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Dynamical phase transitions in glasses induced by the ruggedness of the free-energy landscape

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Abstract. We propose damage spreading (DS) as a tool for investigating the topological features related to the ruggedness of the free-energy landscape. We argue that DS measures the positiveness of the largest Lyapunov exponent associated with the basins of attraction visited by the system during its dynamical evolution. We discuss recent results obtained in the framework of mode-coupling theory and comment on possible extensions to the study of realistic glasses. Preliminary results are presented for purely repulsive soft-sphere glasses.

1. Introduction

The theoretical understanding of a first-principles theory for the glass transition is still lacking. Despite the great advances in the understanding of some generic features associated with the glass transition (such as those predicted by the mode-coupling theory), some questions still remain largely unanswered. Going beyond the schematic mode-coupling theory seems to be an enormous task, so an alternative way of looking at the glass transition may be useful. In this direction, the study of the topological properties of the potential or free-energy landscape may yield further information on the mechanisms responsible for the anomalous viscosity of the glassy phase.

The idea that topological aspects of the potential or free-energy landscape are the ultimate causes for the glass transition goes back to Goldstein [1] and (more recently) Stillinger and Weber [2, 3]. This approach has been recently applied to the study of hard spheres [4], monatomic as well as binary Lennard-Jones glasses [5] and mean-field models of glasses [6].

Here we propose an alternative dynamical approach for studying the topological properties of the potential energy landscape. We will concentrate on the study of the stable local properties of the configurations visited by the system during its dynamical evolution. This is directly achieved through the study of how dynamical trajectories, which evolve following the same stochastic noise, depart from each other in the presence of a potential energy saddle point or a maximum which may induce a negative Lyapunov exponent. The simplest way to study this problem is through damage-spreading (DS) techniques, to be described later on in some detail. Although DS was introduced almost two decades ago as an alternative way to consider thermodynamic phase transitions, the initial enthusiasm for this problem was substantially dissipated when it was realized that DS transitions are not universal and not necessarily related to thermodynamic singularities.

Despite this result, here we will show that these transitions have added interest in that they may be used as a direct way to investigate the local free-energy landscape properties

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by measuring the largest Lyapunov exponent associated with the Hamming distance (to be defined later). In what follows I will explain in more detail why DS is a good way of looking at the rugged properties of the potential energy landscape. Later on I will discuss the analytical results obtained for the schematic mode-coupling theory and finally discuss how to extend these ideas to the study of real glasses. Some preliminary results are shown for the case of binary soft-sphere purely repulsive glasses.

2. Why damage spreading?

Consider two systems evolving under a Langevin dynamics, each one described by a set of N variables x_i, y_i $(1 \leqslant i \leqslant N)$ evolving in a potential energy landscape $\mathcal{V}$ under the same stochastic noise η_t with $\langle \eta_i(t)\eta_j(s)\rangle = 2T\delta_{ij}\delta(t-s)$. Although the present discussion can be generalized for different stochastic noises, here we will concentrate on the simplest case (for a more detailed discussion see [7]). The equations of motion read

$$\dot{x}_i(t) = F_i(\{x\}) + \eta_i(t) \tag{1}$$

$$\dot{y}_i(t) = F_i(\{y\}) + \eta_i(t) \tag{2}$$

where $F_i(\{x\}) = -\partial\mathcal{V}/\partial x_i$. Note that the two trajectories described by the systems x and y never cross in phase space, so two identical configurations such that $x_i(t) = y_i(t)$ remain identical forever (and were identical in the past). The equation for the difference variables $z_i = x_i - y_i$ reads

$$\dot{z}_i(t) = F_i(\{x_i\}) - F_i(\{y_i\}). \tag{3}$$

If the z_i are small we can expand (3) around $z_i = 0$, obtaining

$$\dot{z}_i(t) = \sum_j \frac{\partial F_i(\{y\})}{\partial y_j} z_j = -\sum_j \frac{\partial^2 V(\{y\})}{\partial y_i\, \partial y_j} z_j \tag{4}$$

which may be written in a simplified form:

