence that the relaxation dynamics of glass-forming liquids occurs in a heterogeneous manner but that we still ignore the details on these DH. E.g. we do not know how and why the DH form, what their lifetime is, what their shape is. In the subsequent sections we will therefore present the results of numerical simulations of a simple glass-former that help to advance our understanding on these questions. In Section 2 we will present the model and give the details on the numerical simulations. In Section 3 we will show and discuss the relaxation dynamics and in Section 4 we will present a simple mathematical model that is useful to describe some of the aspects of the observed relaxation dynamics. Finally we end in Section 5 with the conclusions.

2 Model and Details of the Simulations

The system we consider is a simple lattice gas model in which the particles move on the vertices of a cubic lattice of size L^3 [24]. The only interaction between the particles is given by the condition that each vertex can be occupied by at most one particle. This simple interaction Hamiltonian makes that each allowed

particle configuration has the same Boltzmann weight and hence the equilibration of the system is trivial. The non-trivial part of the model is related to the way the particles move on the lattice. This dynamics is given by the following rules: 1) Pick a particle at random. 2) Pick one of the six nearest neighbor sites of the particle. 3) The particle can move to the selected site if the initial site of the particle has less than four occupied nearest neighbor sites and if the target site has less than five occupied nearest neighbor sites. Thus the relevant control parameter of the model is the particle density $\rho = N/L^3$, where N is the total number of particles in the system. Previous investigations have shown that, despite its simplicity, this model does show a glassy dynamics if ρ is close to unity, in that, e.g., its time correlation functions are stretched and the relaxation times are a very strong function of ρ [24, 25, 26, 27, 28, 29, 30]. In particular the simulation results of this model seem to show a divergence of the relaxation time at a *finite* density $\rho_c \approx 0.881$ [24], in apparent contrast to analytical calculations that show that the system is ergodic for *all* densities [28, 29].

We also note that the present system is just one example of a large class of models that are usually denoted "kinetic lattice gas models" and whose dynamical behavior has been investigated intensively in recent years since their simplicity allows to study their static and dynamics properties not only by means of computer simulations but also analytically. See Ref. [31] for an extensive review of these models.

For the present work we have considered lattice sizes of $L = 20, 30$ and 50 in order to avoid finite size effects [24] and densities between $\rho = 0.1$ to $\rho = 0.89$. Time will be measured in Monte Carlo steps (MCS), i.e. N attempts to move a random particle.

Last but not least we point out one important feature of the model: Since, as mentioned above, the interaction potential is trivial, it is not necessary to equilibrate the system. Any allowed configuration, i.e. no double occupancy of a vertex, can be used as an initial state for a simulation *in equilibrium*. This feature allows thus to access *equilibrium* states that have relaxation times that are much longer than the time scale of the simulation.

3   Results

Since the interaction Hamiltonian is trivial, the structural properties of the model are trivial as well. Therefore we start our discussion directly with the dynamical properties of the system.

One of the simplest ways to characterize the relaxation dynamics of the system is to consider the mean squared displacement of a tagged particle:

$$\Delta^2(t) = \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \quad . \tag{1}$$

Here $\mathbf{r}_i(t)$ is the position of particle i at time t and $\langle . \rangle$ denotes the thermal average. In Fig. 3 we show the time dependence of $\Delta^2(t)$ for different densities. As can
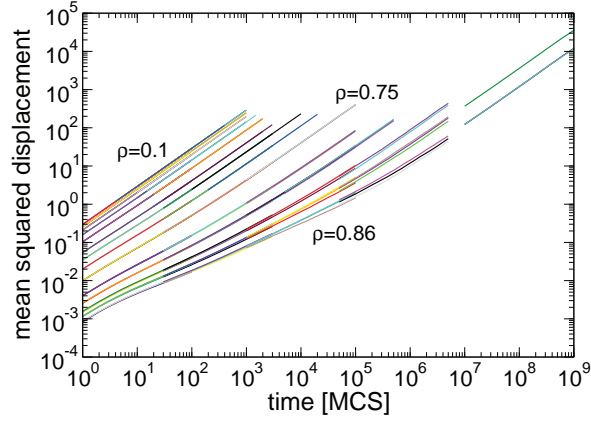
Figure 3: Time dependence of the mean squared displacement of a tagged particle for different densities ρ. The values of ρ are $\rho = 0.1$, 0.2, 0.3, 0.4, 0.5, 0.6, 0.65, 0.7, 0.75, 0.8, 0.82, 0.84, 0.85, and 0.86 (from left to right).

