

Correlations between defect propensity and dynamical heterogeneities in supercooled water

Alejandro R. Verde¹, Laureano M. Alarcón¹, and Gustavo A. Appignanesi^{1*}

¹ *INQUISUR, Departamento de Química,
Universidad Nacional del Sur (UNS)-CONICET,
Avenida Alem 1253, 8000 Bahía Blanca, Argentina*

* *Corresponding author: appignan@criba.edu.ar*

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A salient feature of supercooled liquids consists in the dramatic dynamical slowdown they undergo as temperature decreases while no significant structural change is evident. These systems also present dynamical heterogeneities (DH): certain molecules, spatially arranged in clusters, relax various orders of magnitude faster than the others. But, again, no static quantity (like structural or energetic measures) shows strong direct correlations with such fast-moving molecules. In turn, the dynamic propensity approach, an indirect measure that quantifies the tendency of the molecules to move in a given structural configuration, has revealed that dynamical constraints indeed originate from the initial structure. Nevertheless, this approach is not able to elicit which structural quantity is in fact responsible for such behavior. In an effort to remove dynamics from its definition in favor of a static quantity, an energy-based propensity has also been developed for supercooled water, but it could only find positive correlations between the lowest-energy and the least-mobile molecules, while no correlations could be found for those more relevant mobile molecules involved in the DH clusters responsible for the system's structural relaxation. Thus, in this work we shall define a defect propensity measure based on a recently introduced structural index that accurately characterizes water structural defects. We shall show that this defect propensity measure provides positive correlations with dynamic propensity, being also able to account for the fast-moving molecules responsible for the structural relaxation. Moreover, time dependent correlations will show that defect propensity represents an appropriate early-time predictor of the long-time dynamical heterogeneity.

I. INTRODUCTION

When rapidly cooled below their melting point, most liquids bypass crystallization and enter a supercooling regime characterized by a strong dynamic slowing down until eventually ending up as a metastable amorphous solid, i.e., a glass[1–3] (strictly, while amorphous ices are glasses at a local scale, it has been found that the large-scale density fluctuations keep decreasing well below the temperature of freezing of diffusional and rotational motion[4]). A salient feature of the supercooled liquid state is the presence of dynamical heterogeneities (DH), that is, its local dynamics can differ in orders of magnitude from one region of the sample to another[5–12]. Indeed, the structural or α -relaxation is triggered by certain fraction of the particles that perform large displacements on the order of the interparticle distance, while the rest of the system is basically immobile, and this set of mobile particles is found to be clustered in space (DH cluster)[5–13]. But strikingly, it has not been possible to single out a clear structural source responsible for such a notable spatial variation of the dynamics since different quantities, like various local structural measures, free volume, potential energy of the initial configuration, etc., have failed to strongly correlate with local dynamics [14–17]. Indeed, this lack of a specific static correlator to predict the dynamics resulting from a given initial configuration has recently stimulated the use of machine learning methods[18–26]. A beautiful develop-

ment in this field was the introduction of the concept of dynamic propensity[14–16]. This measure implies the determination of the tendency of the particles to move away from their original position and is calculated by means of diverging molecular dynamics runs originated from a common initial configuration. This indirect approach revealed that the spatial correlations of mobility that define the dynamical heterogeneities are indeed originated from the initial structural configuration, thus revealing that a causal link between structure and dynamics effectively exists, but it does not tell us which particular structural properties are actually responsible. Additionally, it has been shown that the short-time propensity, which represents an estimator of the particle's Debye-Waller factor, represents a good early-time predictor of the long time-dynamic heterogeneity[15, 27, 28].

