Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 337 (2004) 109–114
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Mechanistic view of the relaxation dynamics of a simple glass-former. A bridge between the topographic and the dynamic approaches

G.A. Appignanesi *, Rubén A. Montani

Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, (8000) Bahía Blanca, Argentina

Received 27 January 2004; received in revised form 25 March 2004

Abstract

We provide a link between the two main approaches to the relaxation dynamics of glassy systems: The 'real dynamics' scheme and the inherent dynamics or topographic formalism. The first approach is based on molecular dynamics (MD) simulations, whilst the second one reflects the underlying influence of the energy 'landscape' (within a timescale separation and activated dynamics scenario) and constitutes a widespread picture within the realm of complex systems ranging from glasses to biopolymers. For a model glass-former (a binary Lennard-Jones system), MD studies which characterized in detail the movements of the different particles led to the discovery of dynamical heterogeneities. On the other hand, the topographic approach identified activated events on the potential energy surface of this system corresponding to transitions between different basins of attraction or inherent structures. In this work we demonstrate that at low temperature the relevant events identified by both methods conform to a basic mechanistic phenomenology with elementary steps involving ballistic string-like particle movements. We also show that as temperature increases and the timescales characterizing events of different range become comparable, these elemental steps loose their nature of rare activated events. Concurrently, the system looses diversity and complexity, signatures of glassy behavior. This fact enables us to furnish for the first time the microscopic structural and dynamical basis and conditions for the prevalence of the 'landscape paradigm' for this class of systems.

PACS: 61.20.Ja; 61.20c.Lc; 64.70.Pf

1. Introduction

Even when the dynamics of glass-forming systems in the supercooled regime is an issue of major concern, a complete understanding of the structural relaxation of glassy systems and of the nature of the glass transition are still lacking [1–3]. At low temperatures, this problem has been tackled from a theoretical standpoint mainly by two major avenues: the study of the 'real dynamics' [4,5] (by means of molecular dynamics, MD, simulations) and the topographic approach [1,6–9] (the inherent dynamics) which monitors the exploration the system performs of its potential energy surface (PES). The model systems most studied by these approaches are binary Lennard-Jones (LJ) systems [5,6]. However, despite recent work [8], little effort has been devoted to correlate the inferences obtained, nor to link both approaches.

A series of extensive MD simulations [5,10] demonstrated the existence of dynamical heterogeneities in these systems at low temperatures (T close to T_C, the mode-coupling temperature) structurally characterized by clusters of 'mobile' particles, which in turn are built up by a series of 'strings-like' movements [5,10]. Such strings occur in a highly concerted way, asynchronically and localized within sharp time windows [11]. These results support a heterogeneous scenario for the relaxation dynamics leading to the occurrence of the stretched exponential Kohlrausch law [11], ubiquitous within the context of complex systems ranging from glasses to biopolymers.

* Corresponding author.
E-mail address: appignan@criba.edu.ar (G.A. Appignanesi).

0022-3093/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2004.03.125

On the other hand, the topographic approach [1,6,7], rooted in the early ideas of Goldstein [9], implies the existence of a temperature below which the dynamics of the system on its potential energy surface (PES, the multidimensional surface generated while considering potential energy as a function of particle coordinates) can be decomposed in fast vibrations around and transitions between different energy minima or 'basins of attraction' called inherent structures (in which conuration space is partitioned by potential energy minimizations). Nevertheless, whilst this hypothesis has been recently computationally corroborated for a binary LJ system [6], the microscopic rationale behind it has not been elucidated.

The PES exploration presents three distinct regimes as a function of temperature [6]: At high temperatures the systems performs a (T-independent) free diffusion (characterized by an exponential Debye relaxation law) while at lower temperatures it presents an activated-dynamics or 'landscape influenced' regime (Kohlrausch law) and at temperatures below T_C the dynamics is even slower and is termed 'landscape dominated'. The existence of such distinct exploration regimes has been related to the degree of complexity the conformational search is confronted to at different temperatures [12]. The portion of conformation space visited is more complex as T is lowered. This behavior resembles the situation in biological systems where diversity [13] (as a marker of complexity) is temperature dependent [13,14].

