Chemical Thermodynamics and Thermal Analysis 6 (2022) 100053

Contents lists available at ScienceDirect

Chemical Thermodynamics and Thermal Analysis

journal homepage: www.elsevier.com/locate/ctta

Water structure, properties and some applications – A review

Georgios M. Kontogeorgis*, Andrew Holster, Nomiki Kottaki, Evangelos Tsochantaris, Frederik Topsøe, Jesper Poulsen, Michael Bache, Xiaodong Liang, Nikolaj Sorgenfrei Blom, Johan Kronholm

Center for Energy Resources Engineering, Department of Chemical and Biochemical Engineering, Technical University of Denmark, Building 229, Lyngby 2800, Denmark

ABSTRACT

Water is a fascinating substance with lots of properties not encountered in other compounds. It has been suggested that making use of water's "anomalous" properties can lead to exciting applications in various disciplines e.g. engineering, medicine and physiology. The origin of these anomalous properties is far from clear, with the strong hydrogen bonds of water being only part of the answer. Moreover, water's structure and dynamics are not entirely understood either and new theories have appeared and debated during the 21st century. This review, aiming at a broader/general audience, attempts to review briefly some research trends related to water's structure, properties and applications. New experimental results for the debated phenomena of water bridge and exclusion zone are also presented and discussed. Various explanatory mechanisms for the exclusion zone are reviewed and a new proposal is put forward. A –hopefully- unbiased discussion is presented for both "mainstream" and unconventional theories and trends and future directions are also outlined.

1. Introduction and motivation of this review

"Water is life's matter and matrix, mother and medium. There is no life without water" (Albert Szent-Györgyi, Nobel prize in Physiology or Medicine, 1937).

There is possibly little doubt that water is the most important substance in the world as our blue planet is mainly covered by it and living beings largely consist of water. Numerous books have been written about water [e.g. 1,2], the knowledge about water's structure and properties is immense but is it enough? Are we closer to a more complete understanding?

There are many debates and the two books mentioned [1,2] which we highlight as characteristic examples are no different; they represent two largely opposing views of this debate. The literature about water includes presentation and discussions of a wide range of properties, many of which are anomalous (not encountered in other compounds), and possible link of these properties to water's structure and dynamics. There are numerous theories about water's structure and the discussion has intensified during the 21st century, with hopes we will be arriving to some clarification. Still, even the same spectroscopic or other experimental results appear sometimes to be read or interpreted differently by different research groups.

But, in addition, there are many unexplained experiments, controversial theories and black box inventions e.g. for avoiding scaling or biofilm buildup on diverse installations. Some of these (experiments, theories and inventions) claim or introduce the term "structured water" or maybe that water can exist in a liquid crystalline (coherent) state of matter.

There is a feeling of sensation in many researchers that, in the years to come, great scientific discoveries and novel technological avenues could emerge from a deeper understanding of water. The implications from a greater understanding and link between water's structure and properties can be significant for engineering, chemistry, biology and medicine. Water is the universal solvent, present in all biological processes and reactions. It is the background matrix for all living processes. It is very stable in our environment, and harmless in our bodies. As such it appears inert and passive. But in fact it is a most active and vital participant in the world of molecular interactions.

Our group has been involved in the field of water science and engineering for over 20 years, covering a range of disciplines (thermodynamics, engineering applications, biology and medicine) and approaches (macroscopic modeling, simulation, experiments). We have observed some of the interesting phenomena and investigated some of the important (thermodynamic and other) theories that can be used to describe and explain water. We have witnessed and participated in some of the debates.

The key to describing these water phenomena at a fundamental level, empirically and experimentally, in the first place is through the chemical-thermodynamic analysis. The water molecule is so tiny and mobile in the liquid state that behavior can only be measured and described, first of all, in terms of the bulk properties of the liquid, including spectroscopic absorption rates, NMR measurements, etc. We cannot make images of individual water molecules or their interactions or their bonds in the liquid state. The thermodynamics is based in turn on underlying physico-chemical properties and bonding structures, and more generally potential fields present. Models start from semi-classical

---

* Corresponding author.
E-mail addresses: gk@kt.dtu.dk (G.M. Kontogeorgis), johan@kronholmdevelopment.se (J. Kronholm).

https://doi.org/10.1016/j.ctta.2022.100053
Received 13 November 2021; Received in revised form 22 February 2022; Accepted 18 March 2022

descriptions, e.g. with classical electrostatic fields, and equilibrium states, and extend to dynamic states, inclusion of solutes and ions, surface interactions, electromagnetic (EM) interactions, etc. Water molecules have many states of internal vibration and stretching, which are described by *basic quantum mechanics*. They form complex hydration structures in the presence of larger ions or colloids.

Most modeling for chemical-thermodynamic properties is based on semi-classical and non-relativistic approximations, which can be perfectly accurate, but ultimately models may have to extend to QED (relativistic quantum field theory). This was required to explain the van der Waals forces, the last key attractive-repulsive force not explained by ionic or covalent bonds but by a quantum field interaction (a Casimir type effect). This is essential to explain condensed state physics. QED is considered by some as an important fundamental description in physics at present.

Different types of experimental applications assume different types of models, and there are many specialized developments of techniques, for measurement and interpretation of data, done within different modeling frameworks. Opinions over appropriate types of models regularly come into conflict. There are questions about the effective types of atomic or thermodynamic models, and realistic types of explanatory models for processes.

Perhaps the striking aspect of this field of water chemistry as a whole is how many distinct anomalous phenomena, across different scales and processes, it has come to encompass. This reflects the range of anomalous properties of water. The subject has developed many specialized branches of study, e.g. high and low temp-pressure-density domains, strong and weak EM fields, ionic and solution effects, spectroscopic and vibrational analysis, micro-structure formation at interfaces, unusual time evolution of molecular properties, EM and hydrogen bonded structures, Taylor cones, the floating water bridge, the Mpemba effect, Exclusion Zone (EZ) structures, and others.

These topics have become specialized areas, developing their own traditions as sub-disciplines, with dozens or up to hundreds of publications, partly in parallel but isolated from others while being about similar topics. This is seen in alternative selections of primary references, and background studies and theoretical frameworks. But it is evident they all depend on and describe common mechanisms in water, and we try to review the basis for this in thermodynamics first, and then in several debated areas of research.

Several of the debates related to water's structure, properties and applications are rather "heated" resulting, in some cases, even in specialized - dedicated journals and conferences, depending on the point of view. Several of the reviews in the literature are, despite being very interesting, often rather limited, covering one "side" of the theories related to water's structure and properties.

As water itself is known for the phenomenon of water bridge (see Fig. 1), also discussed later in this review, we believe that a bold, open-minded and transdisciplinary approach bridging different views and methodologies is needed when dealing with water. We hope that this review will be a small effort in this direction. We focus on the positive aspects of the various theories and studies put forward. We hope that it may be of interest to a broader scientific and engineering audience and can contribute to further discussions and research.

This review is structured as follows. Section 2 discusses the extraordinary and sometimes anomalous properties of water from thermodynamic and surface science points of view, as well as the two-state theory of water and peculiar applications of water properties. Section 3 presents water interactions with hydrophobic and ionic compounds. Sections 4 and 5 discuss the phenomena of water bridge and exclusion zone, including various theories for the explanation of the latter, including some of our own experiments, before a final conclusion section. This is a long review, albeit short considering the extensive literature of water research. It is written in such a way that the sections can be read independently.

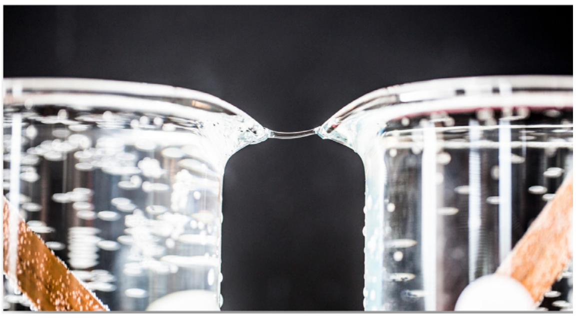

Fig. 1. The floating water bridge. This term indicates the "stiff" water structure adopted by water when high voltage (ca. 15,000 V DC) is passed across two beakers containing distilled water. Water appears to form a bridge between the two beakers and conducts current. The phenomenon is well-known and the experiment was replicated at DTU Chemical Engineering (first time April 11, 2017), but the explanation is far from clear, as can be read here: https://en.wikipedia.org/wiki/Water_thread_experiment.

2. The unusual or anomalous properties of water – the established facts

Anomalous here refers to properties that do not fit with our current models, or cannot be fully explained; or that are very different to the properties of comparable substances.

2.1. Water anomalous properties and thermodynamics

Water is a unique substance. Two thirds of the Earth are covered by water and our own cells contain two-thirds water by volume. While thousands of books and articles have been written about water, it does feel we still know so little about it. As Philip Ball, consultant of *Nature*, has once said: "No one really understands water. It's still a mystery" [3].

Philip Ball (in his 2011 talk) has illustrated the key role of water in biology, as not the "black" background (sometimes used for portraying water), but as the molecule which acts as a plasticizer giving to the protein molecules the flexibility to hold their shape and do their job. As he puts it: "Water is not life's matrix alone, it is a biomolecule in its own right, that interacts with proteins, nucleic acids and membranes".

Water has over 50 anomalous chemical-physical properties; no other substance behaves like this. These properties have important implications for engineering, chemistry, biology and medicine. Yet, so far water research is full of contradictory results. Professor Chaplin has, over many years, maintained a web-site which provided an excellent overview of these "anomalous" water properties (https://water.lsbu.ac.uk/water/water_anomalies.html).

While there are at least partial explanations for most properties, they are not at all fully understood.

Excellent reviews and extensive experimental data of water properties as function of temperature and pressure, with emphasis on the anomalous behaviors have been presented by Mallamace et al. [4,5], Debenedetti [6] as well as by Holten et al. [7].

2.1.1. Characteristic thermodynamic anomalies of water

Perhaps the first and most anomalous property of liquid water could be said to be its liquidity at room temperature. It has surprisingly high melting and boiling points - by rights it should be a gas – but the tiny water molecule sticks to itself very strongly. Among the most characteristic anomalous properties of water are the maximum of density at 4 °C and the high values of heat capacity as well as its minimum with respect to temperature at 35 °C, as shown in Figs. 2a,b.

The density maximum has a role in the floating of ice and the large heat capacity values for stabilizing Earth's climate. In reality, the fact that liquid water is denser than ice is responsible for the floating of ice.

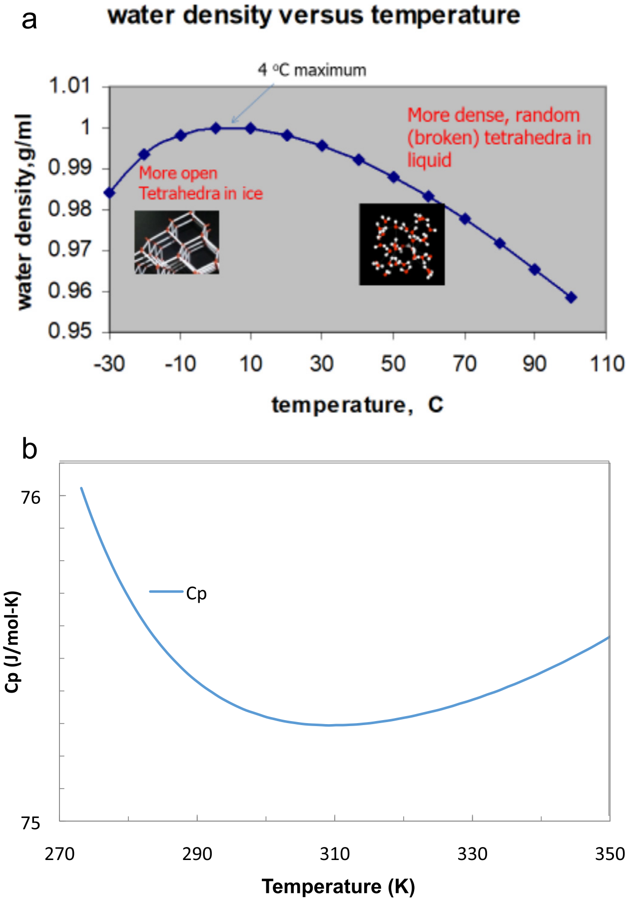

Fig. 2. (a). The Water density as a function of temperature illustrating the maximum at 4 °C. (b). The water heat capacity as function of temperature. The minimum is at 35 °C.

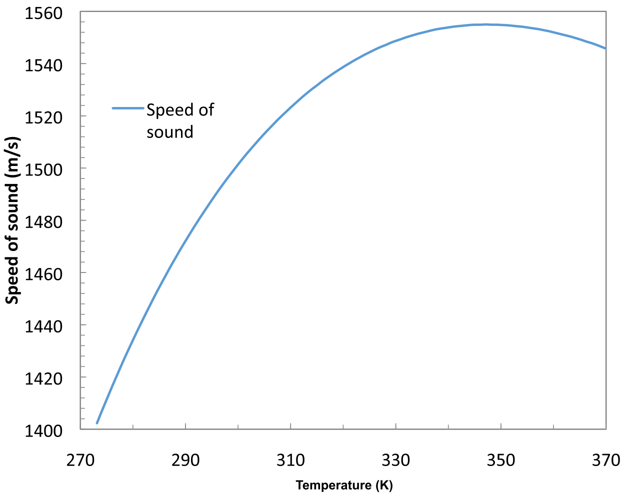

Fig. 3. The water speed of sound as function of temperature.

The values of water's heat of fusion (5.98 kJ/mol) being only 15% of its enthalpy of vaporization (40.5 kJ/mol) indicate that much of water's structure is retained in the liquid state. The standard view is that water has approximately 3.5 hydrogen bonds/molecule in the liquid state (around 5 nearest neighbors) compared to four in the ice. This is currently debated, as explained later. Water has both high values of dipole moment and dielectric constant. The dipole moment often reported in vacuum (1.855 D) is lower than what is expected to be for liquid water (2.4–2.6 D).

The surface tension of water (72.8 mN/m at room temperature) is much higher than any other liquid of similar molecular weight. Water has, moreover, a very high solubility parameter but also a very low co-volume and free volume, considering the size of the molecule. These parameter values indicate strong intermolecular forces in bulk liquid water and these parameters are used extensively in thermodynamic models for describing various thermodynamic properties [8].

There are many more anomalous properties with minima or maxima against the temperature, which we do not see in other compounds e.g. the isothermal compressibility has a minimum at 46 °C and the speed of sound has also a maximum, as shown in Fig. 3.

In the references mentioned earlier [4–7] where extensive data are presented for the properties of water, both the temperature and pressure dependency of the various properties are discussed. Many interesting observations can be made. First of all, the pressure has a significant effect e.g. the density maximum is pressure-dependent and disappears for pressures higher than about 1.8kbar (cross-over pressure). The density-temperature curvature changes from negative to positive as pressure increases. On the other hand, the isothermal compressibility shows the same minimum, at T^*=315 K, at all the reported pressures. Almost the same minimum is observed for the heat capacity, but now this is strongly pressure dependent. Moreover, when plotting the thermal expansion coefficient of water over the entire temperature and pressure range, it can be seen that all curves cross again at the same T^* value. According to Mallamace et al. [4,5], this T^* can have a special thermodynamic role. As the authors phrase it [4] "T^* may be the onset temperature of the hydrogen bonding clustering, the magic point at which liquid water becomes a complex material" and "all indicate that T^* plays a primary role in the physics of water and is the source of its anomalies". Possibly, as the authors imply, the onset of the low-density liquid and hydrogen bonding network organized in a tetrahedral structure occurs near this characteristic T^* temperature, while in the phase regions above T^* (and for pressures higher than the cross-over pressure), liquid water behaves like a normal simple fluid. The same conclusions on the role and importance of T^* and its connection to water's ordered hydrogen bonding structures is obtained by the authors [4,5] by analyzing transport properties such as self-diffusion coefficient data.

As implied in the aforementioned text, the dominant explanation for many of water's special or anomalous properties are its extensive hydrogen bonding, often considered to be present in tetrahedral or similar advanced extensive structures (see discussion below, as the water structure is a debated topic). The hydrogen bonds are today often considered to be of electrostatic nature [9,10]. However, according to a recent mini-review [10], this electrostatic interpretation cannot account for all experimental and theoretical observations. It is discussed that hydrogen bonds should have a complex nature, where the energy of the bond consists of multiple components, such as steric repulsion and cooperativity effects [10]. These observations has led the IUPAC task force and others to advice to change the definition in the IUPAC gold book [9].

It is encouraging to observe that we have today in applied thermodynamics, developed largely over the last 40 or so years, advanced thermodynamic models which explicitly account for hydrogen bonding and other association phenomena (e.g. see [8,11–13] for some pertinent reviews). The capabilities and limitations of these models for water and its mixtures will be discussed later. It is important to mention that the need for explicitly account of association was known for more than 100 years, as professor van der Waals knew, clearly mentioned in his (1910) Nobel prize speech:

> *"In fact, bluntly speaking, the result would be that an equation of state compatible with experimental data is totally impossible. No such equation*

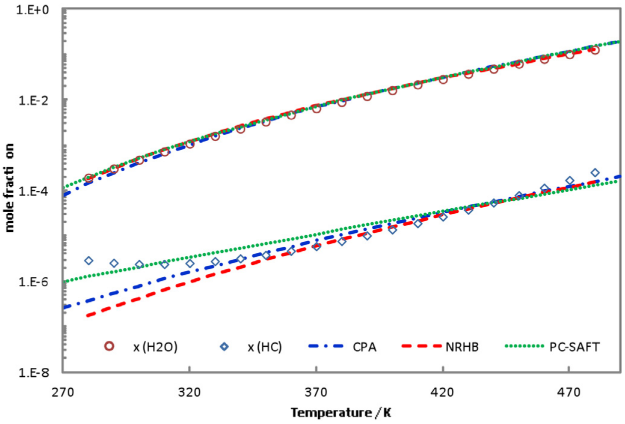

Fig. 4. Liquid-liquid equilibria of water-hexane with three thermodynamic models (CPA, PC-SAFT and NRHB). From Liang, et al. [27]. All models use a single adjustable parameter. Reproduced with permission from [27]. Copyright 2016 Elsevier.

