

Aging in simple liquids: a numerical study

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Abstract

We discuss the phenomenon of physical aging in a well studied atomic model liquid, a binary mixture of particles interacting with Lennard-Jones potentials. We put emphasis on the different dynamical behaviours of the model as well as on the relations between the experimental and numerical timescales. The physics of aging is discussed within a well characterized thermodynamic framework, based on properties of the model potential energy surface.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The slowing down of the dynamics in disordered materials on cooling is among the most interesting topics studied in modern condensed matter research. In the case of supercooled liquids, the effect of the slowing down of the dynamics is dramatic; the self-dynamics and the collective dynamics both slow down by more than 13 orders of magnitude over a small temperature region. At the glass transition temperature T_g [1], the characteristic time becomes of the same order as the experimental time, thus preventing equilibrium studies at lower T . Material properties below T_g depend on the previous history (i.e. on the preparation technique, on the cooling/compression rate and so on) as well as on the time spent in the glass state. This time dependence, generically known as physical aging, highlights the out-of-equilibrium (OOE) condition of glasses and their extremely slow equilibration processes.

In recent years, a substantial amount of work has been devoted to achieving an understanding and to the formal description of supercooled liquid dynamics [2, 3], of the physics beyond the glass transition [4] and of physical aging [5–7]. Numerical simulations of supercooled states, both in equilibrium and in controlled out-of-equilibrium conditions, have played an important role in current developments [8]. Although the timescales probed by numerical simulations are very different to experimental ones (100 ns compared to 1 s), the numerical ‘experiments’ appear to be able to reproduce features of real materials [9, 10]. In view of this, in this article we present results based on one well studied model for a supercooled liquid, using numerical techniques both to generate equilibrium or out-of-equilibrium trajectories in phase space and to analyse them. For simplicity we will restrict our consideration to one single

model and one single isochore, with the implicit assumption that the results presented and the discussion can be generalized to different models and different thermodynamic conditions.

The outcome of the present studies, which are still far from being definitive, supports the possibility that the out-of-equilibrium glassy state, notwithstanding its out-of-equilibrium condition, can be uniquely determined by its kinetic temperature, its volume and one internal parameter which, in the present description, will be identified with the system inherent-structure (IS) energy (to be defined in the following). These quantities allow one to develop a thermodynamic description of the glass state [11–15] which is currently being tested in experiments [16, 17] and further simulations.

The article is organized in sections. Section 2 introduces the selected model. Section 3 briefly discusses the concept of inherent structures. Section 4 contrasts the out-of-equilibrium conditions which are met in numerical simulations with the ones met in experiments. Differences related to the different timescales accessed in simulations and experiments are discussed. Section 5 reports the results of the ‘numerical experiments’ performed on the chosen model system. The role of T in equilibrium and the role of the waiting time t_w , defined as the time spent in the out-of-equilibrium conditions, are compared. Scaling laws for the correlation functions are discussed. Finally, section 6 reviews the recent thermodynamic description of aging based on the inherent-structure formalism [18] and section 7 gives our conclusions.

2. The model

The model that we select is a binary mixture of Lennard-Jones particles (BMLJ), proposed and extensively studied by Kob and co-workers [19, 20]. The model, an evolution of the model presented in reference [21], has been optimized to prevent crystallization. The BMLJ is a binary mixture (80:20) of particles, which in the following we will call type A and type B particles. The interaction between two particles of type α and β , with $\alpha, \beta \in \{A, B\}$, is given by $V_{\alpha\beta} = 4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6]$. The parameters $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are given by $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $\epsilon_{AB} = 1.5$, $\sigma_{AB} = 0.8$, $\epsilon_{BB} = 0.5$ and $\sigma_{BB} = 0.88$. The potential is truncated and shifted at $r_{cut} = 2.5\sigma_{\alpha\beta}$. In the following we will use σ_{AA} and ϵ_{AA} as the units of length and energy, respectively (setting the Boltzmann constant $k_B = 1.0$). The integration time step is 0.01 in units of $\sqrt{(m\sigma_{AA}^2/48\epsilon_{AA})}$, where m is the mass of the particles. We have studied the isochore for number density $n = 1.2$.

The correlation functions reported in this article are the collective (coherent) density-density correlation functions for the majority species A, defined as

$$F^A(\mathbf{q}, t) = \frac{1}{N} \left\langle \sum_{i,j=1}^{N_A} e^{i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle \quad (1)$$

where \mathbf{r}_i are the coordinates of particle i .

3. Inherent structures

Inherent structures of a system are defined as the local minima of the many-body potential energy surface (PES) [22, 23]. A set of points, commonly named a basin, is associated with each IS. The basin includes all points in configuration space which, following a steepest-descent path, end up in the same IS. The \mathbf{r}^N -space is unambiguously partitioned into an ensemble of basins, commonly labelled by the value of the potential energy in the IS, e_{IS} (see figure 1). The trajectory of the system in configuration space is then mapped onto the time series $e_{IS}(t)$.