In turn, water is a system of utmost importance for which the occurrence of slow and heterogeneous dynamics (even above the melting point) becomes determinant for many central fields[1, 29–39]. And provided water is a liquid with directional interactions (hydrogen bonds) which promote local order, it seems reasonable to try to search for such an elusive link between structure and dynamics within its supercooled regime. Additionally, water structural defects are intuitively expected to play a role in its glassy dynamics and, thus, an energetically-based indicator, the V_4 [40] index, has been recently developed to correct overestimations of distorted configurations in which incurred previous indicators[41]. Correlations of different local structural measures (including

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V_4) with dynamical heterogeneities have thus been sought but, at best, they have only produced mild results even in the case of V_4 [17, 42–45]. This might be due to the fact that water defects are short-lived and, thus, a given initial configuration might not provide a good representation of the local structural constraints. Faced with this inability to find a strong direct correlation between structure and dynamics, a very interesting work[17] took the indirect approach to also define a propensity measure based on potential energy which was then correlated with dynamic propensity. However, positive correlations could only be found between the less mobile molecules and the molecules with lower potential energy. This might allow to identify “frozen” regions in the sample but not the molecules engaged in DH clusters which are responsible for the structural relaxation of the system. Thus, this energetic-propensity measure is not able to predict relevant glassy relaxation events.

Within this context and armed with our recently developed structural index[40], in this work we shall define a defect propensity measure. This quantity will be shown to indeed provide positive correlations with dynamic propensity. Moreover, by studying the time dependence of its predictive capability, we shall show that defect propensity represents an excellent early-time predictor of the long-time dynamic heterogeneity, comparable to the short-time dynamic propensity. Finally, the three-dimensional distribution of the high defect propensity molecules will be shown to nicely coincide with that of the high dynamic propensity ones, thus revealing the ability of this new measure to signal the spatial location of the DH clusters.

II. METHODS

A. Molecular dynamics simulations

We performed molecular dynamics (MD) simulations of the TIP4P/2005 [46] model of water by means of the GROMACS package version 5.1.1 [47]. We constrained bonds with the LINCS algorithm and the long range electrostatics was accounted for with the PME method. We used a modified Berendsen thermostat and a Parrinello-Rahman barostat at 1 bar and the time step was 2 fs. Cubic boxes containing $N = 1000$ water molecules with periodic boundary conditions and a cutoff of 1nm for the short range forces were employed. This system size enables us to employ the dynamic propensity approach for which a large number of different trajectories (1000) are generated from a common origin thus building an isoconfigurational ensemble. After equilibrating for timescales much larger than the α relaxation (when the self-intermediate scattering function has decayed to $1/e$), the production runs were generated. We studied a system at $P=1$ bar and a supercooling temperature $T=246$ K (below the melting point of this system), but the results are similar for other supercooling temperatures. Results

are averaged over 10 different replicas. At this temperature, the mean squared displacement, MSD, of the system presents a short-time ballistic and a long-times diffusive regimes[48, 49], separated by a caging regime (a plateau in the MSD) that follows a non-gaussian dynamically heterogeneous behavior. This behavior is most prominent at a timescale called t^* (when the non-gaussian parameter is maximal[48], in our case, $t^* = 5ps$). This timescale is located close to the end of the MSD plateau (at the beginning of the diffusive regime) and is lower (in around one order of magnitude) than the structural or α relaxation time. Mobile molecules are classified as that whose displacement at time t^* is larger than a threshold that is defined as the value at which the van Hove function (the system’s displacements distribution) at such time exceeds a Gaussian distribution with the same mean value. In practice, for temperatures within the supercooled regime, mobile molecules could be selected as the ones that have moved more than around 2\AA within the time interval $[0, t^*]$ [50]. These molecules (only 5 to 10% of the sample) define the dynamical heterogeneities (DH) and are found to be clustered in space. These DH clusters have been shown[50] to present open-like structures similar to the strings typical of binary Lennard-Jones systems[51] but with more branching.

