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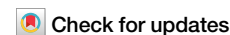
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Machine learning evaluation of structural descriptors for supercooled water



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The anomalous behavior of liquid water is widely associated with a liquid-liquid phase transition between high- and low-density states in the supercooled regime. At the microscopic level, tetrahedral hydrogen-bond networks govern these properties, motivating structural descriptors that characterize local molecular environments. These structural descriptors quantify features such as tetrahedral order, local density, and the separation between the first and second coordination shells; however, they have largely been proposed independently, with limited systematic comparison. Here we evaluate 16 previously proposed descriptors using a neural-network-based temperature classification framework, enabling an objective assessment of their ability to distinguish temperature-dependent structural changes in supercooled water. We further apply an explainable artificial intelligence method that identifies the structural features responsible for the model predictions. This approach reveals how different descriptors encode local structural information and establishes a data-driven framework for benchmarking structural descriptors in liquid water.

Liquid water exhibits significant anomalies, including a density maximum near 4 °C, in response to variations in pressure and temperature; these anomalies arise from rearrangements in the local molecular structure associated with the H-bond network^{1,2}. When liquid water enters the supercooled regime, its anomalous properties become extensively noticeable^{3,4}. In particular, in the supercooled regime, both isothermal compressibility and specific heat sharply increase with cooling, indicative of divergent behavior^{5,6}.

This phenomenon is commonly interpreted within the framework of the liquid-liquid phase transition (LLPT) hypothesis, which proposes that water exists in two liquid states: low-density liquid (LDL) and a high-density liquid (HDL)^{7–10}. Transformations between low- and high-density amorphous ices are further considered to represent the arrested form of the liquid-liquid transition occurring under deeper supercooled conditions, terminating at a liquid-liquid critical point (LLCP)^{11–14}. The LLPT hypothesis has become an important framework that provides a consistent and comprehensive explanation for a wide range of anomalous behaviors observed in supercooled water.

The two-state model describing the competition between HDL and LDL structures is extensively used as an effective framework for elucidating the structural transformations in supercooled water based on molecular dynamics (MD) simulations^{15–33}. To quantitatively examine this framework, scalar structural descriptors have been diversely introduced to characterize the local environment of individual water molecules^{34–38}.

Representative examples include q_{tet} , which quantifies the tetrahedral ordering among the four nearest neighbors of a water molecule^{39–41}, and ζ , which measures the degree of order within H-bond networks⁴². These descriptors enable clear differentiation between the highly ordered open structure associated with LDL and the compact, densely packed structure characteristic of HDL. Furthermore, Local Structure Index (LSI) serves as another structural descriptor that distinguishes HDL-like and LDL-like environments based on local structural fluctuations^{43,44}. Recently, Node Total Communicability (NTC) has been proposed as a graph-theoretical structural descriptor for supercooled water that characterizes not only local arrangements within the first coordination shell, but also medium- and long-range structural orders⁴⁵. Furthermore, Ψ is a descriptor that exploits information on the connectivity of H-bond networks^{46,47}.

Notably, Foffi et al. investigated the correlation between critical density fluctuations near the LLCP in supercooled water and various structural descriptors using MD simulations⁴⁶. Their results reveal that most structural descriptors exhibit strong correlations with density, indicating a close relationship between critical fluctuations and the distinct structural characteristics of H-bond networks in HDL and LDL.

In contrast, studies have demonstrated the occurrence of a “structural crossover,” away from the LLCP under ambient pressure (~1 bar), in which the ratio of HDL-like to LDL-like structures continuously varies across the Widom line, that is, the locus of maxima in thermodynamic response functions^{48,49}. Although this crossover does not correspond to a distinct phase transition, it represents the conditions under which anomalies in

density, specific heat, and related properties become most evident, providing key insight into the structural origins of supercooled water. Accordingly, quantitative evaluation of the structural crossover under ambient pressure is essential for elucidating the universal structural anomalies of liquid water. Therefore, examining the performances of existing structural descriptors under ambient pressure is crucial.

However, because these descriptors qualitatively differ in their definitions and quantitatively vary in their dimensions and scales, a direct comparison is not straightforward. Thus, a consistent framework for estimating and comparing the performances of these descriptors is required, along with assessment methods capable of reliably describing structural variations under supercooled conditions.

This study evaluates the performance of 16 available structural descriptors in distinguishing HDL-like and LDL-like structures within the structural crossover region defined by the Widom line using machine learning. At first, MD simulations of TIP4P/2005 water were performed under isochoric (1 g/cm³) and isobaric (1 bar) conditions, with temperatures ranging from 200 to 300 K, adequately away from the LLC. Note that the temperature, pressure, and mass density at the LLC of TIP4P/2005 water were estimated as (T_C , P_C , ρ_C) $\approx$ (182 K, 170 MPa, 1.017 g/cm³), respectively^{23,24}. Additionally, the crossover between HDL-like and LDL-like states occurs near the Widom line at approximately 230 K under 1 bar^{23,24}. Details of the MD simulations are provided in the “Methods” section, and static and dynamic properties are shown in Supplementary Figs. 1 and 2.

Machine learning using structural descriptors has proven to be a powerful approach for classifying local structures in liquid water, glasses, and colloids^{50–54}. In this study, we propose an alternative machine-learning framework in which structural data obtained from MD simulations of supercooled water were used to construct a neural network model that takes per-molecule structural descriptor values as inputs and temperature as the output. The objective of this study is not merely to identify HDL-like and LDL-like structural states, but rather to quantitatively evaluate, within a unified framework, the extent to which different structural descriptors are sensitive to temperature-dependent structural changes. From this perspective, temperature classification is used as a controlled proxy task for measuring the sensitivity of structural descriptors to such changes. In other words, we assess the extent to which each descriptor captures intrinsic structural information by examining whether it can distinguish structures sampled at different temperatures. Note that we recently employed graph neural networks to perform a similar machine learning-based temperature classification using structural snapshots of glass-forming liquids⁵⁵.

Figure 1 schematically depicts the fully connected neural network (FCNN) model employed in this study. This FCNN model quantitatively assesses the ability of each structural descriptor to distinguish between two different temperatures using the area under the Receiver Operating Characteristic (ROC) curve (ROC-AUC, hereinafter referred to as AUC) as the

evaluation metric. A ROC curve is a graphical tool used to evaluate classification models in machine learning. The AUC quantifies the overall classification performance. An AUC value close to 1 indicates that the model can accurately distinguish between the two classes, whereas an AUC value close to 0.5 corresponds to random classification. Moreover, to enhance the interpretability of neural networks, which are inherently black-box predictive models, we employed explainable artificial intelligence (XAI)^{56–58}. Specifically, we applied Local Interpretable Model-Agnostic Explanations (LIME)⁵⁹, a post-hoc interpretability method, to examine whether the decision-making of the model is consistent with physically meaningful structural changes. Therefore, the advance of this study lies not only in reaffirming the importance of each structural descriptor in distinguishing between HDL-like and LDL-like structures, but also in quantitatively comparing their respective contributions using machine learning and in uniformly evaluating the performance of structural descriptors with different dimensions and scales.

Results and discussion

Correlation coefficients among structural descriptors

Structural descriptors quantify the degree of local order around each molecule; for liquid water, they are often defined in terms of tetrahedrality, local density, interaction energy, and topological properties of H-bond networks. Herein, 16 available structural descriptors were calculated from MD simulations. The definition of each descriptor is provided in the “Methods” section, and corresponding temperature-dependent distributions are shown in Supplementary Figs. 3 and 4.