This temperature dependence of the kind of exploration of conformation space is qualitatively consistent with findings for the more generic context of hierarchical complex systems (ultrametric [15] and constrained-dynamics [16] systems with broken ergodicity used to model from spin glasses to biopolymers). In this context there also exist two dynamical limit behaviors separating three distinct regimes of exploration of conformation space: the limit of convergence of the dynamics or transition from activated dynamics (Kohlrausch law) to diffusive behavior (Debye law), and the limit of compact exploration characteristic of fractal systems (from Kohlausch law to a slower power-law decay). The first limit implies the breakdown of timescale separation (which can be better stated on quantitative grounds in this field) since configuration space is decomposed in components that may be not internally ergodic, depending on T. These limits are dictated by a variational principle embodied by a brachistochrone (inspired by the folding dynamics of natural biopolymers [17]), as we have demonstrated for complex hierarchical systems [18].

2. Results

In this work we aim at providing not only a link between the real dynamics and topographic approaches for a model glass-former but also the microscopic underpinnings of timescale separation. To that end, we performed a series of MD simulations for the binary Lennard-Jones system consisting of a three-dimensional mixture of 80% of A and 20% of B particles, the size of the A particles being 10% larger than the B ones. [1] Within the 'real dynamics' approach, deviation from Gaussian behavior is measured by the 'non-Gaussian parameter' $\alpha(t)$ [5,11]. The time when $\alpha(t)$ presents its maximum value, t^*, defines the time window $[0, t^*]$ in which the behavior of the system is most dynamically heterogeneous. The value of t^* for this system depends strongly on temperature as T_c ($\cong 0.435$) is approached from above, increasing by almost two orders of magnitude from $T = 0.55$ to 0.45 [5,11]. t^* constitutes a characteristic time (including curves collapse) and corresponds to times in the late β-early α relaxation (the transition from localized, or caging, to diffusive behavior) and to the lifetime of the global clusters of mobile particles (implying the mobility of around 5–10% of the particles of the sample, most of which are arranged in string movements: approximately from 75% to 50% as T changes from 0.45 to 0.55) [5,11]. Strings were dynamically characterized as in Ref. [11] for time intervals $[0, t^*]$. We performed MD simulations and identified the 'mobile' particles as the ones whose displacement at time t^*, $\Delta r_i(t^*) = r_i(t^*) - r_i(0)$ (where $r_i(t)$ is the position of particle i at time t), was greater than a value r^*: from approximately 0.6 to 0.7 σ_{AA} depending on temperature [5,11]. Specifically, particles of enhanced mobility are identified by comparing the self part of the van Hove correlation function $Gs(r,t)$ with the gaussian function $Gs^\circ(r,t)$ that measures the probability distribution of a Brownian particle to be located at a distance r from the origin at time t. Mobile particles are the ones whose displacement at t^* is greater than the value r^* where $Gs(r,t)$ (in its long tail) exceeds $Gs^\circ(r,t)$ [5,11]. To study the topology of the dynamical heterogeneities present in this system, in particular to find strings of mobile particles, we calculated the distances $\Delta r_{i,j}(t^*) = r_i(t^*) - r_j(0)$ and recorded the cases when $\Delta r_{i,j}(t^*) < 0.6$. This means that after t^* particle j has moved and particle i has occupied its place to within 0.6 σ_{AA} (represented as $i \to j$). That is, to locate strings two snapshots of the system are used (the configurations at $t = 0$ and $t = t^*$) and we measure the distances between the position of each given mobile particle i at t^* vs. the positions of all other mobile particles j at $t = 0$. When this difference is smaller than 0.6 σ_{AA} the corresponding particles are involved in (a part of a) string $i \to j$. Strings represent chains of first neighbor particles that fulfil this

