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Long-range hydrogen-bond structure in aqueous solutions and the vapor-water interface

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There is a considerable disagreement about the extent to which solutes perturb water structure. On the one hand, studies that analyse structure directly only show local structuring in a solute's first and possibly second hydration shells. On the other hand, thermodynamic and kinetic data imply indirectly that structuring occurs much further away. Here, the hydrogen-bond structure of water around halide anions, alkali cations, noble-gas solutes, and at the vapor-water interface is examined using molecular dynamics simulations. In addition to the expected perturbation in the first hydration shell, deviations from bulk behavior are observed at longer range in the rest of the simulation box. In particular, at the longer range, there is an excess of acceptors around halide anions, an excess of donors around alkali cations, weakly enhanced tetrahedrality and an oscillating excess and deficiency of donors and acceptors around noble-gas solutes, and enhanced tetrahedrality at the vapor-water interface. The structuring compensates for the short-range perturbation in water-water hydrogen bonds induced by the solute. Rather than being confined close to the solute, it is spread over as many water molecules as possible, presumably to minimize the perturbation to each water molecule. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4735267>]

I. INTRODUCTION

The structure of aqueous solutions^{1–4} and interfaces^{5,6} is a long-standing issue, not least because the structure of water is still controversial. Dissolved solutes and interfaces affect the structure of water and thereby exert an influence on numerous processes, from atmospheric reactions⁷ to the workings of biomolecules.² Determining the nature and range of this perturbation is key to understanding how this takes place. That the range extends over many water molecules may be inferred indirectly by non-ideal variations in solution properties such as the activity coefficient⁸ as predicted by the Debye-Huckel theory,⁹ viscosity,¹⁰ and partial volume¹¹ in the limit of infinite dilution, the non-additivity of water's rotational dynamics for different salts,¹² and the suppression of broken hydrogen bonds (HBs) in anion-water clusters.¹³ In further support, computer simulations show an increased mobility of water distant to ions,¹⁴ a non-zero long-range contribution to solvation entropy,¹⁵ and a long-range contribution to surface-tension at the vapor-water interface.¹⁶ Energy in the form of the electrostatic interaction undoubtedly plays a role in explaining this behavior but so too must entropy, which quantifies the structural variability of a system. Otherwise, the long-range perturbation would be invariant to temperature, which is unlikely. Structuring is well-recognized in the first and possibly second hydration shells of a solute as deduced from x-ray absorption and scattering spectra,^{17,18} vibrational spectra,^{19,20} terahertz spectra,^{21,22} distribution functions from neutron diffraction^{23–26} and com-

puter simulation^{25,27–34} tetrahedrality,^{35,36} or a number of hydrogen bonds^{27,35,37–43} from computer simulation. Significant structuring has also been observed in the first water layer or two of the vapor-water interfaces using vibrational sum-frequency experiments^{44–49} or computer simulation.^{50–54} Very few definitive studies have been put forward showing the explicit molecular nature of any long-range structuring. However, the limited ability to detect it does not imply that it is not present. Longer-range structural deviations in water density around ions have been detected in neutron diffraction studies^{24,26} and at the oil-water interface from molecular dynamics simulation.⁵⁵ Nonetheless, little evidence and conflicting thermodynamic, kinetic, and structural data make the topic of long-range water structuring an ongoing, controversial issue.^{56,57}

Here, we examine the nature and range of the HB structure of water in dilute aqueous solutions and at the vapor-water interface using molecular dynamics simulations. The solutes studied are the noble gases Ne, Ar, Kr, and Xe, the halide anions F[−], Cl[−], Br[−], and I[−], and the alkali cations Li⁺, Na⁺, K⁺, Rb⁺, and Cs⁺. The property that we study is the distributions of water molecules in the whole simulation box with a given number of donor or acceptor HBs. Specifically, we examine the number of these HB species compared to bulk, their spatial variation using radial distribution functions, the spatial deviations of their number distributions compared to bulk, and the differences in the number of donors and acceptors. Effects of HB definition, box size, and charge are also examined.