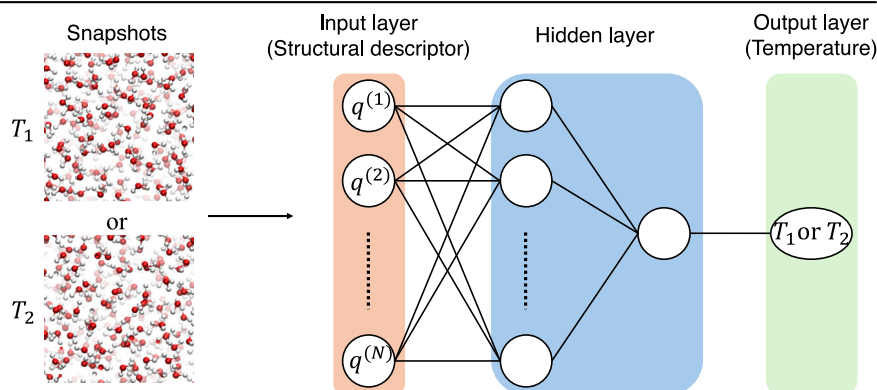
Initially, correlation coefficients were computed to examine the similarities among the structural descriptors. In this study, the correlation coefficient was evaluated in the absolute form of the Pearson product-moment correlation coefficient, denoted as

$$|r| = \left| \frac{\sum_{i=1}^N (X_i - \bar{X})(Y_i - \bar{Y})}{\sqrt{\sum_{i=1}^N (X_i - \bar{X})^2 \sum_{i=1}^N (Y_i - \bar{Y})^2}} \right|, \quad (1)$$

where X_i and Y_i represent the values assigned to the molecule i by the two structural descriptors X and Y , respectively. Note that $\bar{X}$ and $\bar{Y}$ represent the corresponding mean values.

For each simulated temperature in the 200–300 K range, $|r|$ was calculated and subsequently averaged over the 1000 or 500 configurations sampled, and the resulting values obtained were then averaged over all temperatures. Figure 2 depicts $|r|$ among the structural descriptors for isochoric (a) and isobaric (b) conditions. Structural descriptors with large $|r|$ values ($|r| \geq 0.7$) under isochoric conditions were classified into four main groups.

Fig. 1 | Fully connected neural network model for temperature classification. Schematic illustration of the neural network architecture used in this study. Structural descriptors ($q^{(1)}, q^{(2)}, \dots, q^{(N)}$), assigned to individual molecules and computed from MD simulations of the two temperatures, T_1 and T_2 , are provided as the input variables. The number of input nodes corresponds to the number of molecules in the MD snapshots ($N = 1000$). Therefore, the input is a 1000×1 matrix. The network consists of a single hidden layer with the same number of nodes as the input layer, followed by a hidden layer with a single node, and employs a sigmoid function. The output layer produced a binary value (0 or 1, corresponding to T_1 or T_2 , respectively), enabling the model to learn temperature-dependent structural differences. Note that the node representing the bias term is omitted from the diagram.



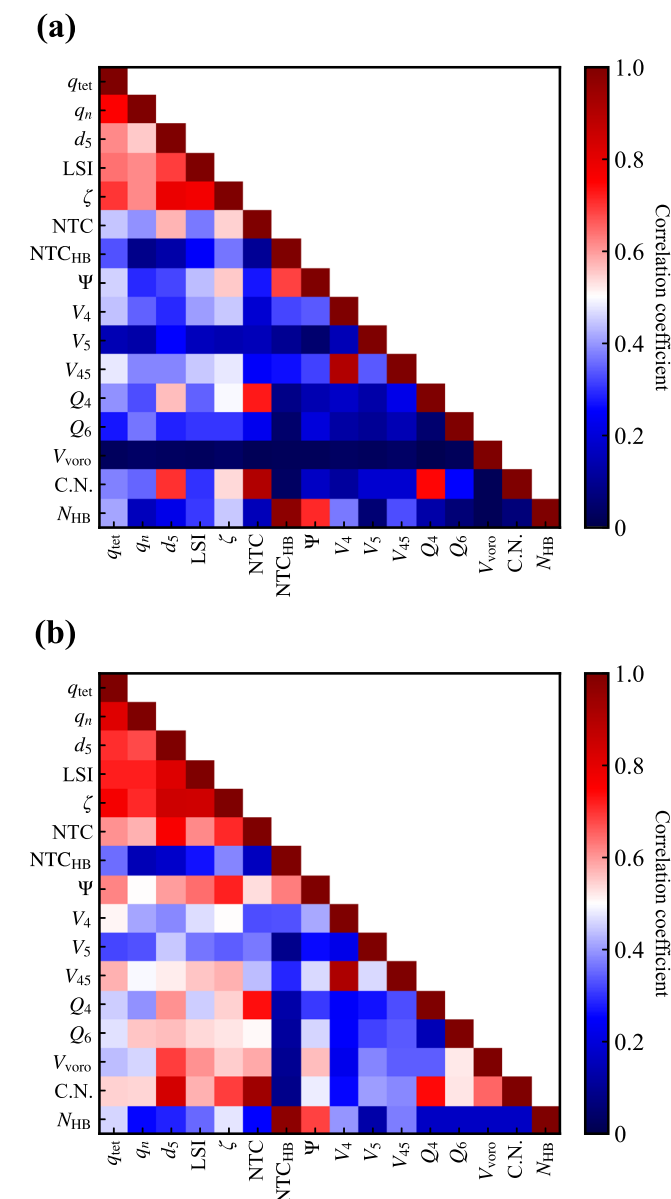


Fig. 2 | Correlation coefficients among structural descriptors. a Isochoric and **b** isobaric conditions.

First group comprises q_{tet} , q_n , d_5 , LSI, and ζ . Among them, q_{tet} and q_n characterize the degree of tetrahedral order according to angular information, whereas d_5 , LSI, and ζ evaluate the degree of separation between the first and second coordination shells using distance-based information.

The second group consists of NTC, Q_4 , and the coordination number (C.N.). Among them, NTC and C.N. quantify local structural fluctuations using distance-based information, whereas Q_4 describes orientational symmetry without explicitly considering local density. The observation that these evidently distinct descriptors are mutually correlated yet uncorrelated with the first group suggests that the second group assesses the ordering associated with local structural fluctuations and lacks geometric information related to the tetrahedral structures formed through H-bonds.

The third group comprises Ψ , N_{HB} , and NTC_{HB} , which characterize the topological features of H-bond networks. In particular, N_{HB} and NTC_{HB} quantify the connectivity of the H-bond network via graph-theoretical approaches. Their relatively weak correlations with the descriptors in the first group imply that the topological properties of H-bond networks are not necessarily strongly related to the tetrahedral structures.

The fourth group consists of V_4 and V_{4-5} , both of which represent energetic quantities associated with negative interactions arising from H-bonds.

Contrary to these four groups, V_{voro} and Q_6 exhibit almost no correlation with other descriptors under isochoric conditions, whereas weak correlations emerge under isobaric conditions. V_{voro} estimates local volume fluctuations, whereas Q_6 describes orientational symmetry in a manner similar to that of Q_4 . These results suggest that density fluctuations enhance the ordering of local structures, specifically under isobaric conditions. Moreover, Ψ in the third group demonstrates stronger correlations with the structural descriptors in the first group under isobaric conditions, implying that variations in H-bond networks are influenced by density changes. Finally, V_5 exhibits no correlations with other descriptors under either isochoric or isobaric conditions.

