

## Potential Energy Landscape Equation of State

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Depth, number, and shape of the basins of the potential energy landscape are the key ingredients of the inherent structure thermodynamic formalism introduced by Stillinger and Weber [F. H. Stillinger and T. A. Weber, *Phys. Rev. A* **25**, 978 (1982)]. Within this formalism, an equation of state based only on the volume dependence of these landscape properties is derived. Vibrational and configurational contributions to pressure are sorted out in a transparent way. Predictions are successfully compared with data from extensive molecular dynamics simulations of a simple model for the fragile liquid orthoterphenyl.

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Recent years have seen a resurgence in studies devoted to modeling the thermodynamics of supercooled liquids [1–5]. Such studies aim to elucidate the physics of the liquid-glass transition, to develop a thermodynamic description of out-of-equilibrium systems and to provide keys for a deeper understanding of the dynamics of supercooled states [6]. Numerical studies are nowadays providing quantitative estimates for the free energy of simple model systems [7–10]. The availability of such data provides stringent tests of the theoretical predictions [9–11] and helps in the understanding of basic mechanisms associated with the behavior of thermodynamic and dynamic quantities close to the glass transition.

Among the thermodynamic formalisms amenable to numerical investigation, a central role is played by the inherent structure (IS) formalism introduced by Stillinger and Weber [12]. Properties of the potential energy landscape (PEL), such as depth, number, and shape of the basins of the potential energy surface, are calculated and used in the evaluation of the liquid free energy [9–11,13]. In the IS formalism, the system free energy is expressed as a sum of an entropic contribution, accounting for the number of the available basins, and a vibrational contribution, expressing the free energy of the system when constrained in one of the basins [12].

Important progress has been made after the discovery that, for models of fragile liquids, the number  $\Omega(e_{\text{IS}})$  of distinct basins of depth  $e_{\text{IS}}$  in a system of  $N$  atoms or molecules is well described by a Gaussian distribution [10,14]

$$\Omega(e_{\text{IS}}) = e^{\alpha N} \frac{e^{-(e_{\text{IS}}-E_0)^2/2\sigma^2}}{(2\pi\sigma^2)^{1/2}}. \quad (1)$$

Here the amplitude  $e^{\alpha N}$  accounts for the total number of basins. Numerical studies of models for fragile liquids have also shown that the basin free energy can be written as the depth  $e_{\text{IS}}$  plus a vibrational contribution which, in the harmonic approximation, has the well-known form

$$F_{\text{vib}}(e_{\text{IS}}, T) = k_B T \sum_{i=1}^M \ln[\beta \hbar \omega_i(e_{\text{IS}})], \quad (2)$$

where  $\omega_i(e_{\text{IS}})$  is the  $i$ th normal mode frequency ( $i = 1, \dots, M$ ) and  $\beta = 1/k_B T$ . The  $M$  normal mode frequencies define the shape of the basin. If relevant, anharmonic corrections can also be accounted for [11,13]. The quantity  $\sum_{i=1}^M \ln[\omega_i(e_{\text{IS}})/\omega_o]$  (where  $\omega_o$  is the frequency unit) is found to depend linearly on the basin depth [10], i.e., can be written, in terms of two parameters  $a$  and  $b$ , as

$$\sum_{i=1}^M \ln[\omega_i(e_{\text{IS}})/\omega_o] = a + b e_{\text{IS}}. \quad (3)$$

Hence, the vibrational free energy can be written as

$$F_{\text{vib}}(e_{\text{IS}}, T) = F_{\text{vib}}(E_o, T) + k_B T b (e_{\text{IS}} - E_o). \quad (4)$$

