Crossover (or Kovacs) Effect in an Aging Molecular Liquid

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We study by means of molecular dynamics simulations the aging behavior of a molecular model of ortho-terphenyl. We find evidence of a nonmonotonic evolution of the volume during an isothermal-isobaric equilibration process, a phenomenon known in polymeric systems as the crossover (or Kovacs) effect. We characterize this phenomenology in terms of landscape properties, providing evidence that, far from equilibrium, the system explores regions of the potential energy landscape distinct from the one explored in thermal equilibrium.

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If two systems in thermodynamic equilibrium with identical chemical composition have the same temperature T and volume V, then they experience the same pressure P. The two systems respond in the same way to an external perturbation and are characterized by the same structural and dynamical properties. In the case of glasses, systems in out-of-equilibrium conditions, knowing T and V is not sufficient for predicting P, since the state of the system depends on its previous thermal and mechanical history. Different glasses, at the same T and V, are characterized by different P values. One can ask if two glasses with identical composition having not only the same T and V but also the same P are the same glass, i.e., if they have the same bulk as well as dynamic and structural properties. If this is the case, the two glasses should respond to an external perturbation in the same way and should age with a similar dynamics.

This basic question is at the heart of a thermodynamic understanding of the glassy state of matter. Indeed, if the glass state is uniquely defined by T, V, and P then it is possible to develop an out-of-equilibrium thermodynamic formalism [1–6] where the previous history of the system is encoded in only one additional parameter.

Back in the 1960s, Kovacs and co-workers designed an experimental protocol [7–9] (Fig. 1) to generate distinct glasses with different thermal and mechanical histories but with the same T, V, and P values. Polyvinyl acetate was equilibrated at high temperature T_h and then quenched at low temperature T_l, where it was allowed to relax isothermally for an elapsed time t_e insufficient to reach equilibrium. The material was then reheated to an intermediate temperature T and allowed to relax. The entire experiment was performed at constant P. The observed dynamics of the volume relaxation toward equilibrium—in the last step at constant T and P—was striking; the volume crosses over the equilibrium value, passes through a maximum, which depends upon the actual thermal history of the system, and then relaxes to the equilibrium value. The existence of a maximum clearly indicates that there are states with the same V (at the left and at the right of the maximum) which, although T, V, and P are the same, evolve differently. Thus, this experiment clearly shows that, in general, one additional parameter is not sufficient to uniquely predict the state of the glass [10].

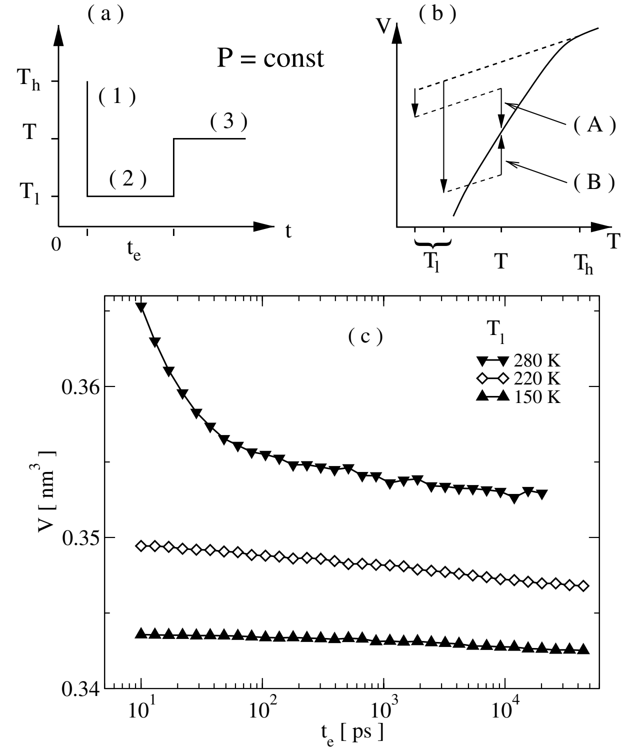

FIG. 1. (a) Temperature protocol in the Kovacs experiment: the system equilibrated at T_h is quenched at several T_l (1) where it relaxes for a time t_e (2). It is finally heated at T (3). (b) Corresponding volume evolution in the cases of low (A) and high (B) T_l. (c) Volume relaxation for the OTP model at different T_l. The fast relaxation taking place on times shorter than the thermostat characteristic time is not reported.