be recognized from this figure, the dynamics of the system does indeed slow down strongly if ρ is increased. For long times $\Delta^2(t)$ shows a linear dependence in time, i.e. the system has a diffusive behavior and, using the Einstein relation one thus can determine directly the diffusion constant D of the tagged particle:

$$D = \lim_{t \to \infty} \frac{\Delta^2(t)}{6t} \qquad . \tag{2}$$

The $\rho-$dependence of D is shown in Fig. 4. As one sees from the figure, the diffusion constant decreases very rapidly if ρ approaches unity, i.e. the system shows indeed a slow dynamics, i.e. it can be used as a simple model for a glass-former.

One should realize that the thermal average in Eq. (1) is equivalent to the ensemble average (i.e. average over all the particles). If the system has dynamical heterogeneities this average will thus include particles that are moving quickly, i.e. contribute, at a given finite time, strongly to the *mean* squared displacement. On the other hand the average will also include the slowly moving particles, i.e. those that contribute only very little to $\Delta^2(t)$. It is easy to see that a quantity like $\Delta^2(t)$ is dominated by those particles that are moving quickly, a fact that we will exploit below.

Another possibility to characterize the relaxation dynamics of the system is to consider the self intermediate scattering function $F_s(\mathbf{q}, t)$ [9] which is defined as

$$F_s(\mathbf{q}, t) = \frac{1}{N} \sum_{j=1}^{N} \exp[-i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \qquad . \tag{3}$$

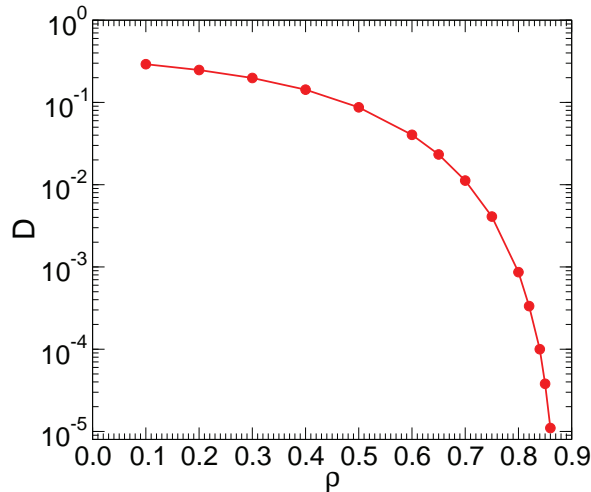Here $\mathbf{q}$ is a wave-vector (which has of course to be compatible with the periodic

339

Figure 4: The diffusion constant D as a function of the density ρ.

boundary conditions of our system). The time dependence of $F_s(\mathbf{q}, t)$ is shown in Fig. 5 for different densities. The wave vector is $q = 10 \cdot 2\pi/L$, with $L = 20$, i.e. the function goes to zero once the particles have moved on the order of a few lattice spacings. Also from this graph we see that the relaxation dynamics of the system slows down strongly if ρ is increased, in agreement with the results for $\Delta^2(t)$ from Fig. 3. We also mention that other wave-vectors show a qualitatively similar t and $\rho-$ dependence [24]. Note that the decay of $F_s(\mathbf{q}, t)$ at long times is very sensitive to the presence of *slowly* moving particles, since they make this correlator finite for long times.

