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 to investigate 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 to 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 how to extend them to the study of realistic glasses. Preliminary results are presented for purely repulsive soft-sphere glasses.

PACS numbers: 64.70.Pf, 75.10.Nr, 61.20.Gy, 82.20.Wt
Introduction

The theoretical understanding of a first principles theory for the glass transition is still missing. Despite of great advances in the understanding of some generic features associated to the glass transition (such as those predicted by the mode-coupling theory) still some questions remain largely unknown. 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 both 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 reason 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], monoatomic as well as binary Lennard-Jones glasses [5] or mean-field models of glasses [6].

Here we propose an alternative dynamical approach to study the topological properties of the potential energy landscape. We will concentrate on the study of the stability 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 describe 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 on this problem strongly decayed when it was realized that DS transitions are not universal and not necessarily related to thermodynamic singularities.

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

1. Why damage spreading?

Consider two systems evolving under a Langevin dynamics each one described by a set of $N$ variables $x_i, y_i; 1 \leq i \leq N$ evolving in a potential energy landscape $\mathcal{V}$ under the same stochastic noise $\eta_i$ 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 [6]). The equations of motion read,

\[ \dot{x}_i(t) = F_i(x) + \eta_i(t) \] (1)

\[ \dot{y}_i(t) = F_i(y) + \eta_i(t) \] (2)
where \( F_i(\{x\}) = -\frac{\partial V}{\partial x_i} \). Note that both 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 where 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 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,

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

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 type 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 being a direct check of the corrugated properties of the free energy landscape. Again, we must insist on the non-universal 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 type of dynamics (such as Monte Carlo dynamics or Glauber) the situation may be different and the physical meaning of DS phenomena more difficult. In some sense, Langevin dynamics is an appropriate tool to explore the topological properties of the potential energy landscape.

### 2. DS in mode-coupling theory

Insight on the previous problem can be obtained through a careful study of the DS equations in the case of ideal mode-coupling theory. It is known since the seminal work by Kirkpatrick, Thirumalai and Wolyness \[8\] 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.
Dynamical phase transitions in glasses induced by the ruggedness of the free energy landscape

The potential energy in this model is defined by,

$$\mathcal{V} = - \sum_{i_1 < i_2 < \ldots < i_p} J_{i_1, i_2, \ldots, i_p} \sigma_{i_1} \sigma_{i_2} \sigma_{i_3} \ldots \sigma_{i_p}$$  \hspace{1cm} (7)

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

$$\frac{\partial \sigma_i}{\partial t} = F_i(\{ \sigma \}) - \mu \sigma_i + \eta_i$$  \hspace{1cm} (8)

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

$$F_i = -\frac{\partial \mathcal{V}}{\partial \sigma_i} = \frac{1}{(p - 1)!} \sum_{(i_2, i_3, \ldots, i_p)} J_{i_1, i_2, \ldots, i_p} \sigma_{i_2} \sigma_{i_3} \ldots \sigma_{i_p}$$  \hspace{1cm} (9)

We define the overlap between two configurations of the spins $\sigma, \tau$ by the relation $Q = \frac{1}{N} \sum_{i=1}^{N} \sigma_i \tau_i$ so a distance between these two configurations is,

$$D = \frac{1 - Q}{2}$$  \hspace{1cm} (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 [3],

$$\frac{\partial C(t, s)}{\partial t} + \mu(t) C(t, s) = \frac{p}{2} \int_{0}^{s} dsR(s, u)C^{p-1}(t, u) + \frac{p(p - 1)}{2} \int_{0}^{t} duR(t, u)C(s, u)C^{p-2}(t, u)$$  \hspace{1cm} (11)

$$\frac{\partial R(t, s)}{\partial t} + \mu(t) R(t, s) = \delta(t - s) + \frac{p(p - 1)}{2} \int_{0}^{t} duR(t, u)R(u, s)C^{p-2}(t, u)$$  \hspace{1cm} (12)

$$\frac{\partial Q(t, s)}{\partial t} + \mu(t) Q(t, s) = \frac{p}{2} \int_{0}^{s} dsR(s, u)Q^{p-1}(t, u) + \frac{p(p - 1)}{2} \int_{0}^{t} duR(t, u)Q(u, s)C^{p-2}(t, u)$$  \hspace{1cm} (13)