Machine learning evaluation of structural descriptors

Figures 3 and 4 show the performances of the structural descriptors that classify two different temperatures, namely, T_1 and T_2 , through the FCNN under isochoric and isobaric conditions, respectively. For each combination, temperatures were selected such that $T_1 < T_2$, and determinations of T_1 and T_2 were set as binary classification tasks when output values were < 0.5 and ≥ 0.5 , respectively. The classification performances of the models were quantitatively assessed using AUC values under both isochoric and isobaric conditions. Table 1 summarizes the average AUC values for each structural descriptor depicted in Figs. 3 and 4. Based on these average values, the descriptors were categorized into four groups: (1) $AUC \geq 0.9$: LSI, ζ , NTC_{HB} , and N_{HB} ; (2) $0.75 \leq AUC < 0.9$: q_{tet} , V_{4-5} , q_n , C.N., V_4 , and Q_4 ; (3) $0.65 \leq AUC < 0.75$: Ψ , d_5 , V_{voro} , and V_5 ; and (4) $AUC < 0.65$: NTC and Q_6 .

Herein, we sequentially discuss the characteristics of each group. (1) LSI, ζ , NTC_{HB} , and N_{HB} all demonstrate high classification performances across all temperature combinations. In particular, LSI achieves nearly perfect discrimination, with $AUC \geq 0.991$ under isochoric conditions and $AUC \geq 0.963$ under isobaric conditions. For ζ , the minimum AUC value is 0.842, indicating that this descriptor also maintains high accuracy. These results suggest that the degree of separation between the first and second coordination shells, a feature common to both descriptors, is a key factor in discriminating temperature-dependent structural changes. Furthermore, compared to ζ , LSI incorporates information from a larger number of surrounding molecules relative to the central molecule, which accounts for its higher classification performance. NTC_{HB} quantifies the graph-based topological feature, in which O atoms and H-bonds are treated as nodes and edges, respectively, whereas N_{HB} represents the number of H-bonds. Both descriptors exhibit high AUC values ($AUC \geq 0.791$ and $AUC \geq 0.739$, respectively). As shown in Fig. 2, NTC_{HB} and N_{HB} exhibit weak correlations with LSI and ζ , revealing that H-bond network connectivity provides an additional structural feature for distinguishing temperature-dependent structural changes, independent of the separation between the first and second coordination shells.

(2) Classification performances of q_{tet} , V_{4-5} , q_n , C.N., V_4 , and Q_4 degrade at high temperatures. Specifically, under isochoric conditions, the AUC values approached those of random classification. This is because these structural descriptors are defined based on angles and distances, and are thus more sensitive to thermal fluctuations at high temperatures than LSI and ζ , which directly include information on H-bonds. In fact, as shown in Supplementary Figs. 3 and 4, the overlap of the distribution functions increases at high temperatures, reducing classification accuracy. Although C.N. is relatively less affected by thermal fluctuations, its distribution differs from that of N_{HB} at high temperatures as compared to the case at low temperatures (see Supplementary Figs. 3 and 4), implying that it does not fully acquire the H-bond information, which reduces the classification accuracy. In contrast, for these structural descriptors, the AUC values under isobaric conditions are generally higher than those under isochoric conditions, indicating that the FCNN model can effectively learn the tendency of local structures to become more ordered due to density changes. In

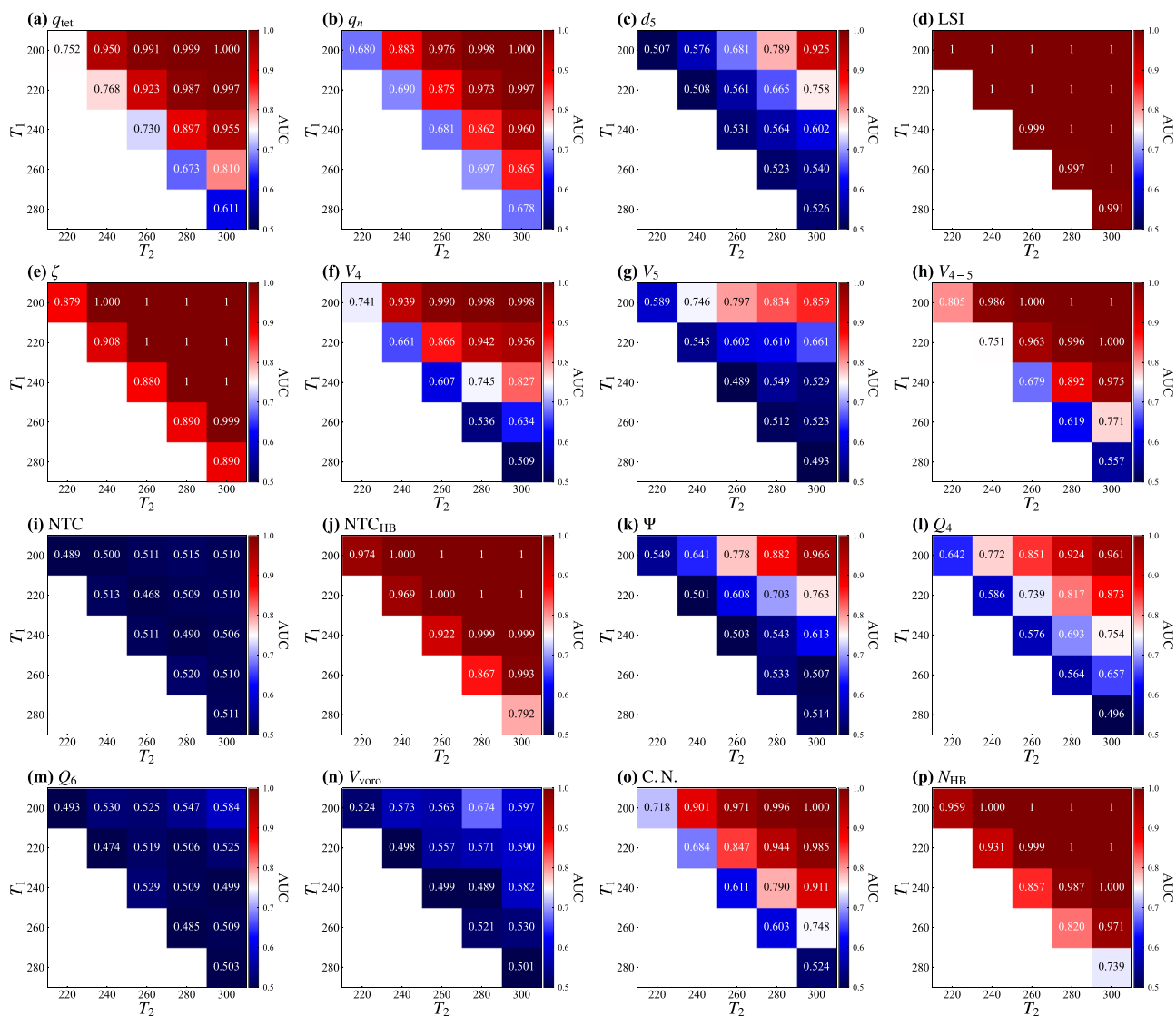


Fig. 3 | Classification performance of structural descriptors under isochoric conditions. Combinations of AUC values for each structural descriptor under isochoric conditions. T_1 and T_2 denote temperature pairs with $T_1 < T_2$. The color bar

represents AUC values in the $0.5 \leq \text{AUC} \leq 1.0$ range. An entry of $\text{AUC} = 1.000$ represents a value of 0.999.... Panels show results for **a** q_{tet} , **b** q_n , **c** d_5 , **d** LSI, **e** ζ , **f** V_4 , **g** V_5 , **h** V_{4-5} , **i** NTC, **j** NTC_{HB} , **k** Ψ , **l** Q_4 , **m** Q_6 , **n** V_{voro} , **o** C.N., and **p** N_{HB} .

particular, AUC values higher than 0.75 are obtained for classification between low temperatures or between low and high temperatures, suggesting that the relationship between structure and temperature is more clearly described in the low-temperature region.

