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On the approach to the equilibrium and the equilibrium properties of a glass-forming model

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Abstract. In this paper we apply some theoretical predictions that arise in the mean-field framework for a large class of infinite-range models to structural glasses and we present a first comparison of these predictions with numerical results.

We find evidence for the energy density relaxation at low temperatures consisting of two steps: the convergence to some metastable state with a mean-field-like behaviour and the decay of metastable states by activated processes. We define an appropriate distance d between states and we study the corresponding equilibrium distribution $P(d)$ that results in being highly nontrivial in the glassy phase.

1. Introduction

In recent years some theoretical progress in our understanding of glasses [1] has been achieved by comparing the results obtained for soluble models of generalized spin glasses [2, 3] with structural glass properties, under the assumption that the phase space of the two systems is similar. This progress is partly due to the use of the replica method and of related concepts such as replica symmetry breaking, coupled replicas, dynamic transitions etc.

In a nutshell many of the ideas of this replica approach are already present in the original papers of Gibbs and Di Marzio [4]. However, the use of the whole panoply of tools developed in the study of spin-glass models allows us to put these ideas into a much sharper form and to test them in numerical (and possibly real) experiments. Moreover the comparison of structural glasses and generalized spin glasses, introduced in [5], has proven extremely useful and the conjecture that the two models have similar energy landscapes has been a fruitful starting point.

In this paper we will not discuss the theoretical basis under which this scenario has been derived but we will concentrate our attention on the physical picture and on the consequences of these predictions on the statistical properties of relatively small samples.

The basic assumption is that, at sufficiently low temperatures but still in the liquid phase, the system is almost always trapped for a long time in one of the exponentially large number of local minima of the free energy. The number ($\mathcal{N}$) of these local minima is related to the configurational entropy or complexity Σ by

$$\mathcal{N} \approx \exp(N\Sigma(T)) \tag{1}$$

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N being the number of particles and formula (1) being asymptotic for large N. The total entropy density S is the sum of two contributions: the entropy density of each minimum and the complexity. This description is valid for $T_K < T < T_D$. The complexity [6] (which starts from a nonzero value at T_D) is supposed to vanish linearly at a lower temperature, (i.e. at the temperature T_K) where the height of the typical barriers becomes infinite. The correlation time diverges at T_K, and one can argue in favour of a Vogel–Fulcher law (e.g. $\tau \propto \exp(-A(T-T_K)^{-\nu})$, where $\nu \simeq 1$).

This scenario is implemented in a large class of infinite-range models [5], where a more detailed picture of the phase space of the system is obtained. Indeed these infinite-range models are soluble because the appropriate mean-field theory is exact. The study of the mean-field theory for these models is not a trivial task: the phase-space structure of the configurations with low energy is quite complex and this shows up in a rather interesting behaviour of the system, both at equilibrium and in its approach to equilibrium. The existence of these complex structures implies the need for modern tools (such as the replica formalism) to study the properties of these systems.

The aim of this paper is to spell out some of the theoretical predictions that are obtained in the mean-field framework for these infinite-range models, to apply them (with the appropriate modifications) to the case of structural glasses and to present a first comparison of these predictions with numerical simulations.

2. A mini theoretical review

The main hypothesis of the Gibbs–Di Marzio's approach is that at low temperatures the system nearly always stays close to a minimum of the free energy and that the long-time dynamics is dominated by the time needed to escape from one valley to another.

As noted in [5] this scenario is implemented in long-range models in which detailed computations can be done and a more precise picture can be obtained [7, 8].

Let us consider, for definiteness, a spin model where the local variables are spins ($\sigma(i)$, $i = 1 \ldots N$). They could be either Ising spins $\sigma(i) = \pm 1$ or spherical spins, i.e. real variables which satisfy the constraint

$$\frac{\sum_{i=1}^{N} \sigma(i)^2}{N} = 1. \qquad (2)$$

The Hamiltonian $H(\sigma)$ has a form that we do not need to specify here. There are many different models with quite different Hamiltonians which share the properties that we are going to describe. In the following we will consider a *finite* large system and only at the end will we send the value of N to ∞.

We suppose that the phase space can be broken into many valleys separated by high mountains. In other words, the free energy (or the energy at low temperature) has many minima and the free-energy barrier [9] which we have to cross to go from one state to another is quite large. In the infinite-range approximation it will be proportional to N. We can consider all the local minima of the energy as functions of the configuration and we can associate a valley to each of them at zero temperature. At higher temperatures we have to consider the minima of the free energy and when increasing the temperature the valleys will disappear.

We could also define the valleys in a dynamical way as regions of configuration space in which the system remains trapped for a long time. This definition is similar to the previous one if we assume that the long time behaviour of the dynamics at low temperature is dominated by activated processes which correspond to the crossing of high free-energy barriers.

Each valley (which we label by α) may be characterized by a magnetization

$$m_\alpha(i) = \langle \sigma(i) \rangle_\alpha \tag{3}$$

where $\langle \cdot \rangle_\alpha$ is the statistical expectation value restricted to the α-valley. One can define a free energy $F[m]$, which is a function of all the local magnetizations, whose functional form depends on the system. The valleys are local minima of this free energy.

2.1. Equilibrium properties

One finds in a very large class of models the following behaviour for the equilibrium properties depending on the temperature [6–12].

• For temperatures higher than T_m there is only one minimum of the free energy $F[m]$ at $m(i) = 0 \forall i$. In this case the total free energy of the system $\mathcal{F}$ is given by $\mathcal{F} = F[0]$.

• At temperatures lower than T_m there is an exponentially large number of minima. The contribution of these minima to the partition function can be estimated by

$$Z_m = \int \mathrm{d}f \ \exp(-N\beta f + N\Sigma(f, \beta)) \approx \exp(-N\beta f^* + N\Sigma(f^*, \beta)) \tag{4}$$

where f is the free-energy density ($Nf = \mathcal{F}$), $\exp(N\Sigma(f, \beta))$ is the number of minima of the free energy density f and f^* is the value of f which maximizes the exponent, that is a function of β.

Below T_m we can distinguish three regions.

• For $T > T_D$ the contribution to the partition function of the nontrivial minima can be neglected and the free energy is still given by $F[0]$.

• For $T_D > T > T_K$ the contribution to the partition function of the nontrivial minima is dominant. The number of minima which dominate the partition function is exponentially large and the total entropy of the system is given by

$$\mathcal{S} = S_m + N\Sigma(f^*, \beta) \tag{5}$$

where S_m is the contribution to the total entropy of one minimum and $\Sigma(f^*, \beta) > 0$.

The magnetization averaged over all the minima is given by $m(i) = \langle \sigma(i) \rangle = \sum_\alpha w_\alpha \langle \sigma(i) \rangle_\alpha$, where $w_\alpha \propto \exp(-\beta F_\alpha)$ is proportional to the contribution of the α-minimum to the partition function ($\sum_\alpha w_\alpha = 1$).

In this region the magnetization averaged over all the minima is zero and the total free energy which is dominated by the contribution of all the nontrivial minima is still given by $F[0]$. The free energy and all the other static equilibrium quantities are fully regular at T_D.

• For $T < T_K$, $\Sigma(f^*, \beta) = 0$. For T slightly larger than T_K one finds $\Sigma(f^*, \beta) \propto (T - T_K)$, so that the complexity (and consequently the entropy) has a discontinuity in the temperature derivative at $T = T_K$, which is the transition point from a thermodynamic point of view. Here the entropy becomes equal to the contribution of a single minimum and this temperature may be identified with the Kauzmann temperature.