II. METHOD

A. Molecular dynamics protocol

The Lennard-Jones parameters for Ne, Ar, Kr, and Xe are those of Guillot and Guissani⁵⁸ and those for Li^+ , Na^+ , K^+ , Rb^+ , and Cs^+ , and those for the anions F^- , Cl^- , Br^- , and I^- are from the parm99 force field as implemented in assisted model building with energy refinement (AMBER) 9.^{59–62} One solute is placed in a cubic periodic box with 375 TIP4P/2005 water molecules⁶³ using the leap module of the AMBER 9 software package.⁶⁴ Five hundred steps of steepest-descent minimization eliminate high forces from any atomic overlaps. This is followed by molecular dynamics simulations in the NVT ensemble at 298 K using a Langevin thermostat for 100 ps and in the NPT ensemble using a Berendsen barostat at 1 bar for a further 2 ns, all using AMBER's sander module. Data collection proceeds over a further 1 ns under the same NPT conditions. All simulations use SHAKE applied to all bonds, a 2 fs time step, a 8 Å cutoff, and particle mesh Ewald⁶⁵ with default AMBER parameters. The sander code of AMBER was altered to print out the hydrogen-bond information. Sander implicitly includes a neutralising background for systems containing ions by omitting the constant, zeroth-order energy term in the reciprocal space Ewald sum.^{66,67} This standard procedure makes no difference to structure because forces, being energy derivatives, which govern motion in molecular dynamics simulations, are unaffected. The same protocol is used for Ar, F^- , and Li^+ in a larger box of 1200 TIP4P/2005 water molecules and the series of artificial sodium ions in the smaller box with charges of ± 1 , ± 2 , and ± 3 . Equilibrated boxes have sides of ~ 2.2 nm and ~ 3.3 nm for the smaller and larger boxes, and concentrations of 0.15 mol dm^{-3} and $0.046 \text{ mol dm}^{-3}$, respectively. The vapor-water interface⁵⁰ is a periodic rectangular prism of 864 TIP4P/2005 water molecules in a box with dimensions $3 \times 3 \times 10 \text{ nm}^3$ such that the water slab occupies the central third, has volume $3 \times 3 \times 3 \text{ nm}^3$, and lies in the xy plane. The same simulation protocol is used as that of the solutions except that they are run in the NVT ensemble throughout to preserve the interface and do not have the extra 1 ns of NPT equilibration. Finally, a simulation of 375 TIP4P/2005 water molecules is run using the same protocol as for solutions to provide a bulk-water reference for comparison with the solutions and vapor-water interface.

B. Structural analysis

HBs are assigned using the topological definition:⁶⁸ a hydrogen donates to the acceptor with the strongest force as long as this is the strongest hydrogen-acceptor force between the two species involved; if it is not the strongest, then that hydrogen is deemed to have a broken HB. Given that the hydrogens in this system have no van der Waals radii, the force is equal to the electrostatic force. The advantages of this definition are that it accurately resolves HBs without recourse to arbitrary parameters and accommodates different types of acceptors according to the size of their force-field charge. Water species are classified according to either the number of donor or acceptor hydrogen bonds. Water molecules with 0,

1, or 2 donors are called non-donors (NDs), single donors (SDs), or double donors (DDs); water molecules with 0, 1, 2, 3, or 4 acceptors are called non-acceptors (NAs), single acceptors (SAs), double acceptors (DAs), triple acceptors (TAs), or quadruple acceptors (QAs); water molecules that have one donor to an ion and no other donor are called ion donors (IDs); and water molecules that have one donor to an ion and one donor to a water molecule are called ion-water donors (IWDs). Given that almost all waters have two donors by the topological definition, SAs, DAs, and TAs can be described as having trigonal, tetrahedral, or trigonal bipyramidal geometry, respectively, even if they are slightly distorted. The HB distributions used here in terms of electrostatic force have slightly more SDs than that obtained using distance⁶⁸ for bulk water with the TIP4P/2005 model,⁶³ 2% versus 1.6%, and a corresponding shift from DAs to SAs. This is because the oxygen's charge used for the electrostatic force calculation is offset by 0.125 Å from the oxygen atom used for distance. To assess whether the results are sensitive to the HB definition, we also apply the distance-angle HB definition⁶⁹ to the solutions of Ar, F^- , Li^+ , and the vapor-water interface. This defines an HB if a donor has an oxygen-oxygen distance less than 0.35 nm and a HOO angle less than 30° ; donor HBs from water to anions are defined using the same distance-angle criterion with the anion in place of the acceptor oxygen. Unless otherwise stated, all HBs are calculated using the topological definition.

Four quantities concerning the number and distribution of the HB species are assessed:

1. ΔN_i : non-ideality of each HB species i in the solution relative to bulk water:

$$\Delta N_i = N_i - N_i^{\text{total}}, \quad (1)$$

where N_i and N_i^{total} are the average number of HB species i in the solution and in bulk water, respectively. Being averages over multiple structures, they are typically not integer values.

2. $g_i(r)$: radial distribution functions of the oxygen of each HB species i :

$$g_i(r) = \frac{N_i(r)}{4\pi r^2 \rho_{\text{w(l)}}}, \quad (2)$$

where $N_i(r)$ is the number of HB species i with their oxygens at distance r from the solute and $\rho_{\text{w(l)}}$ is the density of pure water.

3. $\Delta N_i(r)$: cumulative spatial non-ideality of HB species i integrated from the origin to a distance r :

$$\Delta N_i(r) = \int_0^r d(N_i(r') - x_i N_i^{\text{total}}(r')), \quad (3)$$

where $N_i^{\text{total}}(r')$ is the total number of water molecules with their oxygens at distance r' from the solute, and x_i is the mole fraction of HB species i in bulk water.

4. $\Delta N_{\text{da}}(r)$: cumulative spatial donor-acceptor bias integrated from the origin to a distance r :

$$\Delta N_{\text{da}}(r) = \sum_i^{\text{donors}} d_i \int_0^r dN_i(r') - \sum_i^{\text{acceptors}} a_i \int_0^r dN_i(r'), \quad (4)$$

where d_i and a_i are the numbers of water-water donor HBs and acceptor HBs, respectively, of HB species i .