Here we attempt to reproduce numerically the Kovacs's experiment, performing molecular dynamics simulations for a simple molecular model, to develop an intuition on the differences between states with the same T, V, and P and on the conditions under which one-parameter out-of-equilibrium thermodynamics may be used to describe glass states. We find that only for sufficiently deep quenching temperatures and long aging times, it is possible to reproduce in simulations the crossover effects [11]. Analyzing the numerical trajectories, we examine the differences between configurations with the same T, V, and P, and contrast them with corresponding equilibrium liquid configurations. We discover that when the system ages, following significant T jumps (i.e., low T_l), it starts exploring regions of the potential energy landscape (PEL) which are not explored in equilibrium. Under these conditions, it is not possible any longer to associate a glass to a "quenched" liquid configuration via the introduction of a fictive T or P. This finding suggests that the range of validity of recent out-of-equilibrium thermodynamic theories based on only one additional parameter [3–6,12] is limited to cases when the aging system is close to equilibrium.

We consider a system of $N = 343$ molecules, interacting via the Lewis and Wahnström potential [13], a model for the fragile glass former ortho-terphenyl (OTP). The molecule is rigid, composed by three sites located at the vertexes of an isosceles triangle. Sites pertaining to different molecules interact via the Lennard-Jones potential. Simulation details are given in Refs. [14,15]. The system has been studied in isobaric-isothermal conditions; the time constants of both the thermostat and the barostat have been fixed to 20 ps. In order to accumulate an accurate statistics for the analysis below, averages over up to 200 different starting configurations have been performed. The total simulation time is more than 6 μs.

To reproduce the Kovacs's experiment, equilibrium configurations at $T_h = 400$ K, volume per molecule $V = 0.378$ nm^3, and $P = 16$ MPa are isobarically quenched at several low temperatures T_l [16], and left to age for different t_e values (t_e is never sufficient to reach equilibrium at T_l). Each resulting configuration is then isobarically heated to $T = 280$ K (see Fig. 1). At T the characteristic structural relaxation time is of the order of a few ns, allowing us to follow, with the present computational resources, the dynamics up to equilibrium. The V evolution is recorded along the entire path.

We also perform an analysis of the properties of the PEL explored during the relaxation process. In the PEL approach [17], the $6N$-dimensional configurational space—defined by the $3N$ center of mass coordinates and by the $3N$ Euler angles—is partitioned into a set of basins, each of them associated with a different local minimum of the potential energy landscape. The set of points belonging to the same basin are those which, under a steepest descent minimization procedure, end up in the same local minimum. The local minima in the PEL are called inherent structures (IS). The IS configurations are numerically evaluated performing a steepest descent path on the potential energy surface and can be thought of as the low-T glass generated by instantaneously quenching the liquid. Each IS configuration is characterized by its potential energy (e_{IS}), its pressure (P_{IS}), and by the $6N$ local curvatures (ω_k^2) of the associated basin, which can be estimated in the harmonic approximation by diagonalizing the Hessian matrix. In the OTP model, basins with different depths have different curvatures [14]. We focus, in particular, on the time evolution of e_{IS}, P_{IS}, and of the shape factor of the basin, $S \equiv \sum_{k=1}^{6N-3} \log(\omega_k/A_0)/N$ (here $A_0 = 1$ cm^{-1}).

Figure 2(a) shows the time evolution of V at constant $T = 280$ K and $P = 16$ MPa for samples which have