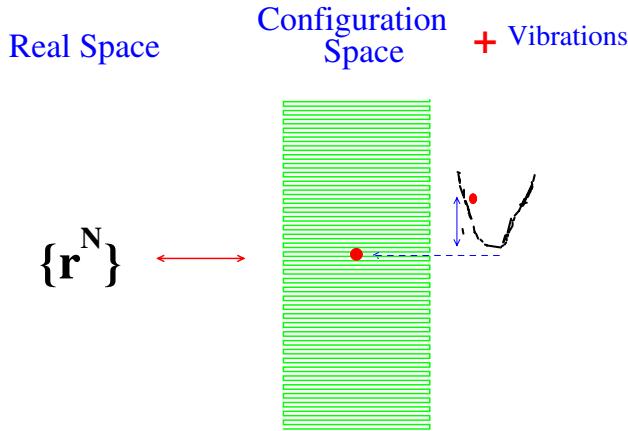


Figure 1. Within the thermodynamic inherent-structure formalism a point in r^N -space is mapped onto one IS plus the position within the IS basin. The occupied basin is commonly identified with the value of the energy of the minimum e_{IS} . The partition function can be written in an exact way as a sum over all possible IS states, each of them weighted with the corresponding basin free energy.

Depending on the value of T , the system explores different parts of the PES, and the frequency of exploration of basins of different depths changes with T . On very general grounds, one can predict that at infinite T the probability of locating the system in a basin is proportional to the basin volume, while at lower temperatures the probability of locating the system in a basin will depend more and more on its depth.

Enhanced computational facilities have allowed exploration of the T -dependence of e_{IS} [24–27]—i.e. which IS are sampled as a function of T —and correlation of such dependence with the changes which are taking place in the liquid dynamics [25]. The location of the system within the basin has also been investigated, to distinguish T -regions where the system is statistically located close to a ridge from T -regions where the system is statistically located close to the IS [28, 29].

In equilibrium—using the BMLJ as a general model—recent numerical work has shown that three different dynamical regions can be detected:

- (1) A high-temperature region, where T is of the order of the depth of the potential energy ($T \sim 1$), where correlation functions show a fast (almost exponential) one-step decay on a microscopic timescale. The distribution of inherent structures in this T -region is T -independent.
- (2) An intermediate region ($1 > T > T_c$), where the liquid starts to explore deeper and deeper potential energy basins. Still the system is always close to ridges separating different basins. This is the saddle-dominated dynamics, which is well captured by the ideal mode-coupling theory.
- (3) A low- T region, where the system only rarely explores ridge regions. In this T -range, lower and lower IS energy levels are populated. When the time required to explore different basins exceeds the experimental time, the system falls out of equilibrium. In the PES description, this condition fixes T_g .

From an experimental (and numerical) point of view these three regions are the only ones relevant to *equilibrium* states. The last T -region is followed by a fourth region where the system is always in an out-of-equilibrium state, commonly named glass. From a theoretical

point of view, equilibrium thermodynamics calculations can often be performed even for this further region. The (unknown) dependence of the number of IS basins on e_{IS} would determine whether, within the model studied, region 3 in principle ends up at a finite temperature (often named the Kauzmann temperature T_K [30]) or at $T = 0$.

Enhanced computational facilities have allowed very accurate modelling of the free energy of several model systems, based on the IS formalism introduced by Stillinger and Weber (SW) [22]. The BMLJ model was among the first to be studied in detail. In the SW formalism the liquid free energy is separated into two contributions: a contribution describing the free energy of one characteristic basin of the PES and a contribution accounting for the number of these independent basins. The liquid is modelled as an ensemble of states, labelled for convenience by e_{IS} , and by the free energy of each of these states. This is formally done by partitioning the configuration space into a sum of basins and by writing the partition function as a sum of the partition functions of the independent basins. In this formalism, a point in r^N -space is indicated by the basin to which it belongs and by the position in the basin. The rationale for this operation is that, in supercooled states, the fast intra-basin dynamics and the slow inter-basin dynamics decouple, allowing a simplified description of the system dynamics and thermodynamics.

More specifically, in the thermodynamic limit, the system free energy $F(T)$ is [22]

$$F(T) = -TS_{conf}(e_{IS}(T)) + f_{basin}(T, e_{IS}(T)) \quad (2)$$

where $-TS_{conf}(e_{IS}(T))$ accounts for the entropic contribution arising from the number of basins of depth e_{IS} and $f_{basin}(T, e_{IS})$ describes the (average) free energy of the system constrained to be in one characteristic e_{IS} -basin. The separation of the free energy into $-TS_{conf}(e_{IS})$ and $f_{basin}(T, e_{IS})$ reflects the separation of timescales which is observed in the supercooled liquid state.

In equilibrium, at each temperature T_{eq} , the system populates basins whose depth $e_{IS}(T_{eq})$ changes with T (see figure 2). Within the SW formalism, the value of $e_{IS}(T_{eq})$ can be calculated from the condition of F being a minimum with respect to e_{IS} , i.e. from

$$\frac{\partial F}{\partial e_{IS}} = -T_{eq} \frac{\partial S_{conf}(e_{IS})}{\partial e_{IS}} + \frac{\partial f_{basin}(T_{eq}, e_{IS})}{\partial e_{IS}} = 0. \quad (3)$$

Equation (3) shows that the rate at which deeper and deeper basins are populated on cooling depends both on $\partial S_{conf}(e_{IS})/\partial e_{IS}$, the way the number of basins of depth e_{IS} changes with e_{IS} , and $\partial f_{basin}/\partial e_{IS}$, the way the basin free energy changes with e_{IS} . If all basins have the same shape—and hence the vibrational contribution is e_{IS} -independent—then the basin free energy change reduces to a change in the energy depth of the local minimum and hence $\partial f_{basin}/\partial e_{IS} = 1$ and, from equation (3),

$$\frac{dS_{conf}(e_{IS})}{de_{IS}} = \frac{1}{T_{eq}}. \quad (4)$$

If basins differ in their shape, the contribution from the change in the vibrational free energy may become relevant [18, 31, 32].