B. The V_4 structural indicator

The calculation of the V_4 index [40] for a central molecule i implies the computation of all its pair-wise interactions V_{ij} , $j \neq i$ to sort them in increasing ordering regarding their intensity. $V_4(i)$ is then the fourth lowest V_{ij} . A good local tetrahedral arrangement implies a $V_4(i)$ value around a linear hydrogen bond (HB) energy, while a distorted local order would produce a higher $V_4(i)$ value. When applied combined with energy minimizations (that is, on configurations subject to a minimization protocol like steepest-descent to reach the so-called inherent structures, IS), V_4 yielded clear bimodal distributions for different water models [40] thus enabling an accurate classification of water molecules in tetrahedral (T, structured) or defect (D, unstructured) molecules. In practice, the index, employed at the IS scheme, classifies molecules with $V_4(i) \leq -12kJ/mol$ as T while D molecules are that which present a higher index value. Thus, $V_4(i)$ is able to discriminate true defects from mere thermally deformed configurations.

C. The dynamic and defect propensity measures

The isoconfigurational ensemble (IC) [14] is built by a set of equal-length MD runs starting from the same initial configuration (at initial time $t=0$) but each one with molecular momenta randomly chosen from a Boltzmann distribution at the corresponding temperature. At the supercooled regime, the different IC runs are diver-

gent and each one presents a different DH cluster since mobility is not reproducible from run to run[14]. The dynamic propensity of a molecule within the time interval $[0, t]$ is calculated as [14]: $P_{dyn}(i, t) = \langle \Delta \mathbf{r}_i^2(t) \rangle_{IC}$ (where $\langle \dots \rangle_{IC}$ implies an average over all the runs of the IC and $\Delta \mathbf{r}_i^2(t) = \Delta \mathbf{r}_i^2 = (\mathbf{r}_i(t = t) - \mathbf{r}_i(t = 0))^2$ is the squared displacement of molecule i within $[0, t]$). This function measures the tendency of a molecule to be mobile, that is, to move away from the initial configuration. At low temperatures within the supercooled regime, it is found that high propensity molecules are not scattered uniformly throughout the sample but tend to be spatially arranged in rather compact clusters [14–16, 27, 28, 44]. If $P_{dyn}(i, t)$ is calculated at very short times (well within the caging regime of the MSD), it is found that it correlates well with the result of $P_{dyn}(i, t)$ at larger times commensurable with the α relaxation, thus revealing the fact that the short-time dynamics (which represents a good estimation of the system's Debye-Waller factors), is able to predict the system's long-time dynamic heterogeneity[15, 27, 28].

In the same spirit as the dynamic propensity, P_{dyn} , we now define a defect propensity, P_{def} . For the different IC runs, each molecule i at time t is classified as D or T and its structural state, $S(i, t)$, is assigned a value equal to $S(i, t) = 1$ if it resides in a D state (defect) at time t or $S(i, t) = 0$ if it is in a T state. Thus, we define a defect propensity, P_{def} , similarly to P_{dyn} : $P_{def}(i, t) = \langle S(i, t) \rangle_{IC}$. This measure quantifies the tendency of a given molecule to be defective at time t in the IC ensemble (different MD runs) that starts from a fixed initial configuration. Thus, it reflects the constraints imposed by the initial configuration on the structural state at later times during the dynamical relaxation.

III. RESULTS AND DISCUSSION

FIG. 1: Typical time evolution of V_4 for a few initially a) D-molecules and b) T-molecules.

For illustrative purposes, Fig. 1 shows the time evolution of the V_4 index for a small set of molecules that, at the initial time of a typical MD run, are either D ($V_4(i)$ value above the dashed line of Fig. 1) or T ($V_4(i)$ value below the dashed line). This plot shows that initially defective molecules tend to alternate between D and T states (defects are short-lived) and, thus, a given initial configuration might not provide a good representation of the defective regions. This fact explains why direct correlations between structural indices, also including $V_4(i)$, could only provide partial correlations with dynamic propensity [17, 42–45]. In turn, the initially structured, T, molecules tend to reside for long times in their structured state (some molecules also experience

certain short visits to D states, but they are minority).