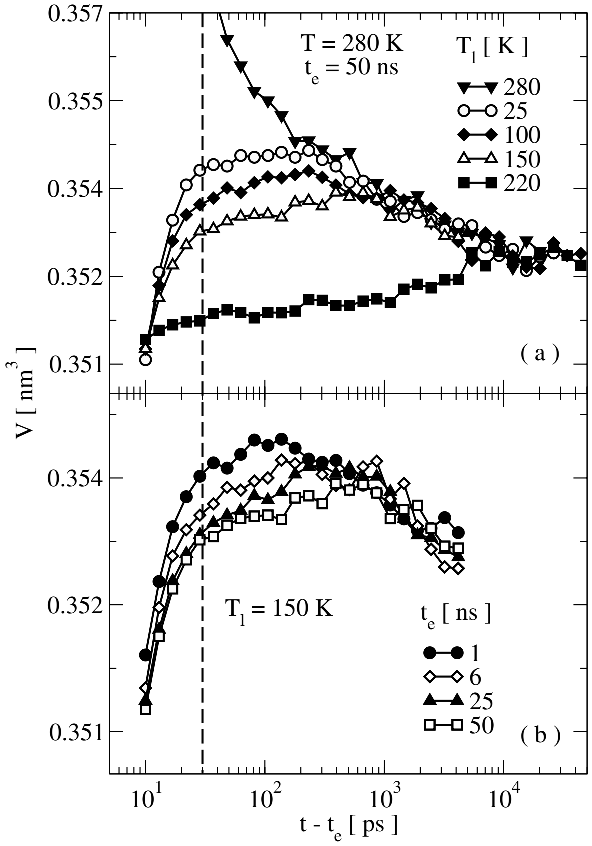

FIG. 2. Volume relaxation showing the crossover effect in a molecular system. (a) A system of 343 OTP molecules at constant $P = 16$ MPa is equilibrated at $T_h = 400$ K, quenched at several low temperatures T_l and left to age for $t_e = 50$ ns, a time insufficient to reach equilibrium at T_l. The system is then heated at the intermediate temperature $T = 280$ K and the V relaxation dynamics is recorded (symbols). For the case $T_l = T$, the system is directly brought from $T_h = 400$ K to $T = 280$ K and hence $t_e = 0$. The vertical dashed lines indicate the transient time, where T and P have not yet equilibrated to the final values. (b) Volume relaxation at $T = 280$ K, at fixed $T_l = 150$ K for different t_e values. Dashed lines delimit the transient region, when neither T nor P have reached their equilibrium value.

previously aged at different T_l for $t_e = 50$ ns [see Fig. 1(c)]. The time evolution of V for the case $T_l = T$ (i.e., for a T jump from T_h to T) is also reported. We note that for large T_l (i.e., $T_l = 220$ K), V relaxes to the equilibrium value from below monotonically. Similarly, for $T_l = T$, V relaxes to the equilibrium value from above, again monotonically. At variance, for deep T_l values, V does not relax monotonically to the equilibrium value. In analogy with Kovacs findings, it goes through a maximum, whose value is higher the lower T_l, before starting to relax toward the equilibrium value. After the maximum, the time evolution of V practically coincides with case $T_l = T$.

The elapsed time dependence of V during the final relaxation at T is shown in Fig. 2(b) for the case $T_l = 150$ K. For all studied t_e values, a maximum is observed, and the value of the maximum is larger the shorter t_e. All together, Figs. 2(a) and 2(b) confirm that the features observed by Kovacs in experiments with polymers are also observable in simulations of molecular glass forming liquids under deep-quench conditions (small T_l values).

Next we study the properties of the region of the PEL explored by the system during the aging process. Figure 3 shows, for the case $T_l = 150$ K for which a clear nonmonotonic V relaxation is observed, the out-of-equilibrium evolution of (a) the volume V, (b) the average inherent structures energy $e_{\rm IS}$, (c) the average inherent structure pressure $P_{\rm IS}$, and (d) the shape factor S. The maximum in the time evolution of V allows us to define two arbitrary points $P_<$ and $P_>$ (marked by arrows), characterized, by construction, by the same T, P, and V values. Although $P_<$ and $P_>$ are indistinguishable from a thermodynamical point of view, the subsequent dynamics is completely different in the two cases: after $P_<$ the system expands, while after $P_>$ it contracts. From a landscape point of view, $P_<$ and $P_>$ differ both in the depth and the shape of the sampled basin. The picture that emerges is that, at $P_<$, the system populates local minima which are systematically characterized by energy higher and basins of attraction steeper than the ones explored at $P_>$.

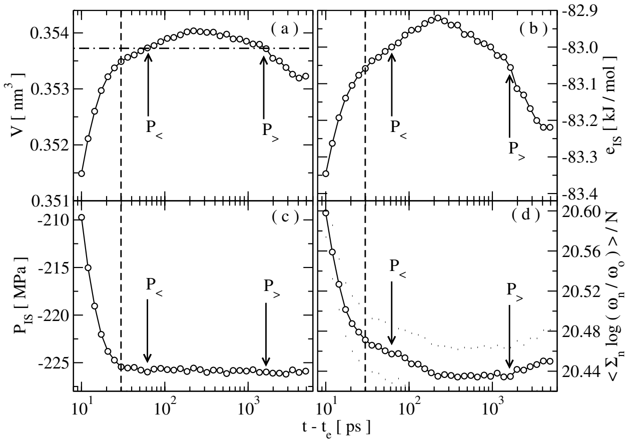

FIG. 3. Kovacs effect for $T_l = 150$ K and $t_e = 25$ ns; average over 200 independent realizations. The out-of-equilibrium evolutions of (a) system volume V, (b) inherent structures $e_{\rm IS}$, (c) inherent structure pressure $P_{\rm IS}$, and (d) shape factor S are shown. Error bars are smaller than the symbols. Two points (labeled $P_<$ and $P_<$), characterized by the same values of T, P, and V, are marked by arrows.