In the case of the BMLJ, there is a clear dependence of the vibrational free energy on e_{IS} [18, 26]. Contrary to the intuitive expectation, at constant volume the average curvature of the basins is smaller in deeper basins and hence, even in the harmonic approximation for the vibrational free energy, an entropic vibrational variation is associated with a change of basin depth. In other words, on moving to a deeper basin, the BMLJ liquid gains in potential energy (going to a lower e_{IS} -state) but also gains in vibrational entropy due to the larger configuration space associated with the smaller frequency. This free-energy gain is counterbalanced by the decrease in configurational entropy, i.e. by the fact that the number of basins with deeper e_{IS} is smaller.

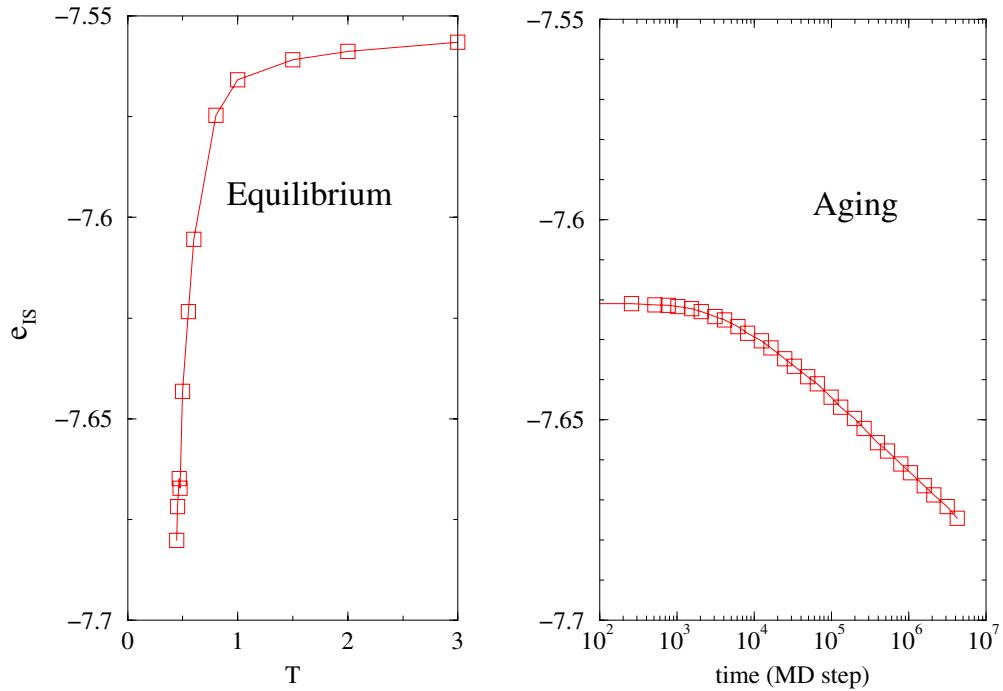


Figure 2. Average inherent-structure energy e_{IS} as a function of temperature (in equilibrium) and as a function of time (in aging, following a density change). The model is the BMLJ at number density 1.2.

4. Experimental and numerical timescales in aging

Any perturbation applied to a liquid (like a change in T or P , or the addition of an external field) determines a dynamics in the system (in the one-time quantities) which evolves in time to adjust to the new external conditions in a characteristic time τ_{equil} . This evolution in time is an OOE process. Are all OOE processes aging processes? In principle, one could answer this question in the affirmative and define as aging all conditions such that the observation time is shorter than the equilibration time. In this simple picture, the possibility of observing aging is only limited by the speed of the measurement technique.

A more restrictive definition may be formulated by requiring that the system under study is—above the glass transition temperature—characterized by different characteristic times, i.e. by a non-exponential correlation function. In this definition, only systems whose equilibrium dynamics is sufficiently complicated to show a separation between microscopic timescales and the structural timescale may show aging. In other words, the structure of the configuration space should not be simple. In the case of supercooled liquids, such a condition is met, since fast (intra-basin) degrees of freedom separate more and more on cooling from the slow (inter-basin) degrees of freedom. In liquids, the essence of the aging process can then be traced back to the slow progressive search for the equilibrium IS (figure 2).

The separation of the equilibrium dynamics into T -regions, presented in section 3, helps in guiding the interpretation of the experimental and numerical results. Experimental studies on aging are usually performed by bringing the system from an equilibrium state point within region 3 to a permanent out-of-equilibrium state point in region 4. Under these conditions, the

system ages for times much longer than the duration of the experimental measurements. Other possibilities (from region 1 to region 3 and so on) are usually not feasible, since the time that it takes to move the system from the initial-state point to the final-state point is comparable to or longer than the duration of the aging dynamics.