> *is possible, unless something is added, namely that the molecules associate to form larger complexes. I have termed it pseudo-association to differentiate it from the association which is of chemical origin. What is the origin of this complex formation, this pseudo association?"*

Today we recognize that the origin of this association is hydrogen bonding and related acid-base interactions.

Many compounds have hydrogen bonds but water's extended hydrogen bonding structures are special. They may be, according to a recent study [14], responsible even for the explanation of the so-called Mpemba effect, a temperature-dependent effect, which is the process according to which hot water can freeze faster than cold water. For this effect, however, have been proposed several alternative explanations, with more factors being recognized in recent years, e.g. including evaporation, temperature gradients, convection currents, ice formation and seeding, impurities and dissolved gasses, molecular bonding and H-bonded structures.

2.1.2. *Thermodynamic association models*

Very characteristic maxima and minima are seen in many more thermodynamic properties of water as function of temperature also for mixtures, for example the minimum hydrocarbon solubility in water at room temperature, which is sometimes related to the well-known hydrophobic effect, see Fig. 4. This figure shows both experimental data, where the characteristic minimum is observed, and three thermodynamic models, which cannot represent this minimum, despite giving an overall good agreement with the data over an extensive temperature range. We have today, as mentioned, in thermodynamics advanced thermodynamic models (the often called "association models") and the three ones shown in Fig. 4 are among the best available (but many more such "association models" provide similar results). These models, based on statistical thermodynamics, can represent very well (various thermodynamic properties for) hydrogen bonding systems, as they incorporate a pre-defined hydrogen bonding structure. In the case of water, all three models shown in Fig. 4 make use of an association scheme which corresponds to the (traditionally accepted to be correct) tetrahedral structure. None of the models can represent the minimum in hydrocarbon solubility at low temperatures, unless temperature-dependent parameters are used. Wu and Prausnitz [15] attribute this problem to so-called entropy-induced hydrophobic effect, according to which the extent of hydrogen bonding in a water-hydrocarbon mixture is larger than in pure water. These authors mention that the inability of even the most advanced association theories to account for this effect is the origin of the poor representation of the phase behavior at low temperatures where this phenomenon is more pronounced. We will discuss the –much debated-hydrophobic effect later in this review.

Moreover, as recently shown [16], none of these advanced thermodynamic models represent any of the anomalous properties of pure water either e.g. maximum of density or maximum of speed of sound or minimum of heat capacity with respect to temperature.

Actually, there are many more association models, some of them accounting for extra effects like dipolar interactions and hydrogen-bonding co-operativity but even these models have very limited success in representing water's anomalous properties (for pure water or mixtures), see Ref. [16] for a recent discussion. In some cases [17] association models have been developed accounting simultaneously with extra terms for dipolar interactions and hydrogen bonding effects of water, but again this has not been very successful, especially for phase equilibria for mixtures. In other cases, some of the association models [18] with suitable parameterization can be shown to represent some of the anomalous properties of water e.g. the heat capacity minimum, with the remaining anomalous properties not been captured. Capturing several anomalous properties of water at the same time with the same thermodynamic model and parameters appear to be something that is not yet accomplished. However, we should mention at this stage the very extensive and recent work of Bennett Marshall published in a series of recent publications [19–26]. In these works, Marshall has extended the Wertheim perturbation theory (of the SAFT model) in various ways (second order contributions, co-operativity, changes in the fundamentals, etc.). He has applied the diverse approaches to water (as well as water-alkanes phase equilibria) including special emphasis on water anomalous properties. None of the approaches represent all properties and anomalous behaviors of water but some of the approaches can capture, at least qualitatively, several of the anomalous behaviors especially for the heat capacity and the isothermal compressibility. Some can also represent well the monomer fraction data, discussed next. None of the approaches can capture the minimum in the hydrocarbon solubility. All these very recent studies by Marshall consider diverse approaches and have not been consolidated yet, neither has it been determined what is the best approach, but these are promising results.

Association models like those shown in Fig. 4 include explicit terms and parameters for the hydrogen bonding. Many of these models are reviewed in literature [8,11-13]. One of the parameters included in these models is the association energy. For water, an experimental value has been reported [28] equal to 1813 K. Quantum chemistry calculations give a similar value [29] (1649 K). Kontogeorgis and Folas [8] present (Table 13.2 of the book) association values for water for almost 30 association models with various choices for association schemes. The reported association values in the various models are, in almost all cases, in the range 1200–2200 K. Overall the agreement is rather satisfactory considering that the association parameter of these models is fitted together with the remaining parameters of the models to experimental data for other properties (vapor pressure and liquid density). Most of the approaches in literature employ either the so-called three-site or four-site (tetrahedral) association scheme, and a consensus appears that the latter (four-site) is the best when a wider range of properties is considered, including mixture phase behavior. This is the standard or conventional point of view, which is in agreement with many experimental and simulation studies [30–39], which indicate numbers around 3.5–3.6 hydrogen bonds per water molecule. Although this issue is not entirely settled as yet, so much evidence would indicate that some consensus appears to have been reached. This is not entirely the case. Several of these references e.g. [34–37] provide extensive data for the number of hydrogen bonds per water molecule as summarized from a wide range of literature sources, including direct measurements (NMR, X-ray diffraction, IR, etc.) and molecular simulation. The agreement is that the degree of hydrogen bonding decreases with increasing temperature, but on the actual values, even at room temperature, there are large disagreements. We see a range between 2 and 4 for the degree of hydrogen bonding at room temperature, with values around 3.3–3.5 proposed by many (this

Table 1

Hydrogen bonding degrees and numbers of hydrogen bonds according to the studies of Kalinichev, Gorbaty and co-workers [39,40]. The degree of hydrogen bonding is calculated from the equation provided by these authors which describes diverse data in the region 280–800K: $\chi = (-8.68 \cdot 10^{-4})T + 0.851$ The number of hydrogen bonds per water molecule n_{HB} is related to the degree of hydrogen bonding via: $4\chi = n_{HB}$. Finally, number of hydrogen bonds and SAFT-theory "site" fractions are connected as follows: $n_{HB} = 4(1 - X_A)$. The limiting values of all parameters are included for comparison purposes.

Temperature °C/K	Degree of hydrogen bonding [39,40]	Number of hydrogen bonds	Site fraction X_A
0 (273 K)	0.614	2.456	0.386
20 (298 K)	0.592	2.368	0.408
100 (373 K)	0.527	2.108	0.473
373 (647 K)	0.289	1.156	0.711
	1	4	0
	0	0	1

is the standard view) e.g. the group of Saykaly and co-workers. Many others show hydrogen bonding number values around 2.2, such as those proposed by the groups of Nilsson-Pettersson and others pioneering the two-state water picture, which we discuss in the next section. Both in Refs. [36,38] is proposed the hypothesis that if we look alone at the strong hydrogen bonds, then the actual numbers are closer to those proposed by Nilsson-Pettersson, but, as mentioned, there is no consensus on this topic as yet. As can be understood, the number of hydrogen bonds is closely related to the actual structure of water molecules and how this changes with temperature, pressure and other parameters. We return to this in Section 2.2, where we discuss the two-state theory.

At this stage it is of particular importance to mention the works of Andrey Kalinichev and Yury Gorbaty, two pioneers in the field. Some of their works are presented in Refs. [39–44]. They have carried out extensive experimental and simulation studies for water, where they mostly focused on supercritical water but they do present hydrogen bonding data also for liquid water. They have presented and interpreted their data as degrees of hydrogen bonding, number of hydrogen bonding, monomer fractions and cluster distributions. Table 1 includes data obtained or inspired from their studies. They have emphasized, on one hand, that hydrogen bonds do not disappear even for supercritical water (despite conclusions from previous studies, see discussion in [45]), but their degrees of hydrogen bonding, even at liquid water, are rather low. Of particular relevance, Gorbaty and Demianets [41] mention that we have about 2.4 molecules at distance 2.8 Å and 2 molecules at 3.3 Å i.e. 0.6 of total number of molecules in liquid water can be simultaneously involved in strong hydrogen bonds. At 3.3 Å they say that features of hydrogen bonds are essentially lost. In this sense, they use the concept of strong hydrogen bonds, as discussed earlier, although they have not particularly pursued this line of research in subsequent studies. For example in Ref. [43] they refer to liquid water over the whole pressure-range having 3.2 hydrogen bonds, without special discussion of strong and weak hydrogen bonds.

Returning to the results shown in Fig. 4, there are several unsettling issues. The first one is that we cannot identify the best theory. The three association models shown in Fig. 4 treat hydrogen bonding in very similar ways but the remaining part of the models (physical forces, etc.) are very different and these models are based on different physical principles (perturbation, quasi-chemical). We have noticed that when such models are developed in the same/similar ways (same number of adjustable parameters, association schemes - input data, etc.), then very small differences are seen between the various approaches, at least when we focus on non-polymeric/non-electrolyte mixtures and only phase behavior. Thus, "fundamentally different" models perform very similarly in very many cases including water-alkanes and one wonders "where is the theory?" Or even worse "is there any theory at all?", if we wish to take a more critical point of view. As a good friend and colleague, the late Michael L. Michelsen once said to the first author: "… which should be a severe warning that our gains are due to the additional flexibility! A number of fundamentally different models are equally good. Since they cannot all be right, this is somewhat scary, as it indicates that flexibility, not fundamentals, are the cause!"

Another point of caution is that most of these models neglect the dipole-dipole interactions of water molecules and only account for the hydrogen bonding. This is partially understood. Hydrogen bonding is a stronger and more long-range interaction compared to dipole-dipole interactions. But the problem is more complex. Attempts with some of these models to account for both dipolar interactions and hydrogen bonding in aqueous systems have not been very successful, as shown by Kleiner and Sadowski [17]. It has been necessary for these researchers to effectively "turn-off" the polar term of water when using such advanced theories e.g. for modeling water-acetone and similar complex systems. Other aqueous systems with acids like acetic acid or benzoic acid are very complex and we are far from being able to understand how we can accurately represent their phase behavior. Once again, while discussing such problems with professor Michelsen, his view was that much of the success of even the most advanced thermodynamic models can be attributed to good parameterization and an overall successful representation of the underlying physics but it is not clear how much "deeper understanding" these models can provide.

In connection to what just said, a final point of caution, often considered a curse of thermodynamics, is the adjustable parameters. The results shown in Fig. 4 are with temperature-independent parameters and very similar results are obtained even in the entirely predictive form, i.e. without using any adjustable parameters. This is a fair comparison, maintaining some rigor and theory, and in this way no solubility minimum is captured, as can be seen, so this special characteristic of water-hydrocarbon liquid-liquid equilibria is not reproduced. If a temperature-dependent interaction parameter is used, the minimum can be captured, as can be seen in Fig. 5 for one of the models. The other models will perform similarly. It has also been shown [46] that advanced composition- and temperature-dependent mixing rules implemented in thermodynamic models also can "force" a representation of the minimum of the hydrocarbon solubility in water. This is no miracle (although it is a good result), and it does not add too much in the theoretical validation and assessment of the models. Capturing the anomaly of the solubility minimum in a predictive way remains an issue!

Another property which most thermodynamic models have difficulty in capturing is the monomer fraction, which can be obtained from spectroscopic measurements e.g. IR or NMR. This is seen in Fig. 6 where the three models mentioned before are compared against the data of Luck [28], molecular simulation data [47] and the dielectric constant theory by Maribo-Mogensen et al. [48]. It is tempting to conclude that Luck's data are wrong as all models/other data/theories disagree.

Liang et al. [27] showed that there is some scatter in experimental water monomer fraction data from literature (1980–1997) from different sources and experimental methods (both IR and X-ray scattering) but there is qualitatively acceptable agreement. Recent monomer fraction data from Mallamace et al. [49] (see discussion by Liang et al. [27]) show even higher monomer fractions for water (fewer hydrogen-

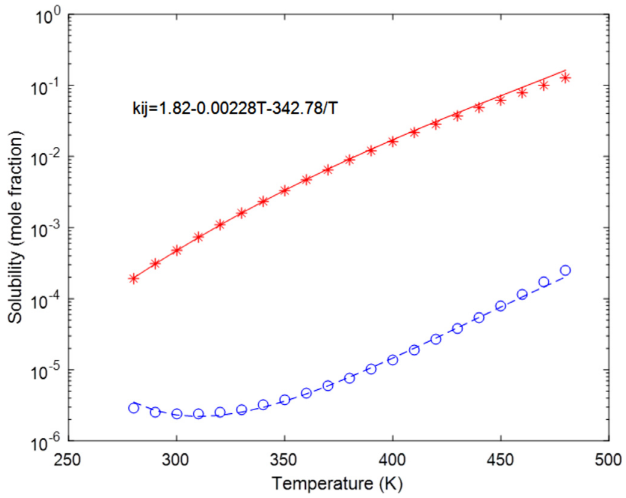

Fig. 5. Liquid-liquid equilibria of water-hexane with the CPA thermodynamic model using a temperature dependent interaction parameter. The other models shown in Fig. 4 are expected to show the same behavior using temperature-dependent interaction parameters. We can see that the minimum solubility of the hydrocarbon in water is accurately reproduced, but at the cost of using adjustable parameters.

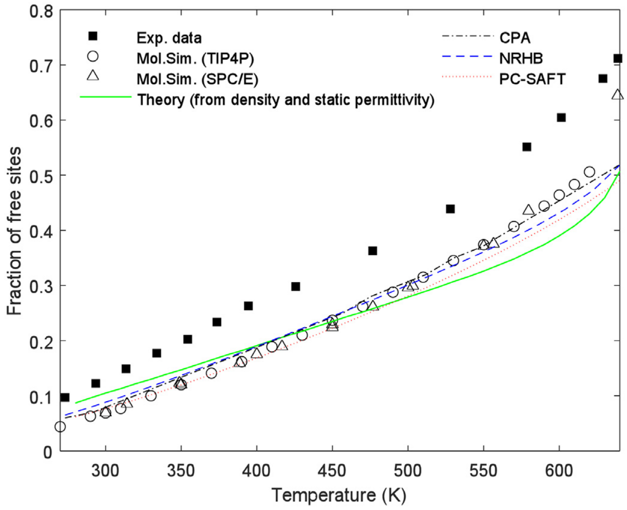

Fig. 6. Free site fraction (free OH groups) of saturated water as a function of temperature using thermodynamic models (CPA, PC-SAFT, NRHB), experimental data, a new theory and recent molecular simulation data. Water is assumed to have a tetrahedral structure with all models. All theories predict more hydrogen bonding than the experimental data. Modified from Liang et al. [27]. Reproduced with permission from [27]. Copyright 2016 Elsevier.

bonded water molecules) compared to Luck and the other sources, indicating thus that there is even further disagreement compared to the thermodynamic models. There are more modeling studies in literature using Luck's experimental data as comparison [34,35,50–55], with varying degrees of success. The role of monomer fraction data in helping or validating association models is discussed in some of these studies [34,55]. In some cases, models were shown to provide good agreement against Luck's data for water at the cost of obtaining accurate representation of other properties such as vapor pressures, liquid densities and most importantly phase behavior for mixtures [56]. It is especially the latter that is the most significant problem. Indeed, as shown in literature [54,56], the "best" model parameters for representing the experimental monomer fraction data for water result to poor representation of liquid-liquid equilibria for water-alkanes, in other words we cannot represent the data and properties shown in both Figs. 4 and 6 with the same advanced thermodynamic model, assuming the four-site (tetrahedral) structure for water. We have arrived to the same conclusion with all three models shown in Figs. 4 and 6, and with others, under the same conditions. Recent efforts to include "additional" effects in some of the association models e.g. account explicitly and separately for the dipolar interactions and hydrogen bonding of water or water's hydrogen bonding co-operativity have not been more successful in representing simultaneously both monomer fraction data of water and phase behavior (liquid-liquid equilibria) with alkanes (with the exception of the very recent works of Marshall [19–26] which show some promise but need much more work and investigation).

We should, however, emphasize that those advanced association theories available today in modern thermodynamics perform overall very well in representing the phase behavior of even complex and multicomponent aqueous systems, containing a wide range of other compounds [8,11–13]. It is when we look at the "details" that the problems become apparent. And by "details", we mean a simultaneous representation of the phase behavior and the extraordinary anomalous properties of water like the density maximum, the heat capacity minimum, the maximum of speed of sound, and of course also the hydrogen bonding degree, as represented by the monomer fraction data.