Similar quantities are calculated at the vapor-water interface as a function of z except that they are averaged per nm^2 over the two 9 nm^2 interfaces and the origin is the Gibbs dividing surface (half the bulk density). Bin-widths used in distance are 0.01 nm for all systems. All quantities are evaluated such that each molecule in the simulation box contributes only once so as to avoid double-counting periodic molecules. Errors in ΔN_i are determined by calculating for N_i and N_i^{total} the standard deviation divided by the square root of the number of independent configurations. Correlation times between independent configurations are determined to be 1 ps for the solutions and 10 ps for the vapor-water interface based on the time for the convergence of the standard deviation. This leads to 1000 configurations for solutions and 100×18 configurations for the vapor-water interface. Errors in $\Delta N_i(r)$ are similar to those of ΔN_i for the respective HB species i while errors in $\Delta N_{\text{da}}(r)$ are smaller and not considered because their integrated total is exactly zero, every donor having an acceptor.

III. RESULTS AND DISCUSSION

A. Non-ideality of the HB species

Non-ideality is first examined using ΔN_i as defined in Eq. (1). These values are listed in Table I. Around noble gases, the water is more tetrahedral, shown by a shift from SAs and TAs to DAs, that increases weakly on average with solute size. There are slightly more broken HBs, indicated by a shift from DDs to SDs and by a greater loss of TAs than SAs. Around anions, there are more species with less acceptor HBs, notably the SAs, fewer broken HBs, and the large expected increase in IWDs at the expenses of DDs. IDs are rare and negligible for larger anions. The broken donors of IDs almost always occur for hydrogens trying to point to a water molecule although about 0.02 water molecules have both donors bound by the anion in the case of F^- . The coordination number of anions, equal to the number of donating hydrogens, is ~ 6 as

TABLE II. ΔN_i of each HB species^a going from bulk water to solution or to the vapor-water interface using the distance-angle HB definition.

Acceptor	Ar	F^-	Li^+	Vapor/water ^b
NA	-0.1	0.2	2.5	0.1
SA	-0.7	3.2	-2.9	1.4
DA	1.1	-2.2	-1.3	-0.8
TA	-0.2	-1.3	1.6	-0.7
QA	0.0	0.0	0.0	0.0
Donor				
ND	-0.1	-0.1	0.0	0.2
SD	-0.6	-1.5	0.4	1.8
DD	0.7	-4.4	-0.4	-2.0
TD	0.0	0.0	0.0	0.0
ID		2.9		
IWD		3.1		

^aErrors are ± 0.1 for NAs, NDs, and TDs (triple donors), ± 0.3 for SDs, SAs, and DDs, ± 0.4 for DAs, ± 0.2 for TAs, and zero otherwise. They are the same at the vapor-water interface but in units of nm^{-2} .

^bUnits are nm^{-2} .

expected.⁷⁰ Around cations, there is a large shift from tetrahedral structure to almost all other species: NAs, TAs, QAs, SDs, and either fewer or more SAs, depending on the cation's size. Smaller cations have a decrease in SAs and more NAs while larger cations have an increase in SAs and fewer NAs. The coordination number of cations is not determined using the topological HB definition because a hydrogen is not involved in the cation-water interaction. For all solutions, there is an absence of NDs. Values of ΔN_i using the distance-angle HB definition⁶⁹ are included in Table II. Most trends are similar and any differences largely arise from the greater number of broken HBs detected by the distance-angle HB definition. There are larger falls in SDs around Ar and F^- , indicating fewer distorted HBs, and small changes in NAs and NDs for Ar and F^- . Even though the coordination numbers are the same around F^- using either definition, the distance-angle definition gives roughly equal numbers of IDs and IWDs versus the dominance of IWDs using the topological HB definition; this is consistent with HBs being more distorted in the first hydration shell of anions.

TABLE I. ΔN_i of each HB species^a going from bulk water to solution or to the vapor-water interface.

Acceptor ^b	Ne	Ar	Kr	Xe	F^-	Cl^-	Br^-	I^-	Li^+	Na^+	K^+	Rb^+	Cs^+	Vapor/water ^c
NA	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	2.2	1.6	1.1	0.8	0.6	0.0
SA	-0.1	-0.4	-0.2	-0.6	3.2	3.1	3.7	3.0	-1.7	-0.6	0.1	0.8	1.2	1.1
DA	0.4	1.0	0.5	1.3	-1.0	-0.5	-1.6	-0.6	-3.0	-3.4	-3.2	-3.6	-3.8	-0.2
TA	-0.3	-0.5	-0.3	-0.6	-2.2	-2.6	-2.1	-2.5	2.3	2.2	1.9	1.9	1.9	-0.8
QA	0.0	0.0	0.0	0.0	-0.1	-0.1	-0.1	-0.1	0.1	0.1	0.1	0.1	0.1	0.0
Donor ^d														
SD	0.1	0.0	0.1	0.1	-0.5	-0.5	-0.2	0.0	0.2	0.3	0.2	0.3	0.3	1.9
DD	-0.1	0.0	-0.1	-0.1	-5.3	-5.8	-6.0	-5.7	-0.2	-0.3	-0.2	-0.3	-0.3	-1.9
ID					0.1	0.1	0.0	0.0						
IWD					5.9	6.4	6.2	5.7						

^aErrors for solutions are ± 0.1 for NAs, QAs, SDs, and DDs, ± 0.2 for SAs, TAs, ± 0.4 for DAs, and zero otherwise. They are the same at the vapor-water interface but in units of nm^{-2} and are $\pm 0.2 \text{ nm}^{-2}$ for SDs and DDs.