$$\dot{z}_i = H_{ij}(\{y\})z_j \tag{5}$$

where H_{ij} is the Hessian matrix evaluated at the configuration y. Always within the linear approximation, the dynamical evolution of the distance between configurations z_i will increase or decrease according to whether the spectrum of eigenvalues of the Hessian matrix contains positive eigenvalues. In this sense, DS probes the spectrum of eigenvalues of the matrix and shows instabilities whenever the matrix develops positive eigenvalues. A more precise condition is given by the maximum Lyapunov exponent defined through

$$\lambda_{max} = \lim_{t\to\infty} \frac{\log(D(t))}{t} \tag{6}$$

where

$$D(t) = \frac{1}{N}\sum_i z_i^2$$

which should be positive whenever $z_i = 0$ is dynamically unstable. Note that the Hessian depends on time through the time evolution of the generic configuration y. This may be an equilibrium or an off-equilibrium configuration. So in principle the maximum Lyapunov exponent depends on time through the time evolution of the systems x and y. We will see later that, in general, the types of initial condition (as well as the initial distance) are not relevant parameters for the DS transition. In this sense DS probes the temperature at which the lowest accessible configurations in the potential energy landscape develop unstable modes,

which is a direct check of the corrugated properties of the free-energy landscape. Again, we must stress the non-universality of the properties of the DS dynamics. The present discussion on the stability properties of the Hessian matrix and its connection with the DS transition is valid in the framework of Langevin dynamics. For other types of dynamics (such as Monte Carlo or Glauber dynamics) the situation may be different and the physical meaning of DS phenomena more difficult to establish. In some sense, Langevin dynamics is an appropriate tool for exploring the topological properties of the potential energy landscape.

3. DS in mode-coupling theory

Insight into the previous problem can be obtained through a careful study of the DS equations in the case of ideal mode-coupling theory. It has been known since the seminal work by Kirkpatrick, Thirumalai and Wolynes [8] that mode-coupling equations can be obtained in the framework of exactly solvable p-spin glass models. Due to their mean-field character, in this class of models it is possible to unambiguously define concepts such as the configurational entropy or complexity and the mode-coupling transition temperature T_c. The description of this type of model is possible in the framework of the TAP analysis [9] where it is possible to show that they contain a large number of metastable states (becoming exponentially large with N) as well as a threshold energy where the system gets trapped in an aging state and the fluctuation-dissipation theorem is violated in a peculiar way [10].

Spherical p-spin models (compared to Ising-spin models) have the clear advantage of being exactly solvable, so it is convenient to perform analytical computations in that case. The potential energy in this model is defined by

$$\mathcal{V} = -\sum_{(i_1<i_2<\cdots<i_p)} J_{i_1,i_2,i_3,\ldots,i_p}\sigma_{i_1}\sigma_{i_2}\sigma_{i_3}\cdots\sigma_{i_p} \tag{7}$$

where the spins σ_i are real valued spins which satisfy the spherical constraint $\sum_{i=1}^{N}\sigma_i^2 = N$. The $J_{i_1,i_2,i_3,\ldots,i_p}$ are quenched random variables with zero mean and variance $p!/(2N^{p-1})$. The Langevin dynamics of the model is given by

$$\frac{\partial\sigma_i}{\partial t} = F_i(\{\sigma\}) - \mu\sigma_i + \eta_i \tag{8}$$

where μ is a Lagrange multiplier which ensures that the spherical constraint is satisfied at all times and the noise η satisfies the fluctuation-dissipation relation $\langle\eta_i(t)\eta_j(s)\rangle = 2T\delta(t-s)\delta_{ij}$ where $\langle\cdots\rangle$ denotes the noise average. F_i is the force acting on the spin σ_i due to the interaction with the rest of the spins:

$$F_i = -\frac{\partial V}{\partial s_i} = \frac{1}{(p-1)!}\sum_{(i_2,i_3,\ldots,i_p)} J_{i_1,i_2,\ldots,i_p}\sigma_{i_2}\sigma_{i_3}\cdots\sigma_{i_p}. \tag{9}$$

We define the overlap between two configurations of the spins σ, τ by the relation

$$Q = \frac{1}{N}\sum_{i=1}^{N}\sigma_i\tau_i$$

so the distance between these two configurations is

$$D = \frac{1-Q}{2} \tag{10}$$

in such a way that identical configurations have zero distance and opposite configurations have maximal distance $D = 1$. Then we consider two copies of the system $\{\sigma_i, \tau_i\}$ which evolve under equation (8) with the same statistical noise and start from random initial configurations.