(3) Ψ , d_5 , V_{voro} , and V_5 overall demonstrate low classification performances. Under isochoric conditions, only structures at low and high temperatures are distinguishable. d_5 and V_5 characterize the fifth nearest molecule from the central molecule and thereby quantify overcoordination. Ψ also serves as an indirect measure of overcoordination characterized by the H-bond network connectivity. Accordingly, these descriptors acquire a common structural feature associated with overcoordination, and significant classification is possible only when the temperature differences are sufficiently large. Notably, although d_5 correlates with LSI and ζ , its classification performance is inferior to that of LSI and ζ because d_5 accounts only for overcoordination and does not characterize broader features of the degree of separation between the first and second coordination shells. Classification performance of V_{voro} is close to random under isochoric conditions, probably because the local Voronoi volume demonstrates slight temperature dependence when the system volume is fixed. Contrarily, under isobaric conditions, the classification accuracy of V_{voro} for $T_1 = 200$ K and 220 K considerably increases. This temperature range is close to and

below the Widom line. Specifically, the high accuracy for temperatures below 220 K implies that V_{voro} is sensitive to the HDL-like and LDL-like structure crossover when the density is allowed to fluctuate.

(4) NTC and Q_6 exhibit low classification performances, particularly under isochoric conditions, where their performances are close to that of random classification. However, in classifications comparing the 200 K state and higher temperatures under isobaric conditions, NTC yields AUC values of at least 0.95. Under isobaric conditions, Q_6 also demonstrates AUC values of 0.85 or lower for the 200 and 300 K classifications, and low accuracy is observed for other temperature combinations. In NTC, O atoms are represented as nodes, and edges are defined between nearest neighbor O atoms, in contrast to NTC_{HB} . While the H-bond-based variant NTC_{HB} in group (1) achieves high classification accuracy, the performance of NTC degrades when edges are defined solely based on distance. This contrast highlights the crucial role of H-bond connectivity in accurately describing the underlying structural features. Q_6 demonstrates inferior classification performance to Q_4 . Note that the values of Q_4 , Q_6 , and C.N. are sensitive to the cutoff distance r_{cut} , and the adopted values are typically based on empirical considerations with respect to the first coordination shell. In this study, $r_{\text{cut}} = 0.35$ nm was adopted to be consistent with the distance criterion for the H-bond state (details are provided in the “Methods” section). As

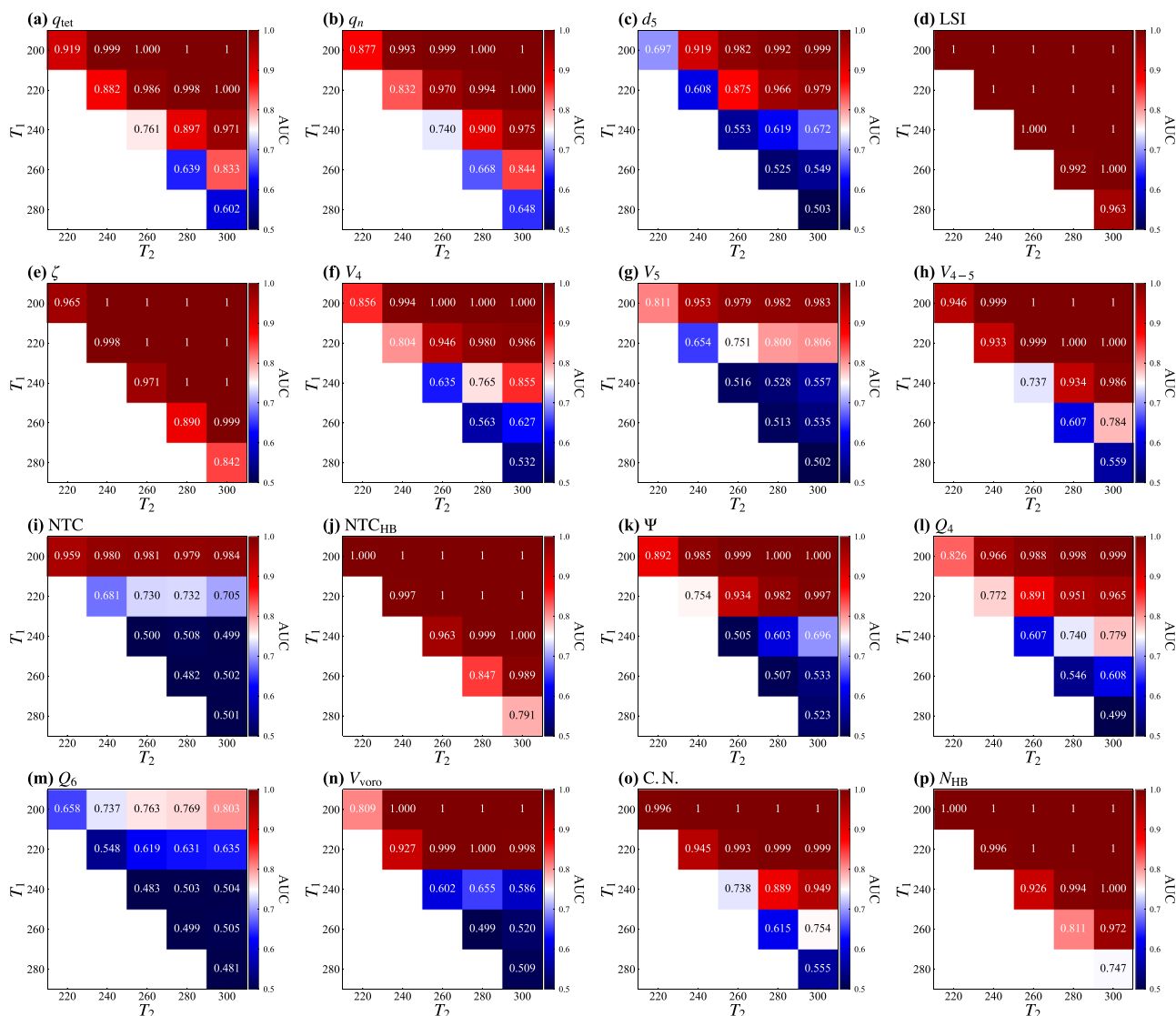


Fig. 4 | Classification performances of structural descriptors under isobaric conditions. Combinations of AUC values for each structural descriptor under isobaric conditions. T_1 and T_2 denote temperature pairs with $T_1 < T_2$. The color bar

represents AUC values in the $0.5 \leq \text{AUC} \leq 1.0$ range. An entry of $\text{AUC} = 1.000$ represents a value of 0.999.... Panels show results for **a** q_{tet} , **b** q_n , **c** d_5 , **d** LSI, **e** ζ , **f** V_4 , **g** V_5 , **h** V_{4-5} , **i** NTC, **j** NTC_{HB} , **k** Ψ , **l** Q_4 , **m** Q_6 , **n** V_{voro} , **o** C.N., and **p** N_{HB} .

these descriptors are sensitive to the choice of r_{cut} , variations in this parameter are expected to substantially affect machine learning accuracy. Consistent with this expectation, Supplementary Fig. 5 shows that the AUC values of Q_4 , Q_6 , and C.N. for the 200 and 300 K temperature classifications under isochoric conditions peak at around $r_{\text{cut}} = 0.3$ nm, which approximately corresponds to the first peak position of the radial distribution function $g(r)$, as depicted in Supplementary Figs. 1 and 2.