Numerical experiments can in principle cover all possible inter-region changes, since the time that it takes to move the system from the initial-state to the final-state point can be made arbitrarily small. The physics of aging, in the restrictive definition, requires that the final state belongs to region 2, 3 or 4. An OOE simulated experiment within region 1 does not qualify as aging physics, since the change in configuration space does not involve a change in the distribution of inherent structures.

With the present computer facilities, it is nowadays possible to study OOE trajectories up to 10 million integration time steps. This amount of time allows one to follow the entire OOE process up to the new equilibrium when the final-state point is within region 2 and the initial part of the aging dynamics in the case of final-state points is in region 3 and 4.

The reason for classifying the aging process according to the region of the final-state point stems from the fact that, as suggested in reference [26] and more recently in references [33] and [34], the dynamics of the system during the aging process differ according to the mechanism of exploration of configuration phase space. For final states in region 2 at all times or in the very early aging dynamics in the other cases, the system always populates ridge regions in configuration space and hence its dynamics is of MCT type. When the system is brought to state points belonging to region 3 or 4, the initial saddle-dominated dynamics crosses over to a different type of dynamics since the system populates the basin of the local minima and the exploration of configuration space requires activated processes of some sort. This crossover in the aging dynamics from saddle to minima, which has been observed in numerical simulations of aging, is the same phenomenon, now taking place as a function of t_w , as the crossover phenomena taking place in equilibrium as a function of T or P when going from region 2 to region 3. Of course, in an OOE experiment, going from region 3 to region 4, only the activated dynamics is present. Hence, in numerical simulations, only the long-time dynamics should be compared with the experimental dynamics.

5. Equilibrium and out-of-equilibrium dynamics

The behaviours of the correlation functions for the BMLJ model in equilibrium have been carefully studied by Kob and co-workers in a series of papers [19, 20]. We refer the interested reader to the original articles. Kob and co-workers have shown that below $T = 1.0$, clear signatures of a two-step relaxation process develop in all correlation functions. The characteristic time of the slow process significantly increases on cooling and appears to diverge (following a power law $\tau_\alpha \approx |T - T_c|^\gamma$) at a crossover temperature $T_c = 0.435$. Very close to T_c , where equilibration times exceeds ten million steps, deviations from the power law are observed, as found experimentally in all glass-forming liquids. T_c has been convincingly interpreted [20] as the mode-coupling-theory dynamical critical temperature.

Figure 3 (top) reports the time dependence of the collective density correlation function (for the A particles) in equilibrium at different temperatures at one specific wavevector ($q = 6.684$). Around $T = 1.0$, a shoulder appears in the correlation function, signalling the separation of the structural relaxation time from the short-time dynamics. While, the short-time dynamics does not present any significant T -dependence (apart for the trivial one, connected to the different thermal velocities), the slow relaxation time shows a power-law T -dependence. (It is important to observe that for the present model, no equilibrium simulations can be performed for T lower than T_c with the present computational resources.)

