Eur. Phys. J. B **30**, 351–355 (2002)
DOI: 10.1140/epjb/e2002-00389-0

THE EUROPEAN
PHYSICAL JOURNAL B

Aging and energy landscapes: application to liquids and glasses

S. Mossa[1,2,a], E. La Nave[1], F. Sciortino[1], and P. Tartaglia[1]

[1] Dipartimento di Fisica and INFM Udr and Center for Statistical Mechanics and Complexity, Universitá di Roma “La Sapienza”, Piazzale Aldo Moro 2, 00185, Roma, Italy
[2] Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA

Received 7 August 2002 / Received in final form 8 October 2002

Abstract. The equation of state for a liquid in equilibrium, written in the potential energy landscape formalism, is generalized to describe out-of-equilibrium conditions. The hypothesis that during aging the system explores basins associated to equilibrium configurations is the key ingredient in the derivation. Theoretical predictions are successfully compared with data from molecular dynamics simulations of different aging processes, such as temperature and pressure jumps.

PACS. 64.70.Pf Glass transitions – 61.20.Ja. Computer simulation of liquid structure – 61.20.Lc. Time-dependent properties; relaxation

Glasses are out-of-equilibrium (OOE) systems, characterized by slow dynamical evolution (aging) and history dependent properties. Their thermodynamic and dynamic properties depend on the preparation method (cooling or compression schedules) as well as the time spent in the glass phase [1]. The extremely slow aging dynamics has often been considered an indication that a thermodynamic description of the glass state can be achieved by adding one or more history-dependent parameters to the equation of state (EOS) [2–13]. Recent theoretical work — mostly based on mean field models of structural glasses, where analytic solutions of the out-of-equilibrium dynamics can be explicitly worked out [14] — supports such possibility.

Here we introduce an equation of state for out-of-equilibrium conditions, based on a generalization of the potential energy landscape (PEL) thermodynamic approach [15–17]. The equation of state is derived under the hypothesis that during aging the system explores basins associated with equilibrium configurations, a condition which, as shown later, is simple to implement in the PEL context. The proposed equation of state for out-of-equilibrium conditions depends on one additional parameter, which for example can be chosen to be the average depth of the explored local minima of the PEL (the so-called inherent structures (IS) [15,16]). Our formulation allows for the first time a detailed comparison between predictions and “exact results” from out-of-equilibrium molecular dynamics simulations. We report such a comparison for a realistic model of the fragile liquid orthoterphenyl, one of the most studied glass forming liquids [18].

The potential energy landscape formalism [15,16] allows for a clear separation of vibrational and configurational contributions in thermodynamical quantities. Indeed, the equilibrium liquid free energy $F(T,V)$ at temperature T and volume V is expressed as a sum of a vibrational contribution f_{vib}, representing the intra-basin free energy [15], and a configurational contribution $(-TS_{conf}+e_{IS})$. Here the configurational entropy S_{conf} accounts for the number of explored basins of the PEL of average energy depth e_{IS}. f_{vib}, for a system of N atoms, depends on the curvature of the potential energy surface, *i.e.*, on the $3N$ eigenvalues ω_i^2 of the Hessian matrix evaluated at the inherent structure. Recently, calculating the V derivative of $F(T,V)$, an analytic equation of state has been derived, based only on the statistical properties of the landscape [19,20].

The separation in vibrational and configurational parts can be carried out for several properties. In our case, it is particularly useful to separate the instantaneous pressure as sum of two contributions: the pressure felt by the system in the inherent structure configuration (P_{IS}), and an additional contribution related to the finite temperature, which we refer to as the vibrational contribution (P_{vib}) [21]

$$P(T,V,e_{IS}) = P_{IS}(e_{IS},V) + P_{vib}(T,V,e_{IS}). \qquad (1)$$

---

[a] *Present address*: Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, 4 place Jussieu, Paris 75005, France
e-mail: `mossa@lptl.jussieu.fr`

In equilibrium e_{IS} is a well defined function of T and V and, as well known, P depends only on T and V. Note that P_{IS}, being the pressure experienced by the liquid in the IS, depends only on the basin's depth and on V, independently from the equilibrium or out-of-equilibrium state of the system. Instead, P_{vib} depends on the basin's depth as well as on T and V [22].