Overall, the isobaric systems exhibited higher AUC values than those of the isochoric systems, and specifically, evident improvements in classification performance are noticed at low temperatures. This indicates that density changes under isobaric conditions are closely related to the ordering of local structures associated with the HDL-like and LDL-like structural crossover, and that the machine learning model successfully describes this behavior. In contrast, in the high-temperature range of 260–300 K, where density variations are small (as shown in Supplementary Fig. 2f), the classification performance decreases for many structural descriptors. Even under these conditions, LSI, ζ , NTC_{HB} , and N_{HB} retain high classification performances, confirming their robustness as structural descriptors for quantifying local structural order in supercooled water.

In addition, to examine the limits of the classification performance of the four descriptors, LSI, ζ , NTC_{HB} , and N_{HB} from group (1), which showed

good performance with the FCNN, we evaluated their classification performance using logistic regression, a linear classification model. The results under isochoric and isobaric conditions are shown in Supplementary Figs. 6 and 7, respectively. The AUC values of LSI remained largely unchanged, while a slight decline was observed for ζ . In contrast, the performance of NTC_{HB} and N_{HB} decreased substantially, with AUC values close to 0.5 for all temperature combinations. These results indicate that the influence of structural descriptors on classification performance depends on the machine-learning model used. From this perspective, LSI and ζ appear to be particularly robust among the structural descriptors examined.

Interpretability of machine learning predictions using LIME

Finally, we applied LIME as XAI to analyze the contribution of each structural descriptor to temperature classification in the FCNN model. Specifically, the LIME values correspond to the coefficients of each input feature when the original FCNN is locally approximated by a linear regression model around the target prediction, representing both the magnitude and the sign of each input's contribution to the classification result. Thus, the absolute value of the LIME value indicates the importance of an input, while its sign indicates the direction of its contribution to the classification outcome. The LIME values were calculated separately for the

Table 1 | Ranking of structural descriptors based on AUC values

Rank	Descriptor	Average	Isochoric	Isobaric
1	LSI	0.998	0.999	0.997
2	ζ	0.970	0.963	0.978
3	NTC_{HB}	0.970	0.968	0.972
4	N_{HB}	0.957	0.951	0.963
5	q_{tet}	0.884	0.869	0.899
6	V_{4-5}	0.883	0.866	0.899
7	q_n	0.875	0.854	0.896
8	C.N.	0.855	0.815	0.895
9	V_4	0.816	0.796	0.836
10	Q_4	0.768	0.727	0.809
11	ψ	0.717	0.640	0.794
12	d_5	0.690	0.617	0.763
13	V_{voro}	0.679	0.551	0.806
14	V_5	0.674	0.622	0.725
15	NTC	0.610	0.505	0.715
16	Q_6	0.563	0.516	0.609

Descriptors are sorted by the average AUC over isochoric and isobaric conditions.

FCNN models using LSI, ζ , NTC_{HB} , and N_{HB} as target descriptors belonging to group (1), using data at 200 and 300 K. In the FCNN, the model was trained to predict the high-temperature state T_2 using binary cross-entropy as the loss function. Accordingly, positive LIME values indicate contributions to the high-temperature prediction, whereas negative values represent contributions to the low-temperature prediction.

Figure 5 depicts the relationship between LIME values and structural descriptors. In practice, the LIME values on the horizontal axis are binned using a fixed bin width, and the average value of the corresponding structural descriptor is evaluated for each bin. LSI and ζ exhibit a clear trend in which the descriptor values increase when the LIME values become more negative and decrease when the LIME values become more positive. This indicates that LDL-like local structures contribute to the predictions of low temperatures, whereas HDL-like local structures contribute to the predictions of high temperatures. These results demonstrate that the classification rationale learned by the machine learning model is consistent with the temperature dependences of the corresponding distribution functions of LSI and ζ (see Supplementary Figs. 3 and 4), particularly highlighting the degree of separation between the first and second coordination shells.

NTC_{HB} exhibits a trend similar to those of LSI and ζ . Physically, this behavior is attributable to the development of H-bond networks at lower temperatures, as shown in the distribution functions in Supplementary Figs. 3 and 4, which leads to significantly larger NTC_{HB} values with a decrease in temperature. Nevertheless, unlike the cases of LSI and ζ , the data are biased toward negative LIME values, implying that machine learning models using NTC_{HB} place considerable emphasis on predicting low temperatures. Additionally, large dispersions are observed in the positive LIME region corresponding to high-temperature predictions, and some values overlap with those at low temperatures where the LIME values are negative, specifically under isobaric conditions. These features are consistent with the reduced classification accuracy between high-temperature states noticed in Figs. 3 and 4, suggesting that NTC_{HB} is predominantly sensitive to low-temperature structures associated with H-bond networks.

N_{HB} values remain close and slightly below 4 across the entire LIME range under both isochoric and isobaric conditions, and only a slight increase is detected with an increase in the LIME values. This behavior implies that LIME emphasizes overcoordination at high temperatures. This interpretation is consistent with the increasing population of $N_{\text{HB}} = 5$

observed in the distribution functions depicted in Supplementary Figs. 3 and 4; however, the population of $N_{\text{HB}} = 3$ remains larger than that of $N_{\text{HB}} = 5$. Nevertheless, the overall variation with respect to the LIME value is marginal possibly because N_{HB} takes discrete integer values in a narrow range from 2 to 5.

These LIME results are consistent with the temperature-dependent changes observed in the distribution functions of the structural descriptors, suggesting that the machine learning models are trained in a manner that does not contradict the known trends in temperature-induced structural changes. While statistical measures such as distribution functions represent trends across the entire system, LIME is characterized by its ability to quantify which molecules contribute to classification predictions within a single snapshot. Evaluating these local contributions provides a complementary perspective for interpreting machine learning models in addition to conventional statistical analyses.

Conclusions

In this study, we examined 16 previously proposed structural descriptors that quantify local structures in supercooled water under isochoric (1 g/cm³) and isobaric (1 bar) conditions using MD simulations. In particular, we assessed the abilities of these descriptors to distinguish temperature-dependent structural changes via neural network-based machine learning.

Specifically, we performed a temperature classification task using the FCNN, with each structural descriptor used as an input feature, and quantitatively evaluated the classification performance using the AUC. The temperature classification in this study serves as proof for measuring the “structural sensitivity” of the descriptors. It is well documented that in supercooled water, the contribution of LDL-like structures increases at lower temperatures, whereas that of HDL-like structures increases at higher temperatures; thus, structural differences associated with temperature changes are closely related to these variations in local structure. Consequently, the classification performance between different temperatures can be interpreted as an indicator of how effectively the descriptors capture the difference between HDL-like and LDL-like environments. Furthermore, the results obtained in this study are consistent with distribution functions, as shown in Supplementary Figs. 3 and 4, indicating that the machine learning model describes structural changes in a manner consistent with established understanding.

The results reveal that LSI and ζ achieve the highest classification accuracies, demonstrating that these descriptors effectively describe temperature dependent-structural changes in supercooled water. NTC_{HB} and N_{HB} , which exhibit the next highest classification performances, quantify the connectivity of the H-bond network. Their weak correlations with LSI and ζ suggest that these descriptors obtain complementary structural features for differentiating temperature-dependent structural changes, independent of the degree of separation between the first and second coordination shells. Overall, these results indicate that structural changes in supercooled water under ambient pressure are governed by both the geometric order of the coordination shell and connectivity of the H-bond networks.

