

Water and its energy landscape

F. Sciortino^{1,a}, E. La Nave¹, A. Scala¹, H.E. Stanley², and F.W. Starr³

¹ Dipartimento di Fisica, Università di Roma La Sapienza, Istituto Nazionale di Fisica della Materia and INFM Center for Statistical Mechanics and Complexity, Piazzale Aldo Moro 2, 00185 Roma, Italy

² Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA

³ Polymers Division and Center for Theoretical and Computational Materials Science, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

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Abstract. We present an overview of the recent studies on the properties of the potential energy surface for a simple model of water. We emphasize the relations between PES properties and dynamics in supercooled states for the model and discuss possible future application of the PES studies.

PACS. 61.43.Fs Glasses – 64.70.Pf Glass transitions – 66.10.Cb Diffusion and thermal diffusion

1 Introduction

Many efforts have been made to elucidate the physics of supercooled liquids [1,2]. The study of the potential energy surface (PES) of simple models, aided by the increased computational resources, has provided important insights into the mechanisms controlling the slowing-down of dynamics on cooling [2–9]. These studies focus on the possible connections between the PES topological properties and both the dynamics and thermodynamics of supercooled liquids. At sufficiently low temperatures, the motion of the system can be separated into motion confined in one PES basin (on the short time scale), and interbasin motion (on the long time scale). The time separation between these two mechanisms allows the development of a thermodynamic approach based on the analysis of the PES geometry [5–9]. This approach has become a powerful formalism for the analysis of the low-temperature physics [3,6–9]. In this paper we review some of the PES properties for a simple model of water, the simple point charge (SPC/E) model [10], and we show how these properties are related to the thermodynamics and dynamics of supercooled water.

Liquid water is one of the most broadly studied liquids, and the dynamic properties in the supercooled region have been the focus of numerous experimental and theoretical studies [11]. Water has a number of anomalous dynamical properties; noteworthy is the fact that water becomes *more* diffusive as pressure P is increased to ≈ 200 MPa at room temperature [12]. For greater P , water becomes progressively more viscous, as expected for simple liquids where increased packing makes motion more difficult.

The presence of a maximum in the diffusivity D along isotherms makes water an ideal choice to test the relations between thermodynamics and dynamics. In fact, for water—in contrast with typical liquids—both the entropy S and the diffusivity D are non-monotonic functions of the density ρ . If monotonic functional dependence between a thermodynamic and dynamic quantity holds—as proposed by the Adam and Gibbs relation [13] for the “configurational” component of the entropy and diffusivity—the loci of the extrema of these quantities in the (T, ρ) -plane must coincide. In this work we test just such a relation.

2 Simulation model

There are a large number of intermolecular potentials for water, most of which provide a reasonable account of the structural and thermodynamics properties under atmospheric conditions. The SPC/E potential [10] models a water molecule as two positive point charges (at the hydrogens positions) rigidly bonded to a negative point charge (at the oxygen position) with a bond length of 1.0 Å with an angle of 109.47°. This model has been studied extensively in the past; the T -dependence of D [14–16] is consistent with the predictions of the mode coupling theory [17], and behaves qualitatively like water over a broad range of (T, ρ) . The ability of SPC/E to reproduce the characteristic features of water is shown in Figure 1, which shows the loci of S extrema and D extrema for water and the corresponding quantities for the SPC/E potential. Note that the loci of S extrema and D extrema do not coincide in either case. Hence the SPC/E potential constitutes an

^a e-mail: fs@phys.uniroma1.it

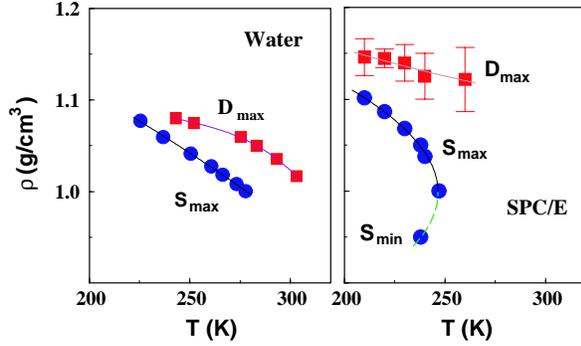


Fig. 1. Lines of entropy extrema and diffusion maximum for water (left panel) and for SPC/E simulated water (right panel). Redrawn from reference [18].