The final equations are [7]

$$\frac{\partial C(t,s)}{\partial t} + \mu(t)C(t,s) = \frac{p}{2}\int_0^s \mathrm{d}u\ R(s,u)C^{p-1}(t,u) + \frac{p(p-1)}{2}\int_0^t \mathrm{d}u\ R(t,u)C(s,u)C^{p-2}(t,u) \tag{11}$$

$$\frac{\partial R(t,s)}{\partial t} + \mu(t)R(t,s) = \delta(t-s) + \frac{p(p-1)}{2}\int_s^t \mathrm{d}u\ R(t,u)R(u,s)C^{p-2}(t,u) \tag{12}$$

$$\frac{\partial Q(t,s)}{\partial t} + \mu(t)Q(t,s) = \frac{p}{2}\int_0^s \mathrm{d}u\ R(s,u)Q^{p-1}(t,u) + \frac{p(p-1)}{2}\int_0^t \mathrm{d}u\ R(t,u)Q(u,s)C^{p-2}(t,u). \tag{13}$$

The dynamical equations involve the two-times correlation, response and overlap functions $C(t,s)$, $R(t,s)$, $Q(t,s)$ defined by (in what follows we take $t > s$)

$$C(t,s) = (1/N)\sum_{i=1}^N \langle \sigma_i(t)\sigma_i(s)\rangle = (1/N)\sum_{i=1}^N \langle \tau_i(t)\tau_i(s)\rangle \tag{14}$$

$$R(t,s) = (1/N)\sum_{i=1}^N \frac{\partial\langle\sigma_i\rangle}{\partial h_i^\sigma} = (1/N)\sum_{i=1}^N \frac{\partial\langle\tau_i\rangle}{\partial h_i^\tau} \tag{15}$$

$$Q(t,s) = (1/N)\sum_{i=1}^N \langle \sigma_i(t)\tau_i(s)\rangle \tag{16}$$

where $\langle\cdots\rangle$ denotes the average over dynamical histories and h_i^σ, h_i^τ are fields coupled to the spins σ_i, τ_i respectively. These equations are complemented with the appropriate boundary conditions $C(t,t) = 1$, $Q_d(t) = Q(t,t)$, $R(s,t) = 0$, $\lim_{t\to(s)^+} R(t,s) = 1$ and the relations

$$\mu(t) = T + \frac{p^2}{2}\int_0^t \mathrm{d}u\ R(t,u)C^{p-1}(t,u) \tag{17}$$

$$\frac{1}{2}\frac{\partial Q_d(t)}{\partial t} + \mu(t)Q_d(t) = T + \frac{p}{2}\int_0^t \mathrm{d}u\ R(t,u)Q^{p-1}(t,u) + \frac{p(p-1)}{2}\int_0^t \mathrm{d}u\ R(t,u)Q(t,u)C^{p-2}(t,u). \tag{18}$$

These equations can be analysed in detail using different methods. Here we summarize the main results obtained [7]:

- *Existence of a dynamical transition T_0.* There is a temperature T_0 such that $D(t) = 0$ (or $Q_d(t) = 1$; see equation (10)) is a stable fixed point for $T > T_0$, becoming unstable below T_0. Because of the non-monotonic character of $D(t)$ it is very difficult to derive T_0 analytically. Nevertheless, it is possible to obtain an upper and a lower bound. One gets

$$\sqrt{\frac{p-2}{2}} \leqslant T_0 \leqslant \sqrt{\frac{p}{2}}. \tag{19}$$

Direct numerical integration of the equations of motion yields $T_0(p = 3) = 1.04 \pm 0.02$ (see figure 1) and $T_0(p = 4) = 1.13 \pm 0.02$. The value of T_0 is well above the mode-coupling temperature T_c and the TAP temperature T_{TAP} below which the number of metastable states is exponentially large (with the system size).