Within the two assumptions of Eq. (1)—Gaussian distribution of basin depths—and Eq. (4)—linear dependence of the basin free energy on  $e_{\text{IS}}$ —an exact evaluation of the partition function can be carried out. The corresponding Helmholtz free energy is given by [10]

$$F(T) = -TS_{\text{conf}}(T) + \langle e_{\text{IS}}(T) \rangle + F_{\text{vib}}(E_o, T) + k_B T b [\langle e_{\text{IS}}(T) \rangle - E_o], \quad (5)$$

where

$$\langle e_{\text{IS}}(T) \rangle = (E_o - b\sigma^2) - \beta\sigma^2 = e_\infty - \beta\sigma^2, \quad (6)$$

and

$$\begin{aligned} S_{\text{conf}}(T)/k_B &= \alpha N - [\langle e_{\text{IS}}(T) \rangle - E_o]^2/2\sigma^2 \\ &= S_\infty/k_B - b\beta\sigma^2 - \beta^2\sigma^2/2. \end{aligned} \quad (7)$$

In the above equations,  $e_\infty$  and  $S_\infty$  are defined as the value of  $\langle e_{\text{IS}} \rangle$  and  $S_{\text{conf}}$  at infinite  $T$ . Equations (5)–(7) show that, along constant volume  $V$  paths, the behavior of the thermodynamic quantities is controlled by the values of the PEL properties, as given by  $\alpha$ ,  $\sigma$ ,  $E_0$  [from Eq. (1)] and by  $a$  and  $b$  [from Eq. (3)].

In this Letter we study the volume dependence of Eq. (5) to provide an expression for the equation of

state (EOS) based completely on landscape properties (PEL-EOS) [15]. This paper provides a significant insight into the understanding of the pressure  $P$ , and favors a detailed comparison between experimental measurements (usually performed at constant  $P$ ) and theoretical approaches based on the IS formalism. It may also help in developing an IS-based thermodynamic description of out-of-equilibrium (glass) states and a theoretical definition of the concepts of fictive  $P$  and  $T$  [16].

In thermodynamics,  $P$  is defined as the (negative)  $V$  derivative of the Helmholtz free energy. Hence  $P$  is fully determined by the  $V$  dependence of the landscape properties  $\alpha$ ,  $\sigma$ ,  $E_0$ ,  $a$ , and  $b$ . Equation (5) shows that  $P$  can be split into three main contributions: a configurational one,  $P_{\text{conf}}$ —related to the change in the number of available basins with  $V$ ; an  $e_{\text{IS}}$  one,  $P_{e_{\text{IS}}}$ —related to the change in basin depth with  $V$ ; a vibrational one,  $P_{\text{vib}}$ —related to the change in the shape of the explored basin with  $V$ . The  $T$  dependence of each contribution can then be studied independently. The explicit expressions for these contributions are

$$P_{\text{conf}}(T, V) = T \frac{\partial}{\partial V} S_{\infty} - \frac{\partial}{\partial V} (b\sigma^2) - \frac{1}{T} \frac{\partial}{\partial V} (\sigma^2/2k_B), \quad (8)$$

$$P_{e_{\text{IS}}}(T, V) = -\frac{\partial}{\partial V} e_{\infty} + \frac{1}{T} \frac{\partial}{\partial V} (\sigma^2/k_B), \quad (9)$$

$$P_{\text{vib}}(T, V) = -k_B T \frac{\partial}{\partial V} (a + be_{\infty}) + \frac{\partial}{\partial V} (b\sigma^2). \quad (10)$$

By grouping together all the contributions with the same  $T$  dependence,  $P$  can be expressed in terms of  $V$  derivatives of only three combinations of the five PEL parameters [18]

$$P(T, V) = P_{\text{const}} + TP_T + T^{-1}P_{1/T}, \quad (11)$$

where  $P_{\text{const}} = -\partial e_{\infty}/\partial V$ ,  $P_T = \partial S_{\infty}/\partial V - k_B \frac{\partial}{\partial V} (a + be_{\infty})$ , and  $P_{1/T} = \frac{\partial}{\partial V} (\sigma^2/2k_B)$ .