^bNA, SA, DA, TA, and QA are non, single, double, triple, and quadruple acceptors, respectively.

^cUnits are in nm^{-2} .

^dSD and DD are single and double donors to water. ID is a single donor to an ion and IWD is a single donor to an ion and single donor to water.

That water is marginally more tetrahedral around non-polar solutes is well-known and consistent with other findings by various measures.^{34,71–73} That water is less tetrahedral around ions, more so for cations than anions, is again consistent with other findings.^{18,73–77} Less well studied have been the distributions of non-tetrahedral species around solutes. The favoring of SAs around anions necessarily arises because of the overall deficiency of donors brought about by the anion. Similarly, the favoring of TAs around cations arises because of the overall deficiency of acceptors brought about by the cation. For the same reasons, there are more broken HBs around cations than around anions. Having fewer broken HBs around anions is similar to what has been observed in anion-water clusters.⁷⁸ Relating the degree of HB breaking primarily to the sign of the solute's charge differs to other studies that relate it to the ion's size and charge density.^{73,74} Examining that trend further, Table I shows little variation in the fraction of broken HBs with solute size for noble gases and cations while there are even fewer broken HBs for the anions of higher charge density. The difference in these interpretations can be explained because HBs are more distorted near the ions of higher charge density and consequently are more likely to be classified as broken by HB definitions with fixed geometric cut-offs.

At the vapor-water interface, there is a shift to species with fewer HBs, namely SAs and SDs and even NDs (0.01 nm^{-2}) and NAs (0.03 nm^{-2}) at the expense of DAs and more so TAs. Some water molecules would be simultaneously SDs and SAs but we have not examined the joint population of donors and acceptors here. The sizeable presence of broken HBs at the vapor-water interface is consistent with the findings elsewhere for the vapor-water interface^{44,52,79–81} and first observed at the oil-water interface.⁸² The surface density of broken HBs at the vapor-water interface in Table I can be converted into a percentage by approximating the interface as a single water layer having bulk density, giving $10.3 \text{ molecules per nm}^2$; the total number of SDs equals the change of 1.9 SDs plus the 1.6% of SDs in bulk water,⁶⁸ giving $1.9 + 0.16 = 2.1 \text{ SDs per nm}^2$. Together with the amount of NDs, this yields 20% of molecules with a broken HB. This is similar to the 25% from sum-frequency generation,⁴⁴ 21% from simulated spectra,⁸³ and 23% (Ref. 47) and 27% (Ref. 84) from molecular dynamics simulations using HB definitions that are less restrictive than those conventionally used but still containing arbitrary parameters. Equivalently, all these values translate to 10%–14% broken HBs, assuming one broken HB per water molecule. This further validates the accuracy and versatility of the topological HB definition. Incidentally, it was the large number of clearly visible free hydrogens at the vapor-water interface that helped us formulate the topological HB definition rather than the case of bulk water in which free hydrogens are fewer and subtler.⁶⁸ The distance-angle HB definition (Table II) also predicts a substantial breakage of HBs but differs by predicting a greater loss of DAs and the non-negligible presence of NDs. The inaccuracy of the distance-angle definition is clear, first because the NDs that it predicts are believed to be negligible at the vapor-water interface,^{52,81} second because the 10% of broken HBs that it predicts in bulk⁶⁸ is surprisingly

comparable to what is measured experimentally at the much more disruptive vapor-water interface, and third that the percentage of molecules with a broken HB at the vapor-water interface is at least double that of experiment at 47%, comparable to $\approx 50\%$ or more from other works,^{51,52,54} which use overly restrictive HB definitions. This significant discrepancy with experiment may be masked by erroneously equating the percentage of broken HBs to the percentage of molecules with a broken HB; on the contrary, the former is about half the latter, the very factor by which the distance-angle definition overestimates broken HBs at the vapor-water interface.