¿From the time dependence of $F_s(\mathbf{q}, t)$ one can define a relaxation time $\tau(\mathbf{q}, \rho)$ via $F_s(\mathbf{q}, \tau) = 1/e$, which is the time scale on which the particles leave their cage. Although this definition is somewhat arbitrary, the results discussed in the following are independent of the exact definition. The plot of the $\rho-$dependence of the relaxation time shows that τ increases rapidly with increasing ρ. If one assumes that the Stokes-Einstein relation holds, one would in fact expect that $\tau \propto D^{-1}q^{-2}$, or equivalently, that $\tau \cdot Dq^2 = const$. In order to test this relation we plot in Fig. 6 the $\rho-$dependence of this product for different wave-vectors $\mathbf{q}$. As one can conclude from this figure, the Stokes-Einstein relation holds very well at low and intermediate densities. However, at high ρ it breaks down in that the product increases with increasing ρ and that the wave-vector at which this breakdown occurs decreases with increasing ρ, i.e. at high ρ one has to consider larger length scales in order to see the normal diffusion behavior. The reason for this breakdown are the dynamical heterogeneities as can be understood as follows: If the system would be homogeneous, i.e. all the particles relax essentially in the same manner, the Stokes-
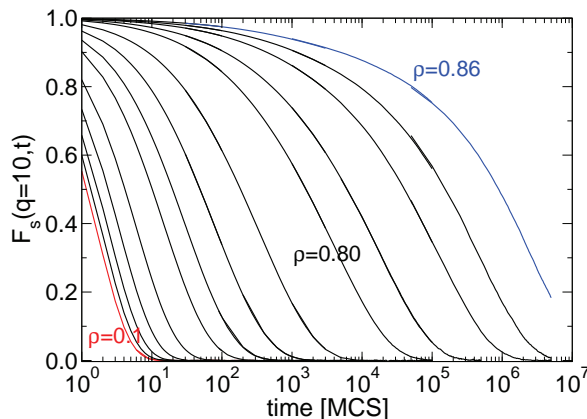
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Figure 5: Time dependence of the self intermediate scattering function for different values of ρ. $\rho = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.65, 0.7, 0.75, 0.8, 0.82, 0.84, 0.85$, and 0.86 (left to right). The wave-vector is $q = \pi$.

Einstein will hold as it is the case in a normal simple fluid. (Having a distribution of *local* relaxation times that has a width of say an order of magnitude will not change this.) However, if the system is very heterogeneous, the distribution of the local relaxation times will have a width of many decades and thus there is no reason why the Stokes-Einstein relation should hold. Since D is dominated by the particles that move quickly and τ by those that move slowly, and since the heterogeneity increases with increasing ρ, it is easy to see that the product of the *averaged* quantities D and τ will increase with increasing ρ [32, 33, 34]. Thus the fact that the Stokes-Einstein relation is violated can be taken as (indirect) evidence that the relaxation dynamics of the system is heterogeneous and that thus in this system the transport properties must be anomalous. Similar findings have been obtained also in other systems and thus presently these results are considered as a hallmark of glassy dynamics [34].

In order to elucidate the nature of these dynamical heterogeneities it is useful to visualize the trajectory of selected particles. For this one has to realize that, at high densities, most of the particles do not move at all for a very long time since they are jammed by the surrounding particles. A much smaller fraction of the particles can move to one (or two) nearest neighbor sites, but then they cannot propagate further, i.e. they have to return to the initial site. Therefore these rattling particles do not contribute to the relaxation of the system either. Finally there is a very small fraction of particles (the exact number depends on the density) that can move larger distances and in the following we call these particles "mobile". In Fig. 7 we show the trajectory of such a mobile particle on the lattice. From this figure we see that the trajectory of mobile particles is very different from the one one would expect for a simple random walk in that it is a sequence of relatively compact blobs that are connected by rather narrow bridges. We also mention that the blob and channel
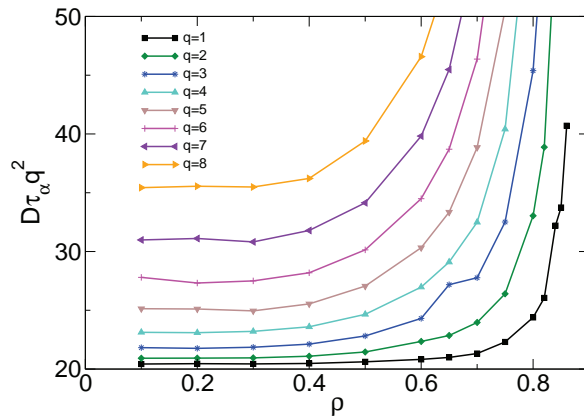
Figure 6: $\rho-$dependence of the product $\tau(\mathbf{q}, \rho) \cdot Dq^2$ in order to test the validity of the Stokes-Einstein relation. The curves correspond to different wave-vectors $\mathbf{q}$ with q measured in units of $2\pi/L$ (here $L = 20$).

structure is not only explored by *one* particle but by *all* particles that are inside this structure, i.e. the blobs and channels form a network in which the particles move relatively quickly [35].