[1] Parameters of the LJ potential: $\varepsilon_{AA} = 1.0$; $\sigma_{AA} = 1.0$; $\varepsilon_{AB} = 1.5$; $\sigma_{AB} = 0.8$; $\varepsilon_{BB} = 0.5$; $\sigma_{BB} = 0.88$; truncated at $r = 2.5\sigma_{AA}$. Ensemble: NPT (but the results do not change if the NVE is used instead); $N = 500$ particles. Step size = 0.0025.

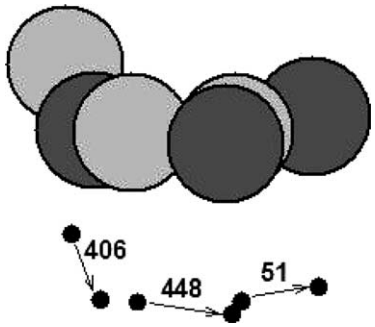

Fig. 1. Top: An example of a short string: $406 \rightarrow 448 \rightarrow 51$ ($T = 0.469$ and $P = 2.296$). The numbers label different particles in the sample. The spheres indicating the positions of the particles at the initial position ($t = 0$) are colored in light gray and the ones for the positions at $t = t^*$ are in dark gray. Bottom: We also indicate the displacements of the particles by arrows connecting the points that mark the centers of the corresponding spheres.

requirement. We found in the simulations that most of the mobile particles were organized in different strings. In Fig. 1 we show an example of a short string of three particles obtained in our MD simulations. In it particle 448 moves towards the position first occupied by particle 51 while particle 406 tends to replace particle 448 (thus the string reads $406 \rightarrow 448 \rightarrow 51$).

A point that emerges from such studies (not stated in Ref. [11]) must be indicated. In Fig. 2 we display the time evolution of the displacements of the particles of the string of Fig. 1. Direct inspection of these kind of figures (for different strings at temperatures $0.45 < T < 0.55$) reveals that *string-like movements are ballistic events* (the fastest possible events in the absence of an external bias). That is, all the particles that take part in a string perform simultaneously coherent ballistic displacements of around $1\sigma_{AA}$, thus revealing the concerted cooperative nature of the string movements. Since each particle is caged by its first neighbors, to perform such a movement its cage must relax properly. Such cage relaxation (by a local fluctuation of density, a 'hole' creation) constitutes the initiation event of the string. Thus, as this 'head' particle of the string is moving ballistically it provides of the space for the second one to perform a ballistic jump and so on, thus producing a kind of 'caterpillar' movement. Long strings usually occur in well differentiated and time spaced steps or 'substrings' of a few particles (we recall that strings were characterized in the whole interval [0, t^*], but substrings also constitute string movements themselves). Nonetheless, the particles taking part of each substring motion perform concerted ballistic displacements. We shall define a ballistic time as the time it would take a particle to perform a ballistic displacement of $1\sigma_{AA}$. This time unit depends slightly on T and represents around 400 MD steps for $T = 0.4685$. For low temperatures this ballistic time is small compared to t^* but for $T = 0.55$ (since t^* decreases with T) these two timescales become comparable (we recall that for all the temperatures studied the number of mobile particles in [0, t^*] was always 5–10% of the total number of particles and the mean squared displacements, MSD, at t^* did not differ appreciable, being around 0.1 σ_{AA}). For higher temperatures, t^* becomes smaller than the corresponding ballistic time. Fig. 3 shows the temperature dependence of the ballistic time and of t^*. We also show the temperature behavior of the time when the MSD equals unity, $\tau_{MSD} = 1$ (the average escape time of the particles from their cages). We can see that t^* (that decreases almost two orders of magnitude from $T = 0.451$ to 0.55) approaches the corresponding ballistic time at temperatures above $T = 0.55$. The curve for $\tau_{MSD} = 1$ displays a temperature dependence similar to t^* ($\tau_{MSD} = 1$ is around ten times t^* for the different temperatures) and approaches the ballistic curve at a higher temperature.