B. Non-ideal spatial distribution of HB species

This is quantified using radial distribution functions $g_i(r)$ of the HB species and their cumulative spatial non-idealities $\Delta N_i(r)$ calculated using Eqs. (2) and (3), respectively. Both quantities are plotted in Figures 1–4 for all systems. Shown in Figure 5 are these same quantities obtained with the distance-angle HB definition⁶⁹ for representative solutes Ar, F^- , Li^+ , and the vapor-water interface. Only those HB species with non-negligible populations are plotted for clarity. The final values of $\Delta N_i(r)$ at the maximum distance equal by definition the total non-idealities listed in Tables I and II. The plots of $\Delta N_i(r)$ reveal more clearly the deviations than those of $g(r)$ because they quantify accumulated differences and are not scaled down by $1/r^2$. A non-zero slope in $\Delta N_i(r)$ implies a non-ideal contribution of species i at distance r . For noble gases (Figure 1), the enhanced tetrahedrality arises more in the first hydration shell, as seen by the steeper slope of $\Delta N_i(r)$, but is still spread over the whole simulation box. SAs and TAs weakly and alternately decrease relative to each other. Most of this decrease happens in the first hydration shell, with the drop in TAs leading that of SAs. This reflects the well-known occlusion of HBs by non-polar solutes,^{23,24,37,85–89} leading to a slight preference for hydrogens to point away from the solute. The pattern persists in the second, third, and fourth hydration shells, and reaches the box edge. This oscillatory structure with a wavelength similar to the size of a water molecule is evidence that water molecules are unable to cancel exactly the perturbation in HBs induced by the solute. Every hydration shell is perturbed and perturbs the next beyond it. Only in the outer 0.4 nm in the box corners do all species level off towards bulk-like behavior to avoid discontinuities with the periodic images. The slower change here is because there are fewer molecules in the box corners. The maximum non-idealities vary non-trivially for each solute, as do the total non-idealities. These quantities likely depend in a complex way on solute size and interaction energy and on box size and shape. The long-range preference for tetrahedrality around non-polar solutes probably arises because of the mutual destabilization of TAs and SAs. There is a small increase in SDs, most of it in the first hydration shell. These trends contrast with those measured using the distance-angle definition (Figure 5(e)), which shows a long-range decrease in SAs and SDs and only a small decrease in TAs.

Around the anions (Figure 2) at short range, the excess IWDs relative to DDs represent the expected donors point-

FIG. 1. Donor and acceptor radial distribution functions $g_i(r)$ of noble gases (a) Ne, (b) Ar, (c) Kr, and (d) Xe, and non-ideality $\Delta N_i(r)$ of HB species i around (e) Ne, (f) Ar, (g) Kr, and (h) Xe. The coloring is the following: total (grey), SA (aqua), DA (blue), TA (green), SD (red), DD (dark blue). The vertical lines are half the box edge (dotted) and half the box long diagonal (dashed).

ing towards the ion. The other species are closer to their bulk populations, consistent with existing findings that anions have a small effect on water structure.^{18,36,75–77,90–93} However, at longer range there is a clear rise in SAs at the expense of TAs, extending to the box edge where they flatten off as for the non-polar solutes. The rate of change is largest in the water shell with radius equal to half the box edge, the shell with the largest number of water molecules. Evidently, the short-

range polarization induced by a solute on water is undone by many water molecules rather than by only those closer to the solute as is commonly assumed. The more water molecules that share in the perturbation out to longer range, the less perturbed each molecule is from bulk behavior. The biases are similar but not identical for all anions. One other minor observation is that the small population of IDs visible in the $g_i(r)$ plot for F^- becomes a peak of SDs for the larger anions. The

FIG. 2. Donor and acceptor radial distribution functions $g_i(r)$ of anions (a) F^- , (b) Cl^- , (c) Br^- , and (d) I^- , and non-ideality $\Delta N_i(r)$ of HB species i around (e) F^- , (f) Cl^- , (g) Br^- , and (h) I^- . The coloring and vertical lines are as in Figure 1 with the addition of ID (yellow) and IWD (orange).

FIG. 3. Donor and acceptor radial distribution functions $g_i(r)$ of cations (a) Li^+ , (b) Na^+ , (c) K^+ , (d) Rb^+ , and (e) Cs^+ , and non-ideality $\Delta N_i(r)$ of HB species i around (f) Li^+ , (g) Na^+ , (h) K^+ , (i) Rb^+ , and (j) Cs^+ . The coloring and vertical lines are as in Figure 1 with the addition of NA (purple).

decreasing strength of anion-water interactions is the likely cause of this trend. Results using the distance-angle definition (Figure 5(f)) are similar except for the shift from IWDs to IDs as noted earlier, the short-range decrease of SDs, and the long-range decrease of DDs.

Around the cations (Figure 3), all the main acceptor species are very non-ideal in the first hydration shell, consistent with the greater perturbation of cations on water structure than anions.^{18,36,75–77,90–93} NAs and SAs dominate the first hydration shell at the expense of DAs and TAs because of cations' strong attraction for waters' oxygens. Concerning long-range structure, there is a shift from SAs to TAs and SDs, the species having more acceptors. This switching of SAs with distance from more to less together with the presence of NAs help explain the mixed SA populations seen earlier in Table I. The $g_i(r)$ plots show that SAs attain values at long range that are almost identical for all cations. Results using the distance-angle HB definition (Figure 5(c)) are similar

but there are more NAs, DAs, and SDs and fewer SAs and TAs at long range.