Fig. 2 displays the probability distributions for the dynamic and defect propensities at $t = t^*$ and at $t = 0.1t^*$. Both measures show non-gaussian distributions with a tail towards large values implying the existence of high propensity molecules. In turn, in Fig. 3 we correlate dynamic and defect propensities at $t = t^*$ for 10 different replicas each one comprising 1000 IC runs. The existence of a good correlation between $P_{def}(t^*)$ and $P_{dyn}(t^*)$ for the different molecules is evident from such contour plot graphs. This means that the molecules that tend to be mobile (take part of the DH cluster) are expected to show good coincidence with the molecules that tend to be defective during the structural relaxation. We also compare the short-time ($0.1t^*$) with the long-time (t^*) dynamic propensities, making evident the existence of a positive correlation (this correlation with the short-time propensity would still hold for larger timescales within the α relaxation time[15, 27, 28]). This means that the short-time propensity represents a good early-time predictor of the system's dynamical heterogeneities.

FIG. 2: Defect propensity distributions, $P_{def}(t)$, and dynamic propensity distributions, $P_{dyn}(t)$, for $t = 0.1t^*$ (squares) and $t = t^*$ (circles)

FIG. 3: Top: Correlations between $P_{dyn}(t)$ at short ($t = 0.1t^*$) and long ($t = t^*$) times; Bottom: Correlations between defect propensity and dynamic propensity at time ($t = t^*$). We show contour plots that depict regions with different density. Thus, the inner region enclosed by the black line (number 95 in the accompanying scale) is characterized by having more than 95 points per unit area (high density of points) while the outer red line (number 5) encloses all the region where there are more than 5 points per unit area.

To quantify the predictive capability of the dynamic and also of the defect propensities as a function of time, we calculated Pearson correlation coefficients between the different quantities. This measure, evaluated at different times, is defined by: $\rho(t) = \sum_{i=1}^N \rho_i(t)$, where:

$$\rho_i(t) = \frac{[X_i(t) - \langle X(t) \rangle][Y_i(t^*) - \langle Y(t^*) \rangle]}{\left\{ \sum_{i=1}^N [X_i(t) - \langle X(t) \rangle]^2 \right\}^{1/2} \left\{ \sum_{i=1}^N [Y_i(t^*) - \langle Y(t^*) \rangle]^2 \right\}^{1/2}}$$

When $X_i(t)$ is $P_{dyn}(i, t)$ and $Y_i(t^*)$ is $P_{dyn}(i, t^*)$, we are correlating the dynamic propensities at different times t with the dynamic propensities at time t^* . As t increases from $t = 0$ to $t = t^*$, Fig. 4 shows that the Pearson coefficient quickly grows and gets $\rho = 1$ at t^* since the function always compares with the dynamic propensity at such final time. The plot shows the ability of the short-time dynamic propensity at predicting the dynamical behavior at later times. Indeed, it is found that the