To study the inherent dynamics of the system we performed periodical quenches of configurations obtained in a given real MD trajectory by means of potential energy minimizations. We used the conjugate-gradient method [19], but a steepest-descent routine (or even a stepwise extraction of kinetic energy) could also be used. This procedure maps each configuration to its

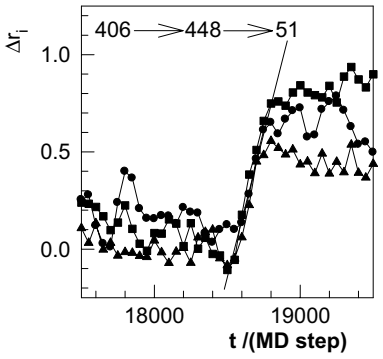

Fig. 2. Time evolution of the displacements of the particles of the string of Fig. 1 in the region where the string occurs (projected onto the global direction of displacement in [0, t^*]). A line indicating perfect ballistic behavior (with velocity extracted from the mean kinetic energy) is drawn for comparison. Time is given in MD steps. Reduced time is obtained when dividing by 0.0025.

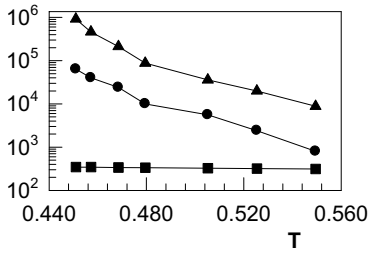

Fig. 3. Temperature dependence of the three relevant times, t: ballistic time (■), t^* (●) and $\tau_{MSD} = 1$ (▲).

corresponding inherent structure (IS). At low enough T, the dynamics of the system can be separated in fast vibrations around the ISs and transition between ISs. That is, at each given time the system spends some time around the current IS before performing a transition to a different IS. Thus, the relaxation can be described at the IS level. This procedure removes the effects of local vibrations that would otherwise obscure the relevant events in the exploration of the PES. To locate transitions between ISs or jumps, we could monitor the inherent structure energy. Instead, we use another quantity, namely the mean squared displacement between successive ISs (this quantity represents a better measure in terms of diversity since structurally distinct ISs do not necessarily differ appreciably in energy): $\Delta R_{\mathrm{IS}}(t) = (\Sigma_{j=1}^{N}(r_j^{\mathrm{IS}}(t+\Delta t) - r_j^{\mathrm{IS}}(t))^2)^{1/2}$ where $r_j^{\mathrm{IS}}(t)$ is the position of particle j in the IS that occurs at time t and Δt is the interval in MD steps between successive quenching minimizations. At each time the system performs a jump in the PES, the time evolution of ΔR_{IS} would produce a peak. This is so, since while vibrating around a given IS each minima would map (by the minimization procedure) to the bottom of its basin of attraction (the same IS) and ΔR is would be around zero. Thus, a peak would indicate an interbasin transition (that is, a transition between two different IS's). In Fig. 4 we schematically depict the topographic approach. In it we qualitatively display the vibrations around and transitions between two consecutive ISs for a given MD trajectory. The corresponding exploration of the PES with a jump in the quenched potential energy and a peak in ΔR_{IS} is indicating the interbasin transition is also shown.