The comparison between isochoric and isobaric conditions aims to examine whether the physical insights derived from distribution functions, as shown in Supplementary Figs. 3 and 4, are consistent with the classification performance obtained through machine learning. Specifically, by considering both isochoric conditions, where density fluctuations are suppressed, and isobaric conditions, where density varies, we investigate how the distinguishability of structural changes differs between these ensembles. Based on the distribution functions, structural changes are expected to be enhanced under isobaric conditions, making classification easier. In this study, an overall improvement in classification performance was observed under isobaric conditions, suggesting that density fluctuations provide additional information useful for discrimination. It is also interesting to note that even for structural descriptors that do not explicitly include density information, such as tetrahedral order parameters, q_{tet} and q_m , classification performance also improves under isobaric conditions. These results suggest

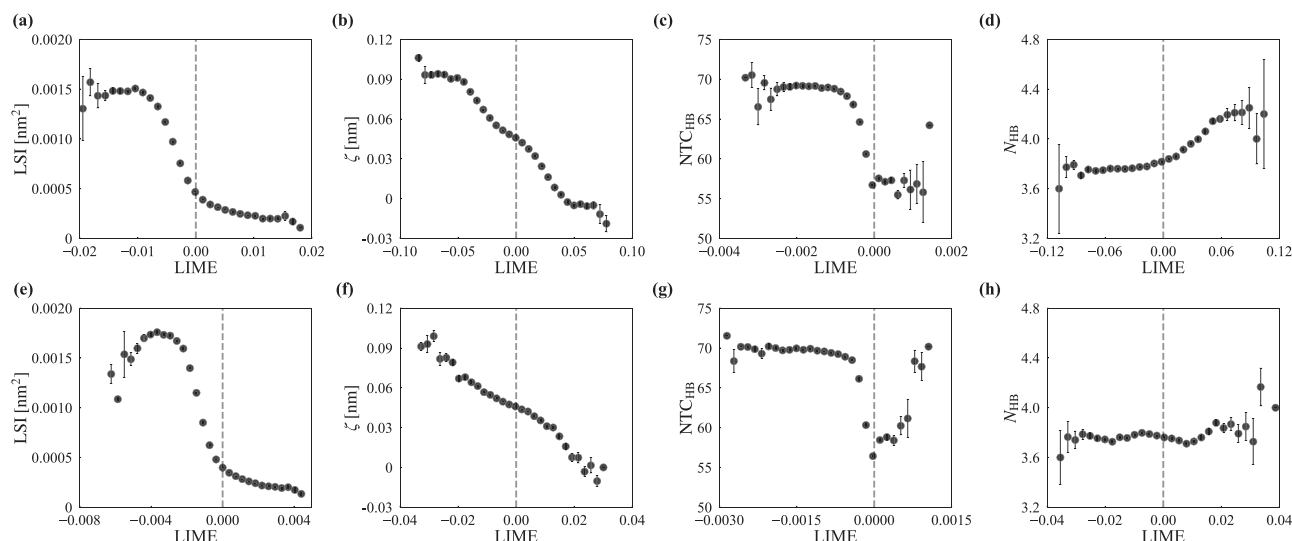


Fig. 5 | LIME-based interpretation of the model predictions. Average values of structural descriptors as functions of LIME: LSI [a, e], ζ [b, f], NTC_{HB} [c, g], and N_{HB} [d, h]. a–d correspond to isochoric conditions, whereas e–h are related to isobaric conditions.

that while density fluctuations contribute to improved performance under isobaric conditions, sensitivity to local tetrahedral structural changes also plays an important role in the classification.

The machine learning model in this study uses descriptor values corresponding to each molecule as input, and the final classification result is obtained by nonlinearly integrating this information in the hidden layers. In this sense, the model performs classification based on the entire snapshot and does not directly identify individual local environments, including HDL/LDL heterogeneous structures or the bimodal nature of descriptor distributions. However, the XAI analysis using LIME elucidates the principle underlying the learned temperature classification of the neural network model. In particular, applying LIME enables quantification of the contribution of each input (i.e., each molecule) to the classification result for a given snapshot. From this perspective, our machine-learning framework can be viewed as a method for indirectly analyzing the relationship between local structures and global classification outcomes.

In fact, the LIME results show that molecules with larger LSI and ζ values preferentially contribute to low-temperature (LDL-like) predictions, whereas molecules with smaller values contribute to high-temperature (HDL-like) predictions. This reveals that these descriptors describe the structural changes in supercooled water through the separation of the first and second coordination shells, yielding a physically plausible interpretation consistent with the temperature dependences of the corresponding distribution functions. Moreover, molecules with large NTC_{HB} values contribute to the low-temperature predictions, highlighting the development of H-bond networks as a key factor driving structural variations with a decrease in temperature. In contrast, although the correspondence between N_{HB} and the LIME values is limited, the analysis emphasizes an enhanced contribution from overcoordination in the high-temperature regime.

In conclusion, this study assessed 16 existing structural descriptors for liquid water in a unified machine-learning framework, explaining the structural features characterized by each descriptor and their temperature dependence. In particular, LSI and ζ were identified as highly efficient descriptors for characterizing local structural changes in supercooled water. Their combination with H-bond network descriptors affords a more comprehensive understanding of the HDL-like and LDL-like structural crossover in supercooled water.

Based on these findings, the development of new structural descriptors that integrate the length scales and information content of available structures is expected. Such descriptors may enable the direct identification of HDL-like and LDL-like environments, establishing a framework to distinguish them, and addressing the transferability across different water models.

Additionally, extending the analysis to higher-order structural representations using nonlinear models, such as graph neural networks, is estimated to further advance this field^{60,61}. Another promising direction is to explore the features of H-bond networks by establishing connections between descriptors used in machine-learning potential frameworks, including atom-centered symmetry functions (ACSF) and smooth overlap of atomic positions (SOAP), and physically inspired and hand-crafted structural descriptors. Studies along these lines have been reported not only at the liquid-gas interface⁶² but also in supercooled water⁶³.

Methods

MD simulations

MD simulations were conducted using the TIP4P/2005 water model^{64,65} with the GROMACS 2020.6 package⁶⁶. Simulated system consisted of $N = 1000$ water molecules in a cubic box with periodic boundary conditions, and a linear dimension of approximately 3.1 nm, corresponding to a mass density of 1 g/cm³. Simulations were performed at the target temperatures of $T = 300, 280, 260, 240, 220$, and 200 K.

We prepared 1000 independent initial structures and performed equilibration for each under NVT conditions while gradually lowering the temperature from 300 K to 200 K. At each temperature, the systems were equilibrated using the Nosé–Hoover thermostat for up to 100 ns, followed by a 1 ps simulation in the microcanonical ensemble to obtain structural data for machine learning. By repeating this procedure at each temperature, we generated a dataset of 1000 structures under isochoric conditions.

Moreover, equilibration under isobaric conditions under 1 bar was performed using the Nosé–Hoover thermostat and the Parrinello–Rahman barostat following equilibration in the NVT ensemble, with an equilibration time of up to 1 μ s. Furthermore, a 10 ps simulation was conducted in the NPT ensemble, and the structure exhibiting the smallest deviation from the average density during this run was selected. Thereafter, a 10 ps simulation in the canonical ensemble, followed by a 1 ps simulation in the microcanonical ensemble, was performed to formulate structural data under isobaric conditions. A total of 1000 structural datasets were produced at each temperature, except for 200 K, where the computational cost limited the dataset size to 500.