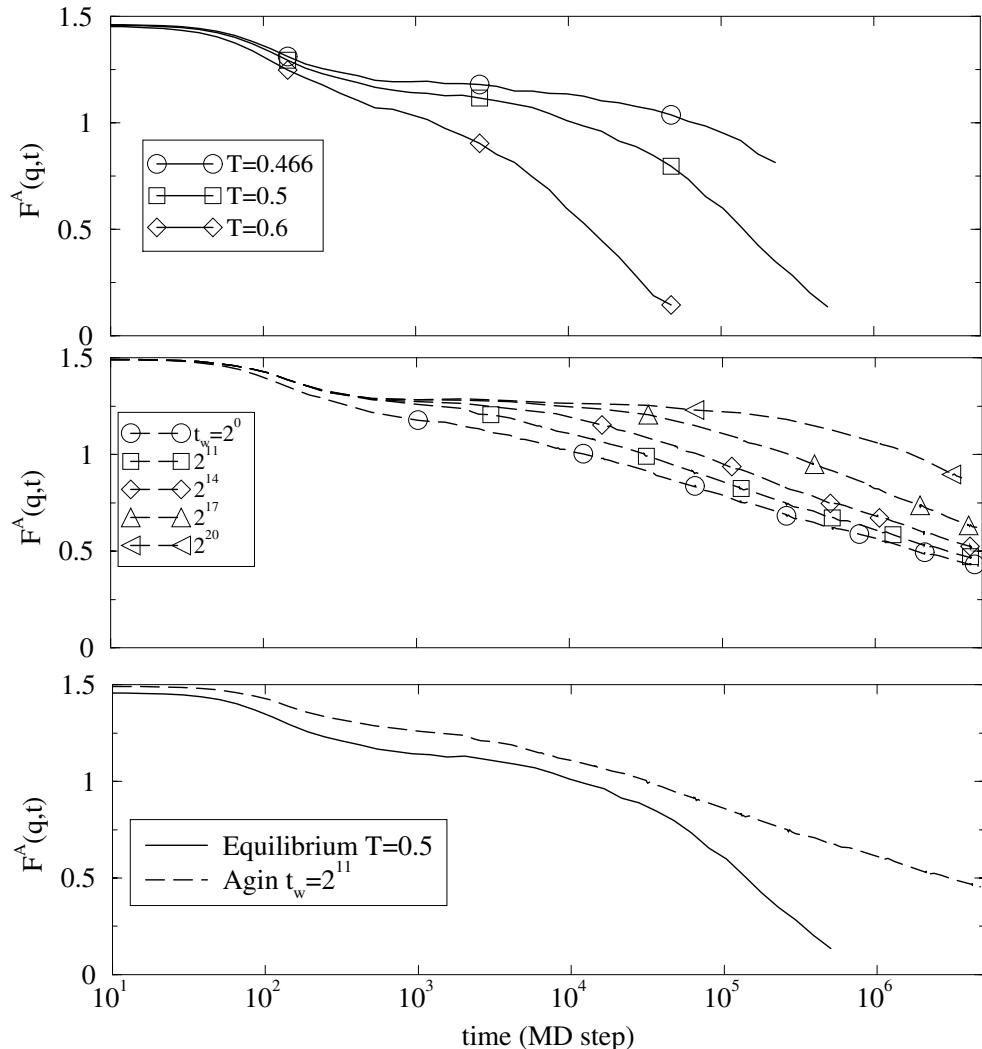


Figure 3. Collective autocorrelation functions for $q = 6.68$ (close to the first minimum in $S(q)$) in equilibrium (top) for different values of T and in aging (middle) for different waiting times from the crunch. The bottom panel contrasts the two different behaviours.

Data in the top panel of figure 3 should be compared with the similar data calculated during an OOE process, reported in the middle panel of figure 3. The specific OOE case reported in the figure is the one originating from a crunch of the system. A rescaling of all particle coordinates by a factor of 1.029 43 is chosen to model a sudden (one MD step!) ten per cent change of the density, from 1.103 65 to 1.2. The final density coincides with the isochore studied in equilibrium. Similar behaviour is observed if the density is kept constant and T is suddenly changed, as shown for the same model and the same isochore in reference [35]. Correlation functions, calculated at different starting times t_w , are shown in the middle panel of figure 3. While in equilibrium, correlation functions depend only on the difference τ between time t and the time at which the calculation of the correlation function was started, under OOE conditions, correlation functions depend both on $t - t_w$ and on t_w .

The correlation functions in aging show again the two-step relaxation phenomenon. Similarly to the equilibrium case, the short-time dynamics is rather insensitive to the time t_w elapsed from the crunch. In contrast, the long-time relaxation shows a significant dependence on t_w . The longer t_w , the longer the time required to lose the memory of the initial configuration. As shown in the bottom panel of figure 3 the shape of the correlation function in equilibrium conditions differs from that under OOE conditions. While the long-time decay of the equilibrium correlation function can be well described by a stretched exponential, the shape of the same function during aging is much wider than the equilibrium one and is better described by a logarithmic decay. A similar observation holds for the OOE condition generated via a T -jump [35].

Another interesting quantity is the behaviour of the mean square displacement $\langle r^2 \rangle$ as a function of temperature and of aging time. The behaviour of $\langle r^2 \rangle$ during aging has been studied previously for short t_w and different potentials in references [36, 37]. Figure 4 shows the mean square displacements for the A particles.