- *Independence of initial conditions.* The asymptotic damage

$$D(\infty) = \lim_{t\to\infty} \lim_{N\to\infty} D(t)$$

is independent of the value of the initial damage $D(0)$ or the class of initial conditions (for instance, random or thermalized; see figure 2). This independence underlines the fact that DS is a true dynamical transition and the asymptotic damage $D(\infty)$ is a dynamical order parameter.

- *T_0 is the lowest DS temperature.* The DS problem can be suitably generalized to the case of correlated noises such that $\langle \eta_i(t)\xi_j(s)\rangle = 2T\mathcal{K}(Q(t,s))\delta(t-s)\delta_{ij}$ where η and ξ are the noises acting on the systems σ and τ respectively. The function $\mathcal{K}$ satisfies $\mathcal{K}(1) = 1$ so the two noises are identical if the two configurations coincide. This implies that $Q_d(t) = 1$ is a fixed point of the dynamics. It can be shown that for any possible function $\mathcal{K} \leqslant 1$ (with $\mathcal{K}(1) = 1$) there is a finite-temperature damage-spreading transition T_0 only if $\mathcal{K}'(1) \leqslant 1$. The case discussed previously of $\mathcal{K} = 1$ (identical noises at all times) yields the lowest damage-spreading transition temperature.
- *T_0 is the end-point of a dynamical critical line.* The DS problem can be also generalized to the case of $\mathcal{K}(Q) \leqslant \lambda$ with $\lambda \leqslant 1$ and $\mathcal{K}(1) = \lambda$. Obviously for $\lambda = 1$, the dynamical trajectories of the two systems may cross. In this case it is possible to show that the function $\mathcal{K}(Q) = \lambda$ yields the lowest DS transition temperature $T_0(\lambda)$ among the set of possible functions $\mathcal{K}$ ($\mathcal{K}(Q) \leqslant \lambda, \mathcal{K}(1) = \lambda$). $T_0(\lambda)$ is a monotonically increasing function of λ which for $\lambda = 0$ coincides with the mode-coupling transition temperature T_c and finishes

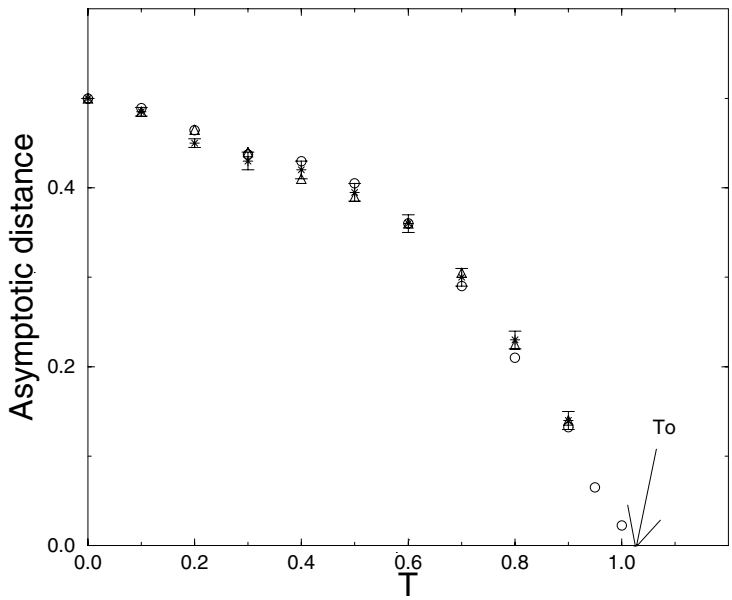

Figure 1. The asymptotic distance D_∞ for $p = 3$ ($\mathcal{K} = 1$) obtained from the Padé analysis of the series expansions for different initial conditions $D_0 = 1$ (circles), $D_0 = 0.5$ (triangles), $D_0 = 0.25$ (stars). Typical error bars are shown for the last case.