The present formalism also provides a possible expression for the so-called inherent structure equation of state (IS-EOS),  $P_{\text{IS}}(T_{\text{IS}}, V)$  [15,19–21], i.e., the relation between the pressure and volume of the typical IS and the temperature  $T_{\text{IS}}$  of the equilibrium ensemble from which configurations were extracted. Indeed, one can assume that the constant  $V$  steepest descent minimization procedure, which realizes the search for the closest local minimum starting from an equilibrium configuration, suppresses all the vibrational components (hence  $P_{\text{vib}} = 0$ ) but keeps  $P_{\text{conf}}$  and  $P_{e_{\text{IS}}}$  frozen at their “equilibrium” initial value. As a result  $P_{\text{IS}}$ , a purely mechanical quantity, can be expressed as

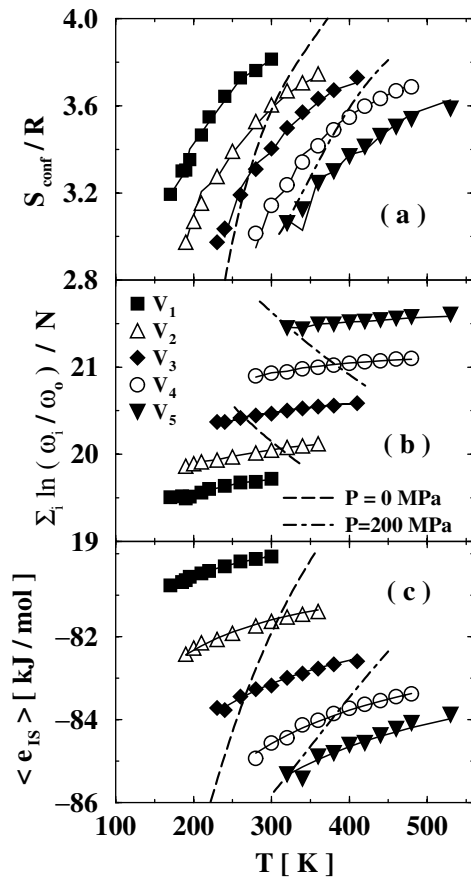


FIG. 1.  $T$  dependence of (a)  $S_{\text{conf}}$ , (b)  $\sum_i \ln(\omega_i/\omega_0)/N$ , and (c)  $\langle e_{\text{IS}} \rangle$  (per molecule) at the five studied volumes  $V_k$  (symbols). Data are from Ref. [13]. The solid curves are simultaneous fits of the three sets of data according to Eqs. (7), (3), and (6). The dashed curves are the constant  $P$  paths (at  $P = 0$  and 200 MPa) calculated according to the IS-EOS, as discussed in the text. The frequency unit is  $\omega_0 \equiv 1 \text{ cm}^{-1}$ .

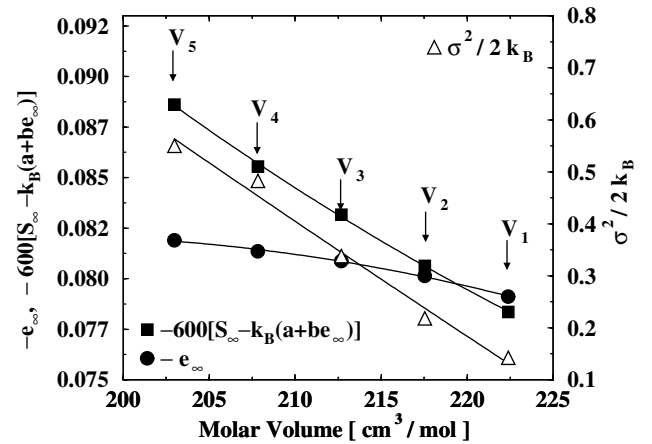


FIG. 2.  $V$  dependence of the three combinations of PEL parameters contributing to the linear (squares), constant (circles), and  $T^{-1}$  (triangles) components of  $P$ , according to Eq. (11). The solid lines are the polynomial fit used to evaluate  $P_{\text{const}}$ ,  $P_T$ , and  $P_{1/T}$ . Tables of the coefficients of the polynomial fit will be reported in Ref. [17]. Here  $e_{\infty}$  is expressed in  $10^6 \text{ J mol}^{-1}$ ,  $S_{\infty} - k_B(a + be_{\infty})$  in  $10^6 \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $\sigma^2/2k_B$  in  $10^6 \text{ J K mol}^{-1}$ .