We performed this study for different trajectories and at different temperatures. We used different values of Δt from 1 to 50. The $\Delta R_{\mathrm{IS}}(t)$ curve for the MD trajectory that contains the string shown in Fig. 1 displays a series of peaks corresponding to transitions between successive ISs. Fig. 5 depicts the $\Delta R_{\mathrm{IS}}(t)$ curve for the regions where two strings take place (including the one of Fig. 1). Similar results were found for other strings of this MD trajectory. A fact that can be learnt from such results is that at times where the real dynamics shows the occurrence of strings (or each step or substring for long strings) a peak is found in the $\Delta R_{\mathrm{IS}}(t)$ curve. Moreover, from the analysis of the particles that contribute appreciably to ΔR_{IS} we find that these are precisely the particles of the string and their neighbors (these last ones displaying smaller displacements compared to the particles that take part in the string). That is, *string movements (strings or substrings) represent relevant events in the exploration of the PES. Additionally, most of the high peaks are found to be a consequence of the displacement of mobile particles that participate in strings. These facts imply a connection between the topographic and the real dynamics descriptions.*

An important fact that arises from these figures is that most of the strings (short strings or substrings) entail a single peak in the $\Delta R_{\mathrm{IS}}(t)$ curve. This means that string movements occur between two consecutive ISs without the presence of intermediate ISs (this is valid

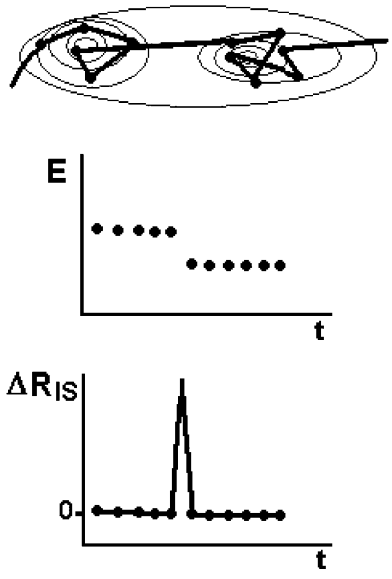

Fig. 4. Schematic representation of the topographic approach or inherent dynamics. Top: MD trajectory that passes through two consecutive basins or ISs. Middle: the corresponding time evolution of the 'quenched' potential energy. Bottom: the corresponding time evolution of ΔR_{IS}. The system spends some time visiting different minima which map to the same IS by a local minimization procedure ('quenching') before performing a transition to another nearby IS.

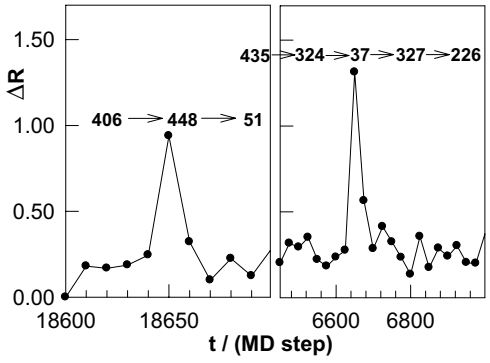

Fig. 5. Time evolution of ΔR_{IS} for the regions where two of the strings take place. The fact that the quantity ΔR_{IS} does not go strictly to zero in the regions between the peaks is due to the use of the NPT ensemble (the usual experimental conditions) instead of the microcanonical ensemble, since the energy and thus the landscape, albeit not changing significantly during the run, is not fixed. This fact introduces small distortions in the positions of the particles in the ISs. Nevertheless, this very small effect does not affect the process to find peaks. Moreover, the results of both the 'real' and inherent dynamics have been regarded as insensitive to the kind of ensemble used (see Ref. [6]). In particular, our results for the 'real dynamics' and the string motions are completely consistent with the results obtained with the NVE ensemble in reference [5].

even if the quenching procedure is made at every MD step). Namely, *string movements represent well-differentiated two-state elementary processes without intermediate steps, thus making the relaxation process amenable of mechanistic description*. We must note that, given the minimization procedure implied in the quenched trajectory, the peaks represent events that demand a certain time of occurrence. We recall that string movements demand ballistic times (≅400 steps). Thus, the transition between the two consecutive ISs (the peak) corresponds to the surmounting of the corresponding barrier or saddle point.