In view of this rapid motion of the mobile particles and the fact that most particles are immobilized (or make only a localized rattling motion), it is evident that the relaxation dynamics of the system is indeed very heterogeneous and therefore it is of interest to investigate the properties of these dynamical heterogeneities in more detail and thus we now address this issue in more detail.

One important aspect for the description of the heterogeneous relaxation dynamics is to characterize the regions in which the system shows a large mobility, i.e. the blob and channel structure seen in Fig. 7, and as a start we calculate the volume of these regions. To this aim we recall that the regions of high mobility see the passage of many *different* particles and hence we can define a vertex to be "active" at time t if within the time span $[0, t]$ the site has been visited by more than one particle or vacancy and the collection of these active sites will thus constitute the mobile regions. Note that, if t is sufficiently large, all sites in the lattice will be active, since the system can be expected to relax, i.e. all particles have moved.

In Fig. 8 we show $n_{\text{act}}(t)$, the number density of active sites as a function of time. We see that, at short times, $n_{\text{act}}(t)$ increases quickly and we find $n_{\text{act}}(t) \sim 1 - \exp(-t/\theta)$ with $\theta \approx 5$, independent of ρ. This regime corresponds to the initial growth of the blobs. For larger times the shape of $n_{\text{act}}(t)$ depends strongly on ρ. For $\rho = 0.80$ the number of inactive sites, $1 - n_{\text{act}}$, decays with a stretched exponential tail, with a stretching exponent of around 0.6, a functional form that is found for all ρ. At even larger ρ, $n_{\text{act}}(t)$ shows three regimes, with the second regime being a period of extremely slow growth, almost logarithmic and thus similar
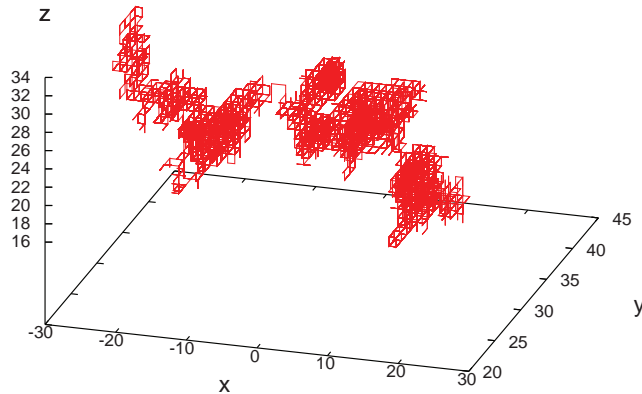
Figure 7: Typical trajectory of a tagged particle that is mobile. The total length of the trajectory is 10^7 MCS and the density is $\rho = 0.87$.

to the coarsening process in disordered media [36]. Note that at short t the typical distance between the blobs increases with ρ and the growth of the blobs slows down with increasing ρ, since it needs the presence of active sites (which are rare at high density). This is the reason why the increase of $n_{\text{act}}(t)$ at intermediate times becomes very slow with increasing ρ. We also observe that at $\rho = 0.89$, which is higher than the density of $\rho_c = 0.881$ at which an apparent divergence of relaxation timescales was observed [24], $n_{act}(t)$ is still an increasing function, suggesting that the system will eventually relax, in agreement with the prediction from Refs. [28, 29].