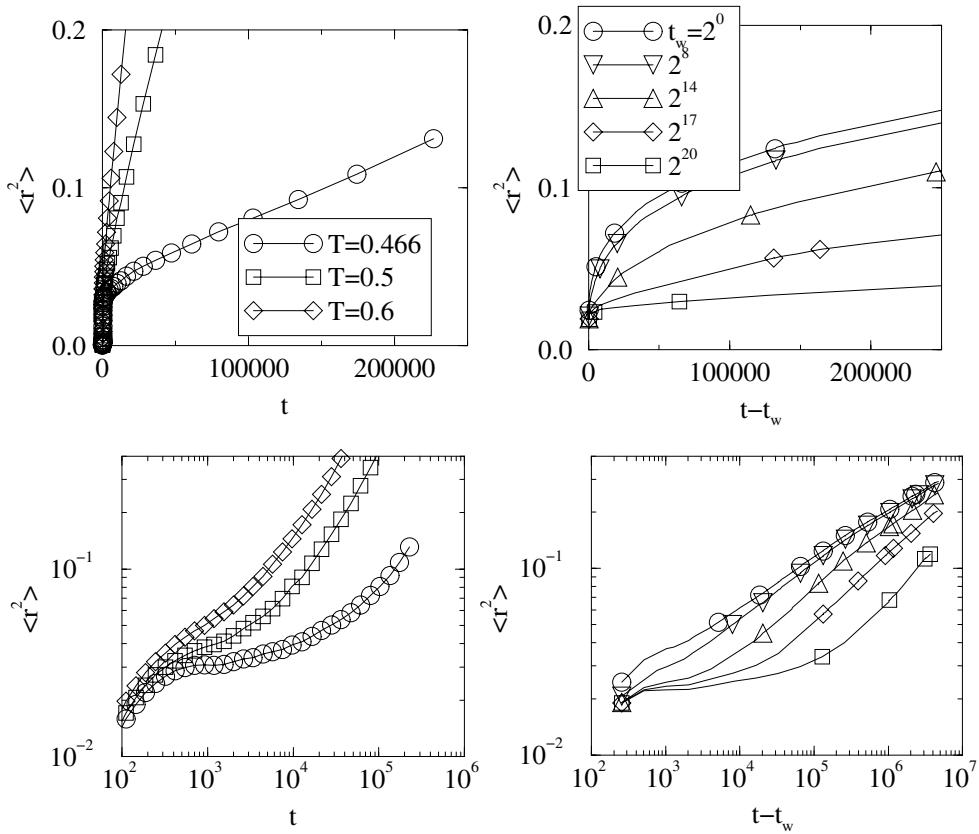


Figure 4. Mean square displacements in equilibrium for different values of T (left column) and in aging for different waiting times (right column). Both linear–linear and log–log representations are reported, to highlight the different t -dependences. Time is measured in MD steps.

In equilibrium, in the T -region where a clear separation of short-time and long-time dynamics is feasible, all curves can be scaled onto a common master curve, the so-called time–temperature representation. A master curve is produced if data are represented as a function of $\log(t/\tau(T))$, as shown in the left-hand panel of figure 5. In the OOE conditions a similar

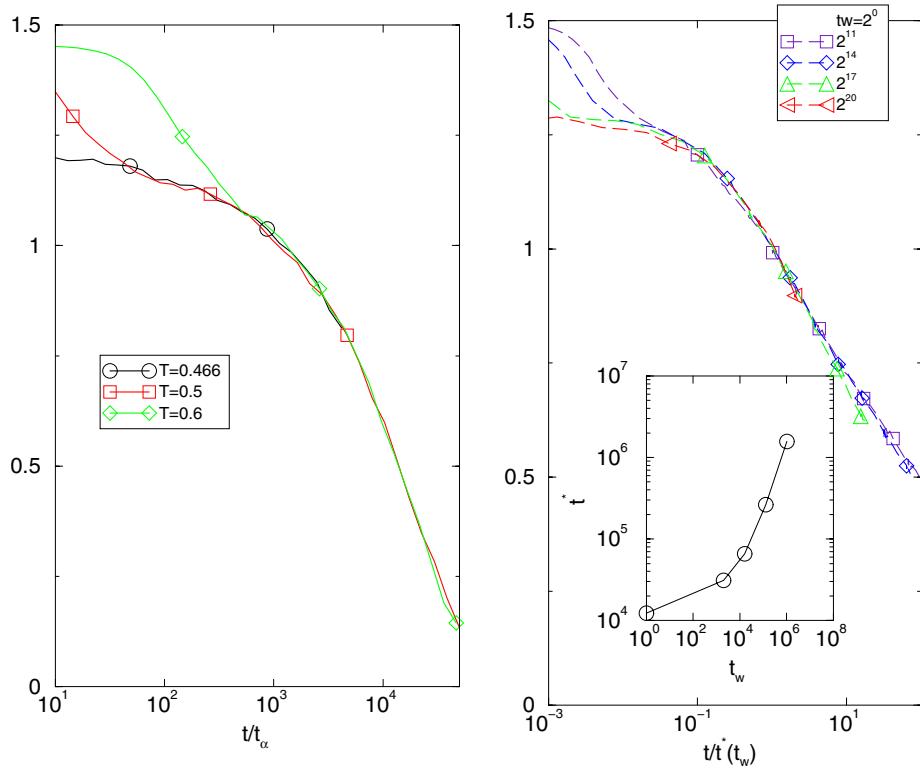


Figure 5. Collective correlation functions as functions of $t/\tau(T)$ and as functions of $t/\tau(t_w)$. The characteristic time τ is defined as the time at which the correlation function has decayed to the value $1/e$. The inset shows, in a log-log representation, the t_w -dependence of $\tau(t_w)$.

scaling can be produced (see the right-hand panel of figure 5), even if the quality of the scaling is not as good as that observed in equilibrium. The t_w -dependence of the scaling time is shown in the inset of figure 5. The qualitative behaviour of the scaling time is similar to that observed in OOE conditions generated during T -quenches (see reference [35]).

All quantities which in equilibrium do not depend on time but show a significant T -dependence, for example the potential energy or the sound velocity, may show a time dependence on t_w . In realistic OOE conditions, the long-time dependence of the one-time quantity $A(t_w)$ can be modelled as a slow logarithmic decay. An example of such decay is shown in figure 2, where the T -dependence of the inherent-structure energy is compared with the same quantity during aging.

The interesting features of aging show up in the slow dynamics. The short-time dynamics does not significantly change with t_w . A possible way to suppress the short-time dynamics is to compare not the instantaneous configurations, but the corresponding inherent structures—the closest local potential energy minimum configuration. The rationale for such an operation stems from the fact that at low temperature, the system dynamics can be efficiently decomposed into fast vibrational motions around the inherent structures superimposed on a slow process associated with changes in the inherent structures. The vibrational motion accounts for the fast decay of the correlation functions, while the long-time motion accounts for the decorrelation among the inherent structures. Figure 6 shows both $F(q, t)$ and $r^2(t)$ for different waiting times as calculated from the inherent-structure trajectories.