The region $T < T_K$ can be characterized by a peculiar behaviour. The partition function is dominated by those states which have the minimum free energy and there are some minima for which the quantities w_α remain of order 1.

In the previous description we have neglected the possibility of crystallization, i.e. the formation of a highly ordered state which leads to a first-order transition. If we consider this possibility we have to distinguish two cases, systems with quenched disorder in the Hamiltonian and systems without disorder (often with a translation-invariant Hamiltonian).

• There are systems whose Hamiltonian contains quenched disorder. A typical example would be

$$H = \sum_{i,k,l} J(i,k,l)\sigma(i)\sigma(k)\sigma(l) \tag{6}$$

where the variables J are random (e.g. Gaussian).

Another example (in which the mean-field approximation is nonexact) would be a system in which the particles interact not only with themselves but also with an external, fixed, random potential. It is clear that if the external potential is strong enough, the free energy of the crystal phase may become quite large, while that of the glassy phase may be much less affected.

• Other systems may not contain quenched variables in the Hamiltonian. A typical example [13] is

$$H = \sum_{i=1}^{N} \left[\sum_{k=1}^{N} \frac{1}{\sqrt{N}} \sin\left(\frac{2\pi \mathrm{i}k}{N}\right) \sigma(k) - \sigma(i) \right]^2 \qquad \text{with } \sigma(i) = \pm 1. \tag{7}$$

Another example would be a system in which the particles interact only with themselves with a given potential.

The two categories of models seem rather different one from another; however, it has been noticed that in the mean-field approximation systems belonging to the two categories behave in quite a similar way, the only difference being that systems without quenched disorder may crystallize.

While these kind of results can be proved in the long-range models, their validity for short-range models (such as structural glasses) remains an open question. In this paper we would like to present numerical evidence for the correctness of these ideas for structural glasses also. Before doing so we will examine in detail the predictions of the mean-field approach.

2.2. Equilibrium properties at low temperature

For simplicity let us consider the predictions that would follow from the application of the replica approach to a system of N particles interacting with a given Hamiltonian in a box.

We will consider for simplicity a system without any type of symmetry (the box is not symmetric and the particles interact with the walls, periodic boundary conditions are not used so that there is no translational invariance). We suppose that for a given value of N the Hamiltonian has many minima which we label by α.

The partition function can thus written as

$$\begin{aligned} Z(\beta, N) &\simeq \sum_{\alpha} \exp(-\beta F_\alpha(\beta, N)) \\ F_\alpha(\beta, N) &= E_{\alpha,N} - TS(\alpha, N) \end{aligned} \tag{8}$$

where for simplicity we label the configurations in increasing free-energy order. For small temperatures the entropic contribution to the free energy will be, as usual, negligible. It is quite evident that for a finite system the partition function is dominated by the lowest energy configurations in the limit of zero temperature, and we will suppose that this property persists in the infinite-volume limit.

For different values of N we will have quite different values of the free energies. The lowest free-energy states will have free-energy differences of order 1, so that by adding a single particle (i.e. going from N to $N+1$) we can strongly change the values of the $F_\alpha(\beta, N)$. If we label by F_0 the lowest free energy, we expect that the quantities

$F_\alpha(\beta, N) - F_0(\beta, N)$ remain of order 1 when N goes to infinity, but they do not go to any limit because they change with N. In this case it is natural to introduce a probability distribution for the differences in free energies, which tell us the probability of finding a given value of $F_\alpha(\beta, N) - F_0(\beta, N)$ if we choose randomly (albeit large) the value of N. In other words if the value of the free energy changes strongly with N it is convenient to introduce the probability distribution of their values.

The precise construction is the following: for any large value of N we introduce a reference free energy $F_R(\beta, N)$ such that, in the whole region $F - F_R(\beta, N) << N$, the probability of finding a minimum of free energy F is given by

$$P(F) = \exp(\beta(x(\beta)(F - F_R(\beta, N))) \tag{9}$$

where the quantity $x(\beta)$ parametrizes the probability distribution.

The condition that the free energy is approximately given by F_R implies that the integral

$$\int_{F_R(\beta,N)}^{\infty} P(F) \exp(-\beta(F - F_R(\beta, N)) \tag{10}$$

is convergent and therefore $x(\beta) \leqslant 1$.

The probability of finding a configuration in the minimum labelled by α is

$$w_\alpha \propto \exp(-\beta F_\alpha) \tag{11}$$

where the normalization condition

$$\sum_\alpha w_\alpha = 1 \tag{12}$$

is satisfied.

In many models x becomes equal to 1 at the temperature T_K. At low temperatures x is proportional to the temperature (it would be exactly proportional to the temperature if we neglected the entropic contribution).

An important property of the model is how different the various minima are. The simplest hypothesis is that they are as different as possible, i.e. the correlations among the particles in one minimum and in another minimum (among those of lowest energy) are zero. For example, the probability of finding two particles in two different minima at a given distance r does not depend on the distance:

$$P_{\alpha,\gamma}(r) = \sum_{i,k} \delta(x_\alpha(i) - x_\gamma(k) - r) = \rho^2. \tag{13}$$

This hypothesis is usually called one-step replica symmetry breaking. More complicated distributions of the distances are discussed in the literature.

If there are symmetries the situation becomes slightly more complex. For example in a translational-invariant system if $x(i)$ are the coordinates of a minimum, $x(i) + \delta$ are the coordinates of another minimum. It is therefore useful to consider all the minima which are related by a symmetry transformation as a single minimum.

2.3. The probability distribution of the distance

The properties of the system may be sharpened by introducing an appropriately defined distance d between configurations of particles and looking at the corresponding equilibrium probability distribution:

$$P_N(d) = \sum_{\alpha,\gamma} w_\alpha w_\gamma \delta(d - d_{\alpha\gamma}). \tag{14}$$

In the limit of large N we have that

$$P_N(d) = a_N\delta(d_0 - d) + b_N\delta(d_1 - d) \tag{15}$$

where $a_N + b_N = 1$. Of course for a finite system the delta function will be smoothed.

The function a_N represents the probability of finding two different configurations in the same minimum and it is given by

$$a_N = \sum_\alpha w_\alpha^2. \tag{16}$$

In the one-step replica symmetry breaking hypothesis two configurations that are not in the same minimum are expected to be orthogonal, i.e. at the maximum possible distance d_1. This happens with the probability

$$b_N = \sum_{\alpha\neq\gamma} w_\alpha w_\gamma. \tag{17}$$

The functions a_N and b_N are naturally dependent on the temperature. In the mean-field framework one finds that the weight of the δ-function in d_1, b_N, that is zero for $T \geqslant T_K$, increases continuously when lowering the temperature below the transition point.

The probability distribution $P_N(d)$ should therefore be an appropriate observable for looking at the transition from the high-T region (where $P_N(d)$ is Gaussian-like for a finite system) to the glassy phase in which it is expected to show a nontrivial behaviour, strongly depending on N.

2.4. *The approach to equilibrium*

For simplicity we will direct attention to the relaxation of the energy density when the system is quenched abruptly (at the time $t = 0$) from a random initial configuration (i.e. infinite cooling rate) to the final temperature.