A common characteristic of these association theories is that when a specific association scheme is assumed e.g. "tetrahedral", then the models do predict a distribution of clusters e.g. for water in monomers, one-, two-, three- and four-bonded (tetrahedral) ones. The models have not been extensively tested against cluster distribution data from simulation and other studies [49,57,58], where water molecules in a mixture may consist of monomers, dimers, trimers, and tetrahedral or, in other studies, where water molecules data are provided simply as monomers, tetrahedral and partially hydrogen bonding molecules. These distributions depend strongly on temperature and are not identical in the various studies. Moreover, in many of these studies, the majority of water molecules are not in tetrahedral structure, unless we are at very low temperatures, as discussed further in Section 2.2, and this would be in disagreement with the dominant tetrahedral structure typically assumed for water in association theories.

In conclusion, we observe a lack of consensus on how water should be modelled, what is the correct hydrogen bonding structure and even, as mentioned, uncertainty on water's degree of hydrogen bonding at various temperatures. A recent discussion on all these aspects is provided in Ref. [16].

On the other hand, the understanding of water anomalous properties can be crucial also in practical applications. As Marcia Barbosa [59] explained, for example, the so-called "diffusion" anomaly (easier mobility of water molecules when there are many) can result in designing better desalination processes. This can be done using nanotubes where water molecules flow faster, while salt does not like nanotubes, thus nanotubes can be used as filter for cleaning water (or aquaporins). And this is a major application related to the better understanding of water properties. "Provide access to clean water" has been identified by the US Academy of Engineering (http://www.engineeringchallenges.org/cms/challenges.aspx) as one of the 14 challenges of engineering in the 21st century.

2.2. The water structure and the two-state theory

Despite the above reservations on the quality and interpretation of water's monomer fraction data, results like those shown in Figs. 4 and 6 and others can make us wonder whether there is something more fundamentally wrong with *all* association theories. Could it be that the predominant in the classical sense tetrahedral structure of water, input to our theories, is not the answer? Indeed, what is the correct water structure and how it is linked to theories has been a debate for 100 years as

Pettersson et al. [60] have written in a recent review. For almost a century, there have been discussions on whether or not liquid water consists of a structured and a non- or less-structured phase. Already in 1892, Wilhelm Röntgen theorized that water is actually a two-state system consisting of a bi-phasic liquid [61]. And several others, over the years, have indicated that water molecules exist in two or more "structures" and with a distribution of diverse hydrogen-bonding formations (e.g. Stillinger [57] in his Science paper – mostly 2 and 3 sites and Franck [58], also Henry Armstrong in 1920s [62], Oleg Samoilov in 1940s [63] and Wilse Robinson et al. in 2000 [64]). In 1970 Franck [58] meant that the two-state model for water is the answer to many of its anomalous properties. He provided three approaches to explain the maximum of density, but he concluded that the two distinguishable species theory (low-energy and high-energy, as he called them) provides an explanation for both the density anomaly and the remarkably high heat capacity of water. He emphasizes that the two states have sizable density differences (several tenths of a gram/cm^3) and he concludes: "when all of the data are taken into account, therefore, the balance of probability seems to have swung to the side of the two-species concept". Both in Frank's paper [58] and several other studies [65–68] are extensive discussions of the much studied Raman spectra of water. The Raman spectra of water have been studied extensively in literature and over wide ranges of temperature and pressure. There is little doubt, see e.g. Ref. [65], that the Raman spectra of water have a complex structure with very broad peaks and shapes which can be approximated with four or five Guassian-shaped constituents (two main and 2–3 minor ones), and it is rather surprising that the exact number of peaks is not precisely known. Still, as shown in many studies [66–68] where water Raman spectra are plotted over a wide temperature range, an isosbectic point appears (where the spectra at different temperatures intersect at a single point). The presence of such a point supports (without entirely proving) the two-state water model.

So, there was plentiful evidence of the two-state water hypothesis during the 20th century. Nevertheless, most of these earlier studies appear to have been forgotten in the meantime.

But it is indeed the group led by the two researchers mentioned in the start of this section (Pettersson and Nilsson) and others [69] who have revolutionized over the recent years the idea that water is best described as a two-state model where most molecules are in the form of rings or chains [60,70–73], and only a smaller portion is tetrahedral. According to them, water is a two-state liquid, having so-called low-density (LDL) and high-density regions (HDL), and actually most of water molecules are in the form of rings or chains (HDL) and only a smaller percentage (15–20% depending on temperature) in tetrahedral form (LDL). A more detailed proposal for the structure of high-density and low-density water has been recently proposed by Camisasca et al. [74]. The HDL structure, according to these authors, implies water molecules forming chains, while in their proposed LDL structure, water molecules have a tetrahedral hydrogen bonding and they are organized in fused dodecahedra.

In the recent years, mechanistic equation of state models using simple entropic considerations and the two-state concept have been proposed for water by Holten–Anisimov [75–77] and used also by others [78,79]. These models are shown to reproduce many of the anomalous properties of pure water (using a rather large number of adjustable parameters). These equations of state also represent the LDL water fraction as function of temperature in qualitative agreement to the data from Pettersson-Nilsson and co-workers as well as earlier LDL data by Mallamace et al. [49]. It is important to note that the Holten-Anisimov model does not assume any specific water structure for the two implied structures. We discuss further the Holten-Anisimov model in Section 2.3.

Nilsson, Pettersson and co-workers have also demonstrated the transition between the two liquid states of water, a phenomenon which could be responsible for a second critical point in water [71,73]. Nilsson and Pettersson have stated that water is, in essence, a mixture of two liquids in a complex relationship, and they have used a wide range of advanced spectroscopic techniques. In Washington Post (2017; article by Ben Guarino) they have stated: "You won't notice it with a cup of tea, but liquid water can flip between high and low densities". And in the same context they said "if we hypothetically do such a simple thing as to pour the different types of liquid water into a cup, there would be a huge effect. The two liquids would separate as oil and water with an interface in-between. The difference in density is 25%, which is huge". This illustrates very well the presence of the two rather different states in water. The same group of authors [80] have presented experimental evidence that the extreme differences seen in the hydrogen bonding environment in the deeply super-cooled region remain in bulk water even at conditions ranging from ambient up to close to the boiling point. They conclude that, based on their experimental data, the density difference contrast seen in Small-angle X-ray scattering is due to fluctuations between tetrahedral-like and hydrogen-bonded distorted structures related to, respectively, low and high density water. The same authors [81] estimate a 2:1 ratio between distorted and tetrahedral species at room temperature.

Other research groups (e.g. Woutersen et al. [82]) had earlier provided additional evidence for two-component water structure using femtosecond IR spectroscopy, and there is further recent experimental observation of the liquid-liquid transition in bulk supercooled water under pressure by Nilsson and co-workers [73]. Some groups [64] have also explained some properties of water, like the anomalous temperature dependency of the refractive index (with a maximum around 0 °C), using a two-state description of water.

The two-state theory has been popularized in the press [83], but it is still a heavily debated topic with numerous papers in *Nature* and *Science* during the 21st century focusing on this, as can be seen by the references cited so far (see also [84], and by researchers who seriously contest this theory [85,86]). While the Pettersson and Nilsson's theory is based on a very wide range of data from diverse advanced spectroscopic and diffraction methods it is far from accepted by all. Saykally and others [85,86] have criticized Pettersson and Nilsson that their interpretation of data is not correct and water is indeed largely a tetrahedral molecule. Saykally has even stated about Pettersson and Nilsson that *"if they are correct, they will win the Nobel prize, but I do not think they are"* [87]. Time will show who is right and who is wrong!

Philip Ball has rather recently (March 2018) stated that "evidence mounts that water exists in two liquids forms" [88] (while he was more skeptical about the two-state water some 10 years earlier [3]), and more evidence continuously appears for the "two-state theory" e.g. by Shi and Tanaka [89]. It does seem, however, that the interpretation of the same/similar spectroscopic and X-ray data by different groups on the structure of water can be done in more than one ways, leading to different conclusions! Somewhat similarly, as seemingly physically different theories can all describe water thermodynamics and hydrogen bonding, as seen in Figs. 4 and 6. Moreover, Poole and Stanley reported in some excitement [83] that so much recent evidence seems to support the existence of water's second critical (liquid-liquid) point, which they "proclaimed" 25 years ago [90].

We can also mention that, in the previously mentioned thermodynamic studies [75,78] by different groups, thermodynamic arguments appear to support the two-state model, even in a somewhat artificial way.

Moreover, a many years molecular simulation debate appears to be won by Professor Pablo Debenedetti's group and the "two-state water model" [91,92], but it is still a heavily debated topic, as previously mentioned, and it does not seem that the final words on water's (two-state) structure have been written. Pablo Debenedetti suspected the existence of the second critical point of water for more than 20 years now [93], but despite diverse evidence he was not convinced. His team's impressive July 2020 manuscript in Science [92] provides even more evidence. In addition to the original Ref. [92], interesting accounts of this breakthrough study are provided elsewhere (https://www.sciencedaily.com/releases/2020/07/200716144719.htm; https://www.chemistryworld.com/news/computational-study-supports-theory-that-water-has-a-second-critical-point/4012153.article).

In this recent work, Debenedetti and co-workers have used two computational methods and two highly realistic and successful computer models of water, the TIP4P/2005 and TIP4P/Ice. Both predict a liquid-liquid critical point in the region Tc=172–188 K and Pc=1739–1861 bar (depending on the model). Thus, the recent results confirm the liquid-liquid critical point predicted with another water model (ST2) in the group's earlier study. The simulations are very time consuming and, as cited in the above references, even with today's powerful research computers, the simulations took roughly 1.5 years of computation time. The web-references cited above provide also interesting comments on this recent work by some of the pioneers in the field (C. Austen Angell, Peter Poole and Anders Nilsson). Of course, the final proof will need to come from experiments, but these are indeed notoriously difficult in the so-called "no-man's land" due to extremely low temperatures involved which make liquid water very difficult to sustain. In addition to Saykally and co-workers, there are more researchers [94,95] who are not convinced about the two-state theory and have stated that water's properties do not indicate two-state behavior, or as Teixeira puts it [95]: "From the large amount of data available, it can be said that liquid water is a homogeneous liquids at all temperatures and pressures". The two-state hypothesis and how experimental data should be interpreted is a topic continuously debated these days [96].

Water's peculiarities do not stop in the aforementioned anomalous physico-chemical properties and the diverse discussions on the possible dual structure. Recent studies indicate separate behavior e.g. on the reactivities for the so-called ortho and para isomers of water [97,98] or a very low dielectric constant when water is in confined media [99].

This has been a very short review of a very extensive topic with rich recent literature. The anomalous properties of water have been discussed in detail in relation to its structure and dynamics in a number of excellent studies (Errington and Debenedetti [100], Debenedetti and Stanley [101], Debenedetti [6], Mallamace et al. [4], Mallamace et al. [5], Nilsson and Pettersson [102], Gallo et al. [103]; Palmer et al.[104]) and the interested reader is referred to these papers for more extensive discussions.

2.3. *Another view on the Holten-Anisimov two-state equation of state*

The Holten-Anisimov equation of state has been often mentioned as a method providing evidence for the two-state theory. We believe, therefore, that it is worthwhile presenting this approach and discuss both the successes and limitations associated with this two-state equation of state specially designed for pure water.

2.3.1. *The model in brief*

First, we outline very briefly the two-state equation of state model from Anisimov group, originally presented in 2014 [77], although there are various versions from the same group [77,75,105,106]. All models are similar in the sense that a chemical equilibrium between the two hypothesized states of water is assumed. The various variants differ mostly on empirical expressions of some properties. The two-state model of 2014 [77] differs from the others as it has many adjustable parameters (77), but at the same time more properties have been investigated and at wider T-P regions is covered with this model. The model was developed to be applied for cold and supercooled water (temperatures up to approximately 23 °C).

While details are presented in the original publications, for our purposes in this review it suffices to say that in the two-state model of Anisimov, pure liquid water is a mixture of two interconvertible states A and B and the mole fraction of each state is controlled by the chemical 'reaction'. These two states could correspond to different arrangements of the hydrogen-bonded network, but details of the hydrogen bonding are not included in the original formulation of the model. The main differences in these states reside in their thermodynamic properties. It is considered that A and B form a non-ideal solution, with all non-idealities expressed by a simple "entropic term". When a chemical equilibrium equations are written, the equilibrium (LDL) fraction can be calculated as function of temperature and pressure. Various thermodynamic properties can be calculated from derivatives of the Gibbs energy and can be obtained at various T/P.

For the development of this equation of state the authors [77] considered experimental data from different sources in order to adjust the parameters of the model; the model has 77 adjustable parameters. The thermodynamic properties that were considered for the fitting include density, isothermal compressibility, thermal expansivity, isobaric heat capacity and speed of sound (5 properties in total). The data that were used extended from the homogeneous ice nucleation line up to the temperature of 300 K and the pressure of 400 MPa. There are data for water beyond this region and the model can also be extrapolated beyond this region, but the accuracy of the model at this region has not been tested extensively by the authors in the original publication [77]. Outside this validity range, the authors showed a few comparisons for density and speed of sound. The model proved to be highly accurate for most of the data with a maximum absolute deviation of 2%. For the model the location of the liquid-liquid critical point needs to be defined.

For the location of the Liquid-Liquid Critical Point (LLCP), they used initially the one from Holten and Anisimov [75] and then it was slightly re-adjusted to fit the experimental data.

A key aspect of this model is the estimation of the phase coexistence line. Along the phase coexistence line, both states have the same mole fraction. The same is true for the LLCP. As mentioned previously, above the phase coexistence line there is the A-rich phase and below there is the B-rich phase. Before traversing the LLCP, the two states can be separated macroscopically. After the critical point there is a single phase region where there could be two states structures at the microscopic level. The model always considers water to be a mixture of the two states (i.e. there is no region where water is pure A or pure B in the model).

As mentioned, there are multiple two-state models published from the Anisimov group. We hereafter outline some of them and discuss some key characteristics and differences. The ones that are going to be discussed are: a) the scaled equation published by Fuentevilla and Anisimov [105] based on Landau's theory of phase transition b) the two state model by Bertrand and Anisimov [106] where they included a chemical equilibrium between the two states and c) the two-state model of Holten and Anisimov [75]. Their later works [76,77] have a very similar framework where they also consider a non-ideal solution of two states and they assumed that the fraction of each state is controlled by a chemical equillibrium. A short summary of some two-state models created by Anisimov is shown in Table 2.

We present some more information about these variations of the two-state equation of state. In 2006, Fuentevilla and Anisimov [105] developed a two-state scaled equation of state in order to describe and predict cold and supercooled water's thermodynamic properties. This study was the first model developed by Anisimov's group and it was mostly based on Landau's phase transition theory. The thermodynamic potential can be expressed as a function of two scaling fields (Landau expansion). The field-dependent thermodynamic potential in this case is the Gibbs energy of the hypothesized mixture. For the scaling fields they used empirical expressions that depend on temperature and pressure. For the values of phase transition coefficients and parameters of the model, they have considered estimates from Mishima [107] and values published by Anisimov and Sengers [108]. Essentially the model had 2 adjustable parameters, one of them being the pressure of the LLCP. They were fitted to thermodynamic properties (isothermal compressibility, thermal expansivity, isobaric heat capacity). Overall, the model showed excellent results for the regions it was tested. The estimated location of the LLCP is at 27 MPa and 232 K.

Table 2
Summary of some two-state models created by Anisimov's group. LLCP stands for the liquid-liquid critical point.

Authors	$N_{param.}$	Properties considered	Estimated LLCP	Comments
Fuentevilla and Anisimov [105]	2	a_p, k_T, c_P	232 K, 27 MPa	Scaled equation First two-state model by Anisimov
Bertrand and Anisimov [106]	~ 6	ρ, a_p, k_T, c_P	227.4 K, 27.5 MPa	Introduction of chemical 'reaction'
Holten and Anisimov [75]	~ 21	ρ, a_p,k_T, c_P, u	227 K, 13 MPa	Chemical 'reaction'
Holten et al. [77]	77	ρ, a_p,k_T, c_P, u	228.2 K, 0 MPa	Chemical 'reaction' More data considered

Notes: A) $N_{param.}$ refers to the number of adjustable parameters in the two-state model B) The column 'Properties considered' refers to the properties considered in the parameter optimization step.

In 2011, Bertrand and Anisimov [106] proposed another two-state model where they introduced a chemical 'reaction' between the two hypothetical states following the works by Ponyatovskii and Moynihan. In contrast to Moynihan, they considered that the two states of water form a non-ideal athermal solution. Under this assumption the liquid-liquid transition is entropy-driven (instead of energy-driven). The formulation is based on the Gibbs energy of the solution and the Landau theory. They also show the case of the lattice gas model which is used to describe liquid-gas phase transition along with differences in the formulation with the liquid-liquid phase transition. Similarly to Fuentevilla and Anisimov [105], Bertrand and Anisimov [106] were able to limit the number of adjustable parameters by adopting values from Anisimov and Sengers [108]. As a result they had approximately 6 adjustable parameters (including the location of the LLCP) which were fitted to density, isothermal compressibility, thermal expansivity and isobaric heat capacity. The model is able to describe these properties with exceptional accuracy. The estimated location of the LLCP in this study is 27.5 MPa and 227.4 K.