Concluding this section, we call the reader's attention to the fact that, in computer simulations, extremely short time windows can be accessed together with infinitely fast changes in the initial conditions (changes of volume or temperature taking place in one MD step). These unphysical conditions may give rise to short-time dependences of one-time and two-time quantities which are not general but depend on the specific OOE realization.

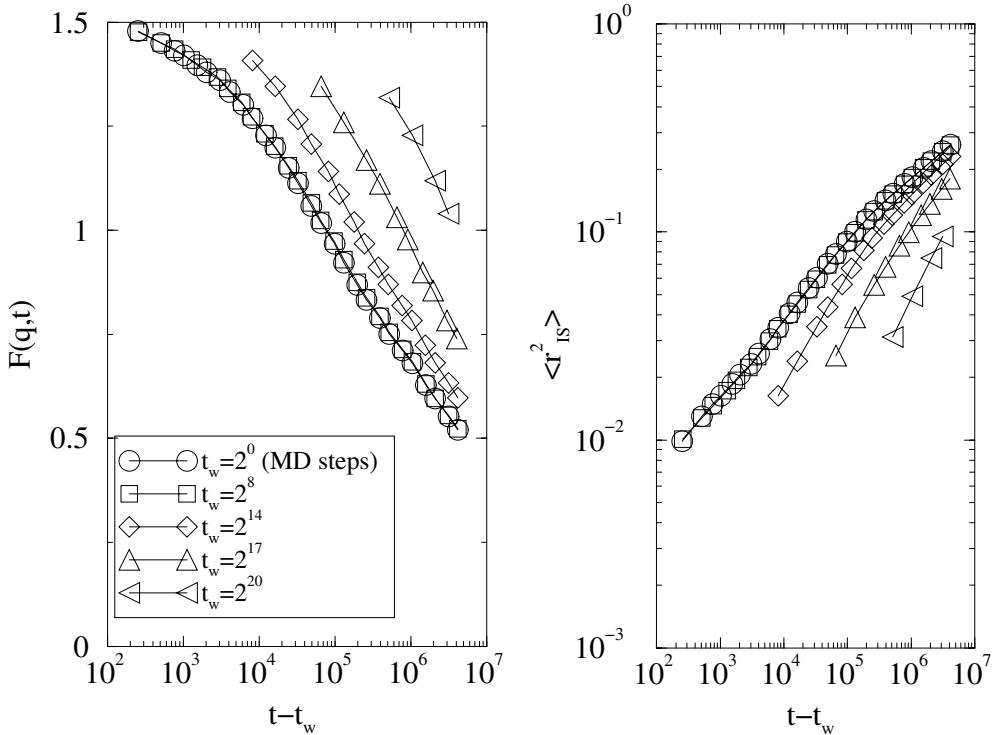


Figure 6. Intermediate-scattering functions and mean square displacements for different t_w -values as calculated from the IS trajectories. Note that the short-time dynamics is lacking and the region of validity of the asymptotic laws is enhanced.

6. A thermodynamic approach to aging

Before reviewing the recently developed thermodynamic description of an aging liquid based on the IS formalism, we discuss the basic ideas behind this theoretical approach.

A schematic view of the aging phenomenon in the IS formalism is shown in figure 7. Following a fast change in density or temperature, the system is located in a basin which is not the equilibrium basin predicted according to equation (3). Hence, the system evolves over time, looking for deeper and deeper basins. As shown in figure 2, the exploration process is very slow. The depth of the basin where the system is located after time t_w , $e_{IS}(t_w)$, decreases as a function of t_w . When $e_{IS}(t_w)$ reaches the equilibrium value $e_{IS}(T)$, the equilibration process is completed. During aging, $e_{IS}(t_w)$ is larger than $e_{IS}(T)$ and hence the system is out of equilibrium.

The expression for the free energy of the liquid during aging is formulated in analogy to the equilibrium free energy, i.e. as a sum of a basin free energy and a configurational

contribution. Since, as has been shown in reference [26], the shape of the basin explored during aging is identical to the shape of the basin explored in equilibrium (under the same basin depth conditions), the only difference in vibrational free energy is in the different values of the kinetic energy in the equilibrium and in the aging case. Hence, the vibrational part is unambiguously given by $f_{\text{basin}}(e_{IS}(t), T_{\text{bath}})$, since the intra-basin degrees of freedom quickly equilibrate with the thermostat at T_{bath} . The entropic contribution to the free energy requires the definition of a temperature, which we call the internal temperature T_{int} , higher than the thermostat temperature [39, 40], to reflect the out-of-equilibrium condition and the slow flow of heat from the system to the thermostat.

Unlike in the equilibrium case, during aging the system selects its own internal temperature depending on the values of $e_{IS}(t_w)$. Assuming quasi-equilibrium for the system, the internal temperature $T_{\text{int}}(e_{IS}, T_{\text{bath}})$ selected by the system when it is populating basins of depth e_{IS} is still a solution of equation (3) but with a fixed e_{IS} -value, i.e.

$$T_{\text{int}}(e_{IS}, T_{\text{bath}}) = \frac{\partial}{\partial e_{IS}} f_{\text{basin}}(T_{\text{bath}}, e_{IS}) \Big/ \frac{\partial}{\partial e_{IS}} S_{\text{conf}}(e_{IS}). \quad (5)$$

Note that, unlike the case in equation (3), f_{basin} is now evaluated at the thermostat temperature T_{bath} . This expression for T_{int} coincides with the expression proposed by Franz and Virasoro [41] in the context of p -spin systems.