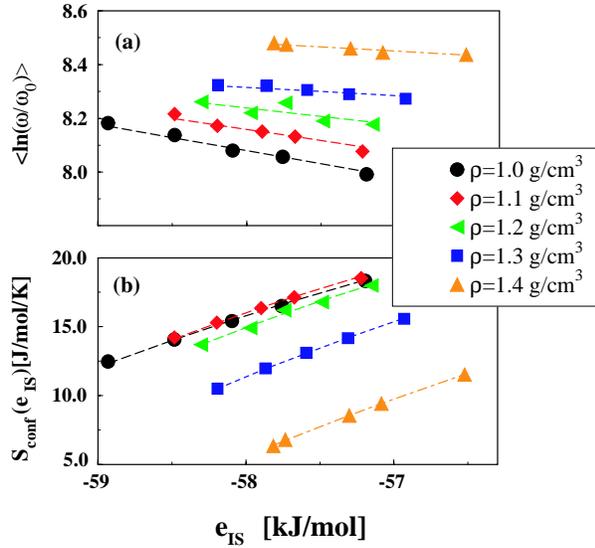


Fig. 2. (a) Average value of $\ln(\omega/\omega_0)$ as a function of e_{IS} for all the studied densities. ω_0 , the frequency unit, is 1 cm^{-1} . (b) Configurational entropy for the same densities as a function of e_{IS} . In both panels, lines are the result of a simultaneous fit according to the equations discussed in the text. Redrawn from reference [31].

appropriate choice for rationalizing both thermodynamic and dynamic properties of water.

The simulation results analyzed in this paper are based on extensive molecular-dynamics simulations of a system of $N = 216$ molecules for six different densities and six different temperatures in the range between $T = 210 \text{ K}$ and $T = 300 \text{ K}$.

3 Results for the potential energy surface

The PES is the surface in the $6N$ -dimensional configuration space generated by the intermolecular potential. Following the “inherent structure” (IS) formalism [5], the

PES can be partitioned in local basins, which are uniquely defined by the set of points connected to a local minimum *via* a steepest-descent path. The configurations corresponding to PES local minima are called inherent structures, and their energies are denoted by E_{IS} . Properties of the PES are quantified by numerical analysis of the configurations of simulated liquid trajectory, classifying basins according to their E_{IS} and local volume (shape). From this knowledge, the configurational component of thermodynamic properties, associated with the topology of the PES, can be evaluated. In the thermodynamic limit, this is formally described using the free energy [3,5,6]:

$$F(T) = -TS_{\text{conf}}(e_{IS}(T)) + f_{\text{basin}}(e_{IS}(T), T), \quad (1)$$

where e_{IS} is the average value of the IS energy at temperature T , $S_{\text{conf}}(e_{IS}(T)) = \log(\Omega(e_{IS}(T)))$ is the entropic contribution arising from the number $\Omega(e_{IS})$ of basins of depth e_{IS} , and $f_{\text{basin}}(e_{IS}, T)$ is the free energy of the system. The separation of the free energy into two contributions reflects the separation of time scales into supercooled liquids. In the T range where two-step relaxation occurs, the intrabasins dynamics is much faster than the interbasins dynamics. The $f_{\text{basin}}(T, e_{IS}(T))$ of a supercooled liquid can be written by expanding the potential energy around the IS configuration:

$$f_{\text{basin}}(e_{IS}, T) = e_{IS} + k_B T \sum_{i=1}^{6N-3} \ln[\beta \hbar \omega_i(e_{IS})] + f_{\text{anharmonic}}(e_{IS}, T), \quad (2)$$

where $k_B T \sum_{i=1}^{6N-3} \ln[\beta \hbar \omega_i(e_{IS})]$ is the free energy of $6N - 3$ independent harmonic oscillators [18], ω_i is the frequency of the i -th normal mode, and $f_{\text{anharmonic}}(e_{IS}, T)$ accounts for the anharmonic contribution to the basin free energy. At the present time, all IS calculations are based on the assumption that the e_{IS} -dependence of $f_{\text{anharmonic}}(e_{IS}, T)$ is negligible, *i.e.* that $f_{\text{anharmonic}}(e_{IS}, T) \approx f_{\text{anharmonic}}(T)$ [18–20], which can be estimated by heating the inherent structure. The harmonic component of the basin curvature depends on the basin depth. In Figure 2(a) we show the e_{IS} -dependence of the average values of $\ln(\omega_i/\omega_0)$ (here ω_0 is the unit frequency cm^{-1} to remove units in the logarithm). From this figure we see that, at constant volume, basins become “sharper” (larger frequencies) on moving to deeper and deeper basins of the PES, in contrast with the results for several “simple” liquids [8, 19]. The same figure shows that the e_{IS} -dependence of the average values of $\ln(\omega_i/\omega_0)$ can be expressed by the linear relation

$$\sum_{i=1}^{6N-3} \ln[\omega_i(e_{IS})/\omega_0] = a + b e_{IS}. \quad (3)$$

Figure 2(b) shows the e_{IS} -dependence of S_{conf} . It has been shown [7, 9, 21] that if equation (3) holds and if the density of state $\Omega(e_{IS})$ is given by the Gaussian expression

$$\Omega(e_{IS}) = e^{\alpha N} \frac{e^{-(e_{IS}-E_0)^2/2\sigma^2}}{(2\pi\sigma^2)^{1/2}}, \quad (4)$$