For models for which the statistical properties of the PEL, *i.e.*, the distribution of shapes and numbers of the inherent structures [19,20] are known, P_{IS} and P_{vib} can be calculated theoretically. In other cases, P_{IS} and P_{vib} can be calculated numerically. In all cases, a landscape-based equation of state can be derived, according to equation (1).

The separation of the pressure in two contributions is crucial for the possibility of extending the equilibrium equation of state to out-of-equilibrium conditions, since it provides a direct way to rebuild the pressure once T, V and e_{IS} are known. In the PEL formalism, the hypothesis that the system explores basins associated with typical equilibrium configurations, *i.e.*, configurations sampled in equilibrium conditions, is equivalent to assuming that the relations — calculated in equilibrium — linking P_{IS} and P_{vib} to e_{IS} and V are valid also in out-of-equilibrium conditions. If this is the case, the knowledge of e_{IS}, T and V is sufficient to calculate both P_{IS}, P_{vib} and their sum P according to equation (1). Similarly, the values of P, T and e_{IS} are sufficient to predict V, since both $P_{IS}(e_{IS}, V)$ and $P_{vib}(e_{IS}, T, V)$ can be estimated as a function of V. The predicted V is the value for which $P_{IS}(e_{IS}, V) + P_{vib}(e_{IS}, T, V)$ matches the external pressure.

Next we apply the ideas discussed above to a system of $N = 343$ molecules interacting *via* the Lewis and Wahnström (LW) model for the fragile molecular liquid orthoterphenyl (OTP) [23,24]. The LW model is a rigid three-site model, with intermolecular site-site interactions modeled by the Lennard-Jones (LJ) potential [24]. We refer to reference [23] for all numerical details. An equilibrium equation of state, based on the assumption of a Gaussian landscape, has been recently presented for this model [19], and successfully compared with the "exact" equation of state calculated from molecular dynamics simulations.

Figure 1 shows the relation between P_{IS} and e_{IS} in equilibrium along different isochores, and P_{vib} as a function of T for the LW model. Both quantities can be parameterized in a quite accurate way. Indeed, for this model, P_{vib} is weakly dependent on V and e_{IS} and it is well represented by a linear T-dependence. The parameterization of P_{IS} and P_{vib} offers the possibility of estimating the system pressure once T, V and e_{IS} are known.

We study four different out-of-equilibrium protocols *via* computer simulation. The imposed external conditions are illustrated in Figure 2. We study i) a T-jump at constant V; ii) a P-jump at constant T; iii) a P-jump at constant T in the glass phase and iv) an isobaric heating of a glass. For the cases i) and ii), conditions are chosen in such a way that within the simulation time window (50 ns) the system reaches the equilibrium state. In all studied cases, averages over 50 independent simulations have been performed.

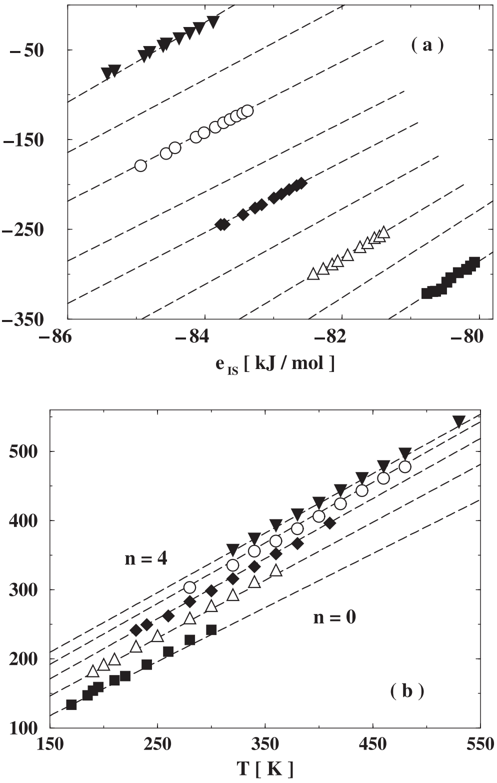

Fig. 1. (a) Equilibrium relation between basin pressure P_{IS} and basin depth e_{IS}. Symbols are simulation results at the five volumes per molecule 0.337 nm^3 (down triangles), 0.345 nm^3 (circles), 0.353 nm^3 (diamonds), 0.361 nm^3 (up triangles), and 0.369 nm^3 (squares) from reference [23]. Dashed lines are calculated using the parameterization discussed in reference [19]. Results at four intermediate volumes are also shown. The local minima are calculated using standard minimization algorithms [23]. (b) P_{vib} as a function of T for the same five volumes. Each curve has been shifted by $n \times 20$ MPa to avoid overlaps. Dashed lines show a suitable parameterization of the e_{IS}, V and T dependence of P_{vib}, as discussed in reference [19].

Case (i). — Figure 3 shows the comparison between the theoretical predictions and the numerical results for the constant-V T-jump case. The numerical experiment is performed by changing at $t = 0$ the thermostat value; the time constant of the thermostat has been fixed to 20 ps. The e_{IS} values, calculated from the simulation (Fig. 3a), are used together with the values of T and V as input to predict the evolution of P (Fig. 3b). Figures 3c and d also show the comparison for P_{IS} and $\mathcal{W}$. $\mathcal{W}(e_{IS})$, defined as $\sum_{i=1}^{3N} \ln(\omega_i(e_{IS}))$, provides an indication of the similarity in basin shape (at the level of the harmonic approximation) between basins explored in equilibrium and in out-of-equilibrium conditions. The quality of the predictions indeed supports the validity of the equation of state and the hypothesis that the basins sampled during aging have the same relationship $\mathcal{W}(e_{IS})$ as in equilibrium.

Case (ii). — Figure 4 shows the evolution of the system after a constant-T pressure jump. In this case, the e_{IS}

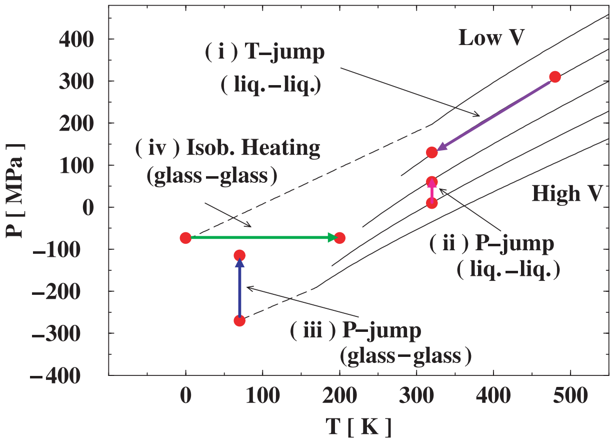

Fig. 2. Paths in the $P-T$ plane of the four out-of-equilibrium simulations discussed in the text. Arrows indicate: (i) a T-jump at constant V between liquid states; (ii) a P-jump at constant T between liquid states; (iii) a P-jump at constant T starting from a glass; (iv) a constant P heating of a glass. P and T-jumps have been simulated by changing the thermostat and barostat value at $t = 0$. The time constant of the thermostat and barostat has been fixed to 20 ps. The full lines indicate the equilibrium $P(T)$ at five V values, from reference [23]. The dashed lines connect the equilibrium state points and the glass states obtained by fast constant-V cooling.

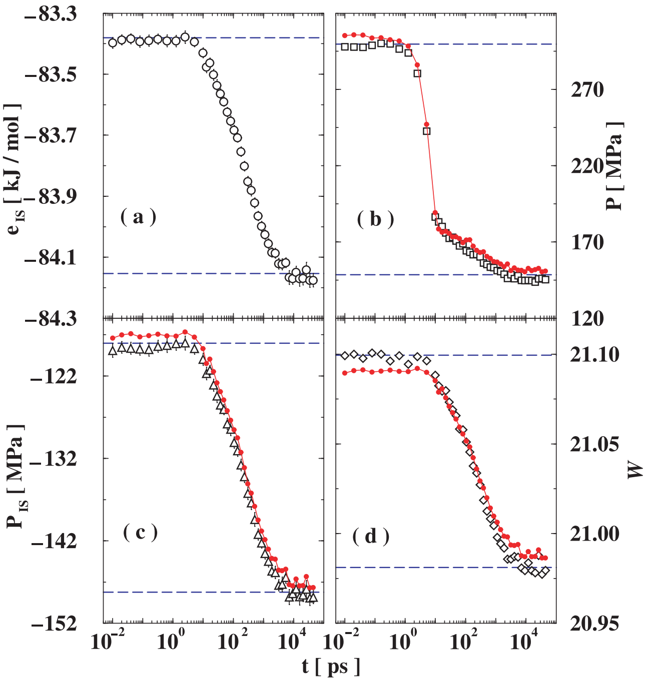

Fig. 3. Dynamics after a T-jump, at volume per molecule $V = 0.345$ nm^3, from 480 K to 340 K. (a) e_{IS}; (b) P; (c) P_{IS}; (d) $\mathcal{W}$ ($\omega_o = 1cm^{-1}$). Open symbols are simulation results, closed circles are theoretical predictions based on the out-of-equilibrium PEL-equation of state and using as input the data shown in panel (a). Dashed lines indicate the known equilibrium values at the initial and final state. The error in the prediction at short and long times, when equilibrium conditions are met, provides a measure of the quality of the equilibrium equation of state [19], which agrees with the simulation data within ±5 M Pa.

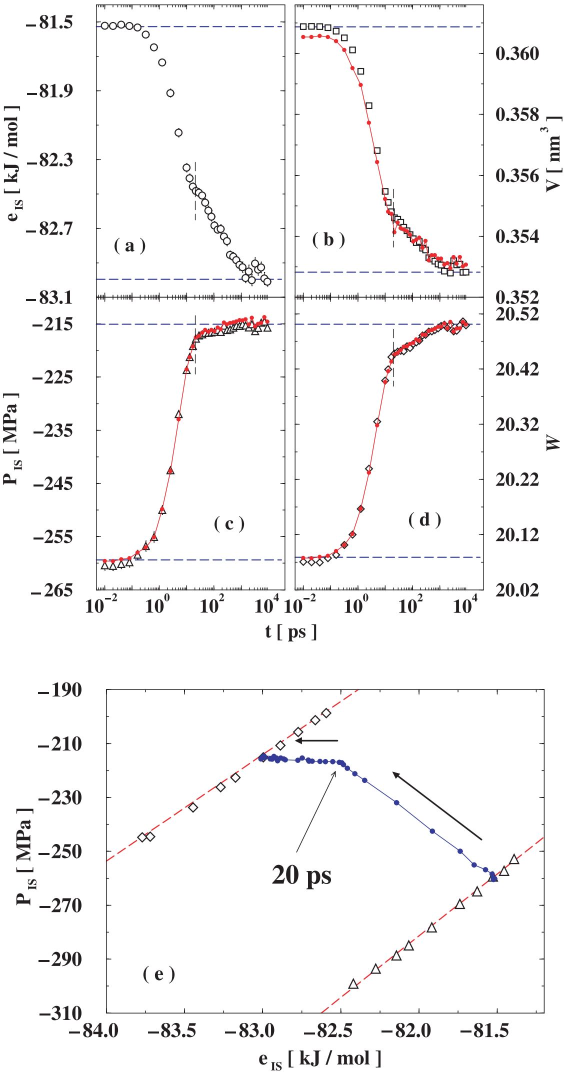

Fig. 4. Dynamics after a P-jump at $T = 320$ K from 13.4 MPa to 60.7 MPa. (a) e_{IS}; (b) V; (c) P_{IS}; (d) $\mathcal{W}$. Open symbols are simulation results, closed circles are theoretical predictions based on the out-of-equilibrium PEL-equation of state, using as input the data shown in panel (a). Horizontal dashed lines indicate the known equilibrium values at the initial and final state. The vertical dashed lines indicate the time at which the external pressure reaches the final value. Panel (e) shows the actual path of the aging process in the P_{IS}-e_{IS} plane. The open symbols are the P_{IS}-e_{IS} equilibrium results at the two densities characterizing the initial and final state of the P-jump.

values calculated from the simulation are used together with the values of T and P as input to successfully predict the evolution of V. For times shorter than 20 ps, the barostat time constant, the fast increasing external pressure forces the system to change the volume with a solid-like response. In this time window, the initial basins in configuration space are continuously deformed by the rapid volume change, in agreement with the findings of reference [25]. For time longer than 20 ps, when the external pressure has reached the equilibrium value,

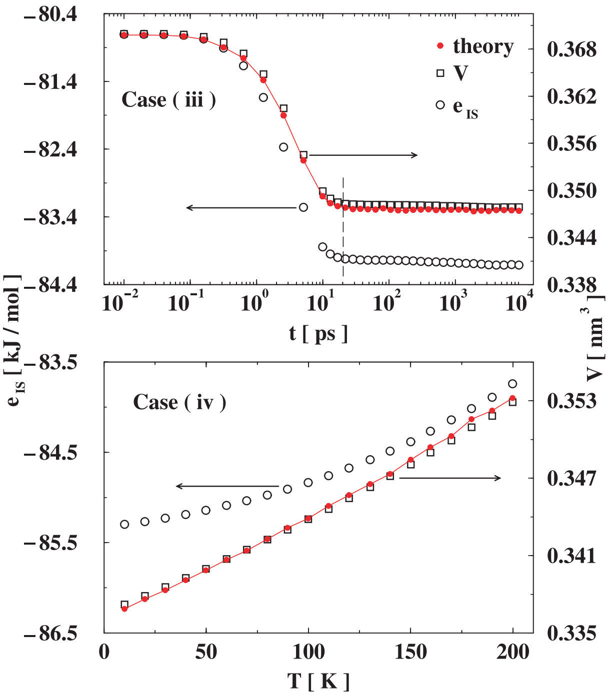

Fig. 5. Top: Simulation of a P-jump from -270.1 MPa to -115.4 MPa, starting from a glass configuration, obtained by quickly cooling to 70 K equilibrium configurations at volume per molecule $V = 0.369$ nm^3 and $T = 170$ K. Bottom: Isobaric heating, starting from the IS at $V = 0.337$ nm^3 per molecule and $T = 320$ K. The heating rate is 1 K / ps. Circles are the e_{IS} values used as input to predict the evolution of V (lines). Squares are the V calculated directly from the simulations.

the system starts to explore basins different from the (deformed) original ones, and the time evolution is controlled by the aging kinetics. To support this interpretation we show in Figure 4e the actual path in the e_{IS}-P_{IS} plane, where the change around 20 ps is clearly evidenced. As shown in Figure 4e, P_{IS} is almost constant at long times. This is due to the fact that the vibrational component to the pressure is mostly controlled by the temperature. Hence, no significant changes in P_{vib} are observed when the system explores states of lower energy. As a result, when the total pressure has reached the value fixed by the barostat (in about 20 ps), P_{IS} must also have reached its final value; the system will then evolve by changing volume and energy depth keeping P_{IS} almost constant.

Cases (iii) and (iv). — The last two cases are respectively a constant T P-jump and a heating at constant P (with an heating rate of 1 K/ps), both starting from glass configurations. These initial configurations are generated by rapid constant-V quenches of equilibrium configurations, as shown schematically in Figure 2. Figure 5 shows the comparison between the theoretical predictions and the numerical calculations for V, using e_{IS} as input. In the case of a P-jump (Fig. 5-top), again two different dynamical behaviors are observed: a fast dynamics process describing the mechanical response of the glass to the external pressure change, followed by an extremely slow aging dynamics, during which basin changes are taking place.

In both cases and for all times, the out-of-equilibrium equation of state is able to predict quantitatively the V changes.

In summary, we have derived an extension of the PEL equation of state to model the thermodynamic properties of liquids under out-of-equilibrium conditions. Such an extension — based on the hypothesis that an aging system evolves through regions of configuration space which are typically sampled in equilibrium — requires an additional thermodynamic parameter which, for convenience, we have associated with the IS energy of the explored basins.

The results reported in this paper (Figs. 3–5) show that the proposed generalization of the PEL equation of state is successful in predicting out-of-equilibrium thermodynamics, at least under the conditions and time scales probed by state-of-the-art numerical simulations. Larger T or P jumps and/or longer aging time could require a more detailed thermodynamic description, with more than one additional parameter. Despite such a possibility, the energy landscape approach developed in this paper is a promising starting point for looking into more complex problems in the physics of out-of-equilibrium liquids and glasses.

We thank A. Angell, P. Debenedetti, T. Keyes, L. Leuzzi, G. McKenna, G. Ruocco, S. Sastry, A. Scala, and M. Yamada for discussions and comments. We acknowledge support from MIUR-COFIN, INFM-PRA and INFM Initiative Parallel Computing.

References

1. P.G. Debenedetti, *Metastable liquids* (Princeton Univ. Press, Princeton, 1996)
2. A.Q. Tool, J. Am. Ceram. Soc. **29**, 240 (1946)
3. R.O. Davies, G.O. Jones, Adv. Phys. **2**, 370 (1953)
4. A.J. Kovacs, Fortschr. Hochpolym.-Forsch. **3**, 394 (1964)
5. G.B. McKenna, in *Comprehensive Polymer Science*, Vol. 2, edited by C. Booth, C. Price (Pergamon, Oxford, 1989), p. 34
6. R.J. Speedy, J. Chem. Phys. **100**, 6684 (1994)
7. L.F. Cugliandolo, J. Kurchan, L. Peliti, Phys. Rev. E **55**, 3898 (1997)
8. Th.M. Nieuwenhuizen, Phys. Rev. Lett. **80**, 5580 (1998)
9. A.C. Angell, K.L. Ngai, G.B. McKenna, P.F McMillan, S.W. Martin, J. Appl. Phys. **88**, 3113 (2000)
10. T.S. Grigera, N.E. Israeloff, Phys. Rev. Lett. **83**, 5038 (1999)
11. L. Bellon, S. Ciliberto, C. Laroche, Europhys. Lett. **53**, 511 (2001)
12. S. Franz, M.A. Virasoro, J. Phys. A **33**, 891 (2000)
13. L. Leuzzi, Th.M. Nieuwenhuizen, J. Phys.: Cond. Matt. **14**, 1637 (2002)
14. L.F. Cugliandolo, J. Kurchan, P. Le Doussal, Phys. Rev. Lett. **76**, 2390 (1996)
15. F.H. Stillinger, T.A. Weber, Phys. Rev. A **25**, 978 (1982)

16. P.G. Debenedetti, F.H. Stillinger, Nature **410**, 259 (2001)
17. S. Sastry, Nature **409**, 164 (2001)
18. A. Tölle, Rep. Prog. Phys. **64**, 1473 (2001)
19. E. La Nave, S. Mossa, F. Sciortino, Phys. Rev. Lett. **88**, 225701 (2002)
20. P.G. Debenedetti, T.M. Truskett, C.P. Lewis, F. Stillinger, Adv. Chem. Eng. **28**, 21 (2001)
21. In equilibrium, P can be unambiguously separated in a configurational $\partial_V[TS_{conf}(T,V) - e_{IS}(T,V)]$ and a vibrational $\partial_V f_{vib}$ contribution. In the inherent structure configuration the vibrational part is strictly zero. Still, the configurational component may not coincide with P_{IS}. Different proposals for P_{IS} arise depending on the meaning of T in the $-TS_{conf}$ term above. See references [19,26]. Such ambiguity affects the theoretical expression for P_{IS} based on the statistical properties of the landscape. Luckily, this ambiguity does not hamper the possibility of developing an out-of-equilibrium equation of state when P_{IS} is calculated directly from the simulation data
22. For example, in an harmonic solid, P_{vib} is related to the V derivative of the eigenfrequencies as $P_{vib}(T,V,e_{IS}) \equiv k_B T \partial_V \sum_{i=1}^{3N-3} \ln(\beta\hbar\omega_i(e_{IS}))$
23. S. Mossa, E. La Nave, H.E. Stanley, C. Donati, F. Sciortino, P. Tartaglia, Phys. Rev. E **65**, 041205 (2002)
24. L.J. Lewis, G. Wahnström, Phys. Rev. E **50**, 3865 (1994)
25. D.L. Malandro, D.J. Lacks, Phys. Rev. Lett. **81**, 5576 (1998)
26. F. Sciortino, P. Tartaglia, Phys. Rev. Lett. **86**, 107 (2001)