Instantaneous Normal Mode Analysis of Supercooled Water

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We use the instantaneous normal mode approach to provide a description of the local curvature of the potential energy surface of a model for water. We focus on the region of the phase diagram in which the dynamics may be described by mode-coupling theory. We find that the diffusion constant depends on the fraction of directions in configuration space connecting different local minima, supporting the hypothesis that the dynamics are controlled by the geometric properties of configuration space. Furthermore, we find a relation between the number of basins accessed in equilibrium and the connectivity between them.

The study of the dynamics of supercooled liquids has received great interest in recent years [1] due to possibilities opened by novel experimental techniques [2], detailed theoretical predictions [3], and by the possibility of following the long time microscopic dynamics via computer simulation [4]. One important theoretical approach is the ideal mode-coupling theory (MCT) [3], which quantitatively predicts the time evolution of correlation functions and the dependence on temperature T of characteristic correlation times. Unfortunately, the temperature region in which MCT is able to make predictions for the long time dynamics is limited to weakly supercooled states [5]. In parallel with the development of MCT, theoretical work [6–9] has called attention to thermodynamic approaches to the glass transition, and to the role of configurational entropy in the slowing down of dynamics. These theories, which build on ideas put forward some time ago [10,11], stress the relevance of the topology of the potential energy surface (PES) explored in supercooled states. Detailed studies of the PES may provide insights into the slow dynamics of liquids, and new ideas for extending the present theories to the deeply supercooled regime.

The instantaneous normal mode (INM) approach uses the eigenvectors (normal modes) and eigenvalues of the Hessian matrix (the second derivative of the potential energy) to provide an "instantaneous" representation of the PES in the neighborhood of an equilibrium phase space point. Examples of INM analysis have appeared for a few representative liquids [12]. In this Letter we present INM calculations for a rigid water molecule model, the extended simple point charge (SPC/E) potential [13], for several temperatures and densities in supercooled states. The reasons for selecting such a system are twofold: (i) The SPC/E model has been studied in detail, and it has been shown that its dynamics follow closely the predictions of MCT [14,15]. Furthermore, the (ρ, T) dependence of the configurational entropy has been calculated and shown to correlate with the dynamical behavior [16]. (ii) The SPC/E model has a maximum of the diffusion constant D under pressure along isotherms, as observed experimentally [17]. The maxima in D can be used as sensitive probes for testing proposed relations between the change in topology of configuration space and the change in D.

We analyze recent simulations [15] for six densities between 0.95 and 1.3 g/cm^3 and five temperatures for each density. For each state point, we extract 100 equally spaced configurations, from which we calculate and diagonalize the Hessian using the center of mass and the three principal inertia momenta vectors as molecular coordinates [18]. For each configuration, we classify the imaginary modes into two categories: (i) shoulder modes and (ii) double-well modes, according to the shape of the PES along the corresponding eigenvector [19]. The shoulder modes are modes for which the negative curvature appears as a result of a local anharmonicity; the double-well modes include only the directions in configuration space which connect two adjacent minima. The classification of the modes is done by studying the shape of the PES along the eigenvector corresponding to the mode, i.e., beyond the point in configuration space where such modes have been calculated. In this respect, the potential energy along the eigenvector direction may be different from the actual curvilinear direction described by the time evolution of the eigenvector under consideration. Furthermore, some modes classified as double-well are related to intrabasin motions [20] and therefore are not relevant to describe diffusivity. Procedures to identify these intrabasin modes have been proposed [20]. In the present study we show that, for SPC/E water, these spurious features are negligible.