For systems for which the basin shape does not change with e_{IS} , the meaning of the internal temperature is more transparent. Indeed, in this approximation the only e_{IS} -dependence in f_{basin} is via the depth of the basin itself, and hence $\partial f_{\text{basin}} / \partial e_{IS} = 1$,

$$T_{\text{int}}(e_{IS}, T_{\text{bath}}) = \left[\frac{\partial S_{\text{conf}}(e_{IS})}{\partial e_{IS}} \right]^{-1} \quad (6)$$

and, from equation (4), $T_{\text{int}}(e_{IS}, T_{\text{bath}}) = T_{\text{eq}}(e_{IS})$. Hence, the internal temperature coincides with the temperature at which, in equilibrium, basins of depth e_{IS} are populated. The liquid can thus be thought of as composed of two subsystems—the vibrational one coupled to the thermostat and the configurational one which is loosely coupled with the vibrational subsystem—hence acting as a microcanonical ensemble. In this spirit, the e_{IS} -value fixes the internal temperature of the configurational part.

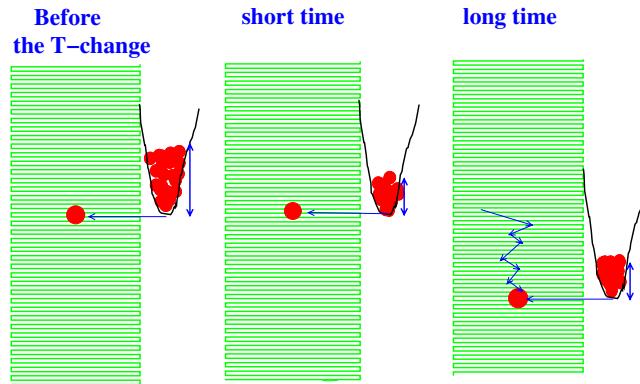


Figure 7. Schematic views of the aging phenomenon in the IS formalism. The case of a T -jump is shown. In a short time, the system equilibrates to the bath temperature within the same basin. Over a long time, the system explores different basins, progressively lowering its configurational energy. During this aging process, the basin free energy is always in equilibrium with the bath temperature.

When the basin shape depends on e_{IS} , the expression for the internal temperature is more complicated but it can still be calculated once a model for f_{basin} is chosen. If T_{bath} is small (as it usually is in the glass state), the harmonic approximation for f_{basin} can be used confidently.

Recently, a preliminary test of the validity of the proposed IS expression for T_{int} has been presented. T_{int} calculated theoretically according to equation (5) has been compared with the result of a numerical ‘experiment’ designed to independently calculate the temperature of the configurational subsystem, i.e. by calculating the ratio between the decay of correlation in thermal equilibrium and the response to an external perturbation. Linear response theory predicts that, in equilibrium, for a suitable choice of the perturbation, the temperature is such a ratio. This calculation, reported in reference [18], has confirmed that in the time window where the decay of correlation is controlled by intra-basin dynamics, the calculated temperature is equal to the bath temperature. In the region where the decay of correlation is controlled by the inter-basin motion, the calculated temperature agrees very well with the theoretical prediction for T_{int} . Hence, the extension of the thermodynamic formalism to the case of an out-of-equilibrium supercooled liquid [12] allows one to predict the response of the (aging) system to an external perturbation and the way in which this response depends on the time spent in the low-temperature glass state. It does not allow one to predict the t_w -dependence of $e_{IS}(t_w)$, an important step toward the full description of aging in glasses.

Before concluding this section, we stress that the thermodynamic analysis based on the IS formalism is strongly connected to the analysis performed in recent years with the aim of obtaining a description of the out-of-equilibrium dynamics of disordered spin models [12, 41, 42]. However we prefer to present our results in terms of quasi-equilibrium of the aging system. Recent extensions to finite-size disordered p -spin systems (the REM model) also support the validity of the thermodynamic approach to aging [43].

7. Conclusions

Numerical simulations of out-of-equilibrium liquids are sharpening our understanding of the aging dynamics and the connection between dynamics and thermodynamics. Simulations are providing a clear reference system to guide the analysis of experiments. At the same time, quantitative comparisons with theoretical descriptions are developing. The IS formalism appears to be able to describe in detail not only the equilibrium thermodynamics but also the non-equilibrium dynamics.

The similarity between the predictions presented here and the theoretical predictions developed in recent years in efforts to describe the out-of-equilibrium dynamics of disordered spin models [42] is very encouraging and suggests that a deep understanding of the physics of supercooled liquid and glasses is being developed. We stress that the IS formulation offers a more microscopic formalization of the thermodynamic approaches to the glass transition [11–13], with the additional possibility of a careful checking of the predictions with numerical simulations of realistic models for liquids.

Concluding, we recall that the time window accessed by the numerical experiments is very different from the experimental one and hence measurements of the internal temperature in aging experiments [16, 17] are very valuable for assessing the range of validity of the approach presented.

Acknowledgments

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