The dynamical equations involve the two times correlation, response and overlap function $C(t, s), R(t, s), Q(t, s)$ defined by (in what follows we take $t > s$),
Dynamical phase transitions in glasses induced by the ruggedness of the free energy landscape

\[ C(t, s) = \frac{1}{N} \sum_{i=1}^{N} \langle \sigma_i(t) \sigma_i(s) \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle \tau_i(t) \tau_i(s) \rangle \]  
(14)

\[ R(t, s) = \frac{1}{N} \sum_{i=1}^{N} \frac{\partial (\sigma_i)}{\partial h_i} = \frac{1}{N} \sum_{i=1}^{N} \frac{\partial (\tau_i)}{\partial h_i} \]  
(15)

\[ Q(t, s) = \frac{1}{N} \sum_{i=1}^{N} \langle \sigma_i(t) \tau_i(s) \rangle \]  
(16)

where \( \langle \ldots \rangle \) denotes the average over dynamical histories and \( h_i^\sigma, h_i^\tau \) are fields coupled to the spins \( \sigma_i, \tau_i \) 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,

\[ \mu(t) = T + \frac{p^2}{2} \int_0^t du R(t, u) C^{p-1}(t, u) \]  
(17)

\[ \frac{1}{2} \frac{\partial Q_d(t)}{\partial t} + \mu(t) Q_d(t) = T + \frac{p}{2} \int_0^t du R(t, u) Q^{p-1}(t, u) \]
\[ + \frac{p(p-1)}{2} \int_0^t du R(t, u) Q(t, u) C^{p-2}(t, u) \]  
(18)

These equations can be analyzed 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 eq. (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 analytically \( T_0 \). Nevertheless, it is possible to obtain an upper and a lower bound. One gets,

\[ \sqrt{\frac{p-2}{2}} \leq T_0 \leq \sqrt{\frac{p}{2}} \]  
(19)

Direct numerical integration of the equations of motion yields \( T_0(p = 3) = 1.04 \pm 0.02 \) with 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 there is an exponentially large (with the system size) number of metastable states.

- Independence of initial conditions
  The asymptotic damage \( D(\infty) = \lim_{t \to \infty} \lim_{N \to \infty} D(t) \) is independent on the value of the initial damage \( D(0) \) or the class of initial conditions (for instance, random or thermalized). This independence stresses 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 for the case of correlated noises such that \( \langle \eta_i(t) \xi_j(s) \rangle = 2TK(Q(t, s)) \delta(t-s) \delta_{ij} \) where \( \eta \) and \( \xi \) are the noises acting on the systems \( \sigma \) and \( \tau \) respectively. The function \( K \) satisfies \( K(1) = 1 \) so both noises are identical if the two configurations coincide. This implies that \( Q_d(t) = 1 \)
Dynamical phase transitions in glasses induced by the ruggedness of the free energy landscape

Figure 1. Asymptotic distance $D_\infty$ for $p = 3$ ($\alpha = 1, K = 1$) 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 $p = 3$ ($\alpha = 1, K = 1$) 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 $\Delta t = 0.01$.

is a fixed point of the dynamics. It can be shown that for any possible function $K \leq 1$ (with $K(1) = 1$) there is a finite temperature damage spreading transition $T_0$ only if $K'(1) \leq 1$. The case discussed previously $K = 1$ (identical noises at all times) yields the lowest damage spreading transition temperature.

