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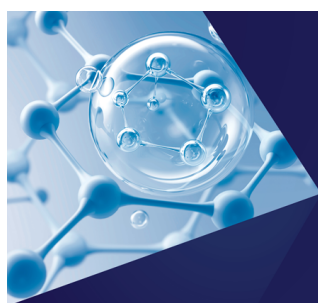
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ABSTRACT

The discovery of high-density liquid (HDL) and low-density liquid (LDL) water has been a major success of molecular simulations, yet extending this analysis to interfacial water is challenging due to conventional order parameters assuming local homogeneity. This limitation previously prevented resolving the composition of the surface layer of the liquid/vapor interface. Here, we apply a recently introduced topological order parameter [R. Foffi and F. Sciortino, J. Phys. Chem. B **127**, 378–386 (2022)] to analyze the composition of the water/vapor interface across a broad temperature range. Our results reveal that LDL-like water dominates the outermost region at all temperatures, while HDL-like water accumulates beneath it, presenting a clear layering roughly below the temperature of maximum density. This structured stratification, previously inaccessible, highlights the power of the topological order parameter in resolving interfacial molecular heterogeneity and provides new insights into the structural properties of water at interfaces.

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I. INTRODUCTION

Water is characterized by a surprisingly rich phase behavior, and several of its anomalies are often attributed to the existence of two distinct liquid forms:¹ high-density liquid (HDL) and low-density liquid (LDL). The concept of liquid polymorphism in supercooled water has been extensively studied, leading to the hypothesis of the existence of a liquid–liquid critical point where HDL and LDL coexist in equilibrium.² This framework is supported by many experimental^{3–8} and computational^{2,9–14} studies, to cite only a few.

At temperatures above the liquid–liquid critical point, fluctuations between HDL-like and LDL-like regions persist, with water existing as a mixture of these two structural motifs. A key open question in this field concerns the composition of water at its liquid/vapor interface, which is known to have markedly different structural and dynamical properties from the bulk.^{15–18} Malek and

colleagues investigated the distribution of HDL-like and LDL-like molecules in water droplets,^{19,20} finding that the interface exhibits structural signatures distinct from the bulk. Several simulations of liquid/vapor interfaces in slab configuration confirmed the presence of a compact layer at the interface, in the shape of a shoulder, or apophysis, in the global density profiles.^{19,21–26} Recently, we have carried out an investigation of flat liquid/vapor interfaces from the normal to the supercooled regime.²⁷ While the main aim of our previous work was to investigate the second inflection point in the surface tension of water, we also noticed the accumulation of HDL-like water in the interfacial region at temperatures lower than, approximately, the temperature of maximum density.

However, our previous analysis excluded the outermost molecular layer due to limitations of the order parameter (the fifth neighbor distance²⁸ criterion) used to distinguish HDL-like from LDL-like water, which assumes a locally homogeneous environment. A variety of order parameters have been proposed to distinguish

LDL-like and HDL-like water, many of which have been shown to be largely equivalent in their ability to distinguish the two motifs.²⁹ The vast majority of the available order parameters assume an implicit homogeneity in the local molecular environment. However, this assumption is problematic in interfacial settings, which are dominated by strong gradients.

Foffi and Sciortino have recently introduced a topological order parameter²⁹ that classifies water molecules based on the distance to their fourth hydrogen-bonded topological neighbor. Unlike local structural descriptors, it does not assume a homogeneous environment and remains well-defined at interfaces. A molecule in the outermost layer can still be classified as long as it has a fourth topological neighbor, making this order parameter particularly suited for interfacial studies.

In this work, we apply the topological order parameter to analyze the molecular-layer composition of the water/vapor interface over a broad temperature range. This approach enables us to overcome the previous limitations and resolve the composition of the surface layer, showing a previously inaccessible layering phenomenon, where LDL-like water dominates the outermost layer while HDL-like water accumulates just beneath it, forming two alternating layers.

II. METHODS

We performed molecular dynamics (MD) simulations using the GROMACS 2019.3 package³⁰ and the TIP4P/2005 water model,³¹ which accurately captures the phase behavior of water, including the presence of the liquid–liquid phase transition.^{32–34}