Some long strings or substrings do not represent a single peak but a series of two or three closely spaced peaks. Nevertheless, these peaks are generally separated by less than ballistic times. Furthermore, if we integrate these peaks (by taking the ΔR_{IS} between ISs before and after the whole set) we find that the displacements of the particles that contribute to the ΔR_{IS} and participate in the string are the sum of the corresponding displacements for the different peaks. That is, the displacements are coherent and the different peaks could be represented by a single peak. This fact is consistent with the overall coherent ballistic behavior found in the real dynamics.

From the study of the particles that contribute to the ΔR_{IS} for the peaks corresponding to the strings, we find that most of them only display small, negligible displacements between such ISs. Nevertheless, the particles that take part in the string do exhibit large displacements (in general greater than 0.5 σ_{AA} and sometimes around 1 σ_{AA}, while the displacement required to be mobile is approximately 0.7 σ_{AA} for $T = 0.4685$). From the rest of the particles, the ones that act as locally adjusting the event show displacements of around 0.2 σ_{AA}, while the rest only perform very small displacements. These facts are also consistent with the ballistic nature of string motions in the real dynamics.

The fact that string motions correspond to single peaks implies that such events are fast once initiated (this is also evident in the real dynamics since, once initiated the string, the different particles move simultaneously and ballistically). For some strings we found a pre-peak close to the string peak. From the study of the contribution of the different particles to the ΔR_{IS} we found that this pre-peak arises as a consequence of the displacement of particles that are first neighbors of the head particle of the string (while the particles of the string itself do not contribute appreciably). Such particles move away from the position the particle head of the string will move to in the string motion, so as to make place for its displacement. For other strings this 'hole creation' or string initiation event occurs concurrently with the string (in the same peak, with no pre-peak present). However, from the study of the quenched configurations and the ones of the real dynamics we never found voids of particle size. Instead, we found small empty spaces in the direction of movement of the particles, as if a wall of the cage had moved. These facts imply that for this system effective holes are small and ephemeral.

The above-expounded description is valid in a timescale separation scenario [9], which has been previously computationally corroborated [6,8] but up to now not properly validated from first principles. In this regard, the comparison between the 'ballistic time' and t^* provides, for the first time, a microscopic rationale for its emergence together with a criterion to estimate its range of application. Thus, for high T ($T > 0.55$) where t^* (and, eventually, $\tau_{\mathrm{MSD}} = 1$, the mean lifetime of the cages) becomes comparable to the corresponding ballistic time, the separation of timescales between transition intra and inter basin starts to break down. [2] For this high temperature regime, the different string-like motions (and thus IS transitions) are not well separated in time, preventing the system to locally equilibrate within each IS. Concurrently, the thermal energy available to the system begins to overlook the landscape of activation barriers and the system tends to perform a free-diffusion characterized by a Debye law. Thus, both the landscape approach and the description of the relaxation in terms of string motions are not applicable in this regime. On the other hand, at low T we find a prevalence of activated dynamics given the fact that the barriers are now sufficiently high (compared to thermal energy) to confine the system for times longer than the ballistic time. Within t^*, the string-like motions that mark the IS transitions occur now well separated in time from each other, allowing for local equilibration. Thus, the relaxation can be characterized in mechanistic terms, dominated by particle rearrangements or defects (strings in our case) leading to the occurrence of Kohlrausch relaxation. These elemental events (in particular their initiation) become now 'rare' events and govern the dynamics.