Figure 1 shows the density dependence of the fractions of imaginary (unstable) modes f_u, double-well modes f_{dw}, and of shoulder modes f_{sh}, where $f_u = f_{dw} + f_{sh}$; we also show D for the same state points. The close correlation of f_{dw} and D is striking. At $\rho \approx 1.15$ g/cm^3, D has a maximum; at this ρ, the increase of diffusion constant caused by the progressive disruption of the hydrogen bond network on increasing the density is balanced by slowing down of the dynamics due to increased packing. At the same density, f_u and f_{dw} also show maxima, supporting the view that these quantities are a good indicator of the molecular mobility. There is also a weak maximum in f_{sh}, but at $\rho < 1.15$ g/cm^3 [21]. The presence of maxima in
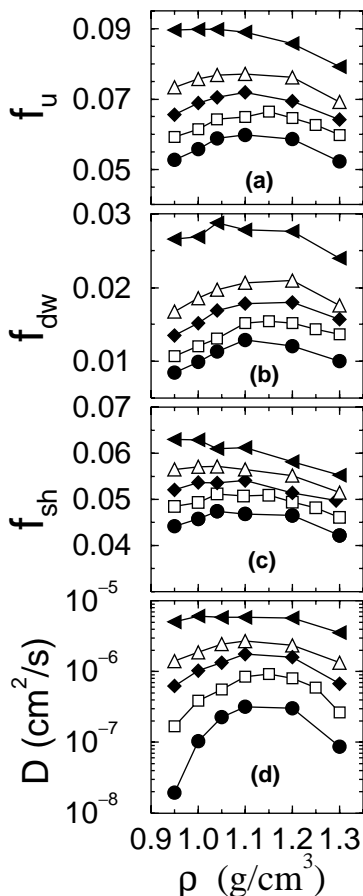
FIG. 1. Density dependence along the studied isotherms of (a) f_u, (b) f_{dw}, and (c) f_{sh}. Temperatures are $T = 210$ K (circles), $T = 220$ K (squares), $T = 230$ K (diamonds), and $T = 240$ K (triangles). (d) shows the ρ dependence of D for the same isotherms [15].

FIG. 2. Diffusion constant D versus f_{dw} for different isochores. The arrow indicates the value $f_{dw} \approx 0.007$, to highlight the presence—even when D approaches zero—of a small number of spurious double-well modes, related to intrabasin motion [20,25].

mainly related to the geometry of the PES, i.e., it is "entropic" in origin.

MCT seems to be able to describe the entropic slowing down of the dynamics associated with the vanishing of f_{dw}. This is consistent with the general consensus that the missing decay channels for the correlations responsible for the failure of MCT at very low T are activated processes. To make closer contact with MCT, we compare in Fig. 3 the density dependence of the MCT critical temperature T_{MCT} [15] with the T at which the fraction of double-well modes goes to zero. We observe that while the $f_{dw} = 0$ locus tracks closely the T_{MCT} line, it does not coincide with it. To test the hypothesis that the differences between

both D and f_{dw} at the same density suggests that, for the SPC/E potential, f_{dw} is directly related to D. The relation between D and f_{dw} is shown in Fig. 2 for all the studied isochores. We note that D in this system is a monotonic function of f_{dw} and that all points fall on the same master curve [22], notwithstanding the large range of D values analyzed. Thus, surprisingly, in SPC/E water, the knowledge of the fraction of directions in configuration space leading to a different basin, f_{dw}, is sufficient to determine the value of D. [23] We also note from Fig. 2 that D vanishes, but at a small nonzero value of $f_{dw} \approx 0.007$ (vertical arrow) [24], suggesting that indeed a small number of double-well modes, not related to diffusivity [20,25], are still included in our classification.

The reduction of mobility on cooling in the studied (ρ, T) range—where MCT provides a description of the dynamics—appears related to the geometrical properties of the PES, i.e., the system mobility is reduced because the number of directions connecting different local minima (needed to explore *freely* the configuration space) is decreasing [26]. Hence, the observed reduced mobility is
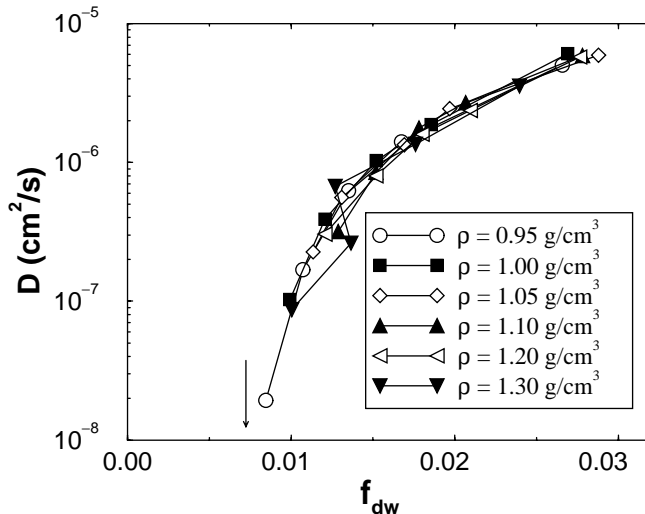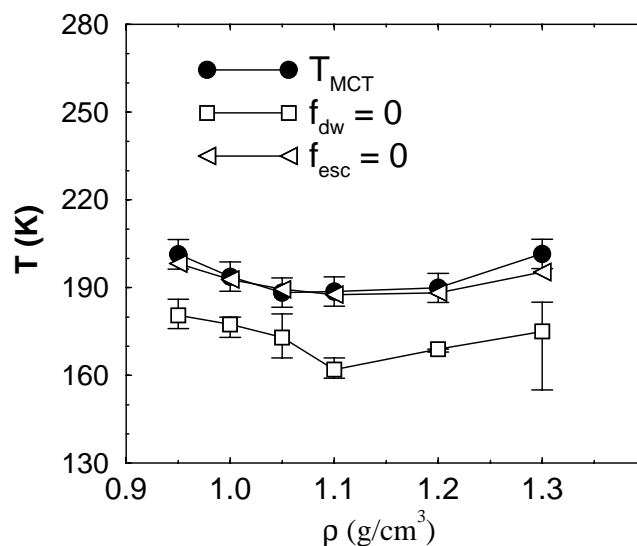