At the vapor-water interface (Figure 4), the rise in water density is first dominated by an excess of SDs followed by an excess of SAs, both of which drop back to bulk-like values beyond 0.5 nm. This is accompanied by slow rises in DAs and TAs. NDs have a tiny peak at the Gibbs dividing surface at a similar point to that of SDs. These profiles are similar to those from other works,^{49–51,53} notwithstanding the effects of HB definition discussed earlier. No oscillatory pattern in the HB structure of SAs and TAs appears at the vapor-water interface as it does for non-polar solutes, presumably because the origin of the Gibbs dividing surface is moved around by the roughness of the vapor-water interface as opposed to the well-defined origin for monatomic solutes. After the large perturbation in the first few water layers, water becomes almost bulk-like but is still very slightly tetrahedral. Averaged over the z -span of 2 nm centered in the middle of slab, this amounts

FIG. 4. (a) Donor and acceptor z -coordinate distribution functions $g(z)$ averaged over both vapor-water interfaces. (b) Non-ideality $\Delta N_i(z)$ of HB species i at both vapor-water interfaces. The Gibbs dividing surfaces are marked as vertical dotted lines. The coloring is as in Figure 1.

FIG. 5. Donor and acceptor radial distribution functions $g_i(r)$ of (a) Ar, (b) F^- , (c) Li^+ , and (d) averaged over both vapor-water interfaces using the distance-angle HB definition, and non-ideality $\Delta N_i(r)$ of HB species i around (e) Ar, (f) F^- , (g) Li^+ , and (h) $\Delta N_i(z)$ for both vapor-water interfaces using the distance-angle HB definition. The coloring and vertical lines are as in Figures 1–4, with red also indicating the small ND deviation.

to one extra DA per nm^2 at the expense of SA and TA, or one extra DA in 70 water molecules. A more tetrahedral structure would be expected to have lower density, and the total $g(r)$ is indeed only 0.98 instead of the bulk value of 1 in the central 2 nm span (Figure 4(a)). This is supported elsewhere by similar reduced densities at the vapor-water interface¹⁶ and at the oil-water interface for a range of box-sizes.⁵⁵ More evidence elsewhere for the long-range structuring comes from a small excess in the pressure normal to the surface over the tangential pressure across the middle of the water slab.¹⁶ This suggests that there is a contribution to surface tension, which depends on this pressure difference, even from water in the middle of the slab. The tetrahedrality is probably enhanced for a similar reason as for the non-polar solutes because of the mutual SA-TA destabilization.

The long-range structuring, even for ions, is not large. It is just about detectable in radial distribution functions, which obscure the structuring because of $1/r^2$ dilution. It was easier to notice in the radial distribution functions using the topological HB definition (Figures 2 and 3) than in the plots using the distance-angle definition (Figures 5(a)–5(c)) because the relative variation of SAs and TAs, being so similar, is more telling. We have resolved this difference more distinctly by focusing on the numbers of HBs, considering differences relative to the bulk or donors relative to acceptors, and removing the dilution owing to the $1/r^2$ scaling that spreads the structuring over more molecules at large distances. Our results demonstrate the importance of looking at all water molecules in the simulation box and not only those near the solute as most simulation studies do^{27,35,38–43,77,88,89}

and as most experimental techniques can either detect, or assume.^{18,19,56,94} Simulation studies also have the advantage of being able to study single ions whereas an experiment has to contend with both cations and anions and their cancelling behavior on long-range structure. In salt solutions, surfaces of bulk-like distributions would be expected to lie in between cations and anions because they generate opposite perturbations in the populations of HB species. Surfaces between like-charged ions would be doubly-perturbed. Some related experimental evidence for a short-ranged HB compensation is seen in the x-ray crystal structures of hydrated molecules.^{95,96} Molecules having more acceptors are surrounded by water molecules with more donors while molecules with more donors are surrounded by water molecules with more acceptors.

The presence of long-range structuring around ions agrees with the polarization out to infinite distance in continuum-solvent electrostatic models such as the Born model⁹⁷ and Debye-Huckel theory.⁹ By explaining how ions are preferentially surrounded by their counterions, regardless of their distance apart, the long-range structuring, together with energy which is also long-ranged, likely contributes to the non-ideal square-root dependence on concentration of the activity coefficients,⁹ viscosity,¹⁰ and partial volumes¹¹ for ions at low ionic concentration. In the case of ions, whose entropies of solvation are much more negative,⁹⁸ the presence of a small, long-range entropic contribution to ionic solvation has recently been detected using quasichemical theory.¹⁵ In the case of non-polar solutes, the well-known and contentious decrease in the entropy of hydration of small non-

polar molecules under ambient conditions^{99–101} is seen in our work to have a long-range contribution. As well as contributing to the non-ideality of partial volumes, our findings further suggest why the partial volumes of cations are more negative than those of anions^{3,102} and why water's density around cations is higher than that around anions, as observed by x-ray scattering and diffraction.^{103,104} While an ion's partial volume is dominated by the ion's size and changes in the first hydration shell, our results show how the positive partial volumes of anions would have a small long-range contribution from the deficiency of water-water HBs brought about by the anion accepting donors. The more abundant SAs have lower density than TAs because SAs have fewer HBs in their coordination shell.⁶⁸ Likewise, our results suggest that there would be a long-range contribution to cations' more negative partial volumes owing to the excess of HBs because of the repulsion of donors from the cation. In this case, there are more high-density TAs than low-density SAs. Our explanation for the structure of solutions in terms of the number of topologically defined HBs bypasses the ambiguities inherent in the concepts of structure-making or breaking,^{2,3,77} which may be used to encompass confinement, degree of tetrahedrality, and water-solute and water-water interactions at any distance. It also gives a clearer structural picture than one in terms of local density fluctuations.^{14,103,104}