In 2012, Holten and Anisimov [75] introduced 2 two-state model similar to the on published by Bertrand and Anismov. They introduced a mean-field and a crossover equation of state, although the published parameter sets and results refer to the crossover equation of state. Here they also assumed a chemical equilibrium between the two states and that they form an athermal solution (entropy-driven phase transition). In this work, they have empirical expressions for the chemical equilibrium constant and the Gibbs energy of the one state. The adjustable parameters have been fitted to experimental data of density ρ, isothermal compressibility k_T, thermal expansivity a_P, isobaric heat capacity c_P and speed of sound u. It is worth noting that they also considered data of high-density and low-density amorphous ice since they have assumed that the liquid-liquid transition should be connected to the phase transition between these two different forms of ice. The experimental data cover the range of 140 K to 310 K and of 0.1 MPa to 400 MPa. The data used in this study covered a wider range of temperatures and pressures compared to the previous ones. The phase transition curve predicted by the model is adjusted to match the estimations of Mishima [109], where they claim that it should have the same curvature as the homogeneous ice nucleation line. In total, the model has approximately 21 adjustable parameters and shows exceptional results for the examined properties. The estimated location of the LLCP in this study is 227 K and 13 MPa.

In all of these two-state models, water is assumed to have a second critical point (a liquid-liquid critical point) at the supercooled region. The critical point proposed in these studies resides at much lower pressure compared to those predicted by computer simulations. For instance, Holten and Anisimov [75] consider the LLCP to reside at 0 MPa and 223 K, while studies on the TIP4P/2005 model estimate it to be at 193 K and 135 MPa. The models are mostly phenomenological and latest versions [77] have a considerable number of adjustable parameters (more than 20). All of these thermodynamic models lack microscopic details of the two states. The models are extremely accurate at describing water's properties in the cold and supercooled region (up to 300 K), but their accuracy at higher temperatures has not been reported. Finally, these models were used to describe a single phase transition at a time and in this case a liquid-liquid phase transition and thus they are not able to describe the vapor phase in their current from.

In this work, the results from the model of Holten, Sengers and Anisimov [77] of 2014 will be presented and analyzed. We typically refer to it as two-state model (2014) [77] in order to differentiate it from the model of Holten and Anisimov [75] (from 2012) which was published in Sci. Reports. This publication is extremely detailed containing extensive information on the framework, on the experimental data that were used for the fitting of parameters and on the model's performance. These factors can positively contribute to a proper analysis and study of the model. We will present results for stable liquid water, one of the major areas of interest even though this is outside the validity range of the model. We will include a few estimations for supercooled water in order to further discuss the two-state hypothesis.

2.3.2. Comparison of LDL fractions

The LDL fractions i.e. essentially the tetrahedral fraction of water molecules can be estimated from the two-state model and is also available from spectroscopic measurements. Some of these data are summarized in Table 3. There are also the spectroscopic data from Mallamace et al. [49].

LDL fractions from various versions of the two-state models and diverse experimental data and molecular simulation studies are compared graphically in Fig. 7. The caption provides information on the sources of the different data and model calculations.

There is a qualitative agreement between data and models/computational results, but considerable differences in the actual values. In all cases, LDL decreases very much with increasing temperature. Despite the differences of the estimates, all seem to have similar sigmoid trends with the exception of the various spectroscopy data which come from different authors and they are scarce.

Pathak et al. [110] and Russo and Tanaka [78] based their estimations on molecular simulations and they used the same method for identifying the LDL structure. The only difference was in the molecular model where Pathak et al. used ST2 model and Russo and Tanaka used TIP5P. It should be mentioned that Pathak et al. [110] indicate that true LDL fractions should be much lower compared to their estimates from ST2 based on experimental estimates of tetrahedrality.

Moore and Molinero [111] found local structures in the mW model for water (molecular simulations) by trying to identify tetrahedral structures. Caupin and Anisimov [76] used another two-state model, also from Anisimov's group and the results are close to those from 2014 two-state model. Overall, computational studies suggest that water is at all times a mixture of the two different structures because of the asymptots, but the data of Mallamace et al. [49] suggest that LDL is (almost) non-existent after ~300 K. Mallamace et al. [49] published more LDL fraction data at even lower temperatures, but these were based from Raman spectroscopy on low-density amorphous ice.

Table 3
LDL fractions from spectroscopy experiments.

Conditions	LDL (tetrahedral) fraction	Technique and author
298 K 0.1 MPa	20% ± 20%	X-ray absorption Wernet et al. [70]
363 K, 0.1 MPa	15% ± 15%	X-ray absorption Wernet et al. [70]
293 K, 0.1 MPa	33.2%	Raman spectroscopy, Sun [112]
280 K, 0.1 MPa	34.5%	X-ray emission, Tokushima et al. [81]
297 K,0.1 MPa	33.3%	X-ray emission, Tokushima et al. [81]
335, 0.1 MPa	27.7%	X-ray emission, Tokushima et al. [81]

Notes: a) For Tokushima et al. [81] we have calculated these fractions based on their ratios of distorted/tetrahedral at these conditions b) Sun [112] did not publish uncertainties and Tokushima et al. [81] published uncertainties for the ratio distorted/tetrahedral. Their estimates should have a maximum accuracy of ± 10%. c) It is likley that there are more data available with lower uncertainty values. d) There are also spectroscopic measurements from Mallamace et al. [49] (which are not shown in this table, but they are discussed in Fig. 7.

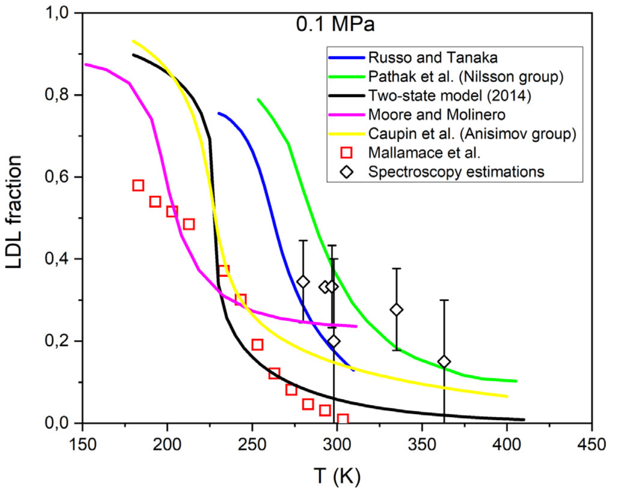

Fig. 7. Comparison of LDL fraction from different sources at 1 bar (0.1 MPa). Solid lines are results from computational studies, while symbols are estimates from experiments. Russo and Tanaka [78] estimated the LDL fraction of TIP5P water model and Pathak et al. [110] estimated the LDL fraction of ST2 water models. Russo and Tanaka [78] and Pathak et al. [110] used the same method for estimating the LDL fraction which was presented by Russo and Tanaka [78]. Moore and Molinero [111] estimated LDL on the mW water model. The yellow line indicates results from the model created by Caupin and Anisimov [76]. Mallamace et al. [49] used Fourier Transformation Infrared spectroscopy (FTIR) on confined water for 183–303 K and Raman spectroscopy on bulk water for 253–373 K. Spectroscopy estimations (diamonds) are from different authors and they are summarized in Table 3.

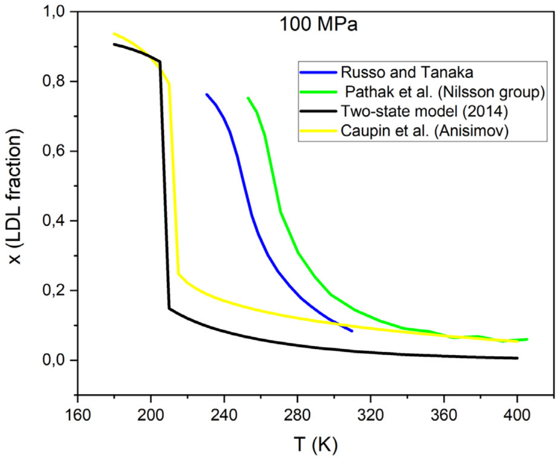

Fig. 8. Comparison of LDL fraction from different sources at 100 MPa. Solid lines are results from computational studies, while symbols are estimates from experiments. Russo and Tanaka [78] estimated the LDL fraction of TIP4P/2005 water model and Pathak et al. [110] estimated the LDL fraction of ST2 water models. Russo and Tanaka [78] and Pathak et al. [110] used the same method for estimating the LDL fraction which was presented by Russo and Tanaka [78]. Yellow line shows results of the two-state model created by Caupin and Anisimov [76].

A comparison of the various approaches at a higher pressure (100 MPa) is shown in Fig. 8. Fewer data/estimates of LDL exist at high pressure but significant differences can still be seen, despite similarities in trends, also between the two versions of the two-state theory [76,77]. Finally, in Fig. 9 LDL fraction as calculated from the two-state model is shown for various temperatures and pressure. We observe that an increase on pressure seems to decrease the LDL fraction. This indicates that higher pressure forces molecules to be closer together promoting the formation of the HDL form. Similar results have also been shown by Russo and Tanaka [78] and Pathak et al. [110]. At high temperatures (above 360 K) the LDL fractions at each pressure have nearly the same values and are close to zero.

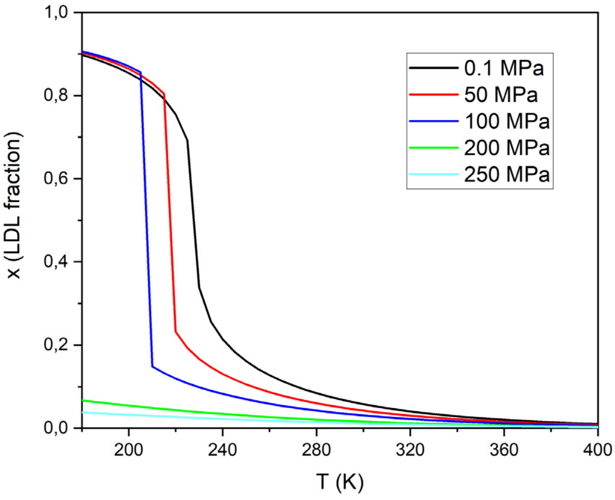

Fig. 9. LDL fraction isobars calculated from the two-state model (2014) [77].

2.3.3. Characteristic results and discussion

We have performed calculations using the two-state model by Holten et al. [77] (2014) for a wide range of properties and conditions in or-

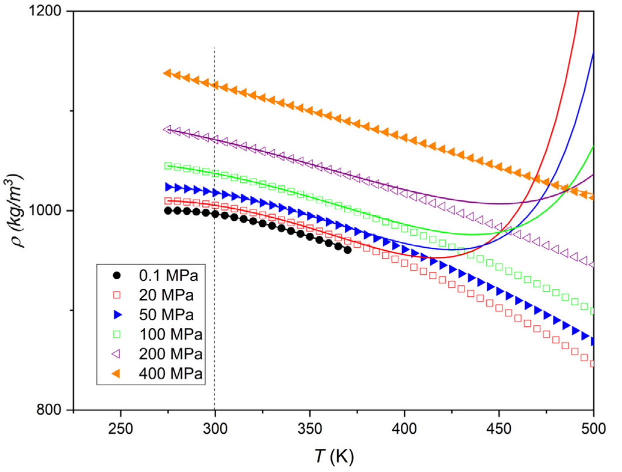

Fig. 10. Density isobars of liquid water. Solid lines are results from the two-state model [77] and symbols represent results from the IAPWS-95 formulation. Dotted line is the line $T = 300K$ and indicates the limit of validity range of the two-state model [77]. Below this temperature, results are the same as the published ones. Beyond this temperature, the results are the model's predictions since they did not consider data beyond 300 K.

der to evaluate the model's applicability, also beyond the range used in parameter estimation. The code provided by the authors has been used. We have considered data for stable liquid water and not for supercooled water, which has been studied extensively in the original publication (where no results were shown beyond 300 K, considered to be the validity range according to the authors). The calculated results are compared to estimates from the NIST Chembook, which is using an empirical model (the IAPWS-95, which is developed based on a multitude of experimental data). Even though it has proven excellent at describing experimental data, there were certain regions where data were lacking. This will be relevant in the further discussion.

Calculated results of the two-state model are shown in Figs. 10–12 for three properties. We do not show but we have also considered isothermal compressibility, thermal expansivity and isochoric heat capacity isobars. Similar conclusions are obtained as for the properties shown here.

We observe that in all cases the model is exceptionally accurate at describing all properties within its validity range (up to 300 K), while deviations are seen at higher temperatures, especially beyond about 350 K. At higher temperatures the curvature of the lines shifts significantly providing unrealistic results and this happens for all 6 properties considered. We cannot say whether the model could produce more accurate results beyond 350 K by including these data in the fit. The two-state model considers only liquid-liquid transition and not vapor-liquid. This is probably one of the reasons why we observe unrealistic results at high temperatures.

In this section, we have briefly presented some results of the two-state model for water developed by Holten et al. [77] in 2014. There are multiple variations created by Anisimov's group, but all share some common characteristics e.g. a chemical equilibrium is considered between the two hypothesized states of water and that the two states form a non-ideal solution. The model is semi-empirical and it does not consider explicitly any microscopic details (i.e. structure, van-der Waals forces, hydrogen bonds, etc.). The different variants have some differences in the final expressions and in the parameters. The two-state model (2014) has 77 adjustable parameters, which are significantly more compared to other studies, but at the same time more properties and over wider regions were considered for its development. In addition, all of these two-state models have been developed for cold and supercooled liquid water and the published results did not exceed 300 K. The model at these conditions is reported to show exceptional accuracy, while it is also able to capture water's anomalies. The fact that the two-state picture can reproduce water's anomalies is an indication that the two-state might indeed be the true origin of water's anomalies. It is worth noting though that the model is incapable of calculating properties of the vapor phase.

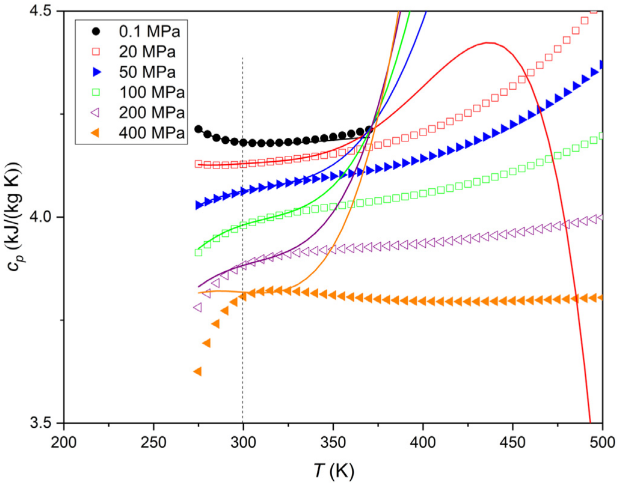

Fig. 11. Isobaric heat capacity isobars of liquid water. Solid lines are results from the two-state model [77] and symbols represent results from the IAPWS-95 formulation. Dotted line is the line $T = 300K$ and indicates the limit of validity range of the two-state model [77]. Below this temperature, results are the same as the published ones. Beyond this temperature, the results are the model's predictions since they did not consider data beyond 300 K. At high pressures and low temperatures Isobaric heat capacity data were scarce during the development of IAPWS-95. New data from Troncoso [113] are closer to the results of the two-state model.

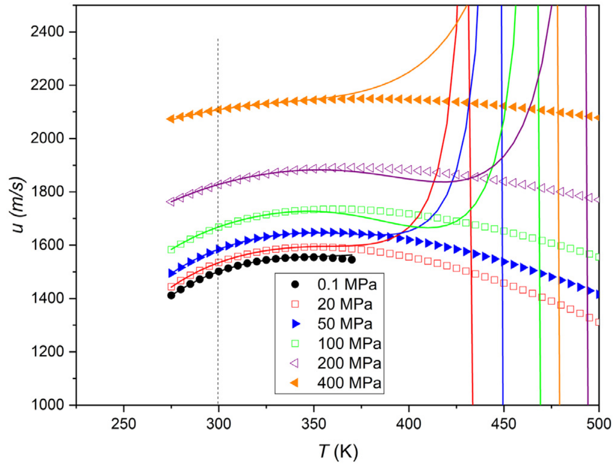

Fig. 12. Speed of sound isobars of liquid water. Solid lines are results from the two-state model [77] and symbols represent results from the IAPWS-95 formulation. Dotted line is the line $T = 300K$ and indicates the limit of validity range of the two-state model [77]. Below this temperature, results are the same as the published ones. Beyond this temperature, the results are the model's predictions since they did not consider data beyond 300 K.

Since the two-state model lacks microscopic detail, some authors have used it in combination with molecular simulations. Some quite noteworthy studies are the ones by Russo and Tanaka [78] and Shi et al. [114] where they applied a similar two-state model, but they did not fit the parameters to thermodynamic properties. They [78,114] fitted the parameters to the LDL fraction and the structure and they were able to predict density anomalies. Shi et al. [114] were also able to predict dynamic anomalies of water with a two-state model. These results provide also evidence that the two-state hypothesis is valid.

One interesting aspect of the two-state model is its ability to estimate LDL fractions, which are important for the two-state theory. By comparing estimations from the various versions of two-state models, molecular simulations and spectroscopy, we can conclude that there is no clear agreement on the LDL fractions. However, all LDL fraction data exhibit similar trends with a sigmoid-like dependence. The exceptional decrease of the LDL population is consistent with the idea of the strong fluctuations between the two states.

The two-state model (2014) was applied for cold and hot liquid water (outside the validity range of the model) in order to test its performance when extrapolated. The two-state model can show exceptional results up to $\sim$ 350 K, but after this point the model shows unrealistic results for all the properties investigated in this study. This fact along with the model's limitations shows that there is clear room for improvement.