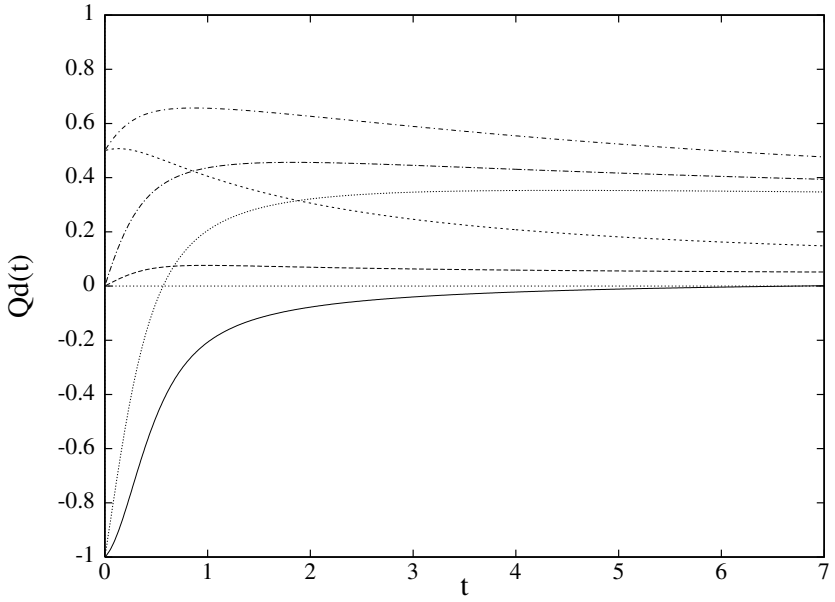

Figure 2. $Q_d(t)$ for $p = 3$ ($\mathcal{K} = 1$) at temperatures $T = 0.1, 0.5$ (from bottom to top at large times) for three different values of the initial overlap $Q_d(0) = -1, 0, 0.5$ as a function of time. The continuous lines are the numerical integrations with time step $\Delta t = 0.01$.

at a critical end-point $T_0(\lambda = 1) = T_0$. So there exists a line of dynamic critical points which connect the mode-coupling temperature T_c with the DS temperature T_0.

- *T_0 is not universal.* The temperature T_0 is not universal. As it depends on the set of correlations of the noises it also depends on the type of dynamics (molecular dynamics, Monte Carlo with Metropolis, heat bath or Glauber). This is a well known result which finds its natural explanation in the physical origin of the DS transition. For a general dynamics it is not possible to map the DS transition onto the local properties of the potential energy landscape. Only for the case of Langevin dynamics or molecular dynamics is this possible. Other dynamics (such as Monte Carlo with heat-bath dynamics) use random numbers in the dynamics which introduce complex correlations between the noises. This yields a DS transition (related to the $T_0(\lambda)$ discussed in the previous paragraph for the Langevin case) which is probably related to the mode-coupling transition temperature, but this issue still needs further investigation.

4. Application to binary soft-sphere glasses

In this section we apply the previous ideas derived in the framework of mode-coupling theory to the case of structural glasses. We consider the binary soft-sphere model introduced in [11] and recently studied in [12]. For the sake of simplicity we consider a gas of N particles such that half of them have diameter σ_1 and the other half have diameter σ_2. The particles interact through a two-particle purely repulsive potential, the energy of the system being defined by

$$\mathcal{V} = \sum_{i<j} \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12}. \tag{20}$$

The choice $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ supposes that diameters are additive during the collision process. The advantage of this potential is that the thermodynamic properties depend on the density $\rho = N/V$ and the temperature T only through the constant $\Gamma = \rho/T^{1/4}$. For the particular case of $\sigma_1/\sigma_2 = 1.2$, crystallization is strongly inhibited and the glass transition (where the dynamics is strongly slowed down) appears in the vicinity of $\Gamma = 1.45$. Larger values of Γ correspond to the glass phase while lower values correspond to the liquid phase. The Langevin dynamics for the soft-sphere model is defined by

$$\dot{\vec{r}}_i = -\sum_{j\neq i}^{N} \vec{\nabla}_i V_{ij}(r_{ij}) + \vec{\eta}_i \tag{21}$$

with $\langle \eta_i^k(t)\eta_j^l(t')\rangle = 2T\delta_{ij}\delta_{kl}\delta(t-t')$ where the superscripts of the noise indicate the different Cartesian components of the vector noise $\vec{\eta}(t)$. The pairwise potential is given by $V_{ij}(r) = (\sigma_{ij}/r)^{12}$.