C. Donor-acceptor biases

The cumulative spatial donor-acceptor bias $\Delta N_{\text{da}}(r)$ calculated by Eq. (4) also quantifies non-ideality in the number of donors or acceptors and implicitly indicates the directionality of HBs. It is plotted for all solutes in Figure 6. $\Delta N_{\text{da}}(r)$ values using both topology and distance-angle HB definitions⁶⁹ are plotted in Figure 7 for water around Ar, Li^+ , and F^- . As expected, large biases are observed for $\Delta N_{\text{da}}(r)$ in the first hydration shells of ions and small ones for noble-gas solutes. The biases grow with distance more rapidly for smaller ions with higher charge densities. However, the extrema are very similar for all solutes of a given charge. Cations blocking water molecules from accepting brings about an excess of

FIG. 6. Donor-acceptor bias $\Delta N_{\text{da}}(r)$ for water around Ne, Ar, Kr, Xe (dark to light green), F^- , Cl^- , Br^- , I^- (dark to light red), and Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ (dark to light blue). The vertical lines are as in Figure 1.

FIG. 7. Donor-acceptor bias $\Delta N_{\text{da}}(r)$ for water around Ar (green) F^- (red) and Li^+ (blue) in the box of 375 water molecules with the topological HB definition (solid), the box of 1200 water molecules with the topological HB definition (dotted-dashed), and the box of 375 water molecules with the distance-angle HB definition (dashed). The vertical lines are as in Figure 1.

7–7.5 donors at the maximum in the cation's first hydration shell. Based on first-shell coordination numbers⁷⁷ of 4.4, 5.8, 6.7, 7.4, and 8.3, first-shell water molecules lose approximately two water-water HBs per water molecule for Li^+ down to one HB per water molecule for Cs^+ . The donating of hydrogens to anions brings about an excess of 6–7 acceptors at the maximum in the anion's second hydration shell, which is slightly smaller than that for cations. Based on first-shell coordination numbers of⁷⁷ 6.1, 6.9, 7.5, and 7.6 and on the populations of IWDs and IDs in Table II, almost all first-shell water molecules around all anions lose approximately one water-water HB, the number being slightly less for larger anions. Beyond the extrema, $\Delta N_{\text{da}}(r)$ decreases slowly to zero, doing so most rapidly in the largest water shell at half the box length, as was seen before for the individual HB species (Figures 2 and 3). $\Delta N_{\text{da}}(r)$ for the noble-gas solutes oscillates slightly above zero on average with values ~ 100 times smaller than for the ions. This matches the weak tendency of hydrogens to point outwards from non-polar solutes.^{23,24,37,85–89} The same small oscillatory behavior in $\Delta N_{\text{da}}(r)$ is also seen for ions in Figure 6 on top of the contribution from the ion's charge. For all solutes, $\Delta N_{\text{da}}(r)$ reaches zero at the furthest water molecule as it must because the number of donor HBs equals the number of acceptor HBs. In all cases, the values using either of the two HB definitions are almost indistinguishable from each other (Figure 7). This further demonstrates that the overall long-range structuring of HBs observed here is not sensitive to the HB definition.

At the vapor-water interface (Figure 8), $\Delta N_{\text{da}}(z)$ detects a tiny deficiency of donors on the vapor side, an excess of donors just within the Gibbs dividing surface, and a comparable deficiency of donors further into the water side. The free hydrogens pointing into the vapor are invisible in $\Delta N_{\text{da}}(z)$ because they are not involved in HBs. No bias is present in the bulk. Similar results are obtained using the distance-angle HB definition, which are also plotted in Figure 8. The main differences using this HB definition are that the peak is smaller and slightly deeper into the interface. The trend in

FIG. 8. Donor-acceptor bias $\Delta N_{da}(r)$ at the vapor-water interface using the topological (solid) and distance-angle (dashed) HB definitions averaged over the two interfaces. The vapor is on the left and the water on the right. The vertical line is as in Figure 4.