This onset of timescale separation is also reflected in the emergence of diversity (which is not intrinsic but depends on temperature and thus on the level of resolution of the conformational search). Thus, diversity is at the heart of the inhomogeneous nature of the relaxation. At high T, where the system has enough thermal energy to visit the whole conformation space, the sampled minima are high and shallow (as the great

[2] Additionally, the ballistic time (the lifetime of the small string-like elemental steps) and t^* (the lifetime of the global cluster of mobile particles), represent timescales related to different scale events: short and long-range, respectively. Moreover, Stillinger (see Ref. [1]) has proposed that similar basins or ISs might be arranged in megabasins (MB) and that transition between MB's (involving large scale rearrangements) would indicate the onset of the α relaxation. t^* marks the crossover from the β to the α relaxation, thus indicating the advent of these long range events.

majority of the minima) [12]. At lower T deeper minima (which are scarce) separated by high barriers are explored and at even lower T the system becomes confined in the deepest minima [12]. Thus, the portion of conformation space visited is more complex as T is lowered [12]. At high T all the minima are similar in which concerns dynamics (since thermal energy is enough to prevent confinement and the system does not spend much time around them). In fact, the liquid state does not present diversity since the sampled minima are all equally unimportant from a dynamical perspective. However, at lower T the system samples (and begins to be confined in) states very different from structural and dynamical standpoints (but not necessarily very different in potential energy), separated by high barriers. Since thermal energy is low, these minima begin to display their own distinct dynamical behavior implying the advent of diversity, and thus of complexity and glassiness.

3. Conclusions

In this work we demonstrate for a binary LJ system that string-like movements (short strings or substrings) of ballistic nature represent relevant exploration events in the PES. These events are clearly two-state and represent activated events. This allows us for the first time to relate the former (static) picture of string inhomogeneities with the topographic inherent structure formalism in terms of a mechanistic description. The comparison of the lifetime of such events with t^* (the characteristic timescale of the global cluster of mobile particles) enables us to provide a microscopic rationale for the up to date only computationally validated timescale separation hypothesis and thus, for the validity and range of application of the landscape paradigm.

Acknowledgements

Financial support from Fundación Antorchas, the Agencia Nacional de Promoción Científica y Tecnológica and the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) is gratefully acknowledged. R.A.M. is Research Fellow of the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC) and G.A.A. is Research Fellow of CONICET.

References

[1] P.G. Debenedetti, F.H. Stillinger, Nature 410 (2001) 259.
[2] P.W. Anderson, Science 267 (1995) 1615.
[3] C.A. Angell, Science 267 (1995) 1924.
[4] C. Bennemann et al., Nature 399 (1999) 246.
[5] C. Donati, J.F. Douglas, W. Kob, S.J. Plimpton, P.H. Poole, S.C. Glotzer, Phys. Rev. Lett. 80 (1998) 2338.
[6] S. Sastry, P.G. Debenedetti, F.H. Stillinger, Nature 393 (1998) 554.
[7] K.D. Ball, R.S. Berry, R.E. Kunz, F.-Y. Li, A. Proykova, D.J. Wales, Science 271 (1996) 963.
[8] T.B. Schrøder, S. Sastry, J.C. Dyre, S.C. Glotzer, J. Chem. Phys. 112 (2000) 9834.
[9] M. Goldstein, J. Chem. Phys. 51 (1969) 3728.
[10] C. Donati et al., Phys. Rev. E 60 (1999) 3107.
[11] G.A. Appignanesi, M.A. Frechero, R.A. Montani, Physica A 329 (2003) 41.
[12] C.A. Angell, Nature 393 (1998) 521.
[13] H. Frauenfelder, P.G. Wolynes, Phys. Today (February) (1994) 58.
[14] I.E.T. Iben et al., Phys. Rev. Lett. 62 (1989) 1916.
[15] R. Rammal, G. Toulouse, M.A. Virasoro, Rev. Mod. Phys. 58 (1986) 765.
[16] R.G. Palmer, D.L. Stein, E. Abrahams, P.W. Anderson, Phys. Rev. Lett. 53 (1984) 958.
[17] A. Fernández, G.A. Appignanesi, Phys. Rev. Lett. 78 (1997) 2668.
[18] G.A. Appignanesi, Physica A 276 (2000) 413.
[19] W.H. Press, B.P. Flannery, S.A. Teukolsky, W.T. Vetterling, Numerical Recipes, Cambridge University, New York, 1987.