We started the simulations from the last equilibrium configuration taken from our previous work.²⁷ The original setup and equilibration protocol consisted in starting from a $50 \times 50 \times 50 \text{ \AA}^3$ cubic box with 4017 water molecules, initially equilibrated in the bulk phase, from which we generated the slab configuration liquid/vapor interface by expanding the box edge along the z -direction to 200 Å. The rigidity of the water molecules was ensured by using the SETTLE³⁵ algorithm. Periodic boundary conditions were applied along all directions. All simulations were conducted in the canonical ensemble at temperatures ranging from 198.15 to 348.15 K. The temperature control was maintained using the Nosé–Hoover thermostat^{36,37} with a time constant of 2 ps. Note that this is well within the safe operating range for this thermostat:³⁸ a test on the lowest temperature system with a time constant of 0.5 ps yielded a statistically indistinguishable mean and variance of the energy. The equations of motion were integrated using the leapfrog algorithm³⁹ with a time step of 1 fs. The long-range contributions to energy and forces were computed using the smooth variant of the Particle Mesh Ewald (PME) method for both electrostatic and dispersion interactions.^{40,41} For the PME algorithm, we used a real-space cutoff of 13 Å, a Fourier grid spacing of 1.5 Å, and a real-space relative contribution at the cutoff of 10^{-5} and 10^{-3} for electrostatics and dispersion, respectively. In our previous work, the systems were simulated at equilibrium for 90 ns, with the exception of the one at 198.15 K, which was simulated for 250 ns. For this investigation, we started from the final equilibrium configurations and added production runs of 80 ns, storing configurations to disk every 20 ps for subsequent analysis. The molecular structure of the liquid/vapor interface was analyzed using the Pytim

package,⁴² which is based on MDAnalysis^{43,44} and available online at <https://github.com/Marcello-Sega/Pytim>. We defined the interface using the Identification of Truly Interfacial Molecules (ITIM) algorithm,¹⁵ as implemented in Pytim. ITIM assigns molecules to the interfacial layer if any of their atoms are reachable from the vapor phase using a probe sphere of a certain radius, here chosen to be 1.5 Å. This approach accurately captures capillary wave fluctuations,^{45–47} allowing for a precise definition of the instantaneous interface. Once the interfacial layer is identified, we repeat the procedure for the remaining molecules iteratively, thereby assigning the successive molecular layers located at increasing depth into the liquid phase.

The fraction of HDL-like and LDL-like molecules in each layer was later determined using the topological order parameter ψ . The order parameter ψ is defined as the distance between the closest of two water molecules that are connected by four hydrogen bonds (i.e., the extremal molecules in a chain of five hydrogen bonded ones, as depicted in Fig. 1). To compute the topological order parameter, we use a graph-based approach. First, we construct the adjacency matrix M_{ij} of molecules i and j that are hydrogen-bonded, where $M_{ij} = 1$ if the i th and j th molecules are hydrogen-bonded, and zero otherwise. A hydrogen bond is identified using a geometric criterion requiring a (donor–acceptor) oxygen–oxygen distance $O_{\text{don}} \cdots O_{\text{acc}} < 3.5 \text{ \AA}$ and an (acceptor) oxygen–hydrogen distance $O_{\text{acc}} \cdots H < 2.5 \text{ \AA}$, roughly corresponding to the (in fact, temperature-dependent) first minima of the corresponding pair distribution functions. Several alternative approaches, including angular or energetic constraints, are possible, but they are all essentially qualitatively equivalent (the reader is referred to the excellent comparison of many criteria by Skinner and co-workers⁴⁸).

Starting from the adjacency matrix, we obtain the shortest paths (in terms of number of bonds) between all molecular pairs using Dijkstra's algorithm⁴⁹ and limiting the exploration of nodes in the connectivity graph to topological distances of at most four links. The molecular pairs with a topological distance of exactly four are extracted, and their Euclidean distances are computed using the minimum image convention. For each molecule, we determine its closest fourth topological neighbor by selecting the

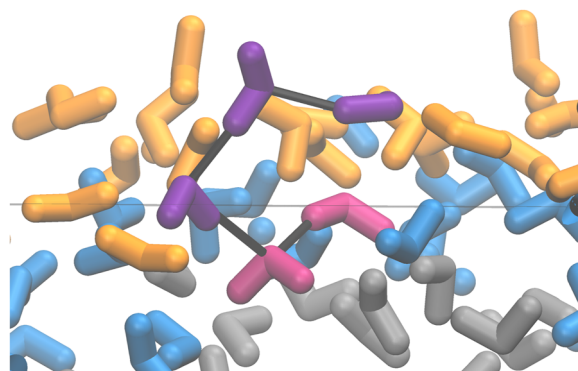


FIG. 1. Simulation snapshot (detail) of the interfacial region. Yellow and purple: first layer, blue and pink: second layer, and gray: other molecules. The purple and pink molecules belong to a chain of four hydrogen bonds (black lines), the first and last molecules of the chain being HDL-like.

pair with the smallest Euclidean distance, which represents the order parameter ψ .

III. RESULTS AND DISCUSSION

To investigate the structure of interfacial water, we define the density profiles across the slab of HDL-like and LDL-like molecules based on the topological order parameter ψ , following the approach introduced by Foffi and Sciortino. A molecule is classified as HDL-like if $\psi < 5$ Å and as LDL-like otherwise. The choice of this threshold is motivated by the apparent separatrix in the bimodal distributions of ψ reported in Refs. 29 and 50. The two peaks corresponding to HDL-like and LDL-like environments are centered at around 3.5 and 6.5 Å, respectively. The threshold at 5 Å represents a natural separation between these two states, effectively distinguishing the two molecular environments.