Finally, it is possible to evaluate the importance of the interaction parameter and the non-ideality role in the model. We have performed the calculations but these results are not shown here. However, we can state that by considering an ideal solution, the LDL fraction changed considerably and the density maximum was no longer described by the model. This suggests that non-ideality is crucial at least for the considered conditions. Shi et al. [114] mention that the interaction parameter can be considered negligible at conditions away from the LLCP. The conditions investigated in this section for the non-ideality were close to the LLCP. Thus the two results may agree, but more investigations would be needed to have a clearer picture.

3. Water interactions with other molecules and the hydrophobic effect

We have discussed in the previous section water molecules, alone or as clusters in complex structures. In Section 4 we will also briefly address the possible effect of impurities. It is of importance, in an effort of achieving a better understanding of water properties, to study the interactions of water with other compounds and the associated, if any, changes to water's structure due to these interactions. We have decided to illustrate this via two examples; the effect of hydrophobic compounds and the interaction of water with ions. Some insights from surface science are provided first.

3.1. Input from surface science

A combined input from thermodynamics – molecular theory and surface science can provide some further information related to the contribution of various forces and hydrogen bonding in water.

From the theory of intermolecular forces and using the van der Waals (vdW) expressions, we can calculate for water that, at 0 °C, 81% of the vdW interactions are due to the polar forces and 15% due to dispersion forces [8,115,126] (with the remaining being the smaller induction forces). The percentages change to about 25% for the dispersion forces at room temperature. For the equally polar ammonia (with 1.47 D dipole moment), the polar contribution is 51% and the dispersion 43% [8,126]. And for the much more polar acetone (with 2.87 D dipole moment), the polar forces contribute 67% and the dispersion 27%. It is clear that the polar contribution of water is significant. The reason being a combined effect of the dipole moment and the polarizability values.

It would be interesting to investigate the contributions of the various intermolecular forces to the surface tension of water, which as mentioned has a particularly high value. This can be done indirectly via "component" theories for surface and interfacial tension, e.g. those proposed earlier by Fowkes and Owens-Wendt and in the more recent years by Good and co-workers and Panayiotou. The references of these methods are provided in the textbook by Kontogeorgis and Kiil [115]. Table 4 presents some pertinent results. There is some consensus that the dispersion contribution to surface tension is about 30%, in agreement to the van der Waals theory of intermolecular forces. There is less consensus on how the hydrogen bonding of water should be represented.

We notice that some authors have considered unequal acid/base contributions for water, presumably in agreement with Kamlet-Taft solvatochromic parameters. Others, however, like in the case of the original values by van Oss-Good and the recent method of Panayiotou maintain that water's acid and base effects should be balanced. It is interesting that there is a disagreement on such a fundamental issue. The performance of the methods for actual applications (liquid-liquid interfaces, wetting and adhesion, etc.) will depend on contributions from other compounds, and other data like contact angle and values for solids, thus the issue of the exact contributions of water's acid/base effects to the surface tension remains largely unresolved.

All these conflicting views about water structure indicate that our understanding of water is lacking. We summarize some recent views next.

3.2. The hydrophobic effect

An important phenomenon, which is much debated [116,117], associated with the interaction of water with non-polar solutes e.g. alkanes or other hydrocarbons, is the so-called hydrophobic effect. As well as the related hydrophobic interaction. Experimental data show, as can be seen in Table 5, that this is an entropic phenomenon. As Israelachvili [118] (and others) explain, non-polar solute molecules (if not too large) can pack around water, without giving up any of their hydrogen bonding sites, thus forming some type of clathrate cage. Thus, we have this negative entropy in the process as the existing water structure is disrupted and a new, more ordered, structure is created surrounding the water molecules. As can be seen in Table 5, at least at room temperature, the entropy decrease contributes a lot to this interaction e.g. 85% for water-butane, while in the case of water-benzene approaches 100%.

It has been shown by many e.g. [119–122] that the Gibbs energy of dissolution of hydrocarbons in water or free energy of solvation is roughly temperature independent and actually can be given [119,123] as linear function of the chain length or hydrogen atoms. This has permitted Gill and Wadso [119] to develop a simple equation (of state) for the hydrophobic effect. Wu and Prausnitz [121] have also shown that the hydrophobic effect is primarily a local phenomenon and that the hydrophobic interaction, which is short-ranged, may be represented by a semi-empirical force field and in a pairwise additive manner. According to the same authors, the hydration of a hydrophobic molecule occurs primarily within a single layer of water molecules and thus the hydrophobic attraction is short-ranged and disappears beyond the overlap of the solvation shells.

On the other hand, as shown by some researchers [120,123,124] the temperature dependency of the enthalpic and entropic contributions to the solvation are very pronounced and in opposite directions, thus tending to cancel out when the Gibbs energy is calculated. At low temperatures, the Gibbs energy is dominated by the entropic effects and at high temperatures by the enthalpic part. It is the large values of the heat capacity changes, see Table 5, which are the reason for these large temperature variations of the enthalpy and entropy terms.

It has been indeed stated [9,116,117] that one of the most central characteristics of the hydrophobicity is this temperature dependency which comes from the interplay of the enthalpic and entropic contributions. And it might provide some insight on the fact that around room temperature, see Table 5, the enthalpy change is close to zero, the entropic term dominates and we typically observe a minimum of the hydrocarbon solubility in water. Based on these observations, several researchers have proposed some explanations [119,120,123] for the solubility minimum (shown in Figs. 4 and 5), although these explanations are not identical and there are some fundamental disagreements on the exact structuring of water around non-polar solutes. The clathrate

Table 4

The surface energy components of water according to various interfacial tension theories. In all cases the total surface energy of water is 72.8 mN/m at 20 °C. All values in the table are in mN/m. For the values and more information, see Kontogeorgis and Kiil, 2016 [115]. The Kamlet-Taft solvatochromic parameters of water are 1.17 (acid) and 0.18 (base). For the references of these methods see the textbook by Kontogeorgis and Kiil (2016) [115].

Theory for surface and interfacial tension	Dispersion or van der Waals	Specific or acid-base	Acid(polar for Hansen method)	Base(hydrogen bonding for Hansen method)
Fowkes/Owens-Wendt	21.8	51.0	–	–
Hansen	21.85	50.94	23.26	27.68
Van Oss-Good, original	21.8	51.0	25.5	25.5
Van Oss-Good with Della Volpe-Siboni, 1997	21.8	51.0	65.0	10.0
Van Oss-Good with Della Volpe-Siboni, 2000	26.2	46.6	48.5	11.2
Lee				
Panayiotou PSP method	15.71 (dispersion)+5.42 (polarity) = 21.13	51.7	25.84	25.84

Table 5

Change in standard molar Gibbs Energy ($\Delta G = \Delta H - T\Delta S$), enthalpy and entropy for the transfer of hydrocarbons from their pure fluids into water at 25 °C. All values are reported in kJ/mol and they are taken from various literature sources [8,115,117,126]. The ΔC_p values are in J/K mol.

Hydrocarbon	ΔG	ΔH	$T\Delta S$	ΔC_p
Ethane	16.3	−10.5	−26.8	150
Propane	20.5	−7.1	−27.6	
n-butane	24.7	−3.3	−28.0	272
n-pentane	28.6	−2.0	−26.6	400
cyclohexane	28.1	−0.1	−28.2	360
n-hexane	32.4	0	−32.4	440
Benzene	19.2	2.1	−17.1	225
Toluene	22.6	1.7	−20.9	263
Ethylbenzene	26.2	2.02	−24.2	318
Propylbenzene	28.8	2.3	−26.5	391

model, is supported by some [118,120] but not by others [3,123,125]. For example, von Stockar [123] states that it is an error to say that restructuring of water in the hydration layer around non-polar solutes makes solubility low. According to von Stockar [123] the opposite is true i.e. restructuring water upon introducing non-polar solutes should actually lower the Gibbs energy change which could be the reason for the increasing solubility of hydrocarbons in water at temperatures lower than room temperature (whereas, we assume, he means that at higher temperatures the structuring is less pronounced and the solubility decreases).

In any case, there is a widespread belief [126] that the water molecules –in presence of a hydrophobic solute- have a higher degree of local order than that in pure liquid water, which results to the decrease of the entropy.

Kronberg [120] has recently presented an alternative explanation for the hydrophobic effect and the associated poor solubility of hydrocarbons in water, which partially also explains why the minimum of the alkane solubility in water is almost universal. In his approach, there are two contributions to the transfer of hydrocarbons into water; cavity formation by water molecules (requiring a large positive energy) and then water structuring i.e. relaxation of water molecules around the hydrocarbon into a more ordered state. He believes that his interpretation is in better agreement with recent spectroscopic data, that water molecules in the hydrophobic solvation shell do not exhibit increased tetrahedral ordering compared to the bulk. He believes that it is the hydrogen bonding dynamics that is different. Moreover, he states that whereas the cavity contribution dominates, the temperature dependency is determined fully by the water structuring in the vicinity of the hydrophobic molecule.

Finally, the work by van Oss and Good [127] should be mentioned. These authors developed an expression between the contact surface areas, the interfacial tension and the solubility. From experimental data of the two latter properties for water-alkanes, they were able to estimate, on average, a contact area for water of about 0.343 nm^2, corresponding to about three water molecules combined. This value agrees approximately to the number of water molecules estimated to be hydrogen-bonded to each other at any given moment at room temperature. Such considerations have been also used when discussing the microscopic basis for the hydrophobic effect. The various quantities (Gibbs energy, enthalpy, entropy and heat capacity) are proportional to the solute surface area, thus hydrophobicity is also considered to be proportional to the number of water molecules in the first solvation shell.

3.3. *Interaction of water with ions*

The presence of water with electrolytes is so frequent that there are numerous applications in chemical, biochemical industries, geothermal, etc. For example, in the area of petroleum engineering, a concept with the characteristic name "SmartWater" includes how injection of water of different salinity or other chemical modifications can improve oil recovery. This is a most interesting practical application, still hampered from the necessity of understanding the water-ion-oil-solid surfaces (rock) interactions.

Returning to the physics of the water-ion systems, as shown by von Stockar [123] and many others, the ion hydration (typically happening when ions are in water) consists first of a structured hydration layer around the ion (size of many molecular diameters) and a more chaotic transition layer in-between the hydration layer and bulk water.

The traditional picture is that several ions (small and/or multivalent) promote the water structure (structure promoters), with decreasing entropy and increasing viscosity, while large/monovalent ions are water structure breakers.

The topic of the effect of ions on water structure is much debated.

We can start with the effect of salt concentration on the dielectric constant of water. The dielectric constant (relative permittivity) of water decreases a lot with both increasing temperature and increasing salt concentration, as can be seen in Fig. 13. This implies that phenomena such as ion pairing and partial dissociation may become significant at high temperatures, concentrated solutions or in presence of organic solvents, and should be considered in models for electrolyte solutions.

The physical picture is, however, somewhat more complex, as the mechanisms for reduction of water's relative permittivity with salts is due to two phenomena [129-131]. First of all, the non-equilibrium originated kinetic depolarization often accounting for 25–75% of the decrease of dielectric constant with concentration and the thermodynamically oriented ion solvation. For this reason, it has been stated that, in principle, only the latter should be considered in thermodynamic modeling, thus a less pronounced decrease of dielectric constant with salt concentration than the experimental one should be incorporated in modeling tools. As the formation of hydration shells around ions cause the

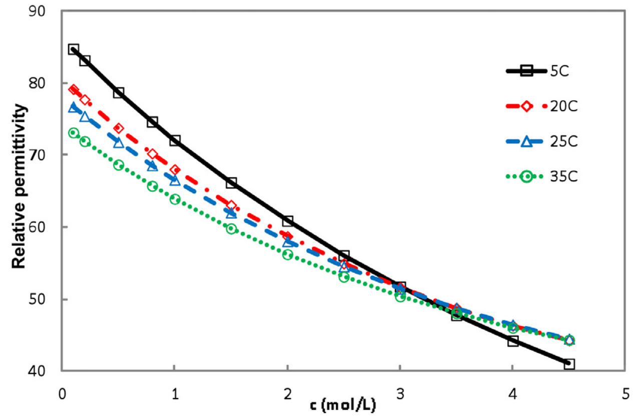

Fig. 13. Relative permittivity of aqueous NaCl solutions at different temperatures. The experimental data are taken from Buchner et al. (1999) [128]. The lines are guide to the eye.

static permittivity to decrease, then the "dielectric saturation" can be modeled using ion-solvent association, as shown by Maribo-Mogensen et al. [131].

Let us now return to the effect of ions on water structure in general.

Omta et al., [132] concluded, using femtosecond pump-probe spectroscopy, that the presence of ions does not lead to an enhancement or a breakdown of the hydrogen-bond network in liquid water outside the first solvation shells of the ions. According to these authors, the increase in viscosity upon adding ions to liquid water can be fully explained based on the rigid nature of the solvation structure formed by the ion and its first solvation shell. Zhang and Cremer [133] share a similar viewpoint and they mention that ions do not affect the bulk water properties and that there is plenty of evidence for that!

On the other hand, Tielrooij et al. [134] presented a combined tetrahertz and femtosecond infrared spectroscopy study of water dynamics around different ions. They conclude that the effect of ions and counter-ions on water can be strongly independent and non-additive and in certain cases extends well beyond the first solvation shell of water molecules directly surrounding the ion. On the same lines, Leberman and Soper [135] find that ions induce a change in structure of water equivalent to the application of high pressures, and that the size of this effect is ion-specific. They believe that ionic concentrations of a few moles per liter have an effect equivalent to that of a few thousands atmospheres in pressure. They also state that these changes could be understood in terms of the partial molar volumes of ions compared to those of water molecules.

Bilde and co-workers [136] have measured osmotic coefficients for aqueous salt solutions using Raman spectroscopy and they were able to obtain good agreement of their measurements with the thermodynamically and independently derived determined values only when water structure change is accounted for (together with electrolyte dissociation). They concluded that the effect of water structure and accounting for it are crucial at higher concentrations. Moreover, the characteristic minimum in the osmotic coefficient values for aqueous salt solutions with respect to concentration can be predicted when the dependence/changes of the structure of water is considered. They conclude that the percentage of hydrogen bonds of water increases with salt concentration and, thus, they see a clear change of water structure in presence of ions.

Nilsson and Pettersson [102], in one of their two-state theory articles, mention that adding NaCl in water has been shown to affect water structure similar to increased pressure, that is by reducing tetrahedrality. Gallo et al. [103], mention that in aqueous NaCl solutions, the heat capacity and density anomalies are still present in dilute solutions, but at higher concentrations of NaCl the heat capacity anomaly disappears. But they add that this fact does not contradict the possibility of a liquid-liquid transition in supercooled aqueous solutions of NaCl, which comes from the liquid-liquid transition in pure water. Moreover, the recent experimental works by de Ninno and co-workers [137,140] with various spectroscopic methods and for several electrolyte solutions appear also to support the two-fluid structure of liquid water.

4. The anomalous properties of water – controversial topics

4.1. More peculiarities and anomalous properties of water

In addition to the well-established anomalous properties of water discussed in Section 2, there are several more controversial properties or concepts related to water's properties and structure which we briefly address here. These range from well-established phenomena where explanations are controversial, to claims of phenomena that are themselves controversial, because the evidence and interpretation are in dispute. In a scale of increasing "weirdness" we could propose the following classification:

1. Central anomalies in mainstream chemistry-thermodynamics, as above (Section 2).
2. The water bridge, the exclusion zone and some other phenomena (Mpemba effect, Kansius effect, electromagnetic interactions with solutions)
3. Structured water, water polymers, liquid crystal phase, QED coherent domains (these are theories, mainly proposed to explain phenomena in point (2))
4. Water memory, imprinting chemical structures on water, homeopathic effects (effects for which there is substantial research but remain highly controversial)
5. Psi effects, mental interactions with water, directed intentions affecting water states (non-physical effects that are claimed to show up in some experiments)

These controversies have become a notable part of water research. The second group of topics (2) is now, as considered by some, within the orbit of mainstream scientific research (although this is only admitted quite recently). These are now subject of extensive ongoing research. (3) are speculative concepts advanced as *explanations* for various water properties, such as the EZ phenomenon (2). These are scientific hypotheses. We review proposed explanations for the *exclusion zone* (EZ) in detail, including comparison of theories (3) with the more conventional diffusiophoresis/chemotaxis theories (2). All topics in (2) have important ongoing recent research.

On the top of this list is the already mentioned so-called exclusion zone (EZ) phenomenon and theory proposed by Pollack [2]. Exclusion zones form in water close (<0.5 mm) to certain solid surfaces. Despite clear evidence of its existence (Henniker [141]), the EZ theory is controversial. Pollack's theory is criticized [142] and the EZ phenomenon explained by some using the mechanism of diffusiophoresis [143,144], while others have tried to explain it using quantum mechanics (De Ninno [145]). Pollack and co-workers proclaim the existence of highly structured water close to hydrophilic surfaces, which "excludes" other compounds from approaching the solid surface for very long distances (in the order of micro-meter and even mm) and even more that water behaves as a battery due to charge separation (EZ being negatively charged). The theory violates classical approaches in colloid science like the DLVO theory and implies that there is evidence that water does not behave like a continuum, but in some cases assumes a more ordered phase, which is directly involved in biochemical processes. According to Pollack [2] his theory can explain many of water's anomalous properties. We are discussing Pollack's theory in detail in Section 5, reporting both new data and a wider range of explanations for the occurrence of the exclusion zone.