Having characterized the volume of the mobile regions, we now can investigate their shape. This can, e.g., be done by calculating the distribution of the cluster size and see how this distribution depends on time. For this we define two active sites to be in the same cluster, if they can be connected to each other by a sequence of active sites that are nearest neighbors. In Fig. 9 we show $P(s,t)$, the probability that at time t a cluster has exactly size s, for the density $\rho = 0.88$ and different times. For short times the active sites are distributed randomly in the system and hence the resulting clusters may or may not touch each other (thus forming a larger cluster). As a result the cluster size distribution is given by an exponential. With increasing time the probability to find a large cluster increases and hence $P(s,t)$ develops a tail at large s. We find that for intermediate and large times the distribution at small and intermediate s can be described well by a power-law, $P(s,t) \propto s^{-\nu}$ with an exponent $\nu \approx 1.6$, which shows that on this time and length scales the structure
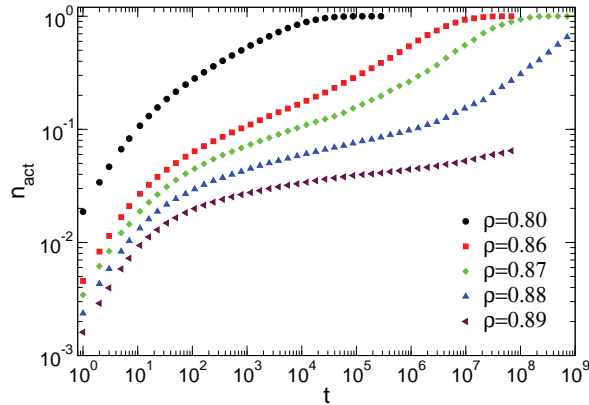
343

Figure 8: Total number of active sites divided by L^3 as a function of time for different densities.

has a fractal shape. Although Fig. 9 shows that for large s the distribution becomes flat, we think that this is an artifact due to the finite lattice. Finally we mention that for very large times the distribution shows a peak at $s \approx L^3$, since the whole system has relaxed and thus all sites belong to the mobile region.

We have argued above that, at any given time interval $[0, t]$ (with t shorter than the $\alpha-$relaxation time), most of the particles are not moving at all, some are making a localized ratting motion, and very few move larger distances. In order to quantify this different behavior we have determined the self part of the van Hove function $G_s(r, t)$ which is defined as [9]

$$G_s(r,t) = \frac{1}{N} \sum_{i=1}^{N} \langle \delta(r - |\mathbf{r}_i(t) - \mathbf{r}_i(0)|) \rangle \quad . \tag{4}$$

Thus $G_s(r, t)$ is the probability that a particle has moved within a time span t a distance r. In Fig. 10 we show the $r-$dependence of $G_s(r, t)$ for different times t. The density is $\rho = 0.87$. From this figure we recognize that for short and intermediate times $G_s(r, t)$ has a high peak at small values of r, i.e. most of the particles have moved not at all or only a small distance since they are totally blocked or just rattling around. In addition to these blocked particles, $G_s(r, t)$ shows a tail at large r, i.e. some of the particles can move a significant distance away from the position they occupied at $t = 0$. For example for $t = 10^7$ we find particles that have covered distances that are as large as 50, i.e. they have crossed the whole system! Thus this is further evidence that the relaxation dynamics of the system is extremely heterogeneous with most of the particles blocked and a few particles highly mobile.

Also remarkable is the fact that the tail in $G_s(r, t)$ at large r seen in Fig. 10 is basically a straight line, i.e. $G_s(r, t)$ is an exponential. Note that for a diffusive
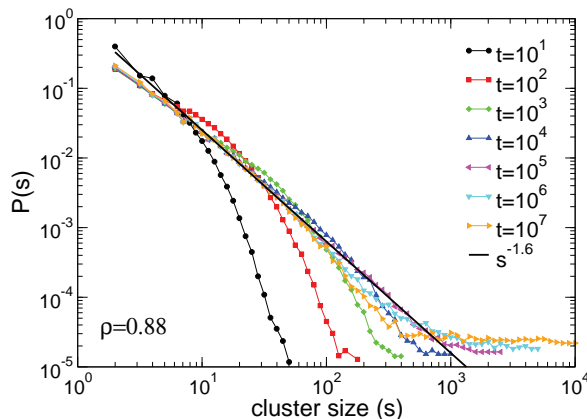
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Figure 9: Probability that a cluster has exactly size s for different times t. The density is $\rho = 0.88$. The straight line shows a power-law with exponent -1.6.

process, one expects the distribution to be a gaussian, i.e. in Fig. 10 one would see an inverted parabola. Instead we recognize from that figure that the gaussian behavior is recovered only at very long times, $t \geq 5 \cdot 10^8 \mathrm{MCS}$, whereas for shorter times we see the mentioned exponential tail, the origin of which will be discussed in the next section. Hence we can conclude that the relaxation dynamics of this system shows only a gaussian dynamics on time scales that are larger than the $\alpha-$relaxation time, which at this density is around $1.7 \cdot 10^7 \mathrm{MCS}$. The reason for this non-gaussian behavior is the presence of the above mentioned blob/channel-like structure that makes that the dynamics is very heterogeneous, i.e. very different from a gaussian process.