Figure 2 shows the probability density distribution of ψ for a selected set of temperatures and for the first four surface layers. Note that while the location of the characteristic peak of HDL-like water at around $\psi = 3$ Å shows no dependence on temperature or layer, the LDL-like water peak location at larger values of ψ (between 5.5 and 7 Å) does indeed have a mild temperature dependence and noticeable shift of ~ 0.5 Å when moving from the first to the subsequent layers. The distributions in layers 2–4 differ only marginally and show that water becomes essentially homogeneous at the structural level already from the second or third layer. The fact that the peak at larger values of ψ has a systematic shift underlines a structural difference in the surface layer only for molecules that are LDL-like.

Figure 3 reports the number density profiles of HDL-like (top panel) and LDL-like (bottom panel) molecules across the liquid/vapor interface. In the bulk region, the relative densities follow the expected temperature trend that sees the concentration of LDL-like water in the bulk increasing upon cooling, especially below the temperature of maximum density. Closer to the interface, we observe a more complex behavior. The HDL-like concentration

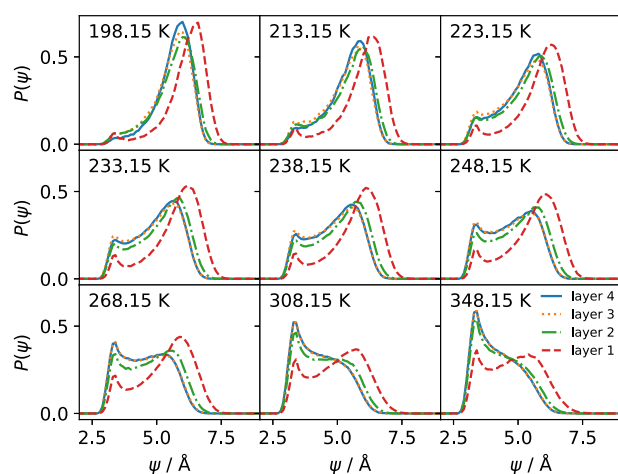


FIG. 2. Probability density distributions of the topological order parameter ψ in the first four layers at selected temperatures.

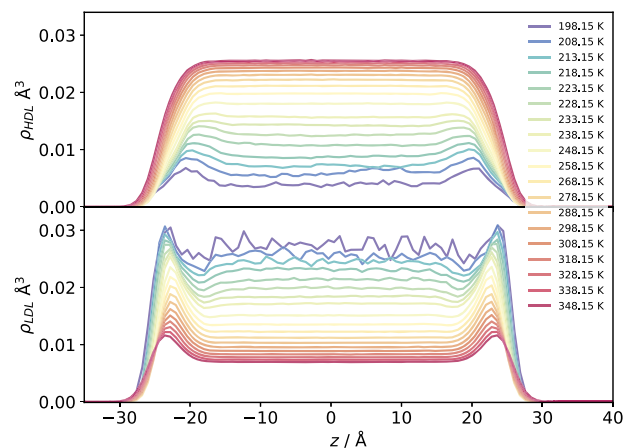


FIG. 3. Number density profiles of (top) HDL-like and (bottom) LDL-like water molecules across the slab.

increases in a subsurface region before decaying toward the interface. This behavior is identical to what we observed in our previous work²⁷ using the fifth neighbor distance as an order parameter. This is not surprising, as the order parameters used to distinguish LDL-like from HDL-like water are quite robust.²⁹ Using the fifth neighbor distance criterion, however, the concentration and fraction of HDL-like water molecules next to the surface is necessarily a lower bound (and, conversely, the LDL-like is an upper bound). With the topological order parameter, instead, we are, for the first time, able to probe in a meaningful way the composition at the boundary of the liquid phase.

Going from the bulk toward the surface, the accumulation of HDL-like molecules observed at low temperatures is followed by a layer where the concentration of LDL-like molecules increases. However, while the peak in the number density profile of HDL-like molecules disappears at high temperatures, this is not true for the concentration of LDL-like molecules, which are always preferentially found at the interface with respect to the bulk.

The locus of the maximum in the LDL density profile in the bottom panel of Fig. 3 exhibits a narrowing that has a minimum around 280 K, confirming what we observed in our previous work,²⁷ which coincides with the density maximum of the TIP4P/2005 model and is far away from the temperature range of several anomalies associated with the Widom lines.^{1,51} From the position of the peaks, one can see that LDL-/HDL-like water layering is taking place at low temperatures. This can be better seen if one overlays the two profiles, normalizing the values to the respective bulk one, as shown in Fig. 4. This normalization highlights the relative variations in concentration and illustrates the emergence of two layers of HDL-like and LDL-like water near the interface.

In the outermost region, where the profiles are dropping to zero, the LDL-like profile always follows or is larger than the total one, meaning that LDL-molecules are always present at the surface in larger concentrations than in the bulk for all systems. A local minimum emerges in the LDL-like profile, just below the apophysis. The normalized HDL-like number density profile, instead, is

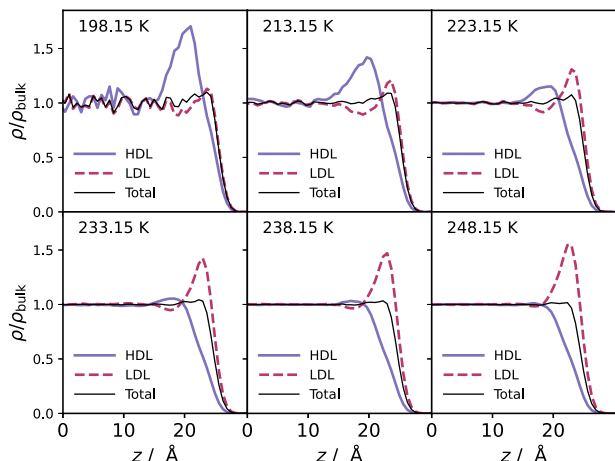


FIG. 4. Number density profiles of HDL-like and LDL-like water molecules (across half of the slab, for clarity) normalized with respect to their bulk values (selected temperatures).

always smaller than the total one in the outer interfacial region, showing a systematic depletion of HDL-like molecules. Below the temperature of maximum density, however, a concentration maximum starts developing at the location of the local minimum of the LDL-like one, suggesting that this is happening in a subsurface layer. This maximum keeps growing upon further lowering of the temperature, eventually developing a large (relative) accumulation of HDL-like water near the surface. The normalized number density profiles clearly show the appearance of alternating layers of increased/decreased concentration (with respect to the bulk value) of HDL-like and LDL-like water molecules. These results highlight the unexpected presence of areas for preferential accumulation of the two structural motifs near the interface.

At low temperatures, the most striking feature is an enhanced layering, where LDL-like water dominates the outermost interfacial layer, while HDL-like water accumulates just beneath it. In correspondence of the LDL-like accumulation, one can notice a small shoulder or apophysis in the total profile that lasts up to temperatures close to the density maximum one.^{25,27} At higher temperatures, both the apophysis and the HDL-like concentration maximum disappear and only LDL-like surface enrichment is observed, in concomitance with the surface depletion of HDL-like molecules.

This behavior is consistent with the previously observed structuring of water^{19,20,25,27} at interfaces but is now resolved in terms of its local hydrogen-bond network topology. At low temperatures, the presence of two alternating layers, one with HDL-like water excess and one with LDL-like water excess, suggests a collective reorganization of the hydrogen-bond network near the interface, possibly linked to the mechanisms underlying water's liquid-liquid transition and the availability of free volume at the liquid/vapor interface.

The persistence of LDL-like water at the outermost molecular layer across all temperatures is particularly noteworthy. This result implies that water at the interface tends to favor the LDL-like local structure even at high temperatures, whereas the enhancement of

HDL-like water at the subsurface region is most pronounced at lower temperatures.

Previously, the topological order parameter has primarily been applied in bulk water studies, raising the question of whether its application to interfacial systems might introduce systematic biases. To check this, we analyzed a control system in which we artificially removed molecules that are farther than 15 Å from the middle of the slab, leaving a 30 Å thick artificially flat interface. We processed this artificial system identically to the initial one. This approach isolates any potential artifacts arising from the order parameter itself, allowing us to determine whether the observed layering is a genuine feature of interfacial water or a more general consequence of structural correlations in bulk liquid water.

Figure 5 presents the HDL-like and LDL-like number density profiles obtained in the artificially truncated bulk region. Maybe unexpectedly, the profiles are not flat. Unlike at the real interface, where LDL-like molecules dominate the outermost layer and HDL-like molecules accumulate in a subsurface region, at the artificially imposed boundary, there is always a systematic accumulation of HDL-like molecules and a depletion of LDL-like ones.

The behavior observed at the artificial interface can be understood by considering the nature of the topological order parameter ψ . Consider two LDL-like molecules at the artificial boundary close to each other and initially at the (shortest) topological distance of three or two links. If one of these links is severed by the cut, but the pair is still connected via another path, this must necessarily have an equal or larger topological distance. Therefore, the two molecules have a chance to be promoted to fourth-bonded neighbors and tagged as HDL-like. The opposite can also happen when a path of four links between two HDL-like molecules is severed. If this is the only path of four links connecting them, they will be tagged as LDL-like. The balance between these two possibilities will depend on the statistics of the number of paths and the state point. The result could be either more or less HDL-like molecules at the artificial cut, depending on the relative number of paths of different lengths, but the balance favors HDL-like molecules in practice.

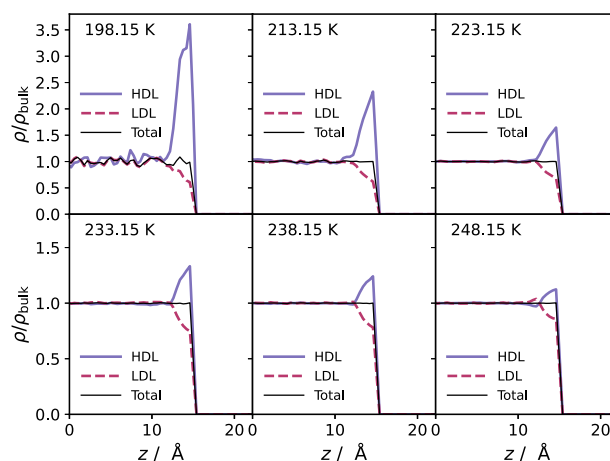


FIG. 5. Number density profiles of HDL-like and LDL-like water molecules in an artificially truncated bulk region, normalized with respect to their bulk values (selected temperatures).

This explanation provides a strong argument reinforcing the validity of our results at the real water/vapor interface. If the layering observed in Figs. 3 and 4 were merely an artifact of the order parameter, we would expect HDL-like molecules to accumulate at the real surface as well, following the same bias seen in the truncated bulk slab. Instead, we observe the opposite trend: LDL-like molecules accumulate at the real interface, while HDL-like molecules preferentially occupy subsurface layers. This result suggests that the alternating HDL-like and LDL-like layering at the interface is a genuine physical feature rather than a spurious effect of the order parameter.

Furthermore, the presence of alternating layers in the real interfacial system but not in the control system indicates that the structuring of water near the interface is not merely a consequence of cutting the system but rather arises from molecular-scale interactions specific to the liquid–vapor boundary. These results confirm that the topological order parameter is a robust tool for analyzing the interfacial water composition and reinforces our previous conclusions.

One further comment is in order. The pronounced peak in the low temperature HDL-like profile at the artificial interface, visible in Fig. 5, is partially a consequence of the normalization to bulk values. As shown in the non-normalized plots in the [supplementary material](#), the excess of HDL-like molecules is compensated by a corresponding depletion of LDL-like ones. Since the artificial conversion of LDL-like to HDL-like molecules (via the path truncation mechanism discussed above) is proportional to the local density of LDL-like molecules, the resulting boundary effect is more pronounced at low temperatures, where LDL-like water dominates in the bulk.

It is also important to note that the HDL-like peak in the artificial system appears exactly at the interface, coinciding with the LDL-like depletion. In the natural interface, by contrast, the HDL-like peak consistently emerges one layer behind the surface, following an LDL-like maximum. This shift is also visible in the layer-by-layer profiles and confirms that the accumulation of HDL-like water at the artificial boundary is a direct consequence of the truncation.

Our analysis of the accumulation and depletion layers has been, so far, necessarily qualitative because the presence of thermal capillary wave fluctuations complicates the interpretation of the number density profiles. In profiles such as those shown in Figs. 3 and 4, molecules at the same elevation relative to the mean interface position may belong to different instantaneous molecular layers due to surface capillary waves. This issue leads to a smearing effect, where properties of neighboring layers mix, making it challenging to resolve finer structural details at the molecular scale. To overcome this effect, we analyzed the fraction x_{HDL} of HDL-like molecules in each layer as identified by the ITIM algorithm. This approach allowed us to investigate how HDL-like water is distributed on a per-layer basis without interference from capillary fluctuations.

Figure 6 shows the fraction of HDL-like molecules, x_{HDL} , resolved on a molecular layer basis. At low temperatures, we observe that HDL-like molecules accumulate predominantly in the second and third layers rather than in the outermost one. At the lowest temperature of 198.15 K, the fraction of HDL-like molecules in the third layer is about 30% higher than in the bulk.

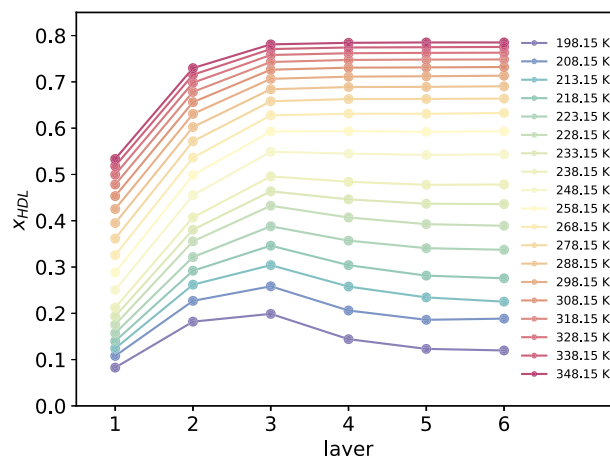


FIG. 6. Fraction of HDL-like molecules as a function of layer index at different temperatures. The layers are labeled starting from the interface (layer 1).

Above 248.15 K, the accumulation of HDL-like water disappears and the fraction of HDL-like molecules across all layers flattens out.

Interestingly, the first layer is consistently characterized by the lowest fraction of HDL-like molecules across all temperatures. This confirms that LDL-like water is always dominant in the outermost molecular layer, reinforcing our previous result that the water/vapor interface preferentially stabilizes LDL-like structural motifs. In contrast, at low temperatures, HDL-like water accumulates just beneath the interface, creating a structured interfacial layering.

IV. CONCLUSION

We have applied the topological order parameter introduced by Foffi and Sciortino²⁹ to analyze the molecular-layer composition of the water/vapor interface in terms of the concentration of local LDL-like and HDL-like molecules, revealing a stratification of the local structural motifs. Our analysis shows that the outermost interfacial layer is consistently dominated by LDL-like water. In contrast, HDL-like water is generally depleted from the surface at high temperatures. However, it accumulates mainly in the second and third subsurface layers when the temperature drops below that of maximum density, with the layering becoming more pronounced upon cooling. By repeating our analysis on an artificially generated interface, we confirmed that the layering effect is due to a genuine structural property of interfacial water rather than an artifact of the order parameter.

Our results demonstrate the applicability of the topological order parameter to interfacial systems, extending its use beyond bulk water, and provide further insights into the structural heterogeneity of interfacial water. We observed a preference for LDL-like local environments in the outermost molecular layer of the water/vapor interface, something that was not possible with conventional order parameters. We confirm the previously observed accumulation of HDL-like water molecules upon lowering the temperature (a trend opposite to the bulk), locating it in the second and third molecular layers. In general, the presence of alternating

layers of HDL-like and LDL-like water suggests a collective reorganization of the hydrogen-bond network near the surface, which may be related to the mechanisms underlying the liquid–liquid transition in supercooled water. Further investigation avenues include understanding how this behavior depends on external parameters, including mechanical tension or electric field, or how it manifests at different interfaces, including those with hydrophobic liquids or in confinement. Of particular importance are the dynamical properties of interfacial water. Single particle dynamics via calculation of the diffusion coefficient within a layer, involving tracking when molecules enter and leave the layer,¹⁸ and collective layerwise dynamics in terms of hydrodynamic modes⁵² or effective layer viscosity⁵³ are possible means to explore the influence of HDL-like and LDL-like molecules on the dynamical properties of water.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for HDL-like, LDL-like, and total number density profiles at selected temperatures, not normalized, for the natural and artificially truncated systems.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Pal Jedlovsky: Conceptualization (equal); Investigation (equal); Writing – original draft (equal). **Christoph Dellago:** Conceptualization (equal); Investigation (equal); Writing – original draft (equal). **Marcello Sega:** Conceptualization (lead); Investigation (equal); Writing – original draft (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- ¹P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley, H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, “Water: A tale of two liquids,” *Chem. Rev.* **116**, 7463–7500 (2016).
- ²P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, “Phase behaviour of metastable water,” *Nature* **360**, 324–328 (1992).
- ³J. A. Sellberg, C. Huang, T. A. McQueen, N. D. Loh, H. Laksmono, D. Schlesinger, R. G. Sierra, D. Nordlund, C. Y. Hampton, D. Starodub *et al.*, “Ultrafast x-ray probing of water structure below the homogeneous ice nucleation temperature,” *Nature* **510**, 381–384 (2014).
- ⁴A. Nilsson and L. G. M. Pettersson, “The structural origin of anomalous properties of liquid water,” *Nat. Commun.* **6**, 8998 (2015).
- ⁵A. Dehaoui, B. Issenmann, and F. Caupin, “Viscosity of deeply supercooled water and its coupling to molecular diffusion,” *Proc. Natl. Acad. Sci. U. S. A.* **112**, 12020–12025 (2015).
- ⁶K. H. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. A. Sellberg, J. H. Lee, S. Kim, J. Park *et al.*, “Maxima in the thermodynamic response and correlation functions of deeply supercooled water,” *Science* **358**, 1589–1593 (2017).
- ⁷K. H. Kim, K. Amann-Winkel, N. Giovambattista, A. Späh, F. Perakis, H. Pathak, M. L. Parada, C. Yang, D. Mariedahl, T. Eklund *et al.*, “Experimental observation of the liquid–liquid transition in bulk supercooled water under pressure,” *Science* **370**, 978–982 (2020).
- ⁸K. Amann-Winkel, K. H. Kim, N. Giovambattista, M. Ladd-Parada, A. Späh, F. Perakis, H. Pathak, C. Yang, T. Eklund, T. J. Lane *et al.*, “Liquid–liquid phase separation in supercooled water from ultrafast heating of low-density amorphous ice,” *Nat. Commun.* **14**, 442 (2023).
- ⁹O. Mishima and H. E. Stanley, “The relationship between liquid, supercooled and glassy water,” *Nature* **396**, 329–335 (1998).
- ¹⁰P. Jedlovsky and R. Vallaury, “Liquid–vapor and liquid–liquid phase equilibria of the Brodholt–Sampoli–Vallaury polarizable water model,” *J. Chem. Phys.* **122**, 081101 (2005).
- ¹¹J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, “Metastable liquid–liquid transition in a molecular model of water,” *Nature* **510**, 385–388 (2014).
- ¹²J. C. Palmer, P. H. Poole, F. Sciortino, and P. G. Debenedetti, “Advances in computational studies of the liquid–liquid transition in water and water-like models,” *Chem. Rev.* **118**, 9129–9151 (2018).
- ¹³R. S. Singh, J. C. Palmer, A. Z. Panagiotopoulos, and P. G. Debenedetti, “Thermodynamic analysis of the stability of planar interfaces between coexisting phases and its application to supercooled water,” *J. Chem. Phys.* **150**, 224503 (2019).
- ¹⁴F. Sciortino, Y. Zhai, S. Bore, and F. Paesani, “Constraints on the location of the liquid–liquid critical point in water,” *Nat. Phys.* **21**, 480–485 (2025).
- ¹⁵L. B. Pártay, G. Hantal, P. Jedlovsky, Á. Vincze, and G. Horvai, “A new method for determining the interfacial molecules and characterizing the surface roughness in computer simulations. Application to the liquid–vapor interface of water,” *J. Comput. Chem.* **29**, 945–956 (2008).
- ¹⁶M. Sega, G. Horvai, and P. Jedlovsky, “Microscopic origin of the surface tension anomaly of water,” *Langmuir* **30**, 2969–2972 (2014).
- ¹⁷M. Bonn, Y. Nagata, and E. H. G. Backus, “Molecular structure and dynamics of water at the water–air interface studied with surface-specific vibrational spectroscopy,” *Angew. Chem., Int. Ed.* **54**, 5560–5576 (2015).
- ¹⁸B. Fábán, M. Sega, G. Horvai, and P. Jedlovsky, “Single particle dynamics at the intrinsic surface of various apolar, aprotic dipolar, and hydrogen bonding liquids as seen from computer simulations,” *J. Phys. Chem. B* **121**, 5582–5594 (2017).
- ¹⁹S. M. A. Malek, P. H. Poole, and I. Saika-Voivod, “Thermodynamic and structural anomalies of water nanodroplets,” *Nat. Commun.* **9**, 2402 (2018).
- ²⁰S. M. A. Malek, P. H. Poole, and I. Saika-Voivod, “Surface tension of supercooled water nanodroplets from computer simulations,” *J. Chem. Phys.* **150**, 234507 (2019).
- ²¹H. Matsubara, T. Koishi, T. Ebisuzaki, and K. Yasuoka, “Extended study of molecular dynamics simulation of homogeneous vapor–liquid nucleation of water,” *J. Chem. Phys.* **127**, 214507 (2007).
- ²²K. Abe, T. Sumi, and K. Koga, “Temperature dependence of local solubility of hydrophobic molecules in the liquid–vapor interface of water,” *J. Chem. Phys.* **141**, 18C516 (2014).
- ²³A. Haji-Akbari, R. S. DeFever, S. Sarupria, and P. G. Debenedetti, “Suppression of sub-surface freezing in free-standing thin films of a coarse-grained model of water,” *Phys. Chem. Chem. Phys.* **16**, 25916–25927 (2014).

- ²⁴A. Haji-Akbari and P. G. Debenedetti, "Computational investigation of surface freezing in a molecular model of water," *Proc. Natl. Acad. Sci. U. S. A.* **114**, 3316–3321 (2017).
- ²⁵X. Wang, K. Binder, C. Chen, T. Koop, U. Pöschl, H. Su, and Y. Cheng, "Second inflection point of water surface tension in the deeply supercooled regime revealed by entropy anomaly and surface structure using molecular dynamics simulations," *Phys. Chem. Chem. Phys.* **21**, 3360–3369 (2019).
- ²⁶V. Vinš, J. Hykl, J. Hrubý, A. Blahut, D. Celný, M. Čenský, and O. Prokopová, "Possible anomaly in the surface tension of supercooled water: New experiments at extreme supercooling down to -31.4°C ," *J. Phys. Chem. Lett.* **11**, 4443–4447 (2020).
- ²⁷A. Gorfer, C. Dellago, and M. Sega, "High-density liquid (HDL) adsorption at the supercooled water/vapor interface and its possible relation to the second surface tension inflection point," *J. Chem. Phys.* **158**, 054503 (2023).
- ²⁸M. J. Cuthbertson and P. H. Poole, "Mixturelike behavior near a liquid-liquid phase transition in simulations of supercooled water," *Phys. Rev. Lett.* **106**, 115706 (2011).
- ²⁹R. Foffi and F. Sciortino, "Correlated fluctuations of structural indicators close to the liquid-liquid transition in supercooled water," *J. Phys. Chem. B* **127**, 378–386 (2022).
- ³⁰M. J. Abraham, T. Murtola, R. Schulz, S. Páll, J. C. Smith, B. Hess, and E. Lindahl, "Gromacs: High performance molecular simulations through multi-level parallelism from laptops to supercomputers," *SoftwareX* **1–2**, 19–25 (2015).
- ³¹J. L. F. Abascal and C. Vega, "A general purpose model for the condensed phases of water: TIP4P/2005," *J. Chem. Phys.* **123**, 234505 (2005).
- ³²J. Russo and H. Tanaka, "Understanding water's anomalies with locally favoured structures," *Nat. Commun.* **5**, 3556 (2014); [arXiv:1308.4231](https://arxiv.org/abs/1308.4231).
- ³³J. L. F. Abascal and C. Vega, "Widom line and the liquid-liquid critical point for the TIP4P/2005 water model," *J. Chem. Phys.* **133**, 234502 (2010).
- ³⁴P. G. Debenedetti, F. Sciortino, and G. H. Zerze, "Second critical point in two realistic models of water," *Science* **369**, 289–292 (2020).
- ³⁵S. Miyamoto and P. A. Kollman, "Settle: An analytical version of the SHAKE and RATTLE algorithm for rigid water models," *J. Comput. Chem.* **13**, 952–962 (1992).
- ³⁶S. Nosé, "A unified formulation of the constant temperature molecular dynamics methods," *J. Chem. Phys.* **81**, 511–519 (1984).
- ³⁷W. G. Hoover, "Canonical dynamics: Equilibrium phase-space distributions," *Phys. Rev. A* **31**, 1695–1697 (1985).
- ³⁸Q. Ke, X. Gong, S. Liao, C. Duan, and L. Li, "Effects of thermostats/barostats on physical properties of liquids by molecular dynamics simulations," *J. Mol. Liq.* **365**, 120116 (2022).
- ³⁹M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, 2017).
- ⁴⁰U. Essmann, L. Perera, M. L. Berkowitz, T. Darden, H. Lee, and L. G. Pedersen, "A smooth particle mesh Ewald method," *J. Chem. Phys.* **103**, 8577–8593 (1995).
- ⁴¹M. Sega and C. Dellago, "Long-range dispersion effects on the water/vapor interface simulated using the most common models," *J. Phys. Chem. B* **121**, 3798–3803 (2017).
- ⁴²M. Sega, G. Hantal, B. Fábrián, and P. Jedlovský, "Pytim: A python package for the interfacial analysis of molecular simulations," *J. Comput. Chem.* **39**, 2118–2125 (2018).
- ⁴³N. Michaud-Agrawal, E. J. Denning, T. B. Woolf, and O. Beckstein, "MDAnalysis: A toolkit for the analysis of molecular dynamics simulations," *J. Comput. Chem.* **32**, 2319–2327 (2011).
- ⁴⁴R. J. Gowers, M. Linke, J. Barnoud, T. J. E. Reddy, M. N. Melo, S. L. Seyler, J. Domański, D. L. Dotson, S. Buchoux, I. M. Kenney, and O. Beckstein, "MDAnalysis: A python package for the rapid analysis of molecular dynamics simulations," in *Proceedings of the 15th Python in Science Conference* (SciPy, 2016), pp. 98–105.
- ⁴⁵F. P. Buff, R. A. Lovett, and F. H. Stillinger, Jr., "Interfacial density profile for fluids in the critical region," *Phys. Rev. Lett.* **15**, 621 (1965).
- ⁴⁶F. H. Stillinger, "Capillary waves and the inherent density profile for the liquid-vapor interface," *J. Chem. Phys.* **76**, 1087–1091 (1982).
- ⁴⁷E. Chacón and P. Tarazona, "Intrinsic profiles beyond the capillary wave theory: A Monte Carlo study," *Phys. Rev. Lett.* **91**, 166103 (2003).
- ⁴⁸R. Kumar, J. R. Schmidt, and J. L. Skinner, "Hydrogen bonding definitions and dynamics in liquid water," *J. Chem. Phys.* **126**, 204107 (2007).
- ⁴⁹E. W. Dijkstra, "A note on two problems in connexion with graphs," *Numer. Math.* **1**, 269–271 (1959).
- ⁵⁰R. Foffi and F. Sciortino, "Identification of local structures in water from supercooled to ambient conditions," *J. Chem. Phys.* **160**, 094504 (2024).
- ⁵¹F. Martelli, "Unravelling the contribution of local structures to the anomalies of water: The synergistic action of several factors," *J. Chem. Phys.* **150**, 094506 (2019).
- ⁵²P. Magaretti, U. Bafle, R. Vallauri, P. Jedlovský, and M. Sega, "Surface viscosity in simple liquids," *J. Chem. Phys.* **158**, 114705 (2023).
- ⁵³P. Jedlovský and M. Sega, "Surface viscosity of liquid interfaces from Green-Kubo relations," *J. Chem. Phys.* **160**, 201101 (2024).