While there is a lot of speculation here, the influence of solids/solid surfaces on water properties still poses a lot of questions. Let us consider for example the influence of solids on the viscosity of water. While results from atomic force microscopy and from molecular simulation indicate that only a few nanometers of water is tightly bound to a solid, studies of friction between plates covered with water indicate that the effective viscosity in water is higher than in free water in a layer up to 100 nm thick [146,147]. In line with this later observation, studies by low field nuclear magnetic resonance indicate that a several 10th of nanometer thick layer of water is magnetically bound to the solid. The effect on friction has been ascribed to countercurrents in the electric double layer opposing the mechanical movement, but whether this is the case is not entirely clear. Similar questions arise due to the apparent low elasticity of water close to solids.

Moreover, since living organisms contain up to 99% water by molecule, any change in the state of water may also influence the biochemical and physiological processes. Methods and technologies for affecting the structure of water towards the more ordered state have been reported and the effects of the structured water on living systems are quite diverse – ranging from increased crop yields to inhibition of bacteria [148,149]. While there have been many reports of the effect of structured water on bacterial biofilm production and plant growth, there is in reality lack of proof of the above, and the link to water structure is not understood at all.

Phenomena like the water bridges (the so-called water thread experiment [150]) under high voltage have not yet found good explanations either. The water bridge is also a rather controversial topic, especially its connection to the exclusion zone (EZ), but it has been the topic of intense scientific studies [151,152]. We will discuss further the water bridge experiment in more detail in Section 4.2, where new measurements will be reported.

Another line of investigation are electromagnetic water treatments, using “devices” claiming to achieve limescale reduction via special water structuring, or being useful for reduction of biofilms, and aiding in plant growth, animal health, concrete production, etc. Many such devices are on the market, for two or three decades, and have found widespread applications [158–160]. The underlying mechanisms are not known, but are generally claimed to involve some physical change of water, e.g. using low-energy ultrasound or electromagnetic fields. There is a lot of criticism about these devices and the lack of experimental proof of the claimed results as well as lack of explanations for the involved mechanisms [161,162] but many results are kept confidential for competitive advantage, while some patents exist [163].

Observations have been presented of long-lasting physical effects (over hours or days) resulting from certain types of water treatments, most notably effects of weak EM or magnetic fields on zeta potentials and related electrical properties of colloid solutions. This phenomenon was investigated by several groups in the 1990′s [164-167]. While the phenomenon is not explained, the reported effects are not found in pure water but in colloidal mixtures or solutions, which contain charged particles and large solute molecules and bubbles, etc. This is less radical than the idea that such EM treatments can change the state of pure water. The effects have been found to be specific to certain EM modulated frequency bands, and certain types of solutes, and while mechanisms are still not well understood, there are partial explanations and applications as mentioned above.

The list of controversial phenomena associated with water is long, including highly debated and controversial studies about water’s memory (initiated by Jacques Benveniste and co-workers [153,154], but later continued by others including the much cited paper by L. Rey [155,156]) and the associations to homeopathy [157].

The literature, scientific and not, is very rich in articles and debates on the above. Jacques Benveniste died in 2004 at age of 69 and obituaries presenting his life and work from different angles have been published [168,169]. In [169], Nobel-prize winner Brian Josephson says “it could be that as we come to understand more about the properties of water, we’ll learn about the conditions required to reproduce the findings of Benveniste”.

Associated with water memory is the work of the Nobel-prize winner Luc Montagnier on DNA waves and water [170], but this is also criticized much in the same way. Elsevier publishes a peer-review journal called *Homeopathy* and numerous articles linking homeopathy to water structure are published there, for some characteristic ones see [171–176].

Associated to the above is the fact that we often do not have “pure water” and water has the tendency to absorb almost everything and the role of impurities is notorious in water research. These impurities may have played a role in “discoveries” like polywater [177–181] (a presumably polymer-like water) and the water memory where water appears to remember the effect of molecules it has been in contact with. In particular, for polywater, similarities between the infrared spectra of polywater and sweat [180] or other impurities [179,181] has indicated that such experiments were, from one side, not reliable and could not be reproduced and from the other side that water’s ability to absorb can often lead to erroneous (but interesting) conclusions. Prominent researchers like Ellis R. Lippincot and co-workers were originally favored about the polywater concept [177] as new unique stable water polymer structure, but shortly after [178] they too have been aware of the serious contamination issues which prohibited them for reproducing the previously reported Raman spectra and they were looking for alternative explanations. Still, it does appear that the polywater story somewhat reappears in the work of Pollack and co-workers during this century which will be presented and discussed later in this manuscript (Section 5).

On the other hand, the four references cited in [173–176] from *Homeopathy* provide diverse views on the topic of water memory, four very passionate articles, each with own characteristics. Yolene Thomas article, previous co-worker of Benveniste is the most favorable about water memory, while the three others are more critical. These latter three papers emphasize that no such material as pure water exists and the effect of impurities e.g. glass tubes and dissolved silica can be a good explanation for the water memory, or even presence of other molecules or dissolved gasses although, according to Elia et al. [175], impurities have an effect but do not provide the full explanation. The effect of shaking can be significant, says M. Chaplin but he also mentions that in the absence of other materials and surfaces, the hydrogen bonding pattern surrounding a solute does not persist when the solute is removed and similar notions can be found in Jose Texeira’s paper [176], possibly the most critical among these four manuscripts [173–176]. Elia et al. [175] are more favorable and believe that many years of experiments have proved the water memory due to structuring and non-equilibrium status, as they say ”within the solutions are molecular clusters of water molecules with hydrogen bonds far from equilibrium conditions”.

The role of water’s structure in connection to Benveniste’s experiment is controversial, to say the list. Philip Ball in his 2011 Talk to the Royal Society of Chemistry maintains that “Benveniste’s idea sadly makes no sense. If Hydrogen Bonds are lasting only a picosecond before they break and reform, how on earth is the shape going to be maintained?”

According to Martin F. Chaplin (London South Bank U.) in one of the aforementioned papers [173]:

> ”Although individual molecules of water cannot retain any memory of past hydrogen bonding for periods of more than a fraction of second, the behavior of water clusters can be entirely different…. Water clusters are proven entities; their size and lifetime dependent on their physical and chemical environment. Liquid water is made up from a mixture of such clusters forming, changing and disappearing”.

See also [253] for interesting claims about water clusters. It is clear that there is no consensus on the topic.

Another related peculiar aspect associated sometimes with water structure is found in gas hydrates, which are solid, ice-like structures formed from small molecules like methane and water at conditions of high pressure and low temperature. For example natural gas at 200 bar forms solid hydrates with water at 25 °C. It is widely accepted [182–184] that it is easier (faster) to make hydrates from water that has previously been in hydrate form than directly from fresh water. By this is meant that if you place gas and water under pressure and cycle the temperature up and down to melt and reform hydrates, each subsequent temperature cycle downwards will form hydrates more quickly. This phenomenon is termed "memory water" by some researchers in this field and is used as an experimental technique to run experiments more quickly. Yet, why it happens and what the possible implications in the understanding of water structure are, nobody knows exactly. Others have contested whether this phenomenon has anything to do with such "water memory" effects and claim it may be due to the persistence of tiny hydrate particles not detectable through traditional means (pressure and heat measurements). This has not been verified and the debate continues.

Finally, we mention the peculiar effect of salts on water structure as claimed in Louis Rey's controversial work [155,156] (one of the papers published in the esteemed journal Physica A). These claims are based on thermoluminescence experiments of ultra-high diluted salt solutions. This work is often associated to water memory and homeopathy, and is thus much criticized. In Rey's studies, ultra-dilute salt solutions have been irradiated with X- and gamma-rays and then warmed up and the stored energy is released. It was found that despite the extreme dilutions (no salt molecules left), the emitted light was specific of the original salts dissolved. Vigorous mechanical stirring has been applied together with the extreme dilutions. As separate peaks of glow have been observed for water, it has been concluded that the structure of pure water hydrogen bonding must be very different from the very dilute solutions and that salt suppresses the hydrogen bonding structure. To the best of our knowledge, these experiments have not been repeated or verified by other researchers.

4.2. *An experimental investigation of the floating water bridge*

We have already mentioned the water bridge and its alledged connection to water structure and maybe also the exclusion zone (theory). We have decided to investigate the phenomenon in more detail and for this reason we have carried out a detailed experimental investigation of the well-known and much discussed phenomenon of the floating water bridge [185] but we have also extended the study to other liquids as well, in an attempt to establish whether the phenomenon characterizes water alone.

The floating water bridge phenomenon [185] concerns the spontaneous formation of a water 'thread' connection between two beakers filled with deionized water, when a voltage of around 15,000–30,000 Vs, is applied across them. This is usually done by placing electrodes in the water, but this is not necessary, only the electric field is required, which can be applied by two plates. It was first reported in 1893 by Sir William George Armstrong, and although not difficult to replicate in the laboratory, the phenomenon is still not fully described by a complete theory [186]. The significance of such a theory, lies in the explanation of water behavior in the mesoscopic scale, which is the scale of interest for the human physiology [187]. Several experimental activities have been published, attracting the interest of modern water science community. The provided information of these works include: density gradients within the bridge [185], OH stretch vibrational changes from infrared measurements [188], stopped mass flow though the water bridge under reduced gravity conditions [189], birefringence and anisotropy observed by neutron and polarized light scattering respectively [190,191], tracking of particles moving on the bridge's surface, as well as measurements of the horizontal force applied by the bridge on the beakers [186]. Although not fully described at a theoretical level, artificial watery channels find applications in the desalination of water [192], development of nanofluidics lab-on-a-chip devices [193,194], as well as drug delivery [195].

While bridges formed with water are of most interest, the same phenomenon occurs with other liquids, and general mechanisms are evident. Experimentally, observations can be made of various types of physical variables (Voltage/EM field, current, ionization, bridge dimensions, shape and topology, bridge motions, electrical currents, mass currents, heat flow, temperature, surface particle motions, mass resonance, discharge events, light absorption, emission, refraction and reflection) and we can relate them to a number of properties of liquids (permittivity, polarity, electrical conductivity, ionic dissociation, acidity, mass density, viscosity, thermal conductivity, heat capacity, surface tension, refractive index).

Theories and models can relate many of these in increasing detail now. Refs. [185–195] and others mentioned above provide studies of many of these aspects, along with attempts to explain features, such as the stability and shape of the structure, and the electrical surface interaction. But there is still no single accepted explanation, or fully settled description. The primary interaction is through the strong electric field along the surface of the bridge. This is very complex at an atomic level, but can be analyzed in classical approximations. This results in a complex dynamic mechanism, of spiraling particle motions and currents. No one could predict this structure from theory yet. But steady progress is being made in explaining various details of the mechanism.

In the remaining of this section, we note features we observed in an experimental reproduction of the water bridge phenomenon. Details on materials and methods are not shown in this review but can be provided by contacting the corresponding author. We have attempted to examine the phenomenon at its extremes and replicated the water bridge at various conditions. First, it can be fairly well determined that the water bridge can take place when the electrodes are outside of the water. In Fig. 14 and the accompanied video an already established water bridge is tested by moving the electrodes out of the bulk water, whereas in the second video, the bridge is generated with the electrodes out of the beakers from the beginning.

These videos show that electrical connection to the bulk water does not contribute to the phenomenon, which only requires the electric field and the water surface.

We have also able to demonstrate a vertical bridge (also reported in [195]), *Video link:* https://youtu.be/z2Lmf6r1sOg, and a so-called 'waving' bridge. A waving pattern of varying wavelength λ, occurred on the body of the water-bridge as it is demonstrated in the video *link:* https://youtu.be/_6huUJaiSzA. The 'waving' took place in a specific distance between the beakers, and the water level was way below the beakers lip. There is this moment when the waving bridge is destabilized but choses to stabilize again instead of collapsing due to gravity.

We were able to form dynamic water columns (https://youtu.be/XWNiuaLKx4s) as well as two water bridges under some conditions. Moreover, it has been possible to generate and stabilize an air bubble inside the body of the water bridge, with the assistance of the pipette. The water continues to flow from one beaker to another, following the path of the bubble's watery surface. The stability of the configuration is tested with water dripping on the top of the bubble, see Fig. 15 and associated video.

We also used a thermal camera for observing the water bridge, see Fig. 16 and associated video. As it is shown, the heat flow is captured, with the maximum temperature observed on the main body of the bridge.

4.2.1. *Liquid bridges beyond water*

This is not a phenomenon unique to water. The liquid bridge formation has also been reproduced with other polar liquids, solutions of low conductivity, as well as colloidal suspensions, but it appears that nonpolar dielectric liquids cannot form the bridge [196]. The key properties towards a liquid bridge formation seem to be low electric conductivity, high relative permittivity as well as a permanent dipole moment of the molecules, and the phenomenon appears possible with any liquid having these properties [197].

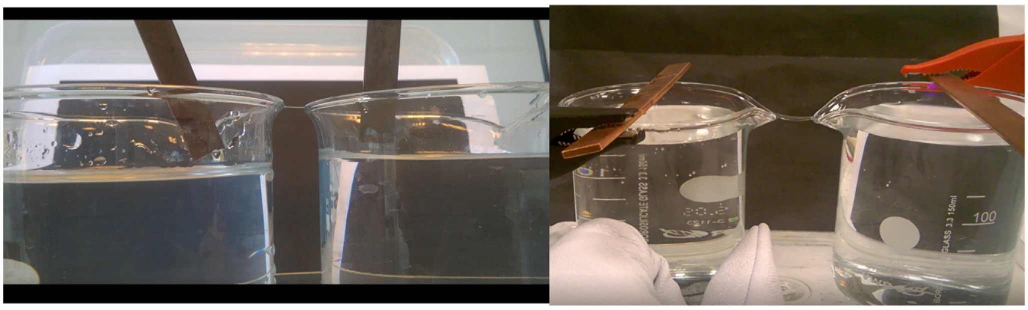

Fig. 14. Moving the electrodes (left). Video link: https://youtu.be/TuXwe1fa_n0. Generating the bridge with the electrodes out (right). Video link: https://youtu.be/WB2Sf50YDVQ.

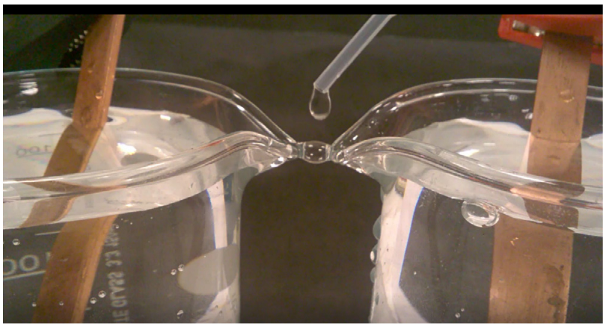

Fig. 15. Stabilized Air Bubble. Video link: https://www.youtu.be/KYh7fPagik0.

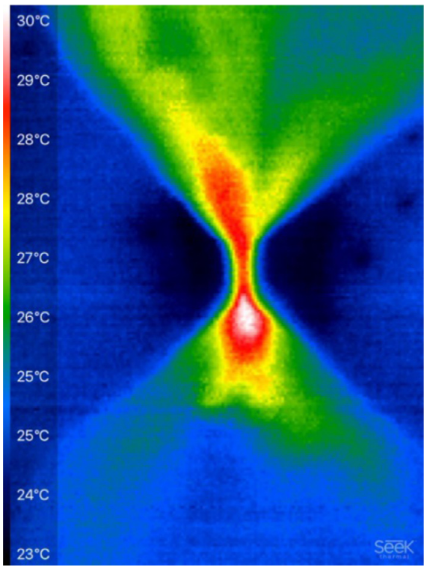

Fig. 16. Thermal Camera on the bridge. Video link: https://youtu.be/_7b9wAWkPQk.

Fig. 17. Glycerol bridge.

According to the references, the experimental procedure applied for the bridges' formation has been the same as with the case of deionized water. So an attempt to reproduce the experiment with Glycerol 99,5% Sigma Aldrich ® was performed in order to justify the similarity of the conditions (for the materials used see the Materials and Methods section). Originally, the first attempt has led to the formation of a thick glycerol film between the beakers after the application of high voltage (almost 30 kV). During the application of the high voltage, there has been a clear mass transfer from the cathode beaker to the anode one, through the film. The film was maintained for around one minute before collapsing. In order to reproduce a bridge formation instead of a film, the glycerol levels should be lower from the spouts, and the 'bridging' was assisted with a pipette. The Glycerol bridge is demonstrated in Fig. 17.

For less viscous liquids which we have tested (Ethanol 96% vol Sigma Aldrich ® and Acetone 99.8% Sigma Aldrich ®) as well as the alcohols methanol, 1-propanol and 2-propanol (mentioned in literature, [135]), similar bridges have been obtained and the reproducibility of these bridges was easier compared to the Glycerol case.

The surface tensions of water and glycerol are high (72 and 63 mN/m), but those of the alcohols and acetone are much lower (21–23 mN/m). The same can be said about the relative permittivity (79.5 and 42.5 for water and glycerol) but about 20–24 for all alcohols and acetone (except for methanol for which it is equal to 33.8). The conductivity (in microS cm^{-1}) is very similar (around 0.05–0.06) for water, glycerol and 2-propanol but much lower for acetone (0.005) and the three other alcohols (0.0014–0.009). From these numbers it does appear a bit difficult to relate the creation of water (polar fluid) bridge to any particular characteristics of the liquids. It appears that the relative permittivity is the most crucial factor as liquids with particularly low relative permittivity (e.g. hydrocarbons with values less than 5) do not appear to form bridges.