4 Continuous Time Random Walks and Glassy Dynamics

In the previous section we have seen that the motion of the mobile particles is very different from the one expected for a particle that makes a random diffusion. In this section we will present a simple model, the continuous time random walk (CTRW) [37, 38], that allows to give a good description of this non-diffusive dynamics [39] (see also [40, 41, 42, 43, 44]).

In order to keep the discussion as general as possible, we will in the following not restrict ourselves to lattice models, but consider an off-lattice glass-former. Experiments, computer simulations, and analytical studies show that the cage effect, discussed in the context of Fig. 2, i.e. the temporary trapping, is observed in all glass-formers that show a slow dynamics [7] and thus is a very generic feature. Therefore it is possible to make the following rough description of the motion of a
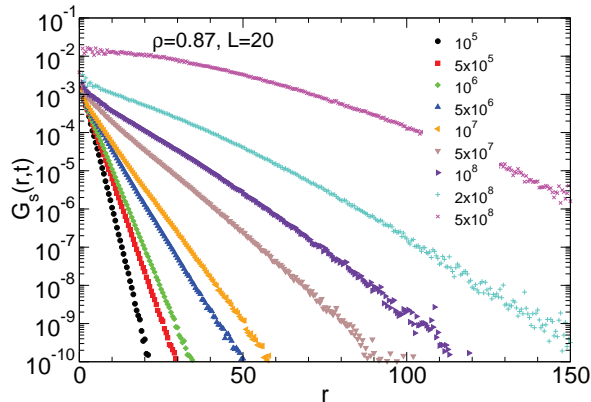
Figure 10: Self part of the van Hove function for different times t. The density is $\rho = 0.87$ and the $\alpha-$relaxation time is around $1.8 \cdot 10^7 \text{MCS}$.

tagged particle: Let us start the observation of the particle at $t = 0$. Typically the particle will be caged by its nearest neighbors and hence make an oscillatory motion around its local equilibrium position. Since the local potential can be approximated by a quadratic form, the deviation from the local equilibrium position is just a gaussian with a width ℓ. We now assume that at a (random) time t_1 the particle jumps out of its cage by making a displacement of size Δ and subsequently starts to oscillate around a new local minimum. These oscillations will typically last for a time t_2, before the particle makes a new jump, again of typical distance Δ, and so on.

Thus this dynamics can be characterized by the distribution of the displacement of the particle within the time t_1, the distribution of the time t_1, the distribution of the jump length Δ, and the distribution of the time t_2. As mentioned above, the distribution for the displacement of the particle inside the cage is approximated well by a gaussian: $f_{\text{vib}}(r) = (2\pi\ell^2)^{-3/2}\exp(-r^2/2\ell^2)$. It is found that the typical width of the cage is around 10% of the distance between neighboring particles, i.e. ℓ will be significantly smaller than an interparticle distance. For the sake of simplicity we will assume that also the distribution of the jump length is given by a gaussian: $f_{\text{jump}}(\Delta) = (2\pi d^2)^{-3/2}\exp(-\Delta^2/2d^2)$, with d being the length scale that characterizes the jump length.

Regarding the distributions ϕ_1 and ϕ_2 for t_1 and t_2, respectively, nothing precise can be said for a system that shows a relaxation dynamics that is as complex as the one of a glass-former. Therefore we make the very simple assumption that these distributions are just exponentials: $\phi_k(t_k) = \tau_k^{-1}\exp(-t_k/\tau_k)$, with $k = 1, 2$. (Note that *a priori* the distributions ϕ_1 can in principle be calculated from ϕ_2. However, in order to keep things as simple as possible and in view of the approximations that we have already made, we consider these two distributions to be independent from
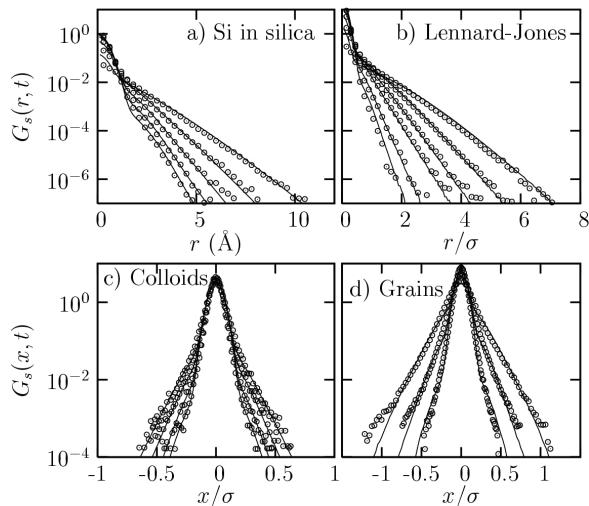
346