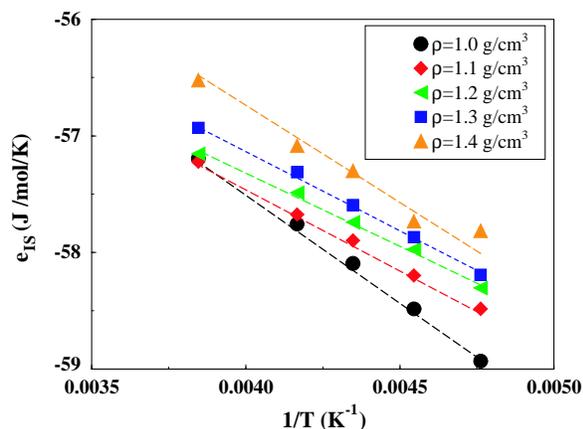


Fig. 3. Average basin energy e_{IS} as a function of $1/T$. For all the studied densities the line can be fit with a linear function. Lines are the result of a simultaneous fit according to the equations discussed in the text. Redrawn from reference [31].

then S_{conf} can be described by an inverted parabola,

$$S_{\text{conf}}(e_{IS}) = \alpha - \frac{(e_{IS} - E_0)^2}{2\sigma^2}, \quad (5)$$

and the T -dependence of e_{IS} can be expressed as a function of the Gaussian distribution parameters,

$$e_{IS}(T) = e_{IS}(\infty) - \sigma^2/k_B T, \quad (6)$$

where $e_{IS}(\infty) = E_0 - b\sigma^2$ is a constant. In equation (4) α is a measure of the total number of states per molecule, while E_0 and σ measure the energy distribution of such α states. The validity of a Gaussian distribution of states (Eq. (4)) can be reinforced by simultaneously fitting the T -dependence of S_{conf} , the T -dependence of e_{IS} and the e_{IS} -dependence of $\ln[\omega_i(e_{IS})/\omega_0]$. The results of such fitting procedure are shown as lines in Figures 3, 2(a) and 2(b). Figure 3 shows that in the case of SPC/E water the linear relation expressed by equation (6) between e_{IS} and $1/T$ holds. Using the same parameter in each case supports the validity of the above assumptions and also validates the numerical estimates for S_{conf} .

Numerical estimates of the PES parameters have been provided mostly for single constant-volume paths. Investigation of both temperature and volume dependences of the PES properties provides new insights into the thermodynamic properties of supercooled liquids and, in the case of water, it sheds light on the possibility of a liquid-liquid transition [22]. Indeed, one of the open topics in the physics of liquid water is the existence of a hidden liquid-liquid critical point at low temperatures and high pressures. The presence of this critical point could explain the anomalous increase of the isothermal compressibility K_T and isobaric specific heat C_P on cooling. The possibility of a liquid-liquid critical point in water was first proposed in reference [23] and supported by numerical investigations of the thermodynamics of water based on the ST2 [24] and (recently) TIP5P [25] models. Although the

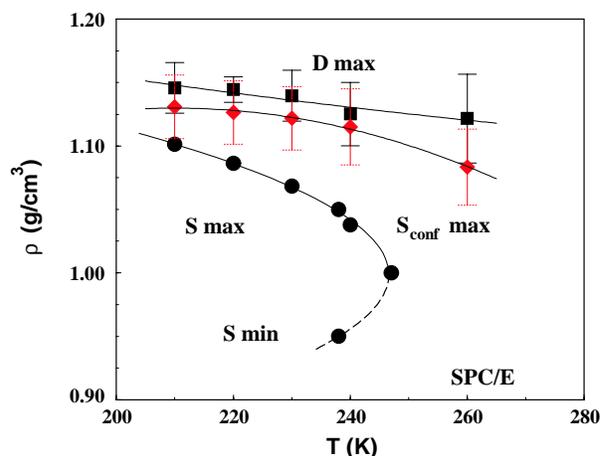


Fig. 4. Isothermal S extrema, S_{conf} maxima and D maxima lines for SPC/E water. The maxima of S_{conf} and D coincide within the numerical errors. Redrawn from reference [18].

estimated temperature T_c of the critical point is below the homogeneous nucleation temperature, and hence difficult to access experimentally, recent experiments in water under high pressure do show evidence of a low- T phase transition [26].