4.2.2. Bridge under the microscope and further discussions

A miniature version of the water-bridge experiment has been constructed, so that the floating water bridge could be placed under the

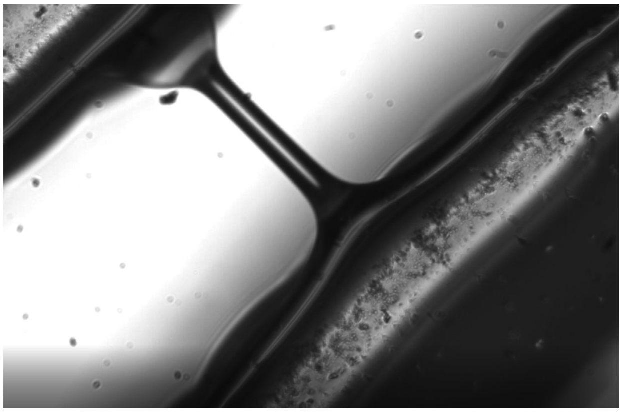

Fig. 18. Water Bridge under the microscope. Thorlabs ® Software used for the filming.

microscope. Thus, using polarized light, birefringence can be observed if present. The setup is established, and tested with regards to the voltage application on the microscope parts. A picture from the water bridge in position is shown in Fig. 18.

Polarometric investigation of the water bridge has been previously reported in other works as well [151,186]. In these studies, no microscope was used, but the bridge was positioned between crossed linear polarizers instead. The observations included bright zones at the longitudinal sides of the cylindrical bridge. The results were discussed regarding the origin of the observation. The bright zones were attributed to either birefringence in the outer layer, or to scattered light from micro-bubbles or density gradients that are present transversely to the water bridge [150,186]. An interesting discussion arises around the bright zones' interpretation. If indeed birefringence is present, that indicates the presence of a structure. Although the microbubbles' hypothesis seems convenient because it can also explain the density gradients [198], it is not impossible for birefringence to occur, in the presence of an electric field according to the Pockel's effect. The aforementioned effect describes how birefringence can emerge or change, inside an optical medium when an electrical field is applied [199]. Similar to the Pockel's effect, the Kerr effect is also mentioned as a possible reason for the bright zones in the water bridge [186]. Further literature review revealed that, these characteristic bright zones under polarized light are also observed in alcoholic liquid bridges as well [200].

So it could be said that the same physics describing the bright zones in the aqueous bridge, could also apply for the case of the alcohol bridges [200]. It seems that the bright zones are not an intrinsic water property, as for example Pollack suggests [2] by linking the characteristic bright zones of the water bridge to the EZ (exclusion zones).

According to Wikipedia [150], the phenomenon of water bridge needs to be studied further but the scientific community agrees that surface polarization at the water surface when a high tangent electrical field is applied is responsible for the extraordinary stability of the system. The same source mentioned that links to special water structure and the Exclusion Zone remain unproven to this date.

According to Skinner et al. [198], who performed diverse experiments (2D X-ray scattering) and molecular simulations, the bulk structure of water within the floating bridge appears to be isotropic and the same as ordinary water at the same temperature. This contradicts other measurements which suggest preferred orientation of water molecules along the electric field within the bridge.

In conclusion, these experiments provide useful insights in the water bridge phenomenon. They may provide some useful input on water's structure under exposure of an external electric field.

It is important to distinguish between intrinsic water properties and general properties of the liquids forming electro-hydrodynamic liquid bridges. The phenomenon reveals information about water, but since it applies to several liquids, it is not a special property of water alone.

We have not been able to determine answers to critical questions, about the stability mechanism, the adequacy of the leaky dielectric/Taylor cone model, the physical processes behind the spiraling charge and spiraling mass flows, the annulus structure, or the role of quantum mechanical effects that have sometimes been claimed as necessary for the explanation. While experimental studies are converging on the phenomenon, there are several different theoretical proposals for the underlying mechanisms. So this is an ongoing area of exciting and open research. For sure the phenomenon reveals information about the water as well, but is it adequate to disclose its peculiar properties? This is yet to be determined.

While the water bridge and water memory appear first as somewhat isolated phenomena, as we investigate these subjects, we become aware that all the water phenomena have common mechanisms and themes. Phenomena in different areas provide checks of the consistency of our fundamental models of water. We now move on to a phenomenon that has drawn a lot of attention in recent years, the *exclusion zone*. Attempts to explain this have confronted water theory more profoundly, and led to proposals for a radical revision of water theory.

5. The exclusion zone (EZ) theory – review, new experiments and proposals for the explanation of EZ

5.1. The Pollack theory for the exclusion zone (EZ) – the big picture

One of the most heated debates in the scientific community in connection to water is the presence of the so-called Exclusion Zone (EZ) near hydrophilic surfaces; whether it exists, how it is formed and whether/how it is related to water.

The EZ theory is pioneered by professor Gerald Pollack and co-workers who also proposed the mechanism for its formation based on some form of structured liquid-crystal water, referred to as the fourth phase of water. The book of Pollack [2] presents an overview of the theory and results until 2013. In this review we summarize also more recent developments.

The first paper was published in 2003 [201] where it was mentioned that *"The solutes (polystyrene microspheres) were excluded from zones on the order of 100 μm from the (polyvinyl alcohol) gel surface"*. The authors stated that the EZ remained for weeks (thus not a temporary phenomenon), and that the migration velocity of the microspheres was observed to be approximately 1.5 μm/s, fast enough to imply that diffusion was not a limiting factor. Moreover, a chemically cross-linked gel was used and it was concluded that the EZ was not formed due to polymer strands projected from the gel into the surroundings fluid, neither due to shrinkage of the gel. A convincing argument was that the EZ was not a characteristic of the specific gel but that other polymers tested (polyHEMA and polyacrylamide) also generated exclusion zone of the magnitude of approximately 100 μm, but there were also exceptions (a copolymer (polyacrylamide with a vinyl derivative of malachite green) generated no exclusion zone).

The 2003 article [201] offered three explanations for the observed phenomena (electrostatic charges – repulsion between gel and microspheres, chemical pH gradients and water structuring). It was shown that the width of the exclusion zone depended on pH, and when NaCl was added to solution the exclusion zone decreased, however much than predicted by the DLVO theory (see discussion in Section 5.3). These and other considerations made the authors to reject the first two explanations and concluded that the most plausible explanation should be the occurrence of some water structuring close to the solid surfaces.

Even though the structuring of water is a phenomenon recognized to exist near hydrophilic surfaces, Pollack and co-workers mentioned that this is typically considered to be in a very small layer. Yet, they also presented that a few earlier papers have opened for the possibility that this structured layer could extend further and this is important

Table 6
Comparison between bulk water and EZ-water according to Pollack and co-workers.

Property	Bulk water vs. EZ water	Comments
Light absorption (UV/visible light)	Big difference. 270 nm peak for EZ water	No peak for bulk water
Infrared absorption	Bulk and EZ water structures differ	Different IR absorption in bulk and EZ water
IR emission	EZ more ordered and crystalline than bulk water	EZ molecules are more stable
Magnetic Resonance Imaging	Chemical difference between EZ & bulk water	More restriction in EZ water molecules
Viscosity	EZ water viscosity is higher	
Optical features	10% higher refractive index for EZ water	EZ water denser than bulk water
Polarizing microscopy	Water in EZ (much) more ordered than bulk water	Huge ordered phase (thousands/1 million water molecules)
Charge	EZ has negative charge	

as if structured water should account for the exclusion zone it need to be made of millions of layers of water molecules. Of particular interest is the review of Henniker from 1949 [141] which summarizes experimental data from 174 published articles. The conclusion from the Henniker review is that the surface layer in liquids, including water) is not a monomolecular layer, but a zone in which orientation (etc. structuring) of the molecules extends hundreds and up to thousands of angstroms, which goes against the accepted DLVO theory.

Several observations in the 2003 manuscript [201] (solvent particle size influences the exclusion of the particles; constant velocity of the microspheres moving away from gel indicating a steady and constant growing “force”) made the authors consider that the built-up of layers of structured water could explain the EZ creation. More evidence for this hypothesis and more experimental results were provided in the 2006 paper [202] from Pollack’s group. In the 2006 paper [202] more materials are shown to form “extended” EZ (gels, optic fibers, monolayers, Nafion) but some don’t (stainless steel).

It was also demonstrated that EZ (close to polyacrylic acid) does not have the same electric potential as the bulk water. According to Pollack and co-workers, this sustained potential gradient within the exclusion zone indicates that the exclusion zone consists of molecules in a stable structure, largely free of mobile charge carriers.

Pollack et al. also performed an analysis of the exclusion zone (close to Nafion-117) using a UV–Vis spectrum setup. They measured [202–205] the absorbance at various distances from the nafion-117 surface and they noticed that there is a significant difference in absorbance, as one gets closer to the Nafion-117 lined surface. The peak absorbance lies around a wavelength of 270 nm. This indicates that the water near nafion-117 differs to a great extent from that of bulk water. Moreover, as the peak absorbance differs from that of Nafion-117 (being at a wavelength of 196 nm), this indicates that the observed absorbance is not caused by Nafion-117 particles diffusing out into water. Pollack in his book [2] discusses this further, and interprets this property as evidence for a liquid crystal state of water, in particular for the hexagonal-lattice model which he proposed for the molecular structure of EZ water. No other independent experimental studies confirming these results have been reported.

If confirmed, the 270 nm peak could be considered one of the most convincing evidence that EZ may be associated with some special water structure. There have been more experiments from Pollack’s group which appear to support the structured water hypothesis. For example, Pollack and co-workers performed IR and NMR measurements of EZ and compared to bulk water. They do see some differences, further indicating that the EZ water structure differs from bulk water. Similar conclusions obtained also from other measurements e.g. density, viscosity, and optical properties. Table 6 summarizes the differences between the structured interfacial (so-called EZ) water and bulk water, as observed by Pollack and co-workers which summarize these systematic experimental studies. Very few of these results have been verified by independent experiments, and the very important UV absorption at 270 nm claimed for EZ water, and also for melting ice has not been replicated by any independent experiments, to the best of our knowledge, neither is reported in standard UV databases. Moreover, Musa et al. [147] have not been able to find any difference of the viscosity and density of water in the EZ and the bulk water.

Anyhow, taken at face value, these experimental results show that, as Pollack suggested, the water in the EZ zone is of a gel-like crystal structure, which is supported by experiments showing that EZ water have different physical characteristics than bulk water, and that these characteristics point to a more rigid structure. Moreover, the results imply that exclusion zones can form in the vicinity to a variety of materials and that these exclusion zones possess significantly different physical properties than that of “normal” water and that several of these physical properties indicate that the exclusion zone water is more rigid, crystal-like, in structure. However, an exclusion zone of 100 μm would have to be built up of approximately 300,000 (structured) water molecules, a number that exceeds all accepted surface chemistry theory e.g. DLVO. These and other factors have led to significant debates about the EZ theory of structured water which we present in Section 5.3, after the presentation of our own measurements of EZ close to Nafion surfaces in the next section.

5.2. New measurements of the EZ in Nafion 117

We performed experiments for investigating the possible EZ in Nafion 117. A ball of Nafion was cut in half, and soaked for 10 min in demineralized water. The ball was then placed in a petri dish, and covered with a solution of demineralized water and polystyrene microspheres (1 μm diameter). Fig. 19 shows the Nafion half ball in the top right corner, and the water with microspheres in the bottom left part of the pictures, after 30, 90 and 230 s. As can be seen the EZ zone formed, pushing the microspheres out of the zone. Fig. 20 shows the size of the EZ layer as a function of time.

We performed the same experiment (with the same size of polystyrene microspheres) using both Nafion and a sheet of glass. We have observed that the EZ zone formed next to the Nafion but not next to the sheet of glass. All experiments have been repeated several times with the same result.

Finally, once the formation of EZ has been established, we have studied the phenomenon for Nafion 117 and polystyrene microspheres over extended periods. The results are shown in Figs. 21 and 22. In order to appropriately document the results, pictures were taken during the experiments. On all pictures the size of the EZ zone was measured and plotted against time as seen Fig. 22.

We should mention that EZ sizes of the same orders of magnitude (200–400 micro-meter) have been presented for Nafion by other researchers as well [143,206]. In particular, Esplandiu et al. [206] in a recent article studied also the effect of salts on EZ and found that salts

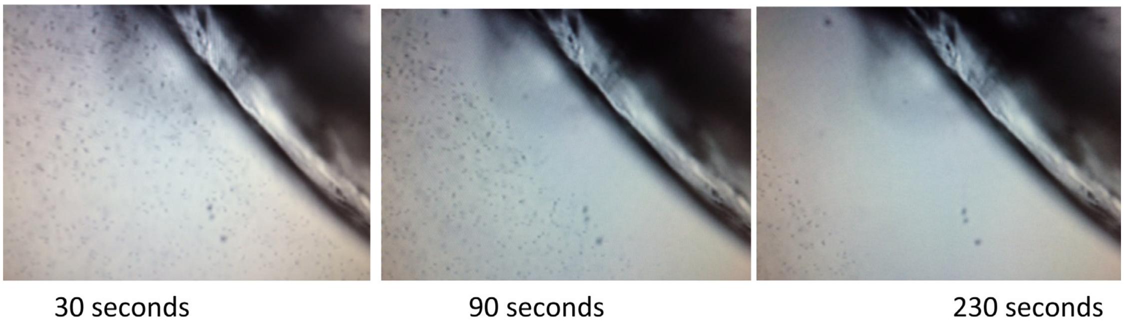

Fig. 19. The formation of an EZ (exclusion zone) in the proximity of a Nafion half ball, resting at the bottom of a petri dish. The dots are microspheres in water covering the half ball.

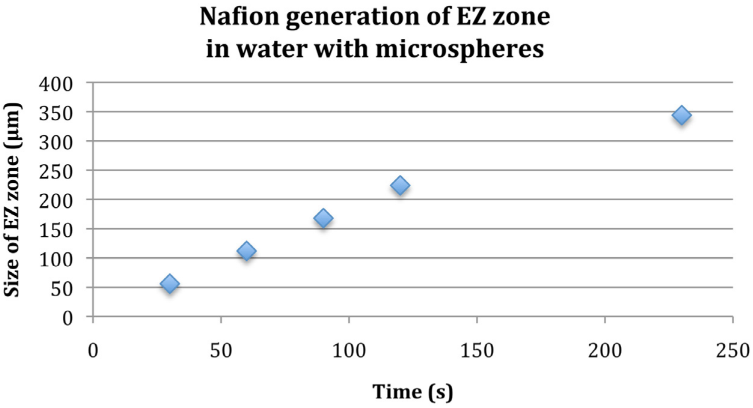

Fig. 20. The size of the EZ layer against time. The EZ instantly started to generate and reached a maximum at approximately 350 μm.

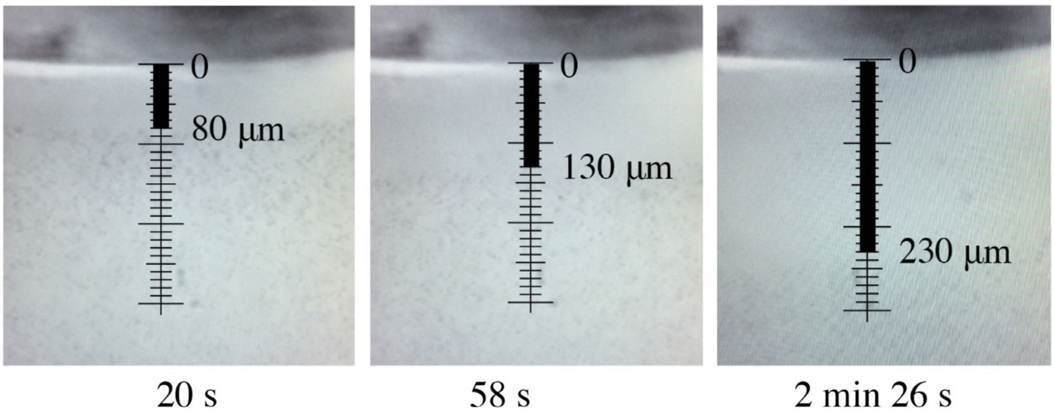

Fig. 21. The formation of an exclusion zone in the proximity of a round Nafion slice. The round Nafion slice is seen at the top of the pictures. The clean zone grows over time, and the “impurities”, consisting of polystyrene microspheres, are seen to have moved away from the Nafion surface.

(NaCl) decrease the EZ considerably e.g. at equilibrium from 350 μm (no salt) to about 100 μm (10^{-3} M NaCl).

5.3. Controversial aspects and debates about the EZ theory

Pollack’s experimental investigations, the establishment of EZ for a wide range of surfaces (gels, Nafion, some biological samples) and his hypothesis for the EZ are interesting.

Possibly the most controversial aspect of the theory is the charge separation in water when it is close to hydrophilic surfaces, looking like water battery from which we can potentially take energy. Those, most typically negative charges, correlate with the length of EZ. Pollack claims that water stores energy in two modes: order and charge separation (battery-like) and that the positive ions (hydronium) which are generated are very important and drive many phenomena.

Pollack believes that there is clear evidence for proton buildup from EZ and not from other sources and that very low pH (1–2) is found in the beyond EZ zone, but he admits that these measurements are difficult. He believes that EZ charge separation resembles the first step of photosynthesis and that the energy needed to drive the water battery comes mainly from infrared radiation.