Figure 11: Self part of the van Hove function for different times and different systems. a) Silicon in a silica system. $T = 3000$ K and $t \in [27, 1650]$ps. b) Lennard-Jones particles at $T = 0.435$ and $t \in [7.5 \times 10^4, 4.1 \times 10^7]$. c) Colloidal hard spheres at a packing fraction $\phi = 0.517$ and $t \in [90, 1008]$s. d) A granular system at $\phi = 0.84$ and $t \in [10, 1000]$ cycles. a) and b) show the distribution of $|\vec{r}(t) - \vec{r}(0)|$, and c) and d) show the distribution of $x(t) - x(0)$.

each other.)

Equipped with the four distributions $f_{\text{vib}}(r)$, $f_{\text{jump}}(\Delta)$, $\phi_1(t_1)$, and $\phi_2(t_2)$ it is not difficult to calculate the self part of the van Hove function for the system [37] and one finds

$$G_s(r, t) = \sum_{n=0}^{\infty} p(n, t) f(n, r) \quad . \tag{5}$$

Here $p(n, t)$ is the probability that the particle makes, within the time t, exactly n jumps and $f(n, r)$ is the probability that it makes in n jumps a displacement r. For the hopping dynamics of our CTRW model it is not difficult to carry out the sum in Eq. (5) and, if one goes into the Fourier-Laplace domain, one finds

$$G_s(q, s) = f_{\text{vib}}(q)\Phi_1(s) + f(q)f_{\text{vib}}(q)\frac{\phi_1(s)\Phi_2(s)}{1 - \phi_2(s)f(q)} \quad , \tag{6}$$

where $\Phi_k := (1 - \phi_k(s))/s$ and $f(q) := f_{\text{vib}}(q)f_{\text{jump}}(q)$. (We mention that Eq. (6) is valid for any choice of distribution $(f_{\text{vib}}, f_{\text{jump}}, \phi_1, \phi_2)$, i.e. is not restricted to the exponential and gaussian distributions considered here.)

Using the four quantities ℓ, d, τ_1, and τ_2 as fit parameters, one can now test whether this simple model is indeed able to describe the time and space dependence of a measured $G_s(r,t)$. We emphasize that for a given system and temperature (or density) a given *fixed* choice of the four parameters must allow to fit the data for *all* r and t.

In Fig. 11 we show the self part of the van Hove function for different glass-forming systems. In panel a) we have the van Hove function of silica, *the* prototype of a network glass-forming system [21, 22, 45]. We see that at short and intermediate times $G_s(r,t)$ shows a gaussian peak at small r, i.e. most particles have not yet left the cage in which they where at $t = 0$. There are, however, particles that have moved already a distance that is significantly larger than $r \approx 2\text{Å}$ and thus form a tail in the distribution. This tail is basically a straight line, i.e. has the same exponential form of the tail found in the lattice gas system discussed above (see Fig. 10). With increasing time the height of the gaussian peak decreases and the width of the exponential tail increases. At even larger times this tail slowly transforms into an inverted parabola, i.e. the gaussian function expected for a diffusive process.

Also included in the graph are the fits using Eq. (6) and we see that these fits reproduce the data points very well for all times considered. Therefore we can conclude that this functional form is indeed able to give a qualitatively correct description of the trajectory. A similar conclusion is reached for a binary Lennard-Jones mixture which is a more fragile glass-former, panel b) with data from Ref. [46], a colloidal system which is basically a hard-sphere system, panel c) with data from Ref. [20], and the data for a the granular system show in panel d) (data from Ref. [47]). (Note that in panel c) and d) we show data from real experiments, which shows that Eq. (6) can also be applied to real systems.) From these graphs we thus can conclude that the CTRW is indeed able to give a reasonably good description of the van Hove function in a system showing glassy dynamics.