It is particularly important to note that, after about 20–30 ps, corresponding to the time requested to bring T and P to equilibrium, the $P_{\rm IS}$ value stabilizes, while both depth and shape of the explored basins continue to change with time. The fact that $P_{\rm IS}$ is constant offers a unique possibility to estimate if the aging dynamics proceed via a sampling of PEL basins similar to the ones which are explored in equilibrium [18]. Indeed, in equilibrium, all landscape properties (i.e., $e_{\rm IS}$, $P_{\rm IS}$, S) are functions only of T and V. By eliminating T in favor of $P_{\rm IS}$, $e_{\rm IS}$ and S can be expressed as a function of V and $P_{\rm IS}$. In this way, precise relations between properties of the landscape

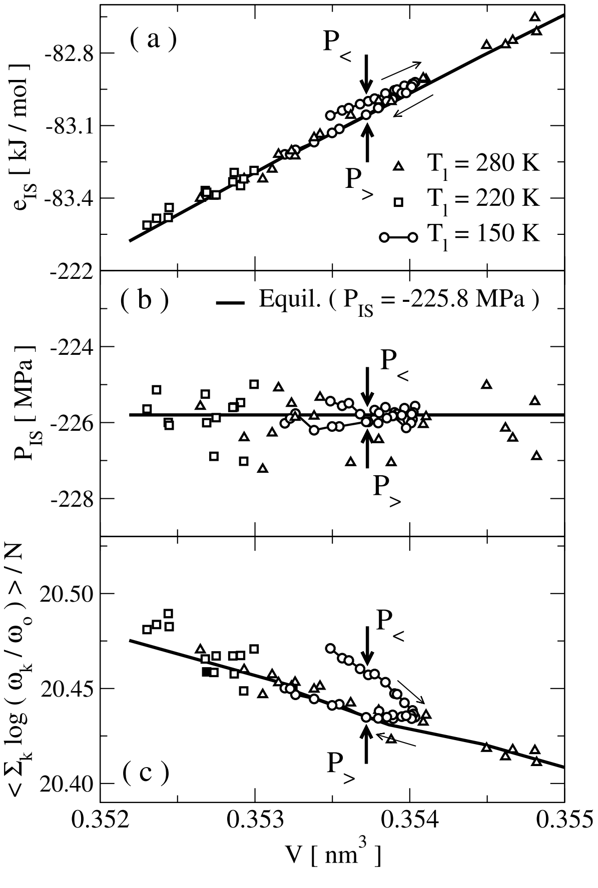

FIG. 4. Landscape relations $e_{\rm IS}(V)$, $P_{\rm IS}(V)$, and $S(V)$ along the constant $P_{\rm IS} = -225.8$ MPa path. Equilibrium data (solid lines) are generated from the analysis of equilibrium simulations at different state points but at constant $P_{\rm IS}$. Symbols refer to the relaxation dynamics at $T = 280$ K, for samples which have aged at $T_l = 150$, 220, and 280 K. Only data for times longer than 20 ps—the time associated with the establishment of constant T and P conditions—are shown. The vertical arrows indicate $P_<$ and $P_>$ (see Fig. 3).

sampled in equilibrium can be established. A set of configurations with the same V and P_{IS} can be considered as a representative of equilibrium configurations if and only if their e_{IS} and S values satisfy the equilibrium $e_{\mathrm{IS}}(P_{\mathrm{IS}}, V)$ and $S(P_{\mathrm{IS}}, V)$ landscape relations.

At fixed P_{IS}, e_{IS} and S become, in equilibrium, unique functions of V. Such equilibrium landscape relations for $P_{\mathrm{IS}} = -225.8$ MPa are shown in Fig. 4. The figure also reports the evolution of $e_{\mathrm{IS}}(V)$ and $S(V)$ during aging for the two cases where a monotonic V relaxation is observed (large T_l values, $T_l = 220$ K, and $T_l = 280$ K), and for the case $T_l = 150$ K where a maximum in the time evolution of V is clearly detected. The important information standing out from the comparison is that, while the relaxation process for the two large T_l cases (280 and 220 K) proceeds via a sequence of equilibrium configurations, in the crossover case ($T_l = 150$ K) only the final part of the dynamics goes via a sequence of PEL basins, where the relations among S, e_{IS}, and P_{IS} are identical to the one found in equilibrium. This shows that only $P_>$ can be related to an equilibrium configuration.