- $T_0$ is the endpoint of a dynamical critical line
Dynamical phase transitions in glasses induced by the ruggedness of the free energy landscape

The DS problem can be also generalized to the case $K(Q) \leq \lambda$ with $\lambda \leq 1$ and $K(1) = \lambda$. Obviously for $\lambda = 1$ dynamical trajectories of both systems may cross. In this case it is possible to show that the function $K(Q) = \lambda$ yields the lowest DS transition temperature $T_0(\lambda)$ among the set of possible functions $K(K(Q) \leq \lambda, K(1) = \lambda)$. $T_0(\lambda)$ is a monotonic increasing function function of $\lambda$ which for $\lambda = 0$ coincides with the mode-coupling transition temperature $T_c$ and finishes in a critical endpoint $T_0(\lambda = 1) = T_0$. 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 on the physical origin of the DS transition. For a general dynamics it is not possible to map the DS transition with the local properties of the potential energy landscape. Only for the case of Langevin dynamics or molecular dynamics this is 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 with the mode-coupling transition temperature but this issue still needs to be further investigated.

3. 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-spheres model introduced in [11] and recently studied in [12]. For sake of simplicity we consider a gas of $N$ particles such that half of them have diameter $\sigma_1$ and the other half $\sigma_2$. The particles interact through a two particle purely repulsive potential, the energy of the system being defined by

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

The choice $\sigma_{ij} = \frac{\sigma_1 + \sigma_2}{2}$ 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 $\Gamma = \rho/T^4$. For the particular case $\frac{\sigma_1}{\sigma_2} = 1.2$ crystallization is strongly inhibited and the glass transition (where dynamics is strongly slowed down) appears in the vicinity of $\Gamma = 1.45$. Larger values of $\Gamma$ correspond to the glass phase while lower values correspond to the liquid phase. The Langevin dynamics for the soft-sphere model is defined by,

$$\dot{\mathbf{r}}_i = -\sum_{j \neq i} N_i V_{ij}(r_{ij}) + \mathbf{\eta}_i \tag{21}$$

with $\langle \mathbf{\eta}_i(t) \mathbf{\eta}_j(t') \rangle = 2T \delta_{ij} \delta_{tt'}$ where the superindex in the noise indicate the different Cartesian components of the vector noise $\mathbf{\eta}(t)$. The pairwise potential is given by $V_{ij}(r) = \left( \frac{\sigma_{ij}}{r} \right)^{12}$. 


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

$$D(t) = \frac{1}{N} \sum_{i=1}^{N} (\vec{r}_i - \vec{s}_i)^2$$  \hspace{1cm} (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 now we must 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 to deal 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 $\rho = \frac{N}{L^3}$. In this case one may numerically solve (21) with two different class of boundary conditions. With periodic boundary conditions particles leave one side of the box and enter the opposite side. This resets completely the coordinates of the particle so the distance (22) is discontinuous if particles cross the boundaries. Concerning 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 considering free boundary conditions so 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 $\langle \vec{r}_i(t) \vec{s}_i(t) \rangle > 0$) and the asymptotic damage is a non trivial function of the temperature.

- **Introducing an spherical constraint**
  For the purpose of studying the local properties of the potential energy landscape we may impose the global constraint $\sum_i r_i^2 = N(\frac{N}{\rho})^2$ 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 (3) 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 $<V>$ and the temperature. The advantage of such a constraint is that now there is no box and $D = 0$ is a fixed point of the dynamics for $\Gamma = 0$. The inconvenience 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 $\Gamma$.

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

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) $\Gamma = 0.8, 0.4, 0.2$

4. 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. 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 regime 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 needs still to be done it is quite probable that DS is a precise tool to investigate the chaotic properties of the free energy landscape. A result in this direction has been recently obtained by Biroli through the study of the instantaneous normal modes spectra of the $p$-spin model. 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. One the one hand it could be very interesting to analyze 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 analog of equation (3) should be very similar except for the presence of oscillations. Still the general argument would be the same and $T_0$ expected to be identical. Such an analysis would be welcome. Finally it would be very interesting to look at the other endpoint of the dynamic critical line. Our present discussion was centered 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 be also analyzed for real glasses.

Acknowledgments

I warmly thank G. Biroli, A. Crisanti, S. Franz, M. Heerema, J. Kurchan and I. Pagonabarraga for useful discussions. This work has been supported by the Spanish Ministry of Education (PB97-0971).

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