We now consider two systems described by the variables $\vec{r}_i, \vec{s}_i$ governed by (21) and evolving under the same realization of the noise. We define the Euclidean distance

$$D(t) = \frac{1}{N}\sum_{i=1}^{N}(\vec{r}_i - \vec{s}_i)^2 \tag{22}$$

which vanishes if the two configurations coincide. If we want to extend the previous ideas for the spherical p-spin model to this system, we must now take into account the fact that at very high temperatures a gas diffuses, so $D = 0$ may not be a fixed point of the dynamics. There are two strategies for dealing with this problem which are discussed below.

- *Particles contained in a box.* This is the most natural choice. To simulate a purely repulsive system one must confine the particles in a cubic box of side L such that $\rho = N/L^3$. In this case one may solve (20) numerically with two different classes of boundary conditions. With periodic boundary conditions particles leave one side of the box and enter the opposite side. This completely resets the coordinates of the particle, so the distance (22) is discontinuous if particles cross the boundaries. For one-system quantities (such as the energy or the pair correlation function) this is not a problem because the relevant quantity is the distance between the particles which may be taken as the minimum value between r_{ij} and $L - r_{ij}$. A similar procedure can be used to define the distance between the two copies. Everything can be easily solved by considering free boundary conditions, because particles are not allowed to cross the boundaries. In this case, it is possible to show that $D = 0$ is asymptotically stable for the purely diffusive case ($\Gamma = 0$).

  Preliminary results show that the DS transition temperature $T_0 = \infty$, so two configurations never coincide at finite temperature. Still both configurations retain some correlation (so $\langle \vec{r}_i(t) \cdot \vec{s}_i(t)\rangle > 0$) and the asymptotic damage is a non-trivial function of the temperature.
- *Introducing a spherical constraint.* For the purposes of studying the local properties of the potential energy landscape, we may impose the global constraint

  $$\sum_i \vec{r}_i^{\,2} = N\left(\frac{N}{\rho}\right)^{2/3}$$

  on the particles in such a way that the average distance between the particles is finite when N goes to infinity. Because the spherical constraint shifts the Hessian matrix (5) by a constant (a Lagrange multiplier), the transition with the spherical constraint may give information on the transition for the unconstrained case. That Lagrange multiplier can be simply obtained from the potential energy $\langle \mathcal{V}\rangle$ and the temperature. The advantage of