In brief, the water battery is charged by IR radiation (from e.g. the sun or other heat sources) which enhances EZ and it can produce electrical current. The phenomenon is reversible and if this energy/light is removed, EZ returns to its original size. According to Pollack, some of

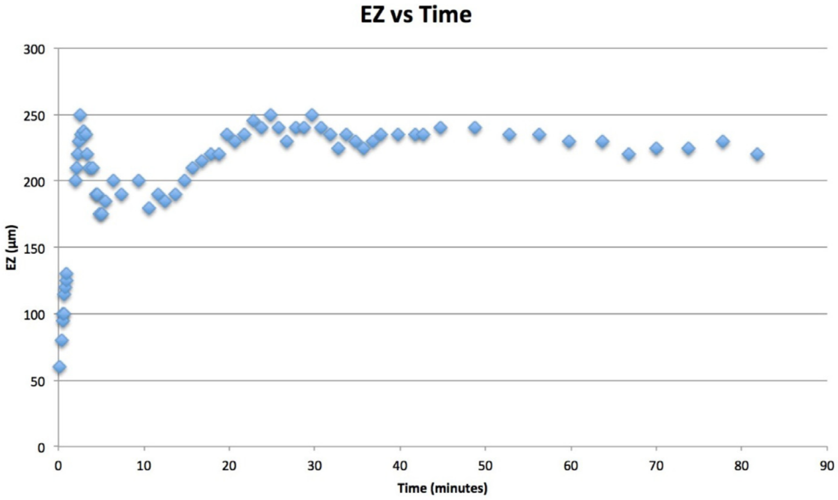

Fig. 22. The exclusion zone length as it develops over time. The zone developed immediately reaching a maximum after a few minutes of about 250 μm equal to a quarter millimeter.

this energy in water can be harvested using the excluding nature of EZ for cleaning water (filtration processes for getting drinking water from contaminated water [207]) as well as developing water desalination devices (as salt is also excluded). He also mentioned numerous applications of EZ water in biology as well. He claims that water can produce useful energy but admits that the amount of energy is small so far. Whether this electromagnetic energy which builds the potential energy in water can be harvested for doing work in quantifiable amounts remains to be seen!

His Book [2] presents, moreover, numerous indications on how this theory can provide explanation for several of water anomalous properties (high heat capacity and surface tension, density maximum,…) but also for other phenomena (why ice is slippery and ice creation, life in ocean depths, Brownian motion, how boiling and evaporation work, catalysis, capillary action, water interplay with salts, etc.). We will get back to these later in this section.

More specifically, the theoretical basis – explanation of the EZ is, according to Pollack, a buildup of many layers of structured water parallel to surface and that the EZ growth is nucleated and is progressed layer by layer. He claims that there is a special “gel/solid” type structure of EZ layer(s) consisting of multiple water-type structures (negatively charged). Pollack hypothetizes a water structure in the EZ zone of the type H_3O_2. Thus, a hexagonal structure, H:O=3:2 (not 2:1), therefore −1 net charge per unit hexagon. In his view, EZ-water looks also like ice but is more fluidic, less structured and negatively charged and it excludes because it is very thick/dense; the hexagonal openings in the structure are very small (only protons and like are small enough to penetrate). He also comments that nature likes hexamer/hexagonal structures and that water hexamers have been identified by many research groups next to many surfaces e.g. metals, proteins, graphene, quartz and in supercooled water.

All these look interesting indeed, some of it maybe even a bit “science fiction” to some extent, but most of the above claims have not been verified by independent researchers. There is no widespread accept of Pollack’s theory, at any level and there is harsh critique of some of the statements. Especially Pollack’s article in Langmuir ”Can water store charge”? [208] has created a firestorm with letters to Langmuir, replies and more…, forcing prof. David G. Whitten, editor-in-chief of Langmuir to state that the paper passed through peer review. More on these will follow next.

The authors of this manuscript consider the work of professor Pollack to be of interest but we wish to present a number of issues which are considered troublesome and present difficulties in the appreciation of the theory or understanding its generality. We illustrate some of these issues in the coming sub-sections.

5.3.1. Interesting results and serious issues

According to Pollack [2], EZs are huge zones of hundreds of micrometer (mm order size, millions of water layers), they occur on numerous hydrophilic surfaces (gel, zinc, nafion, silicon, monolayers, bio-surfaces like muscles), “everything” is excluded from the EZ zones (small and big molecules not just microspheres), there are no ”trivial” explanations (contaminations, etc.) and there are dozen labs which have confirmed EZ existence. We were not able to identify the “dozen labs” which have confirmed its existence for numerous surfaces, according to the 2013 book [2]. But like some other researchers [143,144] we have confirmed the EZ presence for the very hydrophilic polymer Nafion. Videos of the EZ formation, visualized using polystyrene balls with high-speed microscopy, are now commonly available (see experimental section). This confirms the fundamental property of exclusion. However many other properties are more difficult to measure, and are more controversial. However it remains to be seen how general the phenomenon is i.e. for how many surfaces we can observe EZ generation.

Pollack mentions that EZs exist for hydrophilic but not usually hydrophobic surfaces (without explaining this difference in behavior). Moreover, he does not define how hydrophilic the surfaces should be in order to give rise to EZ. The contact angle is a measure of hydrophilicity, but we are not provided explanations on exactly which hydrophilic surfaces would give rise to EZs and how we can test this. Stainless steel and glass apparently do not give EZs, and it is not clear why this is the case. So, the generality of the EZ is one important issue.

Precise factors responsible for the formation of EZ are unknown. This means EZ is not predictable from any theories yet. However some theories can model EZ generation. Pollack does not claim EZ can be predicted by hydrophilicity. Although it may be unpredictable, EZ may be explained in different ways by different theories (see Section 5.4).

So far, it has been observed by numerous researchers only for Nafion, but is claimed to form for several other surfaces, including other polymers or gels, and even metals. However there appear to be very a limited number of independent studies either supporting or rejecting EZ formation, outside water-Nafion experiments.

Another important issue related to the EZ is to what extent it is associated (exclusively) with water. Pollack presents a theory for structured water as an explanation, but he also stresses several times in his book [2] (see [209,210]) that other polar liquids also exhibit EZs.

Liquids like ethanol, methanol, isopropanol, acetic acid and even the polar but not associating DMSO were shown to produce EZs. This

Table 7
Similarities and differences between DLVO theory and Pollack's theory.

DLVO	Pollack/EZ	Comments
Stern/diffuse = Double layer + Electroneutral solution	Separated charges e.g. EZ (-) and protons (typical case)	In EZ theory particles are sensitive to material surface far apart
Debye length – nm order	EZ length – micrometer order or bigger	Both decrease with salt concentration
Both negative and positive surfaces, the latter rare	Negative EZs more common, positive exist but rare	In DLVO explanation based on cations being smaller than anions
Surface charge of mV range	Surface charge of mV range (often around 150–200 mV)	Both depend similarly on distance from surface
Attractive van der Waals forces	vdW forces not mentioned in the EZ theory Attractive forces due to charge separation	DLVO: $V = V_A + V_R$
Presence of third medium can make vdW forces repulsive and electrostatic forces attractive	Principle 4 – "Like likes like via a medium of opposite charge" appears similar to DLVO	

means that EZ is not (and neither was the water bridge) a characteristic property of water alone. Water has unique properties, anomalous properties, that ethanol or acetic acid do not have, but if all these molecules create EZs, what does it really mean? What are the explanations? And if we accept a special water structure for the EZs associated with water, should we do the same for other non-water molecules responsible for EZs? Are there special structures there or other mechanisms? These questions have not been answered.

We should, however, mention that EZs (reported under the same conditions as for water) are smaller for these other polar molecules e.g. (in μm) 102 for methanol, 30–50 for ethanol, acetic acid, isopropanol and DMSO (compared to 220 μm for water). Moreover, DMSO EZ creation was the slowest. These results indicate that EZ creation is not a "privileged" or anomalous property of water, but that other molecules also show it. Pollack and co-workers comment that "it appears that water is less unique than anticipated, at least in terms of exclusion-zone formation" and "how exactly these zones (of these other liquids) differ structurally remains to be elucidated". We can mention that Henniker [141] in that earlier review had also mentioned extended zones also of other polar liquids (than water) close to several surfaces. These papers of Pollack on EZ for other polar liquids are 10 years old, but to our knowledge no extra information has been presented on whether these other polar liquids present special structures close to EZ.

5.3.2. EZ and the DLVO theory

An important and broader discussion point in Pollack's book [2] is the contrast between the EZ theory and the DLVO theory. DLVO is a cornerstone theory of colloid chemistry, typically taught in all courses and presented in books about colloids and interfaces, and it describes stability in colloid systems. In Pollack's book is often mentioned how different are these two theories (EZ and DLVO), but how different are they? Table 7 summarizes their important similarities and differences, as we understand them.

Moreover, unlike DLVO (where the thickness can be calculated via the Debye length), the EZ size depends, according to Pollack, on multiple factors such as surface chemistry, surface roughness, pH of the bulk water, ambient radiant energy and maybe even the atmospheric charge.

As Table 7 indicates, the two theories have many similarities e.g. most surfaces and EZs/diffuse layers in DLVO are negative (and positive surfaces and EZs are more rare). But it is claimed that the negative EZ can grow up to a meter and can keep growing, under certain conditions and this is a serious difference. The same can be said for the surface potential – distance curves in EZ and DLVO theories. We see such curves in both cases but the scales in EZ are orders of magnitude higher compared to DLVO. The size difference between EZ and the double layer length is huge from 5000 to 200.000 ratios (based on 100/200 μm for EZ & 20/1 nm for the double layer).

Finally, we should mention that the "like likes like" principle of Pollack does agree well with the DLVO theory. We have DLVO equations for van der Waals forces (often attractive) which can become repulsive in the presence of a third medium and especially (typically) repulsive electrostatic forces between particles of same charge which can become attractive in the presence of a third medium of another charge. Moreover, in the "classical solution chemistry" the principle "like dissolves like" i.e. the similar molecules form homogeneous solution is also rather well known.

5.3.3. Salts and EZ

As a last note, it is relevant to mention briefly about the effect of salts on EZ, topic extensively discussed by Pollack in his book. What he has observed is that high salt concentrations reduces the size of EZ, which would agree with the DLVO theory (salt concentration decreases the Debye thickness). Pollack goes further and he believes that this decrease of EZ size means also a decrease of the oxygen level and, for example, EZ zones in sea are expected to be disordered / discontinuous networks but still thick and their presence contributes to the stiffness of the water's surface. Moreover, according to Pollack, there are high oxygen levels due to presence of high EZ zones at the upper sea zone level (where salt level is low). Pollack presents several (not entirely convincing) explanations, based on the salt effect on EZ, for the mixing problem between waters with different salt content (or fresh and sea water) as well as for the phenomenon of osmosis.

Staying on the topic of electrolytes, Pollack and co-workers [203] have also performed a single EZ-related spectroscopic study of aqueous solutions of salts (and other chemicals; sugars and amino-acids) in absence of any hydrophilic surface. They found a 270 nm UV absorption peak in all cases, but with different intensities. They conclude that the aqueous region around these solutes resembles the aqueous zone close to hydrophilic surfaces, due to the phenomenon of water ordering around e.g. salts or ions (see also Section 3.2). They used this work to exclude that organic contaminants play some role in the creation of the 270 nm peak. In terms of intensity, LiCl had by far the strongest peak, followed by NaCl, and KCl had the lowest peak. LiCl showed also a very large fluorescence peak (around 480–490 nm), while NaCl and KCl also gave peaks around the same area, but the intensities were weaker.

Note the preparation of these compounds was quite extreme, with baking in high temperature ovens, etc.

Li+ and Na+ are well known as structure-making ions, with Li+ being much stronger. On the other hand, K+ and Cl- are considered to be structure-breaking ions. Marcus [36] reports water structural entropies (in J/K mol) between −70 and −80 (for Li+) and −20 and −30 (for Na+). The values for K+ are between +20 and +40 and for Cl- around +20. Similar observations are mentioned by Frank and Wen [212], that ions like Li+ which are small (or multiply-charged ions like Mg^{2+}) may induce additional structure (entropy loss) of some sort beyond the first water layer. Finally, De Ninno and Francesco [137], in their FTIR study of the isosbestic point in aqueous electrolyte solutions confirmed the order of Li+, Na+ and K+ mentioned above. They concluded that the isosbestic point order coincides with the Hofmeister series and also the effect of ions on the water network.

The line of all these observations are in agreement with those by Pollack and co-workers.

Pollack attempts to explain many of water's special or anomalous properties using his own concept of EZ (with the structured water layers), combined with the associated role of charge and electrostatic phenomena. The effort is interesting but there are issues. He mentions that the reason explaining the observation of several small living creatures (mosquitos, lizards, etc.) walking on water is not so much water's high surface energy but the many EZ layers present on the surface of water in contact with air. But is this answer complete ? As Pollack mentions that ethanol and other polar compounds also give rise to EZ, why don't we see such "walking phenomena" for other fluids as well? Ethanol has a much lower surface tension but are the EZ layers much smaller also? Pollack admits not to have studied ethanol and other polar compounds EZs very systematically.

According to Pollack, water's very high heat capacity is because water must absorb more than the expected energy in order to increase the temperature by a fixed amount because some of the radiant energy goes to build structure! This is interesting, but do we see "structures" for other polar compounds which have much lower heat capacities? Again, the non-uniqueness of EZ for water is an issue.

Pollack attempts also to provide an explanation for the famous density maximum of water based on the fact that the density order follows: EZ water > bulk water > ice (which floats) and that the overall density depends on how much of each phase resides in the container. He states that there is massive freezing near 0 °C, but some ice may begin forming a few degrees higher (2–4 °C) and that at 4 °C we have the minimum volume and thus the highest density. The explanation appears rather speculative and not very convincing.

5.3.4. *General debate about Pollack's "structured water" theory*

Pollack's theory – explanation for the exclusion zone is based on the existence of a special structured water phase close to (certain) hydrophilic surfaces. Water clusters are being reported often in literature e.g. in [205,206] but there is not much accept.

Pollack's work has not been noticed extensively by the "standard" (mainstream) scientific community, with the first two papers from 2003 [201] and 2006 [202] having received (24/11/2020) 129 and 223 citations respectively, all the rest EZ-related articles have, each, fewer than 100 citations. There are many extensive reviews about interaction of water on solid surfaces [216,217] e.g. the Henderson review [216] is from 2002, and the one from Björneholm et al. [217] is from 2016. The latter review contains over 300 references, it is called "Water at interfaces" and it does not mention Pollack, the EZ (with or without connection to water) or even the paper of Henniker [141] which contains plenty of information on extensive layers of water close to a wide range of surfaces. These omissions are surprising.

Both the original papers of Pollack [201,202] and subsequent papers about water and its capability to store charge [208] have met critique and there have been discussions in literature, even from Pollack's colleagues in his own university, such as J.M. Schurr [218,219]. It is important to emphasize that in most of the critiques, the main issue is not so much whether EZs are created for certain systems – surfaces, but mostly whether the exclusion effect is related to water and its structure.

Pollack has replied, however, both on the water-storing-charge comment [208] and also against the theory of macromolecular chemotaxis [220] as a method to justify the exclusion zone.

Nevertheless, the critique against the "structured water hypothesis" for the EZ formation continues and intensifies e.g. from Elton and co-workers [221,223]. Elton was keeping a blog on the EZ and various mechanisms but his investigations were recently published in the aforementioned manuscripts. He does not deny the existence of EZ, on the contrary he and his colleagues mention that by now there are several independent groups which have verified the EZ creation for a few surfaces (though exactly for which surfaces we have EZ and what can be excluded needs further investigation). For example Spencer et al. [223] failed to detect EZ on any material other than Nafion. Thus, while Pollack and co-workers detected EZs in many metals, Spencer et al. [223] failed to do so. Moreover, Li and Pollack [224] observe EZs in many hydrogels including agarose and gelatin but Spencer [225] in his MSc thesis explicitly mentioned those two hydrogels among the examples of materials showing no EZ. So, the generality of the EZ is one serious issue, as there appear clear difficulties in obtaining EZ by independent researchers for materials other than Nafion, at least based on the studies published so far.

Moreover, according to Spencer et al. [223] the detected birefringence is not related to EZ and is not an indication of crystalline ordering of the water molecules. The same is more or less stated by Elton et al. [221,222], who also criticize experiments by others who have measured increased refractive index of water close to the surface of Elton et al. [221,222] mention that neutron radiography experiments do not support the notion of a higher density phase. We do see some issues with the Spencer et al. [223] experiments, but the work is of course highly relevant being one of the few independent studies seriously looking at EZ phenomena.

Moreover, in one of their earlier studies, Musa et al. [144] reported EZ measurements close to Nafion and emphasize the importance of the phenomenon but their measurements show no difference in the viscosity or density of water in the EZ zone and outside of it.

What Elton and colleagues insist is that there are many other more plausible theories for the EZ creation and in their recent manuscript [221] they discuss several of them: diffusiophoresis (long range chemotaxis, ion diffusion and exchange from the material into water), repulsive van der Waals forces, and others e.g. microbubble contamination, nanobubbles in water or dissolved gasses or contamination of plastic nanospheres. They state that the van der Waals repulsion may be useful as explanation for EZ zones in metals.

They conclude that the EZ phenomena may have many applications in engineering such as microfluidics and filtration as well as biology and that their better understanding is crucial and should be pursued. From their manuscripts [221–223], it is clear that Elton and co-workers do not accept that the "structured water hypothesis" is a valid explanation of the EZ formation. The same conclusion is seen from the recent study of Esplandiu et al. [206] who mention that EZ formation is due to interplay of the electric field with the zeta potential of the solute and can be affected by changing ion diffusion coefficients or adