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Identifying a causal link between structure and dynamics in supercooled water

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Abstract – By means of molecular-dynamics simulations we firmly establish the long-awaited existence of strong correlations between structure and dynamics for a glass-forming system: supercooled water. We find molecules with similar structural (and dynamical) properties to be clustered in space, thus revealing the existence of structured regions with low dynamic propensity and unstructured ones with a high-mobility tendency.

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The glass transition represents one of the most fascinating and challenging open problems in condensed matter physics [1,2]. This fact stems mainly from its uniqueness amongst phase transitions since, while the dynamical quantities change dramatically by several orders of magnitude between the melting and the glass-transition temperatures (that is, in the so-called supercooled state), the structural properties only display minor changes, at clear variance from the situation in typical phase transitions. The phenomenological picture implies that as temperature is lowered, the dynamics drastically slows down with the advent of slowly relaxing regions whose dimensions and lifetimes increase significantly upon supercooling. Such a dynamically heterogeneous response (with dynamics that can differ even in orders magnitude from one region of the sample to another) is intuitively expected to be structurally motivated, a belief that has fostered intense research efforts along many years. However, the inability to find a causal link between local structure and dynamics has not allowed such a claim to rise above the status of “article of faith” [2]. Thus, it would be of essence to find some structural correlator to dynamics.

The dominant feature of glassy relaxation, which gets more conspicuous as the temperature of the metastable state is decreased, is the existence of dynamical heterogeneities: Analysis of experiments and simulation data

of glass-forming liquids have shown that dynamics close to the glass transition is characterised by wide variations in the mobility of the different spatial regions of the system [3,4]. The memory of the initial structure is lost in a time, named the structural (or α -) relaxation time τ_α , which increases significantly upon supercooling. Simulation studies have shown that such relaxation is performed by means of rapid events in the form of relatively compact clusters of cooperatively relaxing particles [5] (termed “democratic clusters” or d-clusters) which drive the system from one metabasin (group of similar structures [5,6]) to another. This scenario also holds valid for supercooled water [7] and has received experimental support from a single-molecule technique in a glassy polymer [8]. It seems natural that the emergence of clusters of particles with very different mobility should be motivated by some underlying structural reasons. However, as already indicated, the finding of connections between static and dynamic properties in glass-forming liquids has been elusive, despite the significant amount of work devoted to this topic [9,10]. A newcomer that shed some light to this dilemma was the isoconfigurational ensemble (IC) technique [9]. In it one performs a series of equal length molecular-dynamics trajectories from the same initial configuration (that is, always the same particle positions) but each trajectory with different initial particle momenta chosen at random from the appropriate Maxwell-Boltzmann velocity distribution. This allowed to

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define [9] the propensity P of a particle i to move in the initial configuration ($t=0$) within a time interval ξ as $P_i(\xi) = \langle \Delta \mathbf{r}_i^2 \rangle_{\text{IC}}$, where $\Delta \mathbf{r}_i^2 = |\mathbf{r}_i(\xi) - \mathbf{r}_i(0)|^2$ is the quadratic displacement of particle i in the time interval $[0, \xi]$ for each trajectory of the IC, $\mathbf{r}_i(t)$ is the position of particle i at time t and $\langle \dots \rangle_{\text{IC}}$ is the average over such IC. Particles that can be very mobile in a single particular trajectory from a given initial configuration need not be mobile in other trajectories (within the IC) and might even be highly constrained by the local structure and yield a low P value. In this sense, the dynamic propensity (the tendency to be mobile in the local configuration) is a better dynamical measure to use here since, as it averages out the random thermal effect of the initial momenta which controls the time evolution in a single-trajectory approach, is thus able to clearly reflect the local structural constraints. At difference from the situation at high temperatures, at temperatures within the supercooled regime it has been found that the P of the particles of glass-forming systems are *not* uniform throughout the sample and that high- P particles are confined to certain (relatively compact) regions [9,11]. While particle mobility is not reproducible from trajectory to trajectory, the spatial variation in P is completely determined by the initial configuration, thus surfacing the influence of structure on dynamics [9,11] and making evident the existence of more and less constrained (more or less “jammed”) regions throughout the sample. However, while this heterogeneity in the P distribution clearly demonstrated that the local structure indeed constraints the resulting dynamics, it does not single out which particular aspect of the local structure is in fact responsible so as to unravel the causal link between structure and dynamics. Even when some correlations between local structure and single-trajectory dynamics have already been found [10,12], a firm correlation between any given structural property and the dynamic propensity has not been established. In fact, in ref. [12] it has been shown that different structural quantities like free volume (which has long been thought should play a role in glassy dynamics, as postulated by the so-called free-volume theory) and local composition do not correlate to P . Positive correlations could only be found for the Debye-Waller factors (measured by the very short time motions of the particles) and for the soft modes of the system. However, none of these quantities are strictly speaking “structural” but dynamically originated.

Supercooled water is an interesting system in which to try structural observables to correlate to P given the presence of directional interactions and preferred local structural arrangements. Additionally, water is not only a fascinating and very important system in itself but also the study of structural and dynamical properties of water is essential for several research areas, encompassing solvation, reaction dynamics and biology and for understanding the several anomalies which characterise this liquid and which become more prominent as it is supercooled

[1,13,14]. Such anomalies have been tentatively associated to structural facts: the presence of two competing preferential local structures, identified with molecules characterised by high or low local density [13,15]. Support for this idea comes from the existence of at least two different forms of amorphous glass states, namely low-density amorphous ice and (very) high-density amorphous ice [13,16]. Additionally, supercooled water has been demonstrated to belong to the general dynamically heterogeneous scenario above mentioned. However, a recent work has shown the absence of spatial correlations between the potential energy of the water molecules in a given structural configuration and the corresponding dynamic propensity [10]. Interestingly, spatially correlated clusters of low potential energy molecules in the same spatial region of the low- P clusters of the initial configuration are observable only on the time scale of structural relaxation while not at the initial time, that is, in the initial configuration. In turn, no correlation could be found between the high- P molecules and the high potential energy molecules present during the relaxation.

Different parameters have been proposed to study the local structural order of the water molecules on a quantitative basis. One of them, proposed by Shiratani and Sasai [15], associates a local structure index I to each molecule to quantify the degree of local order. The key observation is the existence of certain molecules which show an unoccupied gap between 3.2 Å and 3.8 Å in their radial-neighbour distribution for certain periods of time (1 Å (angstrom) = 10^{-10} m). Such low-density molecules are well structured and coordinated in a highly tetrahedral manner with four other water molecules. Occupancy of such gap increases the local density and distorts the tetrahedral order of the central molecule. Shiratani and Sasai defined $I(i, t)$ for molecule i at time t . For each molecule i one orders the rest of the molecules depending on the radial distance r_j between the oxygen of the molecule i and the oxygen of molecule j : $r_1 < r_2 < r_j < r_{j+1} < \dots < r_{n(i,t)} < 3.7 \text{ \AA} < r_{n(i,t)+1}$. Then, $I(i, t)$ is defined as [15]: $I(i, t) = \frac{1}{n(i,t)} \sum_{j=1}^{n(i,t)} [\Delta(j; i, t) - \overline{\Delta}(i, t)]^2$ where $\Delta(j; i, t) = r_{j+1} - r_j$ and $\overline{\Delta}(i, t)$ is the average over all molecules of $\Delta(j; i, t)$. Thus, $I(i, t)$ expresses the inhomogeneity in the radial distribution within the sphere of radius around 3.7 Å. A high value of $I(i, t)$ implies that molecule i at time t has a good tetrahedral local order and low local density (and thus a low local potential energy since it is bonded to its first four neighbours by geometrically well-shaped hydrogen bonds), while on the contrary, values of $I(i, t) \approx 0$ indicate a molecule with defective tetrahedral order and high local density (and thus, high local potential energy), even allowing for a fifth neighbour within the coordination shell. Another possibility is the orientational order parameter q , which is defined as follows [17]: $q(i, t) = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\frac{1}{3} + \cos \psi_{jk}(i, t) \right)^2$ where $\psi_{jk}(i, t)$ is the angle between the lines connecting the oxygen of molecule

i with those of its nearest molecules j and k at time t . Then $-3 \leq q(i, t) \leq 1$, and high values indicate that molecule i has good tetrahedral order.

To search for a correlation between local structure and dynamics in supercooled water we simulated a system with $N = 216$ water molecules which interact via the Simple Point Charge (Extended) potential (SPC/E)¹. The system is placed in a cubic box at density 1.0 g/cm^3 , temperature $T = 210 \text{ K}$ and periodic boundary conditions; long-range interactions have been modelled via reaction field (the positions of the molecules will be indicated by the position of their oxygen atoms). In these conditions, this system presents significant dynamical heterogeneities and the P distribution is also clearly heterogeneous. After proper equilibration, from an initial configuration we generate an IC of 250 trajectories and calculate the propensity $P_i(\xi)$ of the different molecules i in time interval $[0, \xi = 160 \text{ ps}]^2$. To seek for correlations between the two mentioned structural parameters and P we start selecting the 18 molecules with the highest P and the 18 molecules with the lowest P , which will form the high- P set (HP) and low- P set (LP), respectively. We indicate that the behaviour we shall show is displayed by other choices for the fraction of particles representing HP and LP. Then, for each of the two sets of molecules and at different times t we calculate their average parameters values in the IC as $\langle \theta(t) \rangle_Y = n^{-1} \sum_{l=1}^n \left(N_Y^{-1} \sum_{i=1}^{N_Y} \theta_i(i, t) \right)$, where θ is the parameter I or q , Y is LP (the set of the $N_Y = 18$ lowest- P molecules) or HP (the set of the 18 highest- P molecules), and $\theta_i(i, t)$ is the parameter θ of molecule i at time t in the trajectory l of the IC of $n = 250$ trajectories. In this manner we calculate respectively $\langle I(t) \rangle_{\text{LP}}$, $\langle I(t) \rangle_{\text{HP}}$, $\langle q(t) \rangle_{\text{LP}}$ and $\langle q(t) \rangle_{\text{HP}}$. For $t = 0$ the calculation is over only one configuration, the initial configuration that generates the IC. For any other t the statistics is improved because we can obtain results from one each configuration (at time t) of the 250 trajectories of the IC. In fig. 1 we show the results. At $t = 0$ a clear correlation can be seen between P and both structural parameters. We can note that the LP (squares), that is the set of 18 molecules with low tendency to be mobile in the initial configuration, displays high values $\langle I(0) \rangle_{\text{LP}}$ and $\langle q(0) \rangle_{\text{LP}}$, which speaks of the highly structured nature of such molecules (recall that the higher the parameter, the better the tetrahedral structure). In turn, the set with the highest- P molecules (circles), or equivalently molecules that exhibit a great mobility tendency, show low values $\langle I(0) \rangle_{\text{HP}}$ and $\langle q(0) \rangle_{\text{HP}}$ which reflects their unstructured local environment. These

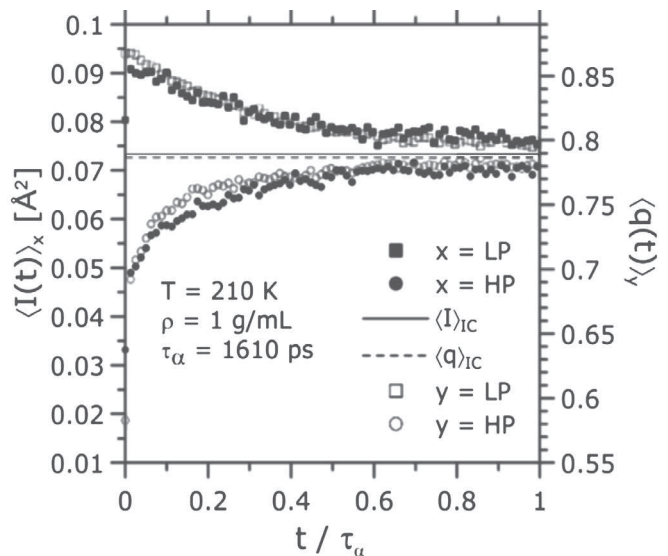


Fig. 1: Time dependence of the averaged parameters I and q ($\langle I(t) \rangle_X$ and $\langle q(t) \rangle_Y$, respectively) over sets X and Y , one set comprising the 18 lowest- P molecules (LP) and the other set comprising the 18 highest- P molecules (HP). Also included are the parameter averages, $\langle I \rangle_{\text{IC}}$ and $\langle q \rangle_{\text{IC}}$, over all the molecules and configurations (times) of the IC.

average values of both sets deviate significantly from the mean values I ($\langle I \rangle_{\text{IC}}$) and q ($\langle q \rangle_{\text{IC}}$) over the IC, as averaged over all the molecules and all configurations (times) of the IC. As the relaxation evolves (that is, at larger times), the loss of the initial structural constraints reflects itself in a decrease in the departure from $\langle I \rangle_{\text{IC}}$ for both $\langle I(t) \rangle_{\text{LP}}$ and $\langle I(t) \rangle_{\text{HP}}$, which at long times it can be seen that tend to the mean value. A similar situation holds for the parameter q , as can be learnt from the same figure.