In summary, while at $P_>$ the system samples landscape properties which are sampled by the liquid at equilibrium at a higher temperature (which can be used as an additional parameter to quantify the glass properties), at $P_<$ the system explores a region of the landscape which is never explored in equilibrium, since the relation between the landscape properties characterizing $P_<$ are never encountered in equilibrium. Under these conditions, it is not possible to exactly relate the glass structure to an equilibrium structure and, hence, define a fictive T for the system.

The present numerical study shows that, only when the change of external parameters is small, or when the aging system is close to the final equilibrium, the evolution of the system proceeds along a sequence of configurations which are explored in equilibrium. Under these conditions, the location of the aging system can be traced back to an equivalent equilibrium state, and a fictive T or P can be uniquely defined. In this case, a thermodynamic description of the aging system based on one additional parameter can be provided. On the contrary, when the external perturbation is significant, like in hyperquenching experiments [19], the aging dynamics propagates the system through a sequence of configurations never explored in equilibrium, and it becomes impossible to associate the aging system to a corresponding liquid configuration. Average values are not sufficient anymore to identify the system and fluctuations around the average values become important to describe the glass state [20].

It is a challenge for future studies to find out if a thermodynamic description can be recovered decomposing the aging system in a collection of substates, each of them associated with a different fictive T—a picture somehow encoded in the phenomenological approaches of Tool and co-workers [21] and Kovacs and co-workers [22]—or if the glass, produced under extreme perturbations, is trapped in some highly stressed configuration which can never be associated with a liquid state.

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[1] R. O. Davies and G. O. Jones, Adv. Phys. **2**, 370 (1953).
[2] R. J. Speedy, J. Chem. Phys. **100**, 6684 (1994).
[3] L. F. Cugliandolo, J. Kurchan, and L. Peliti, Phys. Rev. E **55**, 3898 (1997).
[4] Th. M. Nieuwenhuizen, Phys. Rev. Lett. **80**, 5580 (1998).
[5] S. Franz and M. A. Virasoro, J. Phys. A **33**, 891 (2000).
[6] S. Mossa *et al.*, Eur. Phys. J. B **30**, 351 (2002); J. Phys. Condens. Matter **15**, S351 (2003).
[7] A. J. Kovacs, Fortschr. Hochpolym. Forsch. **3**, 394 (1963).
[8] G. B. McKenna, in *Comprehensive Polymer Science*, edited by C. Booth and C. Price, Polymer Properties Vol. 2 (Pergamon, Oxford, 1989), pp. 311–362.
[9] C. A. Angell *et al.*, J. Appl. Phys. **88**, 3113 (2000).
[10] Indeed, the measured kinetics have been rationalized using an empirical formalism which postulates the existence of nonexponential response functions and of several retardation mechanisms with different time scales [21,22].
[11] G.W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986).
[12] F. Sciortino and P. Tartaglia, Phys. Rev. Lett. **86**, 107 (2001).
[13] L. J. Lewis and G. Wahnström, Phys. Rev. E **50**, 3865 (1994).
[14] S. Mossa *et al.*, Phys. Rev. E **65**, 041205 (2002).
[15] E. La Nave, S. Mossa, and F. Sciortino, Phys. Rev. Lett. **88**, 225701 (2002).
[16] The T-jump magnitudes are large compared to Kovacs's data. For small T jumps (as shown for the case $T_l = 220$), no crossover effects are found. We believe this is due to the fact that activated processes are important in generating the crossover effect. The condition of full relaxation at T during the simulation time fixes the choice of $T = 280$ K which is still a T where "saddle dominated dynamics" is important [14]. Along the $P = 16$ MPa, the estimated ideal mode coupling temperature is $T_{\mathrm{MCT}} \simeq 260$ K. To favor activated processes, we are forced to impose larger T jumps than in the experiment, where T is close to the glass transition temperature. This would suggest that the absence of Kovacs's effect at large T_l values is intimately connected to the location of the final temperature as compared to T_{MCT}.
[17] F. Sciortino, W. Kob, and P. Tartaglia, Phys. Rev. Lett. **83**, 3214 (1999).
[18] E. La Nave *et al.*, Phys. Rev. E **68**, 032103 (2003).
[19] C. A. Angell *et al.*, J. Phys. Condens. Matter **15**, S1051 (2003).
[20] E. M. Bertin *et al.*, J. Phys. A **36**, 10 701 (2003).
[21] A. Q. Tool, J. Am. Ceram. Soc. **29**, 240 (1946).
[22] A. Kovacs *et al.*, J. Polym. Sci., Polym. Phys. Ed. **17**, 1097 (1979).