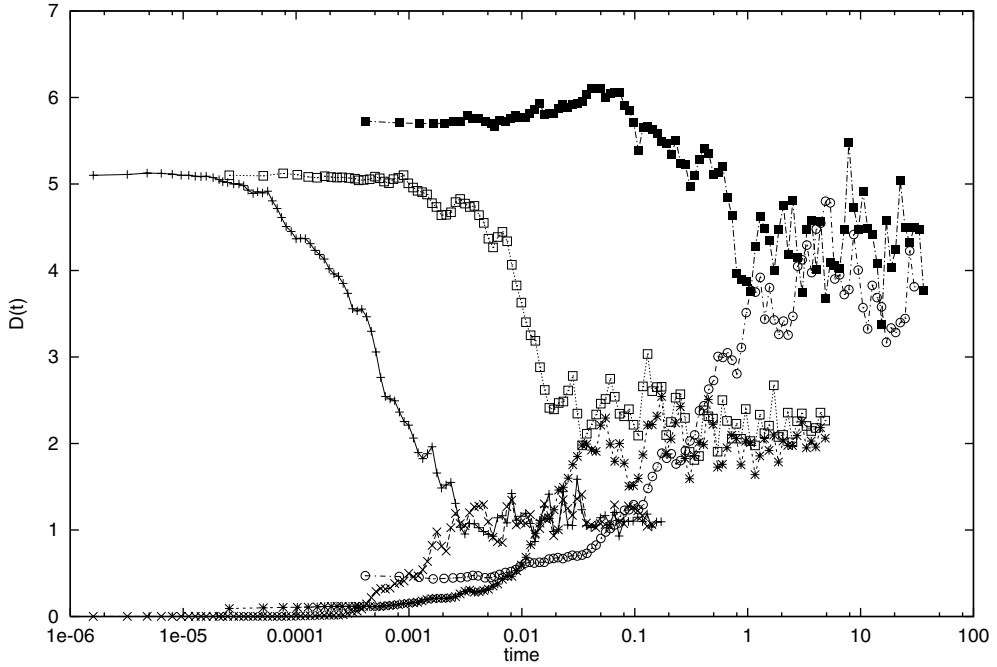

Figure 3. Damage $D(t)$ as a function of time for $N = 32$ starting from two different initial conditions and three different temperatures (from top to bottom) $\Gamma = 0.8, 0.4, 0.2$

such a constraint is that now there is no box and $D = 0$ is a fixed point of the dynamics for $\Gamma = 0$. The drawback is that the simplicity of the original model is lost and the thermodynamics of the new model depends on both density and temperature instead of a unique parameter Γ.

Again, preliminary results show that $T_0 = \infty$ in this case, so $D = 0$ is asymptotically stable strictly only for $\Gamma = 0$. Although this approach is more involved, it is probably the best way to relate the DS transition to the ruggedness of the free-energy landscape.

5. Conclusions

The study of the free-energy landscape may yield valuable information on the glass transition phenomena. A promising description of the glass transition is through the Stillinger and Weber projection of the partition function in terms on inherent structures. That method directly looks at the potential energy landscape described in terms of basins of attraction explored by the system during its dynamical evolution [6]. An alternative approach studies the dynamical properties of the free-energy landscape directly looking at the largest Lyapunov exponent of the Hessian matrix of the potential energy landscape weighted by the size of the basins of attraction visited by the system during its dynamical evolution.

Exact results for the mode-coupling theory reveal that there is a transition T_0 which separates two well defined regimes depending on the value of the asymptotic distance. Below T_0 the asymptotic damage is non-zero and independent of the initial distance as well as the class of initial conditions. Above T_0 the damage vanishes. We argue that the precise value of T_0 is related to the vanishing of the largest Lyapunov exponent defined in (6). Although such an explicit connection still needs to be proved it is quite probable that DS constitutes

a precise tool for investigating the chaotic properties of the free-energy landscape. A result along these lines has been recently obtained by Biroli through the study of the instantaneous normal-modes spectra of the p-spin model [13]. Whether this transition has experimental relevance in the study of real glasses is still an open question. Our preliminary studies of soft-sphere binary mixtures show that T_0 is extremely large. Because liquids are always diffusive at large temperatures (a feature which is directly encoded in the wave-vector dependence of correlation functions, a general feature of liquids) one must be careful when extending the results obtained for the spherical p-spin model to real structural models of glasses. Although a better understanding of the extension of DS to diffusive systems is needed we can point out other interesting open problems. On one hand it could be very interesting to analyse the DS transition for molecular dynamics. In that case, there is no stochasticity in the dynamical equations so the *effective* source of noise comes out directly from the mixing property of the dynamics. The analogue of equation (5) should be very similar except for the presence of oscillations. Still the general argument would be the same and T_0 would be expected to be identical. Such an analysis would be welcome. Finally it would be very interesting to look at the other end-point of the dynamic critical line. Our present discussion was centred on the case of identical noises. For completely uncorrelated noises the dynamical transition temperature is expected to coincide with the mode-coupling transition temperature. This is true in the framework of the aforementioned exact calculations in the spherical model and could also be analysed for real glasses.

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