Having established the existence of a clear link between a structural quantity (the degree of local structural order, as measured by the parameters I or q) with the mobility tendency of the molecules (as dictated by the dynamic propensity P) we now aim at determining the relative spatial arrangement of the different kinds of molecules. It is well known [9] that the high- P particles are not uniformly distributed within the initial configuration but clustered together (the same situation takes place for the low- P particles, as we shall see below). Thus, we expect that the high- and low- I (and also the high- and low- q) molecules are arranged in clusters in the same spatial regions of the corresponding low- and high- P clusters, respectively. In the same manner we did for P , we choose the set of the 18 lowest- I molecules and of the 18 highest- I molecules (LI and HI, respectively), and the set of the 18 lowest- q molecules and of the 18 highest- q molecules (Lq and Hq, respectively). Then we calculate the minimum distance ($\gamma_{XY}(t)$) [20] between the molecules of class X and Y ($X, Y \in \{\text{LI, HI}\}$ or $X, Y \in \{\text{Lq, Hq}\}$), averaged over the IC. This minimum distance is evaluated as $\gamma_{XY}(t) = n^{-1} \sum_{l=1}^n \left(N_X^{-1} \sum_{i=1}^{N_X} \min\{|\mathbf{r}_i^{X,l}(t) - \mathbf{r}_1^{Y,l}(t)|, \dots, |\mathbf{r}_i^{X,l}(t) - \mathbf{r}_j^{Y,l}(t)|, \dots, |\mathbf{r}_i^{X,l}(t) - \mathbf{r}_{N_Y}^{Y,l}(t)|\} \right)$ with

¹This rather small system size is required given the computationally demanding IC we shall use. The dynamics of this system is compatible with that of a larger system, thus no significant finite size effects are present [18].

²The value 160 is somewhat arbitrary. It corresponds to 10% of $\tau_\alpha(T = 210 \text{ K}) = 1610 \text{ ps}$, this last defined as the time when the self intermediate scattering function has decayed to 10% of its initial value using the wave number value 18 nm^{-1} (wave number that gives the first peak in the oxygen-oxygen static structure factor [19]).

Table 1: Minimum distance $\gamma_{XY}(t)$ between molecules within a set X and a set Y , at 10 ps and at τ_α . The values for propensity P are evaluated over the initial configuration. Units are given in \AA .

X	LI	LI	HI	Lq	Lq	Hq	LP	LP	HP
Y	LI	HI	HI	Lq	Hq	Hq	LP	HP	HP
$t = 10$ ps	3.62	4.74	3.89	3.73	4.63	3.95	2.90	6.60	3.03
$t = \tau_\alpha$	3.75	4.73	3.84	3.90	4.39	4.08	3.15	5.94	3.55

the restriction $i \neq j$ if $X = Y$. Here $N_X = N_Y = 18$ are the number of molecules within the sets X and Y and $\mathbf{r}_i^{X,l}(t)$ is the position of molecule i belonging the set X at time t in the trajectory l of the IC. In table 1 we show the results (we choose a very short time of 10 ps, since at this time we do not expect the I and q values have changed much from that of the initial structure and the IC ensemble enables us to gain far better statistics than considering solely $t = 0$, that is, the initial structure).

From these results we can learn that molecules of the same class are much closer together than molecules of different classes. For example, at $t = 10$ ps, on average the closest LI neighbour of an LI molecule is located at 3.62\AA (roughly before the second peak in the oxygen-oxygen radial distribution function occurring at 4.4\AA for actual T and density) while its closest HI molecule is much farther (4.74\AA).

In turn, we determined at time t the relative spatial arrangement of the sets of molecules with different I values and the sets of molecules with different P values. To this end we divided the 216 molecules of each configuration at time t within the IC into 12 sets of increasing I (so that the first set contains the 18 molecules with the lowest- I values and so on, until the set number 12 which contains the 18 molecules with the highest- I values). Similarly, we divided the 216 molecules of the initial configuration into 12 sets of increasing P (we recall that propensity is a measure of the initial local structural constraints and thus we just calculate it for the initial configuration). Then, we calculated the function $\gamma_{XY}(t)$ of the 18 molecules of each of the different I -sets with respect to the 18 molecules of each of the P -sets. Here X and Y can be any of the: 12 I -sets and 12 P -sets, respectively. We note that $\gamma_{XY}(t) \approx \gamma_{YX}(t)$. A similar procedure was carried out by using the q values instead of the I values.