$\Delta N_{da}(z)$ indicates that hydrogens in HBs at the surface tend to point towards the water side because that is where more of the water is. This matches the findings from vibrational sum-frequency experiments,^{46,48} electrostatic theory,¹⁰⁵ and molecular dynamics simulations.^{48,79,80,106–108} It also mirrors what is observed for non-polar solutes. This bias in donors pointing to the water side supports the dipolar explanation^{86,87} for the well-known negative charge at interfaces between water and non-polar phases measured by electrophoretic mobility. The study by Vacha *et al.*¹⁰⁹ also reported a plot of acceptors relative to donors. The results were similar to ours except that that work had a larger excess of acceptors on the vapor side and an excess of donors on the water side. We verified that this was due to the different force fields by running a separate simulation of extended simple point charge (SPC/E) water instead of TIP4P/2005 and obtaining almost identical results to theirs (unpublished data). That study found no long-range bias in the numbers of donors and acceptors¹⁰⁹ and neither did a recent vibrational sum-frequency generation study⁴⁷ that probes HB strength or orientation. However, these studies did not assess structuring in HB tetrahedrality as we discussed earlier.

D. Effect of box size

To examine how the long-range perturbations depend on box size, we repeat the calculations for Ar, Li⁺, and F[−] in a larger box of 1200 water molecules. Figure 7 illustrates that the short-range $\Delta N_{da}(r)$ biases in the larger box are almost identical to those in the smaller box. However, the long-range biases return to zero more slowly and extend over the now larger simulation box. This indicates that the long-range structuring extends over the whole box, regardless of its size. The $\Delta N_i(r)$ plots (Supplementary Figure 1) (Ref. 110) illustrate how the extended long-range structuring occurs for each HB species and the $g_i(r)$ plots indicate that 6–7 hydration shells are enclosed in largest water sphere. This behavior further supports the idea that the structuring would continue outwards indefinitely at infinite solute dilution.

E. Effect of charge

To determine the influence of the solute's charge, we artificially vary the charge of sodium from -3 to $+3$, excluding zero, while keeping its Lennard-Jones parameters fixed. Figure 9 shows the resulting plots of $\Delta N_{da}(r)$. The extrema

FIG. 9. Donor-acceptor bias $\Delta N_{da}(r)$ for Na⁺, Na²⁺, and Na³⁺ (light to dark blue) and Na[−], Na^{2−}, and Na^{3−} (light to dark red). The vertical lines are as in Figure 1.

in $\Delta N_{da}(r)$ are seen to increase linearly with charge, reaching ± 13 for the divalent cation and anion, and ± 20 for the trivalent cation and anion. Whereas water molecules in the first hydration shell of Na⁺ lose just over 1 water-water HB, they lose twice as many around divalent ions, and around trivalent ions, the second hydration shell also loses water-water HBs. Intriguingly, the first hydration shell contributes much less to the bias for the trivalent anion than it does for the divalent anion. The accompanying $g_i(r)$ and $\Delta N_i(r)$ plots show the even stronger long-range biases, which compensate for the higher solute charges (Supplementary Figure 2).¹¹⁰ The linear dependence of $\Delta N_{da}(r)$ on solute charge but not on solute size is consistent with the Gauss's law. The electric field that polarizes water in the ion's first-hydration shell scales according to $1/4\pi r^2$ but there are $4\pi r^2$ as many water molecules being polarized, leading to the same total dipolar polarization in the first hydration shell and the same maximum bias in $\Delta N_{da}(r)$ for all solutes of a given charge. It must be noted that these effects for artificial, highly charged ions are qualitative and likely to be affected by molecular polarization and water dissociation, effects not accounted for in the force-field used here. Nevertheless, the results support the notion that specification effects^{2,4,111} for the series of monatomic ions having the same charge magnitude do not occur at long-range because all such ions exert the same long-range influence; however, effects may be long-ranged for ions having different charge magnitudes. This effect may help explain non-additive dynamics observed recently by Tielrooij *et al.*¹² for the aqueous solutions of cations and anions having charges of different size.

IV. CONCLUSIONS

Long-range deviations have been detected in the number of donor and acceptor HBs of water molecules in the molecular dynamics simulations of dilute aqueous solutions of monatomic ions and noble gases. The long-range structuring is observed over the entire simulation box. It is detected using the spatial variation of the numbers of water molecules with different numbers of HBs compared to those in bulk wa-

ter. It manifests itself as an excess of HB species with fewer acceptors around anions, an excess of HB species with more acceptors around cations, and a weak tetrahedral preference around non-polar solutes and at the vapor-water interface. In all cases, the structuring arises in order to compensate for the short-range perturbation of the water's structure by the solutes and it involves all the water molecules in the system in order to reduce the perturbation per water molecule. It is independent of the HB definition, box size, and the solute's Lennard-Jones parameters and its extent depends linearly on the solute's charge. It can explain in structural terms the non-ideality of activity coefficients, viscosities, and partial volumes of ions at dilute concentration and gives new explanations for the entropy of solvation and partial volumes. It appears to have remained hidden from spectroscopic techniques, which are currently unable to resolve water structure spatially in liquids to the level of detail done here, a challenge exacerbated by the small size of the structuring, the radial dilution, low solute concentrations, and opposing effects of anions and cations. Radial dilution is probably the primary reason why the effect has been obscured in previous simulation studies. Long-range structuring of HBs in water is likely to occur for any solute, given that it is observed here for the extreme cases of strongly and weakly interacting solutes and the vapor-water interface. Greater understanding will come from further computational studies and better experimental techniques to characterize structure in water.

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