$$\begin{aligned}
P_{\text{IS}}(T_{\text{IS}}, V) &= P_{\text{conf}} + P_{e_{\text{IS}}} \\
&= -\frac{\partial}{\partial V} E_o + T_{\text{IS}} \frac{\partial}{\partial V} S_{\infty} \\
&\quad + \frac{1}{k_B T_{\text{IS}}} \frac{\partial}{\partial V} (\sigma^2/2). \quad (12)
\end{aligned}$$

Note that in this expression  $T_{\text{IS}}$  is assumed to be the  $T$  controlling the configurational contribution. Different formulations for the out-of-equilibrium free energy [16] would lead to different expressions [17].

The present approach also predicts the behavior of  $P$  when an IS configuration is heated from  $T = 0$  at constant  $V$ . While the system remains in the same basin,  $P$  is given by  $P_{\text{IS}}(T_{\text{IS}}, V) + P_{\text{vib}}(T, T_{\text{IS}}, V)$ , where the only (linear)  $T$ -dependent part arises from

$$P_{\text{vib}}(T, T_{\text{IS}}, V) = -k_B T \frac{\partial}{\partial V} [a + b e_{\text{IS}}(T_{\text{IS}})]. \quad (13)$$

We now apply the present derivation to the simple Lewis and Wanström (LW) model for the fragile molecular liquid orthoterphenyl (oTP) [13,22]. The LW model is a rigid

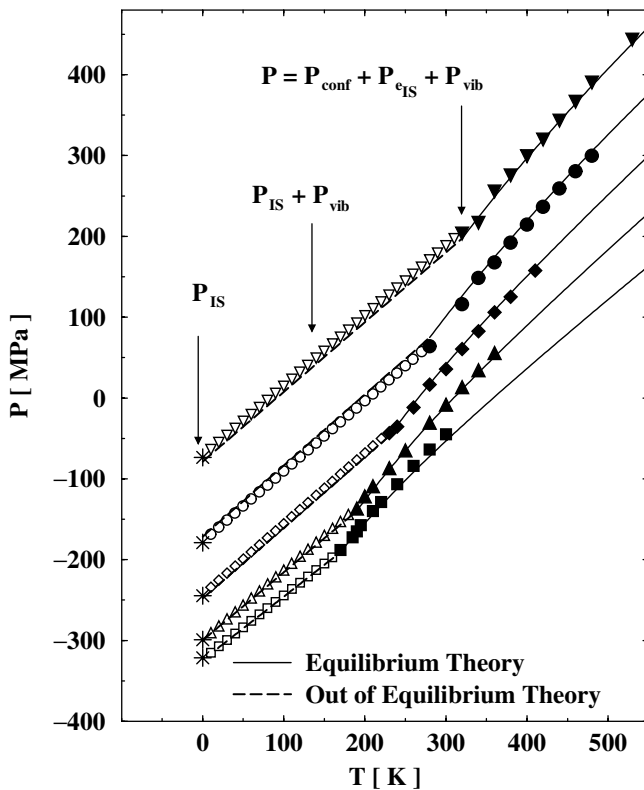


FIG. 3. Comparison between  $P$  evaluated according to the  $V$  derivative of PEL properties (lines) and  $P$  evaluated in the MD simulation using the virial expression (symbols). The solid symbols are equilibrium values. For each  $V_k$ , the symbol \* indicates  $P_{\text{IS}}$  for the coldest equilibrated state point. The open symbols are MD data calculated during a constant heating procedure starting from the IS configuration marked with \*, as explained in the text. Lines are PEL-EOS for equilibrium [solid lines, Eq. (11)] and for the heating procedure [dashed lines, Eq. (13)].

three-site model, with intermolecular site-site interactions described by the Lennard Jones (LJ) potential [22]. Its simplicity allows one to reach simulation times of the order of  $\mu\text{s}$  [13]. In this model, as in the LJ case, the anharmonic contributions are negligible,  $e_{\text{IS}}(T)$  goes as  $1/T$ , and  $\sum_{i=1}^M \ln[\omega_i(e_{\text{IS}})/\omega_o]$  is linear in  $e_{\text{IS}}$  [13]. Hence this model is a perfect candidate for testing the validity of the PEL-EOS proposed here.

We use the excellent data base of state points presented in Ref. [13] (i) to calculate the  $V$  dependence of the PEL parameters; (ii) to derive the EOS for the oTP model, and (iii) to compare it with the “exact” EOS calculated using the virial expression, as commonly implemented in molecular dynamics (MD) codes.

Figure 1 shows, for five constant  $V$  paths, the simultaneous fit of the  $T$  dependence of  $S_{\text{conf}}$ , the basin curvatures, and of the  $\langle e_{\text{IS}}(T) \rangle$ , according to Eqs. (7), (3), and (6). The possibility of fitting simultaneously, with the same values of  $\alpha$ ,  $\sigma$ ,  $E_o$ ,  $a$ , and  $b$ , the quantities  $\langle e_{\text{IS}}(T) \rangle$ ,  $\sum_{i=1}^M \ln[\omega_i(e_{\text{IS}})/\omega_o]$ , and  $S_{\text{conf}}(T)$ , supports the validity of the two main assumptions, i.e., Eqs. (1) and (4).

The  $V$  dependence of the three combinations of fit parameters,  $-e_{\infty}$ ,  $S_{\infty} - k_B(a + b e_{\infty})$ , and  $\sigma^2/2k_B$  is shown in Fig. 2.  $P(V, T)$  can be calculated from the  $V$  derivative of these quantities according to Eq. (11) and compared with the MD data. Such a comparison is reported in Fig. 3.

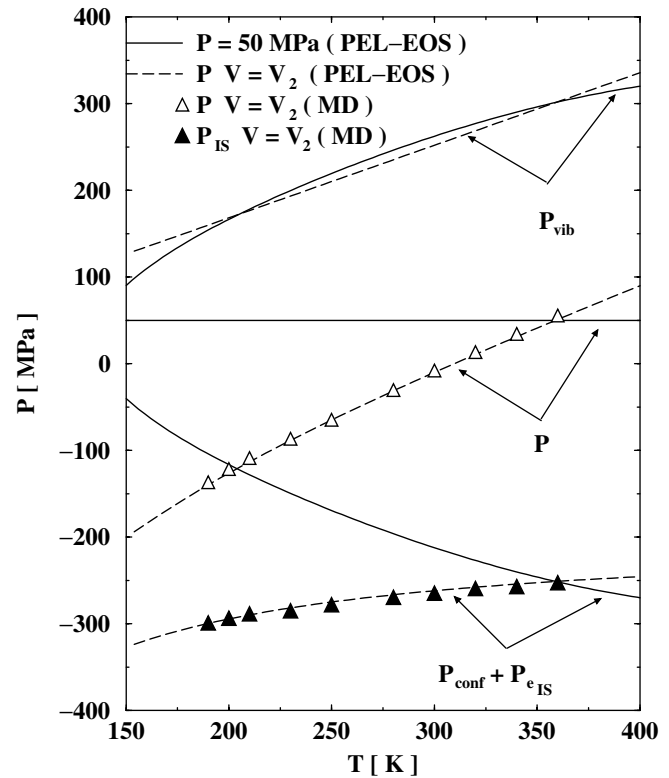


FIG. 4. Total ( $P$ ), vibrational ( $P_{\text{vib}}$ ) and  $e_{\text{IS}}$  plus configurational ( $P_{e_{\text{IS}}} + P_{\text{conf}}$ ) contributions to  $P$  along constant  $V$  (dashed lines) and constant  $P$  (solid lines) paths. At constant  $V$ ,  $P_{\text{vib}}$  is linear in  $T$  [Eq. (10)].

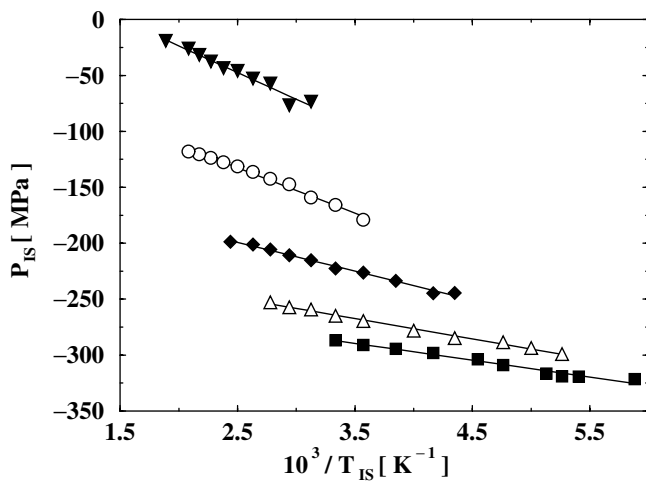


FIG. 5. Inherent structure equation of state. Symbols are MD calculations, lines are PEL predictions.

The  $T$  dependence of the individual contributions can be evaluated according to Eqs. (8)–(10). The volume dependence of  $b\sigma^2$  and  $(a + be_\infty)$  has been evaluated from the best fit of  $P - P_{IS}$  which, according to Eq. (12), coincides with  $P_{vib}$ . Figure 4 shows—along a constant  $V$  and a constant  $P$  path— $P_{vib}$  and  $P_{conf} + P_{e_{IS}}$ . We note that, at constant  $V$ , both  $P$  components are increasing with  $T$  while, at constant  $P$ ,  $P_{conf} + P_{e_{IS}}$  decreases on heating to compensate for the increase of  $P_{vib}$ .

The PEL-EOS allows us to also contrast the isobaric and isochoric  $T$  dependence of  $S_{conf}$ ,  $\langle e_{IS}(T) \rangle$  and  $\sum_{i=1}^M \ln(\omega_i/\omega_o)$ . Such comparison is reported in Fig. 1. Here we note the faster decrease of  $S_{conf}(T)$  and  $\langle e_{IS}(T) \rangle$  along constant  $P$  paths as well as the different trend in the change of the basin shape [23].

As a further check of the quality of the calculated EOS for the oTP model, Fig. 5 compares the MD (virial) and PEL [Eq. (12)] IS-EOS. Since for the oTP model the term linear in  $T$  in Eq. (12) is negligible [17],  $P_{IS}$  follows, to a good extent, a  $1/T_{IS}$  law. The quality of the comparison supports the interpretation of  $P_{IS}$  as the  $V$  derivative of the depth and number of basins sampled in the corresponding thermodynamic equilibrium state.

Finally, Fig. 3 compares MD data (open symbols) and PEL (dashed lines) predictions in a run where  $T$  is increased starting from the  $T = 0$  IS configuration, as previously discussed. The entire simulation is much shorter than the time needed to change the basin, so that only the vibrational degrees of freedom are thermalized. Also in this case, the PEL expression accounts for the observed linear increase of  $P$ .

The present EOS, based exclusively on PEL properties, can be used to address important issues in the thermodynamics of supercooled liquids [24], such as the study of the intrinsic limit of stability of the liquid state [15,20,21] and the IS-based thermodynamic description of aging [16].

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