Supplementary Figs. 1 and 2 depict the temperature dependences of the O–O radial distribution function $g(r)$, mean-square displacement (MSD) of O atoms, H-bond time correlation function $P_{HB}(t)$, HB lifetime τ_{HB} , diffusion coefficient D , potential energy V , and pressure p or mass density ρ under isochoric and isobaric conditions, respectively. Although gradual temperature dependence is observed for $g(r)$ and V , dynamical properties

such as D and τ_{HB} demonstrate evident changes with a decrease in temperature.

According to the conventionally accepted definition, a pair of water molecules is considered to be in a H-bond state when the O–O interatomic distance is within 0.35 nm, and the H–O⋯O angle is within 30°^{67,68}. $P_{\text{HB}}(t)$ is defined using the H-bond index $h_{ij}(t)$ for the molecular pair of (i, j) as follows^{67–70}:

$$P_{\text{HB}}(t) = \frac{\langle h_{ij}(t)h_{ij}(0) \rangle}{\langle h_{ij}(0) \rangle}, \quad (2)$$

where $h_{ij}(t)$ is 1 if the molecules i and j form the H-bond at the time t , and 0 otherwise. Herein, $\langle \dots \rangle$ represents the ensemble average over all molecular pairs and initial times. From the fitting of $P_{\text{HB}}(t)$ to the Kohlrausch–Williams–Watts (KWW) function, namely, $P_{\text{HB}}(t) = \exp[-(t/\tau_{\text{KWW}})^{\beta_{\text{KWW}}}]$, the HB lifetime τ_{HB} was evaluated by $\tau_{\text{HB}} = (\tau_{\text{KWW}}/\beta_{\text{KWW}}) \Gamma(1/\beta_{\text{KWW}})$ with the Gamma function $\Gamma(\dots)$. Moreover, the diffusion coefficient D was obtained by dividing the long-time limit of the MSD by $6t$. Note that the equilibrium times of 100 ns and 1 μs under isochoric and isobaric conditions, respectively, correspond to the durations required for $P_{\text{HB}}(t)$ to decay to zero at 200 K.

Structural descriptors

Structural descriptors are metrics that quantify the degree of order of a molecular structure by assigning scalar values based on the local environment of each molecule. For liquid systems, the structure has generally been characterized using two-body correlation functions, for example, radial distribution functions and static structure factors. As these quantities are averaged over spherical symmetry, they cannot adequately describe the local geometric order. This limitation is particularly noticeable in supercooled liquids, in which temperature-dependent variations in the local structure play crucial roles. To address this issue, various structural descriptors have been proposed that incorporate local many-body correlations based on geometric features such as angular arrangements and intermolecular distance^{34–38}. Furthermore, in liquid water, the production of a tetrahedral network is regarded as a low-density, highly ordered state, whereas coordination defects and more compact configurations correspond to high-density disordered states^{71,72}. Hereinafter, we summarize the definitions of the 16 structural descriptors employed in this study. The temperature dependences of the descriptor distributions under isochoric and isobaric conditions are shown in Supplementary Figs. 3 and 4, respectively. Note that in addition to the structural descriptors considered herein, additional structural descriptors, including helicity³¹ and local order metric^{30,73}, have been proposed.

(a) q_{tet} measures the degree of tetrahedral coordination of liquid water and is defined by^{40,41}

$$q_{\text{tet}} = 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2, \quad (3)$$

where ψ_{jk} is the angle formed by lines connecting the O atom of the central molecule to the O atoms of its two nearest neighbor molecules, that is, j and k . The summation is taken over all unique pairs among the four nearest neighbor molecules. If a molecule is located at the center of a regular tetrahedron created by its four nearest neighbors, $\cos \psi_{jk} = 1/3$, yielding $q_{\text{tet}} = 1$. In contrast, for a random molecular arrangement such as that in an ideal gas, the six angles associated with the central molecule are statistically independent, and the average value of q_{tet} approaches 0.

(b) q_n is a generalized form of q_{tet} that accounts for the possibility that the four nearest neighbor molecules do not necessarily belong to the first coordination shell⁷⁴. This quantifies the extent to which the local H-bond environment approaches tetrahedral coordination. The definition is

presented by

$$q_n = 1 - \frac{9}{2n(n-1)} \sum_{j=1}^{n-1} \sum_{k=j+1}^n \left(\cos \psi_{jk} + \frac{1}{3} \right)^2, \quad (4)$$

where n is the number of H-bonds of the central water molecule, i.e., $n = 2, 3, 4$, and 5.

(c) d_5 is expressed as the O–O distance between the central molecule and its fifth nearest neighbor¹⁸. d_5 classifies molecules as HDL-like when its value exceeds 3.5 Å. This descriptor contains only distance-based information and characterizes the local structure up to the first coordination shell.

(d) LSI (Local Structure Index) for the molecule i is defined by ordering the O–O nearest-neighbor distances between the central molecule i and its neighboring molecules, denoted as r_j , such that $r_1 < r_2 < \dots < r_j < \dots < r_{n(i)} < 0.37 \text{ nm} < r_{n(i)+1}$. Herein, $n(i)$ is chosen such that $r_{n(i)} < 0.37 \text{ nm} < r_{n(i)+1}$. Based on this ordered set of distances, the LSI is expressed as^{43,44}

$$\text{LSI} = \frac{1}{n(i)} \sum_{j=1}^{n(i)} [\Delta(j) - \bar{\Delta}], \quad (5)$$

where $\Delta(j) = r_{j+1} - r_j$ and $\bar{\Delta}$ is the average of $\Delta(j)$ over all the nearest neighbors j of the molecule i . Herein, 0.37 nm lies between the first and second coordination shells, which is determined to optimize the sensitivity of the distribution function. LSI quantifies the degree of separation between the first and second coordination shells of a target water molecule, thereby characterizing the local structure beyond the first coordination shell. A large LSI value indicates a well-ordered first coordination shell, with no water molecules located between the first and second coordination shells. In contrast, a small LSI value implies either a disordered first coordination shell or the presence of water molecules between the first and second coordination shells.

(e) ζ is defined as the difference between the distance to the nearest no H-bond molecule (r_{NHB}) and the distance to the farthest H-bond molecule (r_{HB}), i.e., $\zeta = r_{\text{NHB}} - r_{\text{HB}}$ ^{42,75}. ζ is a descriptor designed to measure local order extending to the second coordination shell by explicitly incorporating the existence or absence of H-bonds. $\zeta \approx 0 \text{ nm}$ indicates a locally disordered (HDL-like) environment in which the second coordination shell is disrupted, whereas $\zeta \approx 1 \text{ nm}$ corresponds to a locally ordered (LDL-like) structure with a clear separation between the first and second coordination shells.

(f) V_4 is expressed as the fourth-largest negative interaction energy among the interaction energies between a central water molecule and its surrounding molecules⁷⁶. If a local tetrahedral structure is approximately formed, V_4 is expected to correspond to a typical H-bond energy; when the tetrahedral arrangement is disrupted, V_4 approaches 0. Therefore, V_4 serves as a descriptor for identifying coordination defects.

(g) Similar to V_4 , V_5 is defined as the fifth largest negative interaction energy to primarily highlight overcoordinated molecules, contrary to the case of V_4 ⁷⁶.

(h) V_{4-5} is the difference between V_4 and V_5 , i.e., $V_{4-5} = V_4 - V_5$, which is used to discriminate the four-fold tetrahedrally coordinated water molecules from both the three-fold-coordinated and overcoordinated molecules⁷⁷.

(i) NTC (Node Total Communicability) is a graph-theoretical metric that evaluates the cumulative connectivity of each water molecules⁴⁵. To apply graph-based analysis to molecular structures, atomic coordinates are converted into a graph representation. Following the literature, O atoms are treated as nodes, and an edge is assigned between two nodes when the O–O distance is less than or equal to 0.35 nm⁴⁵. This procedure yields an

undirected, unweighted graph. NTC of the node v_i is expressed as

$$\text{NTC} = [e^{\beta A} \mathbf{1}]_i = 1 + \beta [A \mathbf{1}]_i + \frac{\beta^2}{2!} [A^2 \mathbf{1}]_i + \frac{\beta^3}{3!} [A^3 \mathbf{1}]_i + \dots, \quad (6)$$

where A is the adjacency matrix of the graph consisting of N nodes, where N is the number of molecules in the system. Thus, A is an $N \times N$ square matrix with the element a_{ij} . If an edge exists between the nodes v_i and v_j , then $a_{ij} = 1$; otherwise, $a_{ij} = 0$. Additionally, $\mathbf{1}$ is the vector of all ones, and β is a parameter that weights medium- and long-range effects. In this study, $\beta = 1$ was employed based on the corresponding literature⁴⁵. This descriptor includes the influence of network connectivity over medium- and long-range, and a large NTC value indicates a highly connected and dense network.

(j) We define an alternative descriptor, namely, NTC_{HB} , as a variation of NTC, in which edges are constructed based on the H-bond expression rather than the distance-based criterion used in NTC.

(k) Ψ is a structural descriptor that characterizes topological changes in H-bond networks across the liquid–liquid transition in water^{78,79}. It is defined as follows^{46,47}: for a specific molecule i , molecules connected to i by the chemical distance $D = 4$, that is, molecules separated by four H-bond links along the network, are identified at first. These molecules constitute the fourth bond-coordination shell of i . O–O distances among the molecules in this shell are evaluated, and the shortest of these distances is expressed as Ψ for molecule i . In the LDL-like state, the tetrahedral H-bond network is adequately developed, affording $\Psi \approx 0.6$ nm. In contrast, in the HDL-like state, the H-bond network adopts a disrupted structure, resulting in $\Psi \approx 0.35$ nm.

(l) and (m) Bond-orientational order (BOO) describes the degree of local orientational order in liquids⁸⁰. To quantify the orientational symmetry of neighboring particles around particle i , the complex order parameter $q_{lm}(i)$ is defined as follows:

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\hat{\mathbf{r}}_{ij}), \quad (7)$$

where $N_b(i)$ represents the number of neighboring particles within the first coordination shell of i . In this study, the first coordination shell was expressed as the region within the cutoff distance of $r_{\text{cut}} = 0.35$ nm, consistent with the H-bond definition. Herein, $Y_{lm}(\dots)$ denotes the spherical harmonic function of the degree l , and order m , with $m = -l, \dots, +l$, and $\hat{\mathbf{r}}_{ij}$ is the unit vector pointing from particle i to particle j . To ensure rotational invariance, the BOO is described as

$$Q_l = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |q_{lm}(i)|^2}. \quad (8)$$

Generally, the choice of l is arbitrary. In this study, we employed Q_4 (l) and Q_6 (m), which are sensitive to cubic and hexagonal symmetries, respectively. The combination of these parameters is widely used to distinguish between liquid-like and crystalline local structures. All Q_4 and Q_6 calculations were performed using the Pyboo code⁸¹.

(n) V_{vor} is the local volume associated with each molecule based on Voronoi tessellation^{82,83}. Herein, V_{vor} was evaluated using the Pyvoro code⁸⁴.

(o) C.N. is defined as the number of molecules within the first coordination shell, determined by the O–O distance within the cutoff $r_{\text{cut}} = 0.35$ nm utilized in the H-bond definition. To guarantee that C.N. is

smooth and continuous, it is defined as follows⁶²:

$$\text{C.N.} = \sum_{j=1}^N \frac{1 - \left(\frac{r_j}{r_{\text{cut}}}\right)^{12}}{1 - \left(\frac{r_j}{r_{\text{cut}}}\right)^{28}}, \quad (9)$$

where r_j denotes the distance between a central O atom and the j th O atom. (p) N_{HB} is described as the number of H-bonds of the central molecule.

Neural network model

An FCNN was employed to classify the structures between two temperatures. As shown in Fig. 1, the network architecture comprises an input layer with 1000 nodes, two hidden layers (with 1000 and 1 nodes, respectively) using the LeakyReLU activation function (leak parameter = 0.01), and an output layer with a sigmoid activation function to predict the temperature, T_1 or T_2 . Note that each node contains a bias term. For each structural descriptor, we constructed an independent neural network model for a total of 15 temperature combinations. For all models, the outputs were assigned as $T_1 = 0$ and $T_2 = 1$, with $T_1 < T_2$, and the network was trained by minimizing the binary cross-entropy loss function. In general, the model's representation capacity can be improved by adjusting hyperparameters such as the number of hidden layers and the number of nodes. This implies that high-precision classification may be achievable for many of the structural descriptors considered in this study. However, the primary objective of this study is to evaluate the classification performance of structural descriptors within a unified framework while introducing minimal nonlinearity between inputs and outputs; therefore, we adopted a relatively simple FCNN with two hidden layers.

Training was conducted using TensorFlow⁸⁵ with the optimization algorithm Adam, a learning rate of 10^{-6} , and a batch size of 32. At each temperature, the dataset was divided into training, validation, and test datasets at an 8:1:1 ratio. Epoch dependences of the training and validation loss functions for the case using q_{tet} as the structural descriptor are depicted in Supplementary Figs. 8 and 9. To enable performance comparisons under equal conditions across temperature combinations for each descriptor, we determined the epoch at which the validation loss shifted from decreasing to increasing and evaluated the model's AUC at that point. In addition, to prevent biases arising from the arbitrary assignment of molecular indices in MD simulations, the molecular indices used as input were randomly shuffled. To account for the permutation-invariant nature of the data, training and evaluation involving this shuffling procedure were performed independently ten times for each structural descriptor, and the AUC was calculated as the average of these values.

For comparison, we also used logistic regression as a linear classification model without nonlinearity. As shown in Supplementary Fig. 10, the model has an input layer with 1000 nodes, similar to the FCNN, followed by a single output layer performing binary classification using a sigmoid activation function. As with the FCNN, the model was trained separately for each structural descriptor. Training was performed using TensorFlow with the Adam optimization algorithm, a learning rate of 10^{-6} , and a batch size of 32, identical to those used for the FCNN. The loss function was binary cross-entropy. Training was repeated 10 times with randomly shuffled molecular indices, and the average AUC was calculated.

LIME analysis

To interpret the temperature classification predictions generated by FCNNs, we applied LIME, an XAI method⁵⁹. Because FCNNs are typically black-box models, identifying input features that contribute to their predictions is difficult. LIME addresses this issue by locally approximating the original model with an interpretable model, thereby quantifying the contribution of each input variable. Specifically, LIME explains the prediction for a certain input instance by creating a local linear regression model that reproduces the behavior of the original classifier in the neighborhood of the instance.

Herein, LIME value computations were performed using the available Python code⁸⁶.

Data availability

The data that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.19938177>.

Code availability

The codes that support the findings of this study are openly available in Zenodo at <https://doi.org/10.5281/zenodo.19938178>.

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Author contributions

K.Y., K.K. and N.M. designed the research. K.Y. and S.K. performed the research. K.Y., S.K. and K.K. analyzed the data. K.Y., K.K. and N.M. wrote the paper.

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Competing interests

The authors declare no competing interests.

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