Figure 2(a) shows the results for parameter I for a very short time of $t = 10$ ps. From such plot we can easily learn that γ between P -set 12 (former HP, highest P) and I -set 1 (former LI, lowest I) is close to 2.957\AA (a value that lies within the position of the first peak of the oxygen-oxygen radial distribution function thus indicating that many of the highest- P and lowest- I molecules are common to the two sets or are first neighbours). In turn, P -set 1 (former LP, lowest P) and I -set 12 (former HI, highest I) present a $\gamma \approx 3.39 \text{\AA}$. However, γ between P -set 1 and I -set 1, and that between P -set 12 and I -set 12 is around 4.60\AA and 4.76\AA , respectively. These values are rather large and lie within the second peak of the radial distribution function.

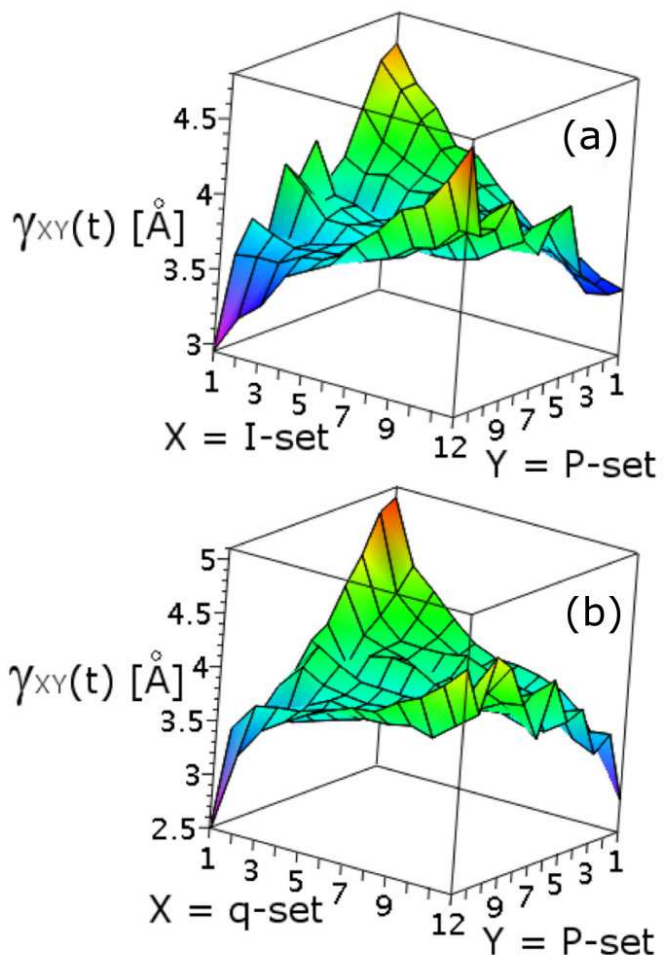


Fig. 2: (Colour on-line) Minimum distance $\gamma_{XY}(t)$ for a short time of $t = 10$ ps between the molecules within an X -set and a Y -set, where Y is one of the 12 P -sets. a) In this case X is one of the 12 I -sets. b) In this other case X is one of the 12 q -sets.

These values are also much higher than the flat portion of the surface, thus, these classes of molecules are the ones that lie farther from each other. We also performed an analogue treatment with the q parameter, shown in fig. 2(b). The results are very similar to those shown in fig. 2(a), thus the conclusions taken from it remain the same as for fig. 2(a). Additionally, we found that for both parameters (X is an I -set or a q -set) the shape of the $\gamma_{XY}(t)$ function (Y is a P -set) for time $t = \tau_\alpha$ is a flat surface, indicating that spatial correlations between

structural (at long times) and dynamical (at $t = 0$, signed by P) quantities are lost.

To summarise, our work has provided clear evidence for the existence of correlations between structural and dynamical quantities in a glass-forming system. For supercooled water, well locally structured (tetrahedrally coordinated) molecules present a low tendency for mobility, while unstructured molecules display the highest dynamic propensities. As is the case for molecules with similar dynamic propensity, molecules with similar structural characteristics are clustered in space, thus determining the existence of spatial regions in the sample where the different structural constraints determine wide variations in the dynamical behaviour.

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