short-time dynamic propensities are very good predictors of the long-time DH: For example, at $t = 0.1t^*$ ρ is around 0.6. However, for very short times, the correlation falls: For example, at $0.02t^*$ we find that $\rho < 0.3$. Of course, this is a very short timescale, located at the beginning of the caging regime in the MSD plot. In Fig. 4 we also correlate $P_{def}(i, t)$, the defect propensity at time t with $P_{def}(i, t^*)$ (that is, in this case $X_i(t)$ is $P_{def}(i, t)$ and $Y_i(t^*)$ is $P_{def}(i, t^*)$). From such plot we can learn that the correlation is excellent at all times. Indeed, the time evolution of the defect propensity correlation is faster than that of the dynamic propensity since at $0.02t^*$ $\rho \approx 0.6$. This means that the long-time defectiveness of the sample is predictable from the very beginning. Finally, in Fig. 4 we also correlate $P_{def}(i, t)$ with $P_{dyn}(i, t^*)$ (by making $P_{def}(i, t)$ as $X_i(t)$ and $P_{dyn}(i, t^*)$ as $Y_i(t^*)$) to see how well the early time defects can predict the dynamical heterogeneities of the system. From direct inspection of Fig. 4 it is evident that the curve grows extremely quickly. The final value is not unity but a bit below $\rho = 0.6$ since here at $t = t^*$ we are comparing different quantities: defects with mobilities. However, such a final value speaks of a nevertheless good correlation since it falls around the maximum correlation values found in machine learning studies of glass-forming liquids[18]. It also makes sense that the curve tends to a value lower than unity when we bear in mind the open-like nature of the DH clusters [5–7, 9, 10, 50] and the intermittent nature of the glassy relaxation events (large periods of inactivity to then suffer rapid bursts of mobility[13, 27]) Thus, not all the molecules comprising the mobile object need to be defective at times before the relaxation event. It is expected that in each IC run some defective molecules alternate between D and T states as shown in Fig. 1, to perform a coherent collective motion at a later time. Once these molecules perform their displacements (they move roughly more than 2\AA), they create defective environments to previously non-defective molecules which immediately move to complete the DH cluster.

In turn, what is even more notable from Fig. 4 is the quick growth of the $P_{def}(t)$ vs $P_{dyn}(t^*)$ curve, which speaks of the fact that the short-time defects work even better as very early predictors of the final dynamical heterogeneities than the short-time dynamic propensity itself. The $P_{def}(t)$ vs $P_{dyn}(t^*)$ curve starts at higher correlation values than that of the $P_{dyn}(t)$ vs $P_{dyn}(t^*)$ (even when, of course, it is later on surpassed since its saturation value is lower than unity). We have also included a normalized curve $P_{def}(t)/P_{def}(t^*)$ vs $P_{dyn}(t^*)$, which displays a behavior similar to the excellent correlation of the $P_{def}(t)$ vs $P_{def}(t^*)$ curve. Thus, by defining a defect propensity measure we have been able to indeed reveal the existence of a strong correlation between high-mobility and high-defectiveness, a result that could not be achieved by the previously defined energetic propensity measure[17].

In Fig. 5 we show the spatial arrangement of the different high propensity molecules for one typical IC run.

Namely, we plot the three-dimensional (3D) distribution of the 5% highest propensity molecules for $P_{dyn}(t^*)$, $P_{dyn}(0.1t^*)$, $P_{def}(t^*)$ and $P_{def}(0.1t^*)$. From these plots it is evident that the different sets of molecules are located in the same spatial region including several coincidences, a fact that speaks of the close similarity between the different high propensity regions. We note that the study of total correlation functions for the D molecules together with partial radial distribution functions has evidenced certain clustering tendency for the D molecules[40] (also, D molecules are the only ones that can locate at around 3.5\AA of any other molecule, thus populating the interstitial position of the radial distribution function). This is consistent with the rather compact nature of the clusters of Fig. 5.

FIG. 4: Pearson correlation coefficients for the correlation of the different propensity measures. Red circles: $P_{dyn}(t)$ and $P_{dyn}(t^*)$; black squares: $P_{def}(t)$ and $P_{def}(t^*)$; purple triangles: $P_{def}(t)$ and $P_{dyn}(t^*)$; blue stars: $P_{def}(t)/P_{def}(t^*)$ and $P_{dyn}(t^*)$

FIG. 5: Top right: 3D distribution of the 5% highest propensity molecules for $P_{dyn}(t^*)$ (water molecules are simple depicted as spheres, colored in red). Top left: Distribution of the molecules within the 5% of highest $P_{dyn}(0.1t^*)$. The water molecules are colored in yellow but, when additionally to belonging to the 5% of highest $P_{dyn}(0.1t^*)$ they also take part of the 5% highest propensity in $P_{dyn}(t^*)$, they are instead painted in green color. Bottom right: Set of molecules within the 5% highest $P_{def}(t^*)$ (yellow spheres, unless they also belong to the 5% highest propensity in $P_{dyn}(t^*)$ when they are painted in green). Bottom left: 5% highest $P_{def}(0.1t^*)$ set (yellow spheres, or green in the case they also take part of the 5% highest $P_{dyn}(t^*)$ set). In all cases, the rest of the molecules of the system are depicted in a very light gray color.