FIG. 3. Comparison of the mode-coupling critical temperature T_{MCT} [15], with the $f_{dw} = 0$ locus and with the $f_{esc} = 0$ locus.
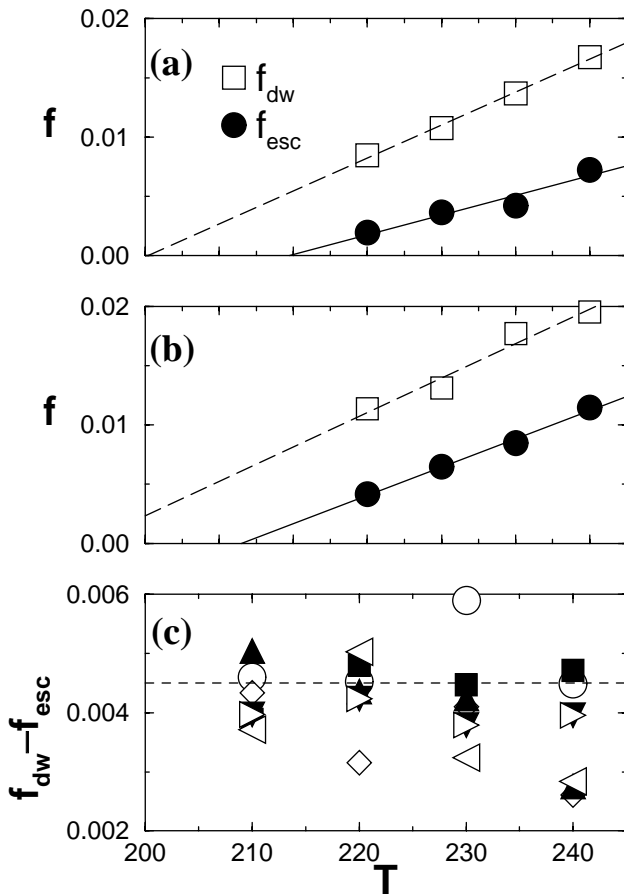
FIG. 4. T dependence of f_{dw} and f_{esc} for (a) $\rho = 0.95$ g/cm^3 and (b) $\rho = 1.05$ g/cm^3. Straight lines show the linear extrapolation used to define the locus of $f_{dw} = 0$ and $f_{esc} = 0$, reported in Fig. 3. (c) T dependence of $f_{dw} - f_{esc}$ for all densities. (○: $\rho = 0.95$ g/cm^3; □: $\rho = 1.$ g/cm^3; ◇: $\rho = 1.05$ g/cm^3; △: $\rho = 1.1$ g/cm^3; ◁: $\rho = 1.2$ g/cm^3; ▽: $\rho = 1.3$ g/cm^3).

the T_{MCT} locus and the $f_{dw} = 0$ locus are due to the small overcounting intrinsic in the mode classification (i.e., to the presence of false barriers), we perform the analysis suggested in Ref. [20]. Thus, for each double-well mode, we perform a potential energy minimization starting from the two apparent minima—*à la* Berne [20]—and we calculate f_{esc}, the fraction of modes which allows the system to escape from a basin [27]. The T dependence of f_{esc} is shown in Figs. 4(a) and 4(b). We find that at all state points, $f_{dw} - f_{esc} = 0.005 \pm 0.002$ [Fig. 4(c)], accounting for most of the overcounting included in f_{dw}. The locus of $f_{esc} = 0$, shown in Fig. 3, nearly coincides with the T_{MCT} line.

The results presented here suggest that the liquid dynamics in the MCT region of SPC/E water is controlled by the average connectivity in configuration space. On the other hand, for the same model, the (ρ, T) dependence of the configurational entropy S_{conf} — which, in the Stillinger-Weber [10] formalism, can be defined as the logarithm of the number of different basins Ω in configuration space — has also been calculated and shown to correlate with D
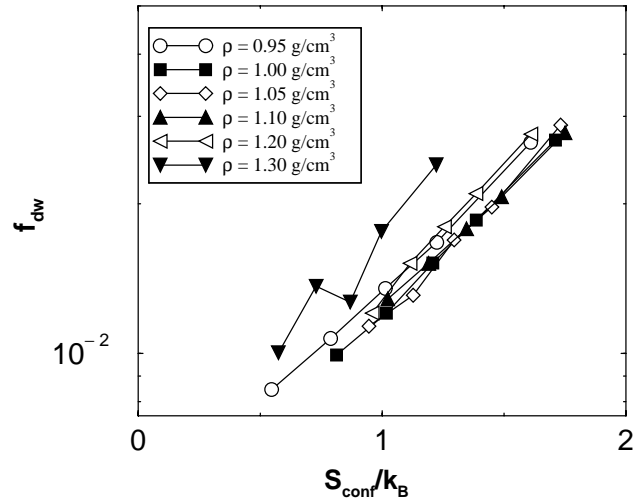

FIG. 5. Dependence on S_{conf}/k_B (from Ref. [16]) of $\log f_{dw}$.

[16]. Since no *a priori* relation is expected between the connectivity of the local minima and their number, we consider particularly interesting the observation of such a relation. For this reason, we show in Fig. 5 a "parametric plot" (in the parameter D) of f_{dw} versus S_{conf} for all studied densities. Figure 5 shows a linear relation between $\ln(f_{dw})$ and S_{conf}, i.e., between f_{dw} and the number of basins [since $\Omega = \exp(S_{conf}/k_B)$] and highlights the existence of an unexpected relation between the number of basins accessed in equilibrium and the connectivity between them, in the region of the phase diagram where the liquid dynamics are dominated by the presence of saddles and can be well described by the predictions of MCT. This novel feature of the PES contributes to a better understanding of the water dynamics, and may contribute to the understanding of the dynamics of glass-forming liquids [28].

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[21] Thus far, we cannot distinguish if the shift in the maximum of f_{sh} is connected to a change of the anharmonicity as a function of density, or to spurious leakage of double-well modes into shoulder modes in the classification procedure.

[22] We note that for $D \gtrsim 0.3 \times 10^{-6}$ cm^2/s, the relation between D and f_{dw} is approximately linear, in agreement with the finding of Keyes and co-workers for different liquids [12,30].

[23] The observed relation $D(f_{dw})$ is material dependent. Studies of the INM spectrum in different materials have shown that D may correlate with f_u or with the product $\omega_u f_u$, where w_u is defined as the average frequency of the f_u distribution [12].

[24] The approximate value 0.007 has been obtained by fitting D vs f_{dw} with a cubic polynomial and evaluating the value at which $D = 0.0$.

[25] Reference [20] has shown that some of the eigenvector of the double-well type may indeed point, in both directions, to the same local minimum; an example is the Mexican hat surface.

[26] A connection between glassy dynamics and the mechanism of "reduction of free directions" was proposed in R. Botet *et al.,* in *Universalities in Condensed Matter,* edited by R. Jullien, L. Peliti, R. Rammal, and N. Boccara (Springer-Verlag, Berlin, 1987), p. 250; see also A. Cavagna *et al.,* Phys. Rev. B **57**, 11 251 (1998).

[27] To separate the double-well directions into true double-well modes (modes connecting distinct minima, or inherent structures) and false modes (intrabasin modes), we perform a conjugate gradient minimization with tolerance 10^{-15}, starting from the two apparent double-well minima. We then calculate the distance between the two inherent structures $d \equiv [\sum_i^N (r_i^0 - r_i^1)^2 / N]^{1/2}$, where r_i^α is the ith atom position in inherent structure α. In agreement with the recent work of Ref. [31], we find that the distribution of d is bimodal, with peaks separated by more than 1 order of magnitude. Modes which contribute to the peak located at "large" $d \approx 0.067$ nm are classified as true double-well modes (f_{esc}). All other modes, widely distributed around 0.004 nm, are classified as false double-well modes. The very small differences between the two inherent structures that we associate with false modes is in large part due to the finite tolerance and to the numerical imprecision of the conjugate gradient technique [31]. A detailed analysis of these distributions will be submitted separately.

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