Configuration Space Connectivity across the Fragile-to-Strong Transition in Silica

Emilia La Nave,[1] H. Eugene Stanley,[1] and Francesco Sciortino[2]
[1]Center for Polymer Studies, Center for Computational Science, and Department of Physics, Boston University,
Boston, Massachusetts 02215
[2]Dipartmento di Fisica, INFM and INFM Center for Statistical Mechanics and Complexity, Universitá di Roma "La Sapienza,"
Piazzale Aldo Moro 2, I-00185, Roma, Italy

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We present a numerical analysis for SiO_2 of the fraction of diffusive direction $f_{\rm diff}$ for temperatures T on both sides of the fragile-to-strong crossover. The T dependence of $f_{\rm diff}$ clearly reveals this change in dynamical behavior. We find that for T above the crossover (fragile region) the system is always close to ridges of the potential energy surface (PES), while below the crossover (strong region), the system mostly explores the PES local minima. Despite this difference, the power law dependence of $f_{\rm diff}$ on the diffusion constant, as well as the power law dependence of $f_{\rm diff}$ on the configurational entropy, shows no change at the fragile-to-strong crossover.

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A useful approach for relating dynamics and thermodynamics of glass-forming liquids in their supercooled states is offered by the study of the liquid's potential energy surface (PES) [1]. The PES is the multidimensional surface generated by the system's potential energy as a function of all atomic coordinates. Numerical and theoretical studies [2–10] are providing evidence that several aspects of the liquid dynamics have a clear signature in the properties of the explored regions of the PES. For example, correlation functions display stretching in time in the same temperature (T) range in which the system explores regions of the PES associated with local minima of deeper and deeper energy [11]. Similarly, the rapid slowing down of the dynamics which takes place in the weakly supercooled region is associated with the exploration of regions of the PES close to saddles of lower and lower order [12–17]. Recent numerical studies for fragile liquids [18] have suggested the possibility that a crossover T, $T_\times$, marks a change in the geometrical properties of the PES explored. In this picture, above $T_\times$ the system trajectories are mostly located close to the ridges between different PES basins ("border dynamics"), while below $T_\times$ the system only rarely samples the regions connecting different PES basins ("minimum-to-minimum dynamics"). $T_\times$ has been associated [13,14,19,20] with the critical temperature predicted by the ideal mode-coupling theory (MCT) [21].

Instantaneous normal mode (INM) analysis [12] is a powerful technique to investigate the connectivity properties of the PES explored at different temperatures. The curvature of the PES along each of the $3N - 3$ independent directions (the eigenvectors of the Hessian matrix) is calculated and analyzed to estimate the fraction of diffusive directions $f_{\rm diff}$ [22].

If the representative configuration is crossing a ridge separating different PES basins, some of the local curvatures are negative. A computationally expensive but well-defined screening procedure to sort out the negative-curvature directions contributing to diffusion [7] has been developed [14,23,24]. For all model potentials for which such analysis has been performed, it has been shown that the T and density ρ variation of $f_{\rm diff}$ controls the behavior of the long-time dynamics, supporting the hypothesis that information about the local properties of the PES may be sufficient to describe long-time dynamical processes.

The analysis of the PES connectivity has been limited to models for fragile glass-forming liquids and to temperatures above $T_\times$, due to the difficulty in generating equilibrium configurations at low T. In all studied cases, it was consistently found that $T_\times$ locates the T at which $f_{\rm diff}$ appears to extrapolate to zero [13,14,24].

Here, we present an evaluation of the fraction of diffusive directions (using the INM analysis) for the well-studied Beest, Kramer, and van Santen (BKS) model for silica [25], for which we generate *equilibrium* configurations for temperatures both above and below $T_\times$. The INM spectrum of BKS silica has been previously calculated by Bembenek and Laird [26] for equilibrium states above $T_\times$ but no evaluation of $f_{\rm diff}$ was reported. For the BKS model, the high T dynamics has been shown to be consistent with the predictions of MCT at both a qualitative [27] and a quantitative [28] level. At lower T, the T dependence of the characteristic times [27] shows a crossover toward an Arrhenius T dependence which has been interpreted as a clear case of fragile-to-strong transition [29]. In the Arrhenius region, the activation energy is 54 000 K and 60 000 K, for oxygen and silicon, respectively. The crossover temperature $T_\times$, about 3330 K at $\rho = 2.36$ g/cm^3, has been interpreted by Horbach *et al.* as the MCT critical temperature [27]. It is interesting to note that, in silica, the T region, where correlation functions start to show the two-step relaxation characteristic of glassy dynamics, is well above the silica melting temperature (about 2000 K). In this respect, silica is not supercooled from a thermodynamics point of view [30].

We find that the T dependence of both the diffusion constant D and the $f_{\rm diff}$ shows a clear signature of the two different dynamical behaviors—fragile above and strong below $T_\times$. Despite these differences, the relation between D and $f_{\rm diff}$ is *not* sensitive to the presence of dynamical changes. Moreover, we find that $f_{\rm diff}$ does not vanish around $T_\times$ but changes to an Arrhenius T dependence, similar to the T dependence of D. Finally, we show that the number of diffusive directions is related to the number of basins of the PES, providing a possible explanation for the recently observed validity [4,29,31] of the Adam-Gibbs (AG) equation [32] in the T region where border dynamics dominates.

Our results are based on extensive simulations of a system of 999 atoms, for $\rho = 2.36$ g/cm^3, close to the density of ambient pressure silica. We investigate eleven T, in the range from $T = 2650$ K to $T = 7000$ K. We carry out simulations in the constant volume, energy, and number of particles ensemble, using a 1 fs integration time step. We evaluate the long range interaction by implementing the Ewald summation. To guarantee proper equilibrium conditions all simulations lasted longer than several times the slowest collective structural relaxation time; low T runs lasted longer than 50 ns. We also performed averages over eight different realizations. For each studied state point we calculated eigenvalues and eigenvectors for 96 configurations. For each of the eleven T studied, we performed approximately 2600 minimizations, using a total of about 50 000 CPU hours.

The INM analysis requires the evaluation of the eigenvectors and associated eigenvalues of the potential energy, second derivative matrix, the Hessian. According to the procedure described in Refs. [23,33], all eigenvectors associated with negative eigenvalues are inspected in order to eliminate those associated with intrabasin anharmonicities ("shoulder" and "false barrier" modes). Figure 1 shows (i) the T dependence of the fraction of directions with negative eigenmodes f_u, (ii) the fraction of directions whose one-dimensional profile is double-well shaped $f_{\rm dw}$, and (iii) the number of diffusive directions $f_{\rm diff}$, calculated by eliminating from the double-well set all false barrier modes [23,34]. Above $T = 3330$ K, all three quantities show a fast decrease with T. While f_u and $f_{\rm dw}$ assume nonzero values, $f_{\rm diff}$ appears to approach zero on cooling. A clear change of concavity in the T dependence of $f_{\rm diff}$ takes place above $T = 3330$ K. As found previously for fragile liquids for $T > T_\times$, the fast decrease of $f_{\rm diff}$ confirms that, above $T = 3330$ K, (i) the slowing down of dynamics is associated with a progressive decrease of the number of possible directions that lead to a different basin, (ii) the system trajectories are located close to PES ridges (*border dynamics*), (iii) even for BKS silica, the dynamics properly described by the ideal MCT are border dynamics, supporting the identification of $T_\times$ with the MCT critical temperature.

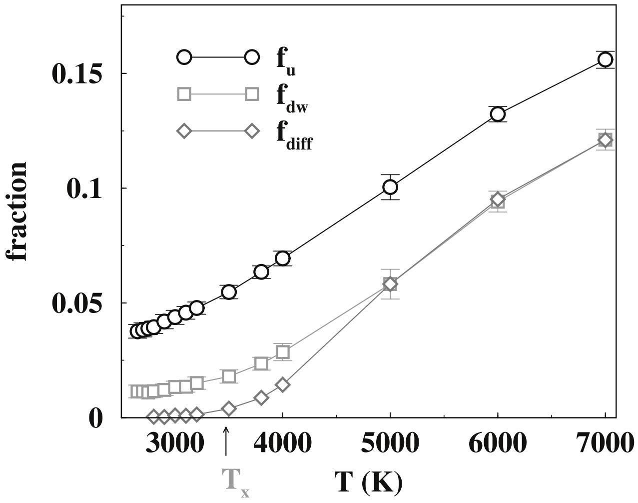

FIG. 1. Temperature dependence for the BKS model of the fraction of modes with negative curvature f_u, the fraction of modes with double-well-shaped one-dimensional profile $f_{\rm dw}$, and the fraction of diffusive directions $f_{\rm diff}$. The arrow marks $T_\times$ for the isochore studied [27].

For T below 3330 K, the system spends most of the time far from the PES ridges. To support this statement, Fig. 2 shows the probability $P(f_{\rm diff})$ of finding a configuration with a specific $f_{\rm diff}$ value for $T = 2800$ K ($<T_\times$) and $T = 4000$ K ($>T_\times$). Above $T_\times$ all examined configurations have a nonzero $f_{\rm diff}$, while below $T_\times$ the distribution is peaked at about zero and most of the configurations are characterized by the absence of diffusive directions.

We next investigate the functional relation between $f_{\rm diff}$ and D. The T dependence of both quantities, shown in an Arrhenius plot in Figs. 3(a) and 3(b), shows a change in the T dependence above and below $T_\times$. Despite this

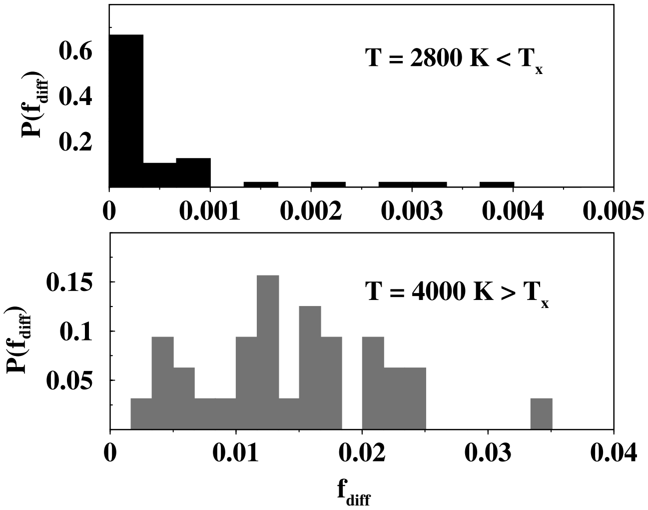

FIG. 2. Probability $P(f_{\rm diff})$ of finding a configuration with a given $f_{\rm diff}$ value above $T_\times$ ($T = 4000$ K) and below $T_\times$ ($T = 2800$ K). While for $T > T_\times$ all examined configurations have a nonzero $f_{\rm diff}$, below $T_\times$ the distribution is peaked around the origin.

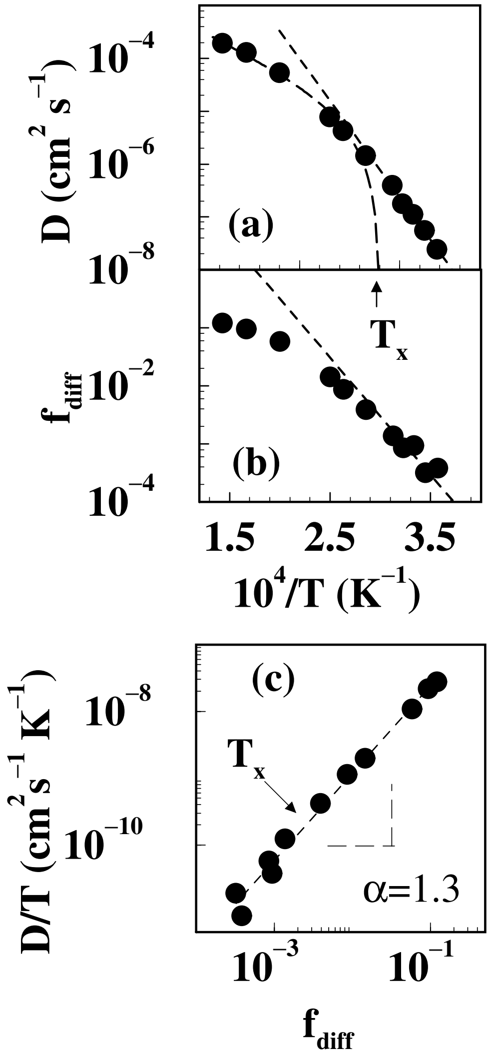

FIG. 3. Arrhenius plot of (a) the diffusion constant D for Si atoms; (b) f_{diff}. The short-dashed lines have slope 54 000 K in (a) and 41 000 K in (b). The long-dashed line in (a) indicates the MCT fit of $D \sim (T - T_{\times})^{\gamma}$. Part (c) shows the parametric relation D/T vs f_{diff} in a log-log scale. The data are perfectly smooth through the transition at $T_{\times}$.

different dynamical behavior, the quantity f_{diff} is related to D by the same power law relation both for $T > T_{\times}$ and for $T < T_{\times}$ [Fig. 3(c)]. In the entire studied T region, D follows the law

$$D/T \sim (f_{\mathrm{diff}})^{\alpha}, \qquad (1)$$

with $\alpha \approx 1.3 \pm 0.2$ over more than two decades in f_{diff} and more then three decades in D/T. The same functional form describes the relationship between D and f_{diff} both above and below $T_{\times}$ showing that, while the T dependence of both D and f_{diff} is sensitive to the microscopic mechanisms controlling the dynamics, the fragile-to-strong transition does not affect the relation between D and f_{diff}. We also stress that the same functional form has been found to describe the relation between D and f_{diff} in the case of the extended simple point charge (SPC/E) model for water [14], for which calculations were limited to $T > T_{\times}$.

The interpretation of the dynamics in terms of the fraction of diffusive directions is complementary to the analysis which attributes the slowing down of the dynamics to the decrease of the liquid configurational entropy S_{conf} [32]. In the case of BKS silica, S_{conf} has been recently calculated and shown to describe, via the Adam-Gibbs relation, the slowing down of the dynamics both above and below $T_{\times}$ [29]. Since S_{conf} is a measure of the number of distinct PES basins explored by the system—if the description in terms of S_{conf} and the description in terms of f_{diff} are both valid—a relation must exist between the number of basins and the number of directions connecting them. Figure 4 shows the relation between S_{conf} and f_{diff} for the case of BKS silica. Within the numerical uncertainty, the fraction of diffusive directions appears to be proportional to the number of explored basins, $\Omega \equiv e^{S_{\mathrm{conf}}/k_B}$, irrespective of the strong or fragile character of the dynamics. Data in Fig. 4 are consistent with similar findings which were limited to the SPC/E model for water to the T region above $T_{\times}$. The present results suggest that the linear relation between $\log f_{\mathrm{diff}}$ and S_{conf} is not model dependent; indeed it has been recently derived within the random energy model [35]. We also note that the relation between D and f_{diff} [Fig. 3(c)] and the relation between f_{diff} and S_{conf} (Fig. 4) suggest a relation between D and S_{conf} which would mathematically coincide with the AG 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 us to distinguish if the AG 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.

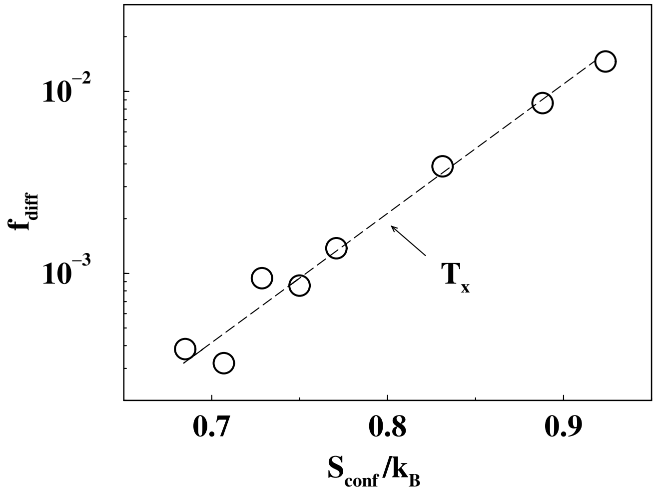

FIG. 4. Parametric plot of the fraction of diffusive modes f_{diff} as a function of the configurational entropy S_{conf} for the BKS model of silica.

The fact that the linear relation between $\log f_{\mathrm{diff}}$ and S_{conf} holds even above $T_{\times}$ is particularly interesting; since above $T_{\times}$ the system dynamics is a dynamics of borders, there is no clear reason why such border dynamics should be well described by the Adam-Gibbs relation which focuses on the number of basins explored as a function of T. The observed relation between $\log f_{\mathrm{diff}}$ and S_{conf} may offer a key for the resolution of this apparent paradox. It is a challenge for future studies to find out if f_{diff} is a potentially richer quantity for describing dynamics in deep supercooled states, as the results reported here seem to suggest.

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