Finally, in Fig. 6 we present the curve $n(t)$, calculated as the fraction of molecules that are within the 5% of the molecules with the largest $P_{dyn}(t)$, and within the 5% of the molecules with largest $P_{def}(t)$ for the replica shown in Fig. 5. Thus, the final point ($t = t^*$) of this curve would be the number of green molecules divided by the total number of molecules in the bottom-right box of Fig. 5 (similarly we can get the value at $t = 0.1t^*$ from the bottom-left box). The function grows up to around $1/4$ since, as already indicated, there is a coincidence between regions of high dynamic propensity and high defect propensity but not all the molecules coincide (note that the probability to get such a coincidence on a random basis is almost completely null). We recall that the high defect propensity molecules predict the events triggering the DH clusters but not the whole object since certain

DH molecules are not defective on times previous to the relaxation event but get defective and move once a neighboring defective molecule has managed to move within the event triggering the DH cluster.

FIG. 6: Function $n(t)$ depicting the fraction of top 5% high defect propensity molecules that are also within the top 5% high dynamic propensity ones for the replica shown in Fig. 5.

Before concluding, it is worth noting that a recent work has shown that close to water's second critical point, several structural indicators nicely correlate with the system's density, even displaying almost identical distributions of fluctuations[52]. However, such strong equivalence between different structural descriptors stems for the fact that the system is close to the critical point[52] and does not hold when we are far from it[53]. The latter is the case of the present study since we are interested in a relaxation regime dominated by glassy behavior rather than by critical fluctuations. Additionally, to define a Defect Propensity we needed to accurately characterize water defects at the single-molecule level and, thus, the existence of a clear bimodal index distribution (two maxima separated by a deep minimum) was essential. This requisite has not been met by most previous indicators until V_4 [40] which fulfills it both for the supercooled regime and for the liquid above the melting point. Moreover, the distributions of the energy per molecule of the structured (T) and defective molecules (D) are well separated for V_4 at the inherent structures scheme (while they are less separated when, instead using energy minimizations, they are calculated at the real dynamics)[40]). This fact underlies the behavior of the time evolution of the value of V_4 illustrated in Fig. 1 which safely enabled us to perform the digitalization of the structural state $S(i, t) = 1$ used for the definition of

the Defect Propensity. The only other structural indicator whose distribution has displayed a rather similar bimodality is the local structure index (LSI) applied at the inherent dynamics[53], but the population of the unstructured state has been found to be dominant even in a great part of the supercooled regime and, hence, this indicator overestimates the population of defect molecules[53] and precludes a proper definition of Defect Propensity.

IV. CONCLUSIONS

Based on the recently introduced V_4 structural indicator for supercooled water, we have defined a defect propensity measure. At variance from a previously defined static propensity measure[17], the use of V_4 enables the defect propensity to appropriately discriminate the role of water structural defects since it employs potential energy minimizations to filter out the randomizing effect of the thermal fluctuations. We have shown that this defect propensity measure indeed correlates positively with the previously defined dynamic propensity of the water molecules. Moreover, by studying the time evolution of the defect propensity measure, we have shown that it is able to act as an excellent (very) early-time predictor of the later dynamical events responsible for the system's structural relaxation. In the same trend, the spatial distribution of high defect propensity molecules was found to nicely coincide with that defined by the cluster of the dynamical heterogeneities, a goal that has been out of reach for long times in spite of copious efforts[17].

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