Last but not least we come back to the exponential tail seen at intermediate times in $G_s(r,t)$ [39, 48, 49]. In order to keep things simple, we will in the following consider only the case that there is no vibrational motion, i.e. $\ell = 0$, but as we will see below, the result can be easily extended to $\ell > 0$. In addition we will assume that $\tau_1 = \tau_2$. For this choice of parameters one finds immediately that

$$G_s(r,t) = G_0 + \frac{4\pi e^{-t/\tau_1}}{r} \int_0^\infty dq [e^{tf(q)/\tau_1} - 1] q \sin(qr) \quad , \tag{7}$$

where $G_0(r,t) \equiv \delta(r)\Phi_1(t)$. We now can expand the exponential term in the integrand into a power series, integrate each term, and convert the resulting sum into an integral. This gives

$$G_s(r,t) = G_0(r,t) + \frac{\pi e^{-t/\tau_1}}{4d^3} \int_1^\infty dn \frac{e^{-f(n)}}{n^2} \quad , \tag{8}$$

with $f(n) := n \ln n - n \ln(t/\tau_1) - n + r^2/(8d^2n)$. For large r, Eq. (8) can be evaluated

348

using a saddle point approximation and one obtains

$$G_s(r,t) \sim \frac{(\pi Y)^{3/2} e^{-t/\tau_1}}{(rd)^{3/2}\sqrt{1+Y^2}} e^{-r[Y-1/Y]/2d} \quad , \tag{9}$$

where Y is defined via the equation $Y^2 \exp(Y^2) = r^2/(2dt/\tau_1)^2$, i.e. $Y^2 \sim 2\ln(r^2/(2dt/\tau_1))$ if r is large. Thus we find that $G_s(r,t)$ has for large r indeed an exponential tail (with logarithmic corrections), as found in the simulation and experimental data (see Figs. 10 and 11). Note that, in order to obtain this result we have not made use of the fact that $G_s(r,t)$ is described well by a CTRW, i.e. the result on the exponential tail is much more general. In fact, the exponential tail is just the result of the fact that the probability that a particle has made exactly n jumps, with n significantly larger than the average number of jumps, decreases exponentially in n, leading to an exponential suppression of $G_s(r,t)$ at large distances, and Eq. (9) is just the formalization of this simple but hand-waving argument.

5   Conclusions

We have discussed some of the properties of glass-forming systems. In particular we have emphasized that these systems do not only show a strong dependence of their relaxation dynamics on external control parameters (temperature, density,...) but also have a dynamics that becomes strongly heterogeneous if the coupling increases. In order to study the nature of these dynamical heterogeneities in more detail, we have investigated the relaxation dynamics of a simple model for a glass-forming system. We have demonstrated that at high density this system does indeed show many features of realistic glass-formers, such as a very rapid increase of the $\alpha-$relaxation time upon increasing density, a breakdown of the Stokes-Einstein relation, etc., i.e. the system has qualitatively the same behavior as off-lattice systems that show dynamical heterogeneities. By studying the trajectories of the individual particles we can show that the relaxation of the system occurs on different levels: At short and intermediate times a small fraction of the particles form dynamical entities that move relatively quickly and explore the local environment. With increasing time these zones of local mobility expand and form a percolating cluster. At long times this cluster fattens until it invades the whole system. Similar results have also been found for other lattice systems [50, 51, 52] which shows that this relaxation behavior is not just a particularity of the present system, but more general feature of glass-forming systems.

Last but not least we have shown that the self part of the van Hove function of the present lattice model, as well as of other glass-forming systems, can be described very well by a continuous time random walk. For intermediate times this distribution shows an exponential tail in r, a feature which is due to rare events in the relaxation dynamics of glass-forming systems.

In summary we can conclude that the diffusive motion of glass-forming systems is very different from the one found in normal liquids or in crystals. Although

we have so far already identified quite a few unusual features (dynamical heterogeneities, breakdown of the Stokes-Einstein relation,...) one can expect that glassy systems have further unexpected features in their dynamics that we have not yet discovered. Hence the investigation of these systems remains highly interesting and a challenging task for the future.

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