4 Role of configurational entropy in dynamics

Recent work has shown that the slowing-down of the dynamics approaching the glass transition can be related both to the reduction of the connectivity between local minima, the diffusive directions f_{diff} [27–30], and to the decrease in the number of available local minima, *i.e.* to S_{conf} [8, 18–20, 31]. It has been suggested that the dynamical behavior above and below the mode coupling critical temperature [17], T_{MCT} , can be explained in terms of geometrical PES properties [27]. In this picture, developed with the aid of the instantaneous normal mode approach [32], T_{MCT} is a crossover temperature between temperatures at which the system efficiently samples pathways between PES basins (for $T > T_{\text{MCT}}$), and temperatures for which the system is almost always inside a local basin (for $T < T_{\text{MCT}}$) [30, 33, 34].

The availability of accurate estimates for S_{conf} makes it possible to address the connection between the number of basins accessed by the system and diffusivity, *i.e.* the relation between a thermodynamic quantity S_{conf} and a dynamic one, D . Figure 4 shows the comparison between the line of the isothermal S extrema and S_{conf} maxima with the line of D maxima in the case of SPC/E water. This figure shows that the lines of S_{conf} and D maxima coincide (within numerical error), supporting the possibility that dynamics in supercooled states is indeed controlled by the geometrical information contained in S_{conf} . A functional form that relates S_{conf} to diffusion was proposed by Adam and Gibbs [13] —also recently supported by novel

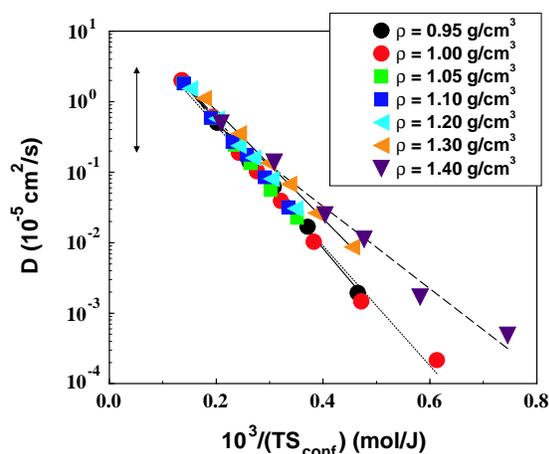


Fig. 5. Test of the Adam-Gibbs relation in SPC/E water. For all the densities studied the diffusivity follows the Adam-Gibbs law, for about four decades in diffusivity. The arrow indicates the range of diffusivity values accessible to experiments. Redrawn from reference [18].

theoretical approaches [35]— who predict a linear relation between $\log D$ and $(TS_{\text{conf}})^{-1}$. Figure 5 shows that in the case of SPC/E water, this relation holds for more than three decades in D , supporting the hypothesis that the configurational entropy is a key for understanding dynamics in supercooled states.

If the descriptions of dynamics in terms of S_{conf} as well as basin connectivity are both valid, a relation must exist between the number of basins and the number of directions connecting them, since S_{conf} is a measure of the number of distinct PES basins explored. The possibility of such a relation has been considered for the SPC/E model, and it has been shown that the fraction of diffusive directions appears to be proportional to the number of explored basins. This result has been derived theoretically in the case of a random energy model by Keyes [36].

We also note that the relation between D and f_{diff} and the relation between f_{diff} and S_{conf} [29,30] suggest a relation between D and S_{conf} which would mathematically coincide with the Adam-Gibbs equation only for a specific T -dependence of S_{conf} . The limited range of values of D explored with the present computation does not allow to distinguish if the Adam-Gibbs equation and the relation between D and S_{conf} parametric in f_{diff} are equivalent or which of the two has a larger validity range. This remains an important open problem to be addressed in the future.

5 Discussion and summary

In this paper we have reviewed some of the recent studies of the PES of a simple model for water. We have discussed the IS formalism and the relations between thermodynamics, dynamics, and the PES geometrical properties. We showed that, through the IS formalism, it is possible to express the thermodynamic properties of the liquid as a

function of the geometrical properties of the PES. Moreover, we showed that the dynamics of supercooled water is strongly tied to the PES topology. The PES for supercooled liquids therefore appears to be central in the understanding of the slow dynamics in liquids. Further work is required for a complete description of the supercooled liquids thermodynamics in terms of PES parameters.

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