In the mean-field picture [14] one finds two different relaxation behaviours, depending on the final temperature value.

- At high temperatures the energy reaches its equilibrium value exponentially, i.e. $e(t) = e_{\mathrm{eq}} + c\exp(-t/\tau)$. The relaxation time τ increases when lowering the temperature and it diverges for $T \rightarrow T_D$.
- Below the dynamical transition point T_D the energy behaves linearly as a function of $t^{-\alpha}$ [15], i.e. $e(t) = e_D + ct^{-\alpha}$, the exponent α being weakly depending on T. Here the system is evolving towards some metastable states (with an infinite lifetime) and correspondingly the asymptotic energy value e_D is higher than that of the equilibrium.

The infinite lifetime of metastable states is just an artefact of the mean-field approximation. In a real system we expect the approach to the equilibrium for $T < T_D$ consisting of two steps.

- The convergence to some metastable states with a mean-field-like behaviour.
- The slow decay of metastable states due to activated processes. In this second step the system reaches the true equilibrium state that will still be the replica-symmetric one for $T \geqslant T_K$.

This means that by looking at $e(t)$ it is in principle possible to find numerical evidence for the reminiscence in real glasses of the mean-field dynamical transition. Here T_D is expected to mark the onset of the two-steps relaxation.

3. The model

We study a binary mixture of soft spheres, half of the particles being of type A with radius σ_A and half of type B with radius σ_B. The Hamiltonian is

$$\mathcal{H}_{\text{pbc}} = \sum_{i<k=1}^{N} \left(\frac{\sigma(i) + \sigma(k)}{|\boldsymbol{r}_i - \boldsymbol{r}_k|} \right)^{12}. \tag{18}$$

This model has been carefully studied in the past [16–24]. It is known that the choice $\sigma_B/\sigma_A = 1.2$ strongly inhibits crystallization. We also follow the convention of considering particles with an average diameter of 1 by setting

$$\frac{(2\sigma_A)^3 + 2(\sigma_A + \sigma_B)^3 + (2\sigma_B)^3}{4} = 1. \tag{19}$$

Thermodynamic quantities only depend on $\Gamma \equiv \rho/T^{1/4}$, where $T = 1/\beta$ is the temperature and we have taken the density to be $\rho = 1$ ($\Gamma \equiv \beta^{1/4}$). The N particles move in a $3d$ cube of size $L = N^{(1/3)}$. The glass transition is known [17] to happen around $\Gamma_c = 1.45$.

In order to obtain numerical results on the equilibrium properties comparable with the mean-field theoretical picture we attempt to measure the equilibrium probability distribution $P(d)$ of the distance d between states. Following the usual strategy in spin-glass simulations we introduce two replicas of the system evolving contemporaneously and independently. $P(d)$ is then given by

$$P(d) \equiv \langle \delta(d - \mathcal{D}) \rangle \tag{20}$$

$\mathcal{D}$ being the appropriately defined distance between the configurations of the two replicas.

Labelling by $\{\boldsymbol{r}_i\}$, $\{\boldsymbol{s}_i\}$ the positions of the N particles in the two replicas, a natural definition of $\mathcal{D}$ is the Euclidean one, minimized over permutations π, rotations and reflections R and, when using periodic boundary conditions, translations T:

$$\mathcal{D}^2 \equiv \frac{1}{N} \min_{\pi,\mathrm{R},\mathrm{T}} \left(\sum_{\text{type A}} (\boldsymbol{r}_i - \boldsymbol{s}_{\pi(i)})^2 + \sum_{\text{type B}} (\boldsymbol{r}_i - \boldsymbol{s}_{\pi(i)})^2 \right). \tag{21}$$

An analogous definition of distance between configurations of particles has been considered in [25] and in [26], in studies of potential energy minima for Lennard-Jones systems.

We minimize over permutations by an approximate procedure. For each particle i of one configuration we take $\pi(i)$ being the nearest one of the other. We expect this to be a reasonable approximation in the considered temperature range (from $\Gamma = 1$ to $\Gamma = 2$) since the probability for two particles of the same system of being at a distance lower than $2\sigma \simeq 1$ is very close to zero at not too high temperatures (the radial density–density correlation function in a simple liquid shows the well known behaviour $g(r) \simeq 0$ for $r < 2\sigma$).

Minimization over rotations and reflections is easily performed since in the case of a $3d$ cube R results a discrete group that includes 48 symmetry operations, corresponding to the 2^3 reflections and to the 3! permutations of axes. On the other hand, minimization over the continuous group of translations is a hard task and we prefer to avoid it by not using periodic boundary conditions.

To measure $P(d)$ we consider a slightly modified model in which particles are definitely confined in the cubic box of size L by a soft walls-repulsive potential term:

$$\mathcal{H}_{\text{sw}} = \mathcal{H}_{\text{pbc}} + c_1 \sum_{i=1}^{N} \sum_{\mu=1}^{3} \left(\frac{1}{(c_2 + r_i{}^{\mu})^{10}} + \frac{1}{(L + c_2 - r_i{}^{\mu})^{10}} \right). \tag{22}$$

We have chosen the values $c_1 = \pi/5$ and $c_2 = 0.6$ that give a behaviour of the energy as a function of Γ quite near to that of the periodic boundary conditions case.

4. Numerical results on the dynamics

4.1. Algorithms

Both for finding the best numerical approach to the simulations of structural glasses at the equilibrium and for studying the dynamical properties of the model we have implemented different algorithms, considering stochastic and deterministic dynamics.

• Monte Carlo (MC). We start from a random configuration and we quench abruptly the system by putting it at the final temperature (i.e. infinite cooling rate). During one step each particle is suggested to move by a random quantity and a maximum shift permitted is chosen in order to obtain an acceptance ratio near 0.5.

• Molecular dynamics (MD). Using MD to start with a completely random spatial configuration may cause difficulties. Here the initial spatial configuration is obtained from a random one by 60 MC steps at the final temperature. At the beginning and again each 100 steps we extract momenta $\{\boldsymbol{p}_i\}$ according to the Boltzmann distribution (we have taken the masses of particles $m_A = m_B = 1$) and we impose the condition $\sum_{i=1}^N \boldsymbol{p}_i{}^2 = (3N - f_{\mathrm{MD}})T$, where f_{MD} is the number of frozen degrees of freedom. $f_{\mathrm{MD}} = 3$ when using periodic boundary conditions since the three components of the total linear momentum $\boldsymbol{P}$ are conserved (we have taken $\boldsymbol{P} = 0$), otherwise $f_{\mathrm{MD}} = 0$. We use the velocity-Verlet algorithm [27] with $\delta t = \frac{1}{250}$ (a value that we have checked to be reasonable in our case, e.g. the total energy results perfectly constant).

• Isothermal molecular dynamics (IMD). The system evolves according to the Gaussian isokinetic equations of motion [27]:

$$\dot{\boldsymbol{r}}_i = \boldsymbol{p}_i \qquad \dot{\boldsymbol{p}}_i = \boldsymbol{F}_i - \lambda \boldsymbol{p}_i \qquad \lambda = \frac{\sum_{i=1}^N \boldsymbol{F}_i \cdot \boldsymbol{p}_i}{\sum_i \boldsymbol{p}_i{}^2}. \tag{23}$$

At the beginning we extract momenta and we fix the constraint $\sum_{i=1}^N \boldsymbol{p}_i{}^2 = (3N - f_{\mathrm{IMD}})T$, where $f_{\mathrm{IMD}} = f_{\mathrm{MD}} + 1$. Also in this case we start from a spatial configuration obtained from a random one by 60 MC steps at the final temperature. We implement the algorithm by using a variant of the leap-frog scheme [27] again with $\delta t = \frac{1}{250}$.

• Parallel tempering (PT). Algorithms in which the temperature is allowed to become a dynamical variable [28] are very effective for thermalizing systems with a complex free-energy landscape. In this recently introduced [29] method a set of n different β values $\beta_1 < \cdots < \beta_k \ldots \beta_n$ is chosen *a priori* and n replicas of the system evolve contemporaneously. The extended Hamiltonian $\mathcal{H}_{\mathrm{PT}} = \sum_{a=1}^n \beta(a)\mathcal{H}[C_a]$ is defined and exchanges of temperatures between replicas

$$(\beta(a_1) = \beta_{k_1}, \beta(a_2) = \beta_{k_2}) \to (\beta(a_1) = \beta_{k_2}, \beta(a_2) = \beta_{k_1})$$

are allowed with probability $p = \min[1, \exp(-\Delta\mathcal{H}_{\mathrm{PT}})]$. The whole process is itself a Markov chain and, when equilibrium has been reached, each replica moves between different temperatures of the set remaining at the equilibrium. We start by extracting independently the n random initial configurations and we quench each replica at a different one of the chosen temperatures. In a PT step, sequentially for $a = 1 \ldots n$:

—replica a makes one MC step at its temperature $\beta(a) = \beta_k$;

—a random number $j = \pm 1$ with equal probability is extracted;

—for $1 \leqslant k + j \leqslant n$ the exchange of temperatures between replica a and replica b, where $\beta(b) = \beta_{k+j}$, is suggested and possibly accepted.

The set of β values should be chosen carefully. We find that for the numbers of particles considered (up to $N = 36$) PT works well down to $\Gamma = 2$ with $n = 13$ different temperatures ($\Gamma = 1, 1.05 \ldots 1.2, 1.3 \ldots 2$).

- We have implemented and tested a combined technique of PT and Isothermal molecular dynamics (IMDPT). The n initial spatial configurations are obtained from random ones by 60 MC steps at $\Gamma = 1$. After extracting momenta we impose the constraints $\sum_{i=1}^{N} (\boldsymbol{p}_i{}^a)^2 = (3N - f_{\mathrm{IMD}}) T_a$, $a = 1 \ldots n$ (we have taken the same set of temperatures as in PT). Replicas evolve accordingly to IMD and each 10 IMD steps the exchanges of temperatures happen with probability $p = \min[1, \exp(-\Delta \mathcal{H}_{\mathrm{PT}})]$, where in $\mathcal{H}_{\mathrm{PT}}$ only potential energies appear. Here to change temperature $T_{\mathrm{old}} \to T_{\mathrm{new}}$ means to transform momenta as $\boldsymbol{p}_i \to (T_{\mathrm{new}}/T_{\mathrm{old}})^{1/2} \boldsymbol{p}_i$, $i = 1 \ldots N$.
- Finally we have performed MC simulations of large systems (2000 and 8000 particles) in the periodic boundary conditions case, by putting a cut-off on the soft spheres' potential:

$$V_{ik} = \begin{cases} \left(\dfrac{\sigma(i) + \sigma(k)}{|\boldsymbol{r}_i - \boldsymbol{r}_k|} \right)^{12} & \text{for } |\boldsymbol{r}_i - \boldsymbol{r}_k| < R \\ \left(\dfrac{\sigma(i) + \sigma(k)}{R} \right)^{12} & \text{otherwise.} \end{cases} \tag{24}$$

The algorithm is then implemented in such a way that for each particle the map of those which are at distance lower than $R + 2\delta$ is recorded and updated during the run (δ being the maximum shift permitted to a particle in one MC step). We have chosen $R = 1.7$ that means a practically negligible $V_{ik}^0 \sim \mathrm{O}(10^{-3}) (V_{ik} \sim 1$ for $|\boldsymbol{r}_i - \boldsymbol{r}_k| \sim 2\sigma)$.

4.2. On the energy relaxation behaviour

We look at the (potential) energy density relaxation when the system is quenched abruptly from a random initial configuration to the final (low) temperature. We compare results obtained by different numerical methods for $N = 34$ particles and we extend the analysis to large systems ($N = 2000$ and $N = 8000$) in the MC case. Here periodic boundary conditions are used.

In figures 1–3 we present data obtained by MC, MD and IMD, respectively. Our results show no evident difference between stochastic and deterministic dynamics. Not only in the MC case, as already observed in previous simulations on the same model [22], but also when using MD techniques the energy density relaxation is well compatible on a large-time window with a linear behaviour as a function of $t^{-\alpha}$. We obtain a nonsmall exponent $\alpha \sim 0.8$, weakly Γ-dependent in the considered range (the dependence seems slightly more pronounced in the IMD case).

Moreover the energy values at a fixed temperature that one can estimate by asymptotically extrapolating the linear behaviours obtained by different methods are nearly the same. On the other hand we are going to show that these asymptotic values (apart from the case of $\Gamma = 1.4$) are not the real equilibrium energy values of the system.

We present in figures 4 and 5 PT and IMDPT data. There is a reminiscence of the linear behaviour but here the system moves between the high and the low temperatures of the set, this prevents it from becoming trapped. At the end of the (quite large) time window, equilibrium is nearly reached and the energy values are definitely smaller than those estimable by extrapolating simple MC or MD data. The difference is already detectable at

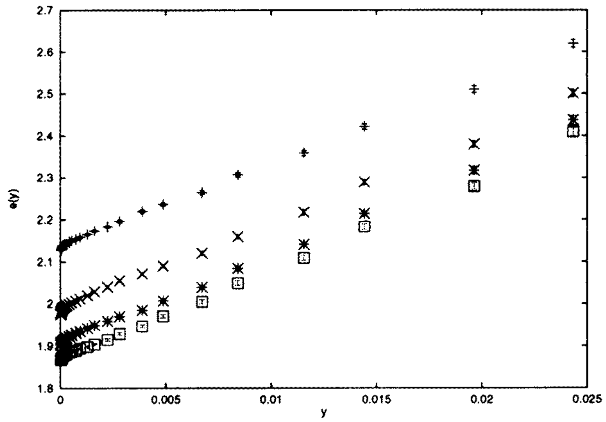

Figure 1. MC data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 1.4$ (+), 1.6 (×), 1.8 (∗) and 2.0 (□). Here 150 different initial conditions are considered.

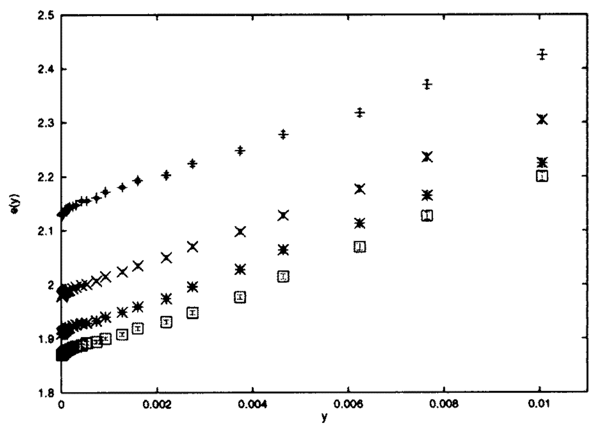

Figure 2. MD data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 1.4$ (+), 1.6 (×), 1.8 (∗) and 2.0 (□). Here 100 different initial conditions are considered. When using MD techniques the need for a not completely random initial configuration (i.e. the first 60 steps are MC steps) induces some short-time effects and the linear behaviour takes place at a slightly larger time than in the MC case.

$\Gamma = 1.6$ and it becomes more pronounced at lower temperatures. To further outline this result we plot in figure 6 data obtained by various methods at $\Gamma = 2.0$.

We have found numerical evidence for the energy relaxation at low temperatures consisting of two processes that happen on remarkably well-separated timescales. Both in the MC and in the MD data the first step is clearly observable, corresponding to the convergence to some metastable states with a mean-field-like behaviour (note that α is weakly dependent on the temperature over a large range). The fact that the extrapolated energy values are not the real equilibrium values gives evidence for the presence of a second step, the slow decay of metastable states dominated by activated processes.

These results are inadequate for understanding whether the curvature of low-temperature data on $e(y)$ at very large times (small $y = t^{-\alpha}$) is related to the quite small N value that we are considering or it actually represents the beginning of the second step (possibly with

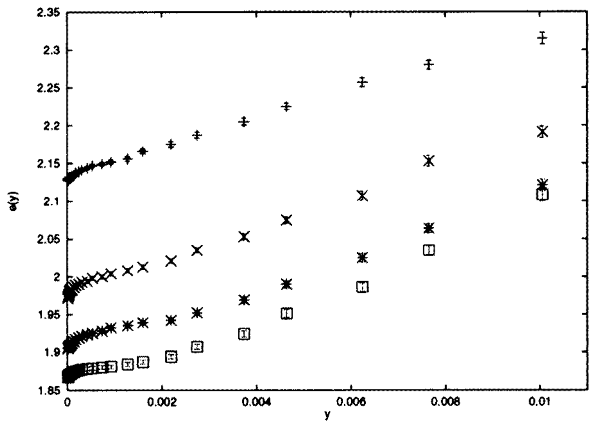

Figure 3. IMD data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 1.4$ (+), 1.6 (×), 1.8 (∗) and 2.0 (□). Here 100 different initial conditions are considered. The dependence of α on Γ seems slightly more pronounced in this case, our best estimates ranging from $\alpha \sim 0.8$ at $\Gamma = 1.4$ to $\alpha \sim 1.1$ at $\Gamma = 2.0$.

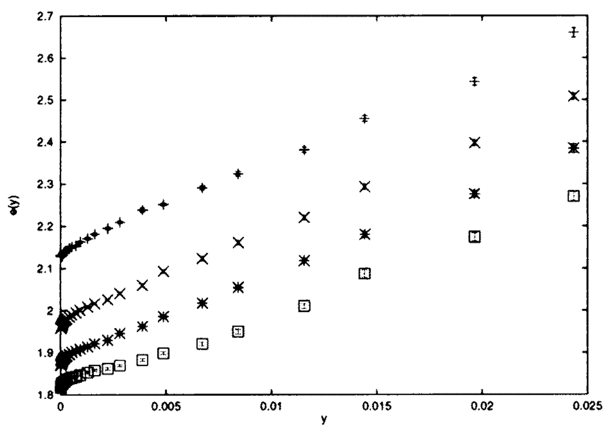

Figure 4. PT data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 1.4$ (+), 1.6 (×), 1.8 (∗) and 2.0 (□). Here 24 different initial conditions are considered. Note that in both this case and the IMDPT one, the obtained behaviour depends on the entire set of temperatures.

an intermediate *plateau*). In order to clarify this point we consider definitely larger systems.

We plot in figure 7 $e(y)$ as obtained by MC simulations for $N = 8000$ at $\Gamma = 1.4$, 1.5, 1.8 and 3.0. At $\Gamma = 1.8$ we also present data for $N = 2000$ the results of which are almost indistinguishable from the $N = 8000$ ones and remarkably similar to MC data for the significantly smaller $N = 34$ system. This means that we are actually looking both at the first relaxation step and at the beginning of the second one.

The different behaviours observed when varying the temperature agree well with the previously discussed theoretical picture.

• At $\Gamma = 1.4$ no two-steps behaviour is observable and the energy reaches the equilibrium value in the considered time window. The system still appears to be above T_D but quite near to it (the relaxation time τ seems to be very large and the expected exponential decay is not distinguishable from a linear behaviour as a function of y).

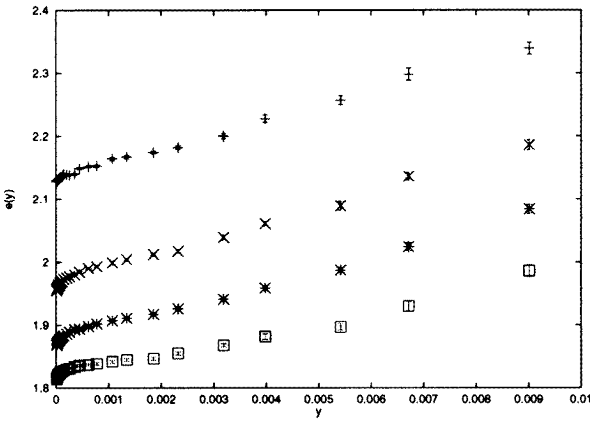

Figure 5. IMDPT data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 1.4$ (+), 1.6 (×), 1.8 (∗) and 2.0 (□). Here 24 different initial conditions are considered. Data are nearly compatible, within error, with the PT ones.

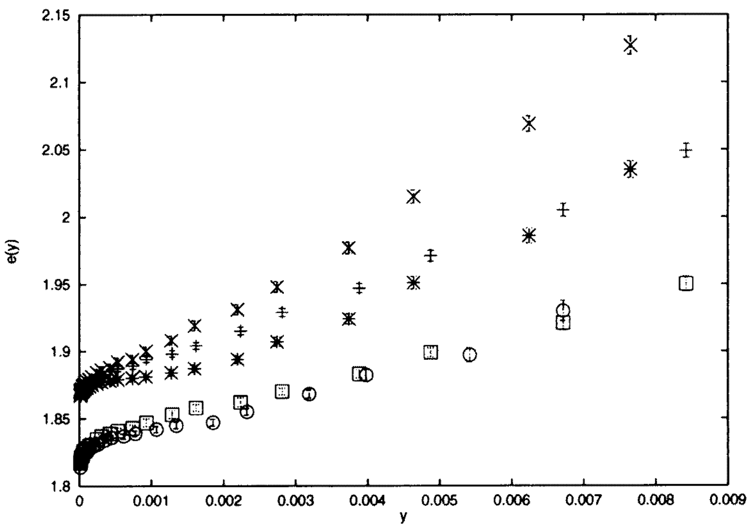

Figure 6. Data on e as a function of $y = t^{(-0.8)}$ at $\Gamma = 2.0$ obtained by MC (+), MD (×), IMD (∗), PT (□) and IMDPT (○).

• For $\Gamma \geqslant 1.5$ the system is definitely below T_D. The energy relaxes linearly as a function of y to a value e_D higher than that of equilibrium, the slow decay of metastable states happens on a much larger timescale.

• The beginning of the second step is clearly observable at $\Gamma = 1.5$ and still quite evident at $\Gamma = 1.8$ but disappears at $\Gamma = 3.0$. Here data behave linearly over the entire time window. This seems reasonable since the timescale that controls the second step (i.e. the onset of activated processes) is expected to increase when lowering the temperature.

To fit the two-steps behaviour is a difficult task. In figure 8 we show our best results at $\Gamma = 1.5$ and 1.8 ($N = 8000$), obtained by fixing $\alpha = -0.8$ and considering $e(t) = at^{(-0.8)} + bt^{\gamma} + c$ It is interesting to note that in both cases we obtain a positive γ value of the same order, $\gamma \sim +0.1$. It seems reasonable that the second step corresponds

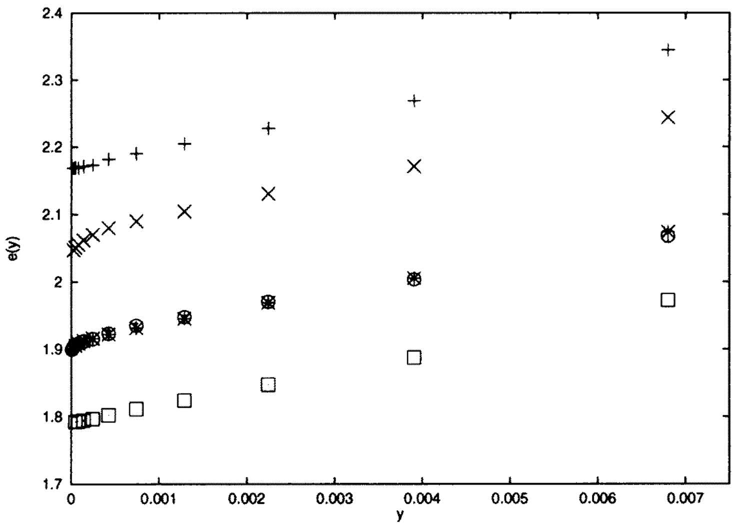

Figure 7. MC data on e as a function of $y = t^{(-0.8)}$ respectively for $N = 8000$ (one initial condition) at $\Gamma = 1.4$ (+), 1.5 (×), 1.8 (∗) and 3.0 (□) and for $N = 2000$ (two different initial conditions) at $\Gamma = 1.8$ (○).

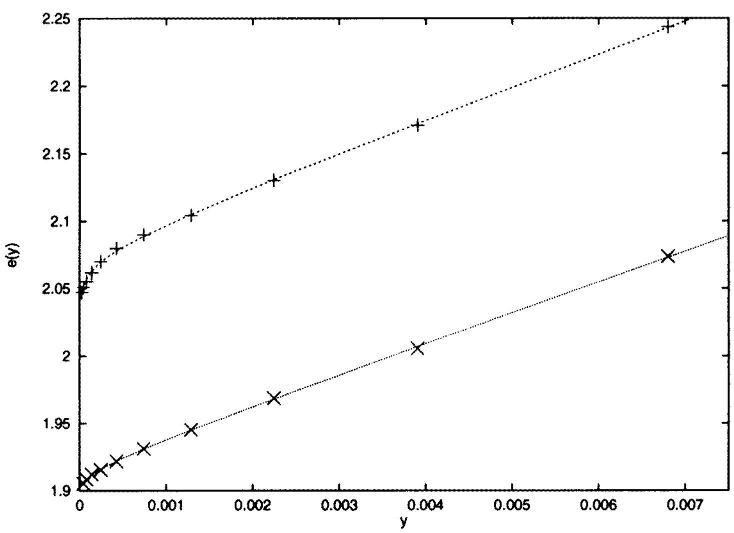

Figure 8. MC data on e as a function of $y = t^{(-0.8)}$ for $N = 8000$ at $\Gamma = 1.5$ (+) and 1.8 (×). The lines are the corresponding best fits to $e(t) = at^{(-0.8)} + bt^{\gamma} + c$ obtained by the plotted points.

to a streched exponential decay, i.e. $e(t) = a_1(t/\tau_1)^{-\alpha} + a_2 \exp(-C(t/\tau_2)^{+|\gamma|}) + e_{\text{eq}} \simeq at^{(-0.8)} - |b|t^{+|\gamma|} + e_{\text{plateau}}$ for $t \ll \tau_2$. However, we stress that this is a purely indicative result, since quite different γ values (possibly of the opposite sign) are obtainable by slightly varying α or the time window.

To conclude this section, we note that IMDPT works well but seems to be no more effective than usual PT. We have also performed some dynamical simulations with different methods in the case of the Hamiltonian (22). We do not show the results that are qualitatively similar to those obtained by using periodic boundary conditions, the only difference being that here the onset of the second step becomes evident at shorter times.

5. Numerical results on the statics

5.1. Simulations at the equilibrium

In order to obtain the equilibrium behaviour of $P(d)$ we use PT, simulating contemporaneously two independent sets of replicas. Thermalization is a hard task and we limit our analysis to quite small numbers of particles ranging from $N = 28$ to $N = 36$. For each N value we perform an extensive simulation of 2^{22}–2^{24} PT steps (i.e. up to more than 16 million MC steps for each one of the 26 replicas). We measure all the quantities we are interested in during the last $\frac{3}{4}$ of the run.

Thermalization is checked in different ways.

- We divide the last part of the run, in which statistics is collected, into 16 equal intervals and we look for possible shifts of the corresponding mean values (particularly we do not find evident changes in the behaviour of $P(d)$).
- We check that each replica moves more than once from an extrema of the temperature range to the other and back in the last part of the run.
- We valuate the specific heat c using both $c = \partial\langle e\rangle/\partial T$ and $T^2c = \langle e^2\rangle - \langle e\rangle^2$, checking for compatibility of the results.

Errors are estimated from the mean values obtained in each of the 16 intervals.

Despite our efforts it is not possible to exclude the presence of lower minima in the free energy landscape that are not accessible to the system on the considered time scale. To clarify this point it is interesting to look at the particular value $N = 32 = 4^3/2$. Here particles are allowed to fill all the sites of a fcc structure. Once this crystalline equilibrium state has been reached (in about 2^{24}–2^{25} PT steps) the system rests definitely trapped in it, the crystalline configuration corresponding to a 'golf-hole' shaped minimum in the free-energy landscape. The energy density results in a discontinuous function of Γ as expected for a first-order (liquid-crystal) transition.

It seems unlikely to us but particles could also be able to arrange themselves in some sort of crystalline configuration that we have not detected for $N \neq 32$. On the other hand we would like to look at the glass equilibrium states, apart from the possible presence of lower crystalline minima. We therefore find it reasonable to assume that on the timescale studied, the system extensively explores the entire phase-space region we are interested in.

5.2. On the behaviour of $P(d)$

Data on the energy density $e(\Gamma)$ for different N values are plotted in figure 9. Note that the equilibrium energy density is not a regular function of the number of particles since it is definitely smaller for $N = 34$ than for $N = 36$. The nontrivial N-dependence of the model at low temperatures is outlined when looking at the specific heat $c(\Gamma)$ (figure 10).

It should be stressed that for each given N value the energy appears a continuous function of Γ and correspondingly the behaviour of $c(\Gamma)$ looks quite smooth, this gives evidence that the physics phenomenon we are studying is not a crystallization process. Moreover, we never observed the system definitely trapped in a configuration as in the previously discussed $N = 32$ case.

In figure 11 we plot data on $P(d)$ for different N values at the highest temperature considered ($\Gamma = 1$). The shape is Gaussian-like, characteristic of the liquid phase and it

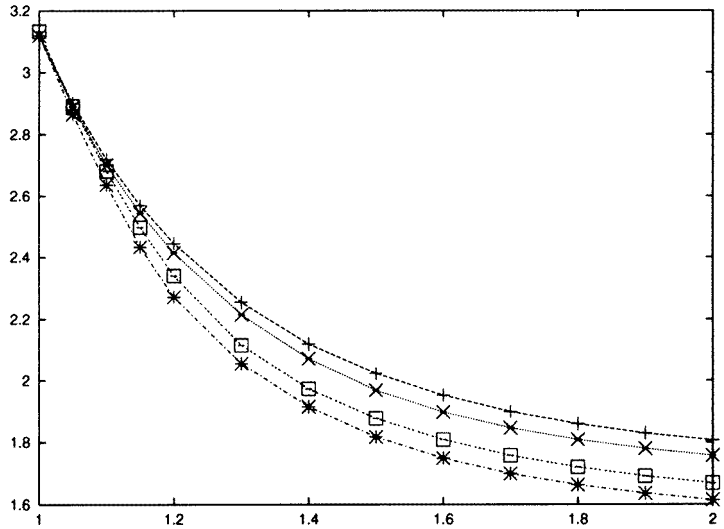

Figure 9. Data on the energy density e as a function of Γ for $N = 28$ (+), 30 (×), 34 (∗) and 36 (□). Lines are only to join neighbouring points.

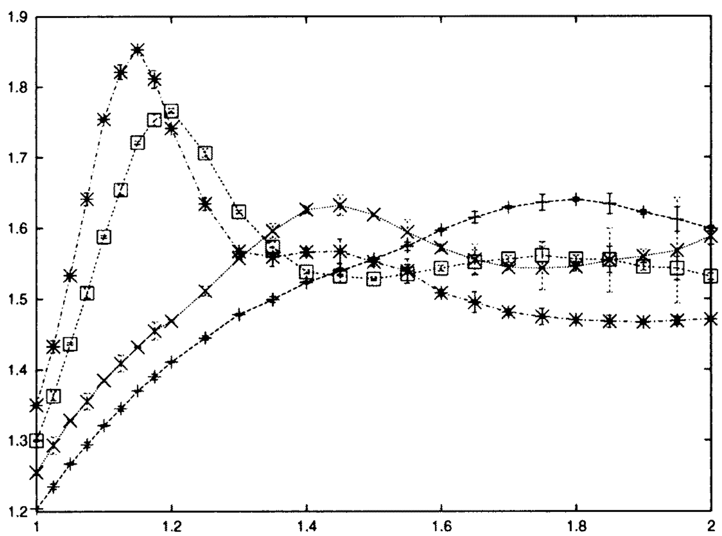

Figure 10. Data on the specific heat c as a function of Γ for $N = 28$ (+), 30 (×), 34 (∗) and 36 (□). Lines are only to join neighbouring points.

changes very little when varying the number of particles.

Finally in figures 12–15 we present the low-temperature data on $P(d)$ respectively for $N = 28$, 30, 34 and 36. The qualitative features are the same for different numbers of particles. The behaviour changes in a remarkably short Γ range around $\Gamma = \Gamma^*$ and $P(d)$ looks highly nontrivial at higher Γ values. The physical meaning of the peaks shown by the equilibrium probability distribution of distance between states in the low-temperature region comes from the mean-field theoretical picture. In this region the data are well consistent with the scenario that in the glassy phase a small number of valleys in the free-energy

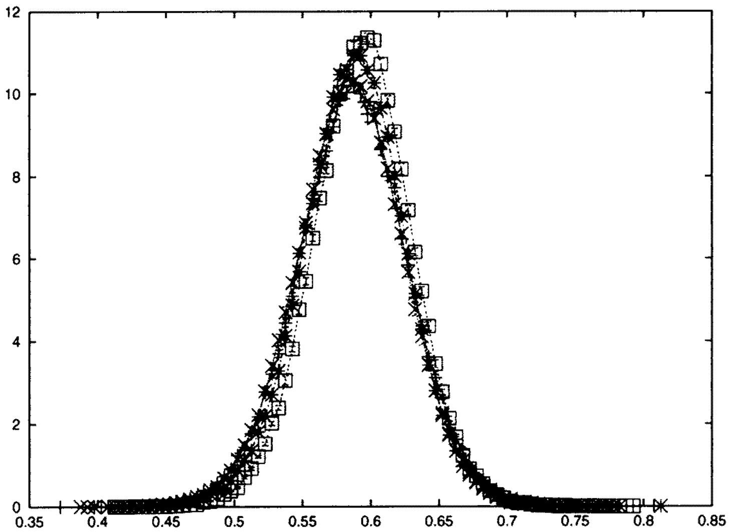

Figure 11. Data on $P(d)$ at $\Gamma = 1$ for $N = 28$ (+), 30 (×), 34 (∗) and 36 (□).

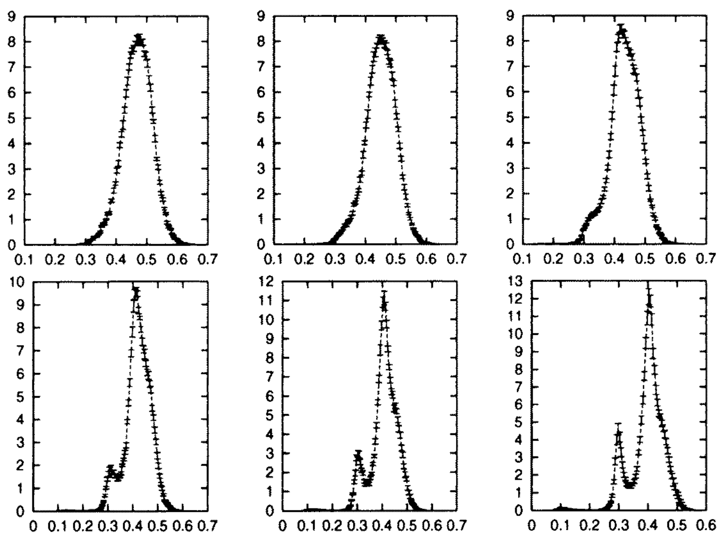

Figure 12. Data on $P(d)$ for $N = 28$. From left to right and top to bottom $\Gamma = 1.5$, 1.6, 1.7, 1.8, 1.9 and 2. Plotted data have been measured during a 2^{24} PT-step run but we stress that they are perfectly compatible with those obtained by a previous 2^{22} step run.

landscape give the dominant contribution to the partition function.

Both the value of Γ^* and the $P(d)$ shape in the glassy phase are strongly dependent on N. Differences are also evident when the number of particles is varied by only 2 (i.e. between $N = 28$ and 30 or $N = 34$ and 36). This is easily understandable since a little difference in N can change abruptly the kinds (and the number) of configurations that maximize and that are near to maximizing the relative distances between the particles (minimizing the Hamiltonian). On the other hand, the observed nontrivial dependence of the behaviour of the model on the number of particles seems to agree with N affecting

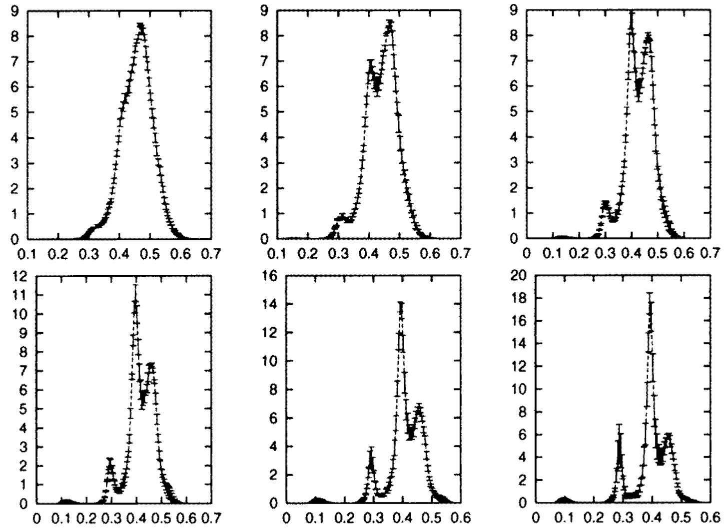

Figure 13. Data on $P(d)$ for $N = 30$. From left to right and top to bottom $\Gamma = 1.5$, 1.6, 1.7, 1.8, 1.9 and 2 (i.e. the same values as in figure 12). Here data have been measured during a 2^{22} PT-step run.

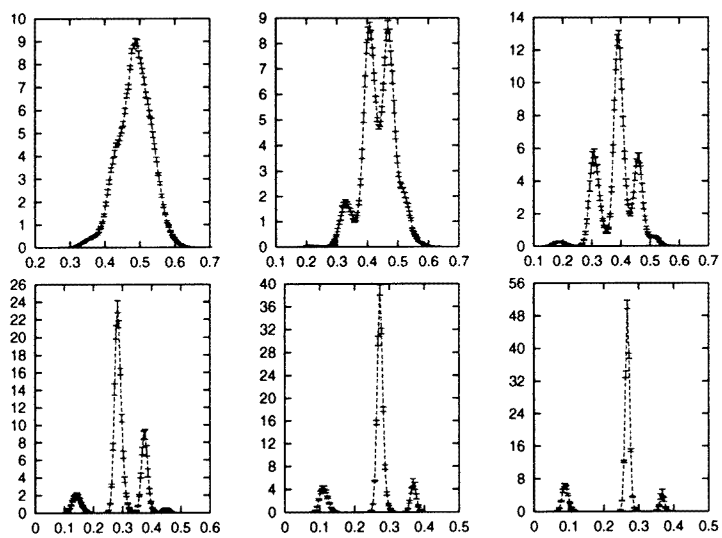

Figure 14. Data on $P(d)$ for $N = 34$. From left to right and top to bottom $\Gamma = 1.2$, 1.3, 1.4, 1.6, 1.8 and 2. Here and in the next case of $N = 36$ data have been measured during a 2^{24} PT-step run.

structural glasses in some way in the same role that quenched random variables play in spin glasses.

As a last remark we note that when reaching Γ values much higher than Γ^* some peaks of $P(d)$ disappear and the height of the other ones (usually corresponding to smaller d values) goes up. This seems quite reasonable in a finite-size system with continuous degrees of freedom since, in spite of the absence of a perfectly crystalline ground state only

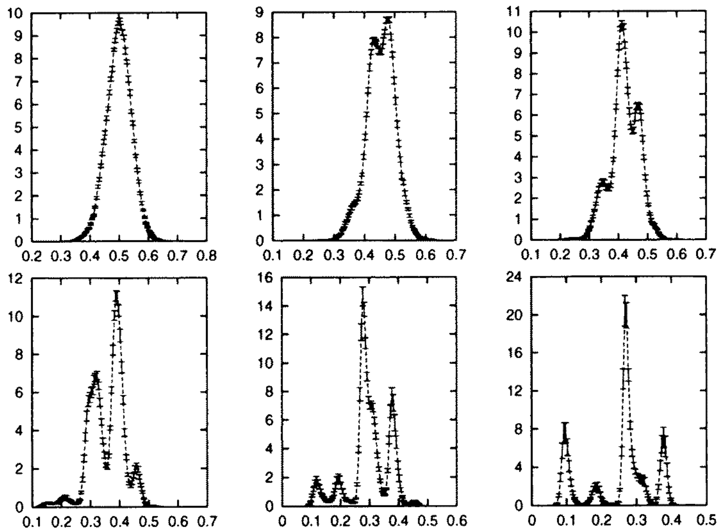

Figure 15. Data on $P(d)$ for $N = 36$. From left to right and top to bottom $\Gamma = 1.2$, 1.3, 1.4, 1.6, 1.8 and 2.0 (i.e. the same values as in figure 14).

a few configurations of the particles are really expected to minimize the Hamiltonian.

The natural next step in this analysis should consist of trying to find the behaviour of quantities averaged over different N values. We advance that from early new results [30] a slightly different definition of distance seems to be more suitable for mixtures and it could make this kind of study easier, permitting us to gain further insight into structural-glass properties.

6. Conclusions

We find numerical evidence for the behaviour of the considered glass-forming model being well consistent with some theoretical predictions obtainable by applying to structural glasses (with the appropriate modifications) the mean-field scenario that is implemented in a large class of infinite-range models.

To sum up our main results:

• When the system is quenched abruptly from a random initial configuration to a final low temperature, the energy density relaxation consists of two clearly distinguishable steps that happen on remarkably well-separated timescales.

The first step corresponds to the convergence to some metastable states with the mean-field-like behaviour $e(t) \propto t^{-\alpha}$, where the exponent $\alpha \simeq 0.8$ is weakly dependent on T in the considered range (we obtain very similar results by a MC dynamics and by MD techniques).

The fact that the extrapolated energy values are not the real equilibrium values indicates the presence of a second step, the slow decay of metastable states dominated by activated processes. The beginning of this second step is observable at very large times and its presence is confirmed by simulations on quite large systems.

We find therefore numerical evidence for a reminiscence in structural glasses of the mean-field dynamical transition, T_D being here the temperature that marks the onset of the two-steps relaxation.

• The equilibrium probability distribution $P(d)$ of an appropriately defined distance d between states, that is Gaussian at high temperatures, quite abruptly becomes nontrivial at low T values. $P(d)$ seems, therefore, a suitable observable for describing the thermodynamical transition of the system from the liquid to the glassy phase.

In the mean-field picture only a small number of valleys in the free-energy landscape give the dominant contribution to the partition function in the glassy phase. The pronounced peaks that $P(d)$ shows at low temperatures are well consistent with this scenario.

The qualitative behaviour of $P(q)$ is the same for the different N values considered but the shape in the glassy phase results strongly and nontrivially N-dependent. This seems to confirm the hypothesis that the number of particles N in some way affects structural glasses, the same role that quenched random variables play in spin glasses.

Unfortunately, to achieve equilibrium and measure d in a reasonable time, one is forced to consider systems that are not too large and to not use periodic boundary conditions. On the other hand, one also needs to carefully avoid possible crystalline minima that, in the case of quite small systems, could be reached on the same timescale of the glass equilibrium states. These difficulties make the study of $P(d)$ a difficult task, preventing us from a more quantitative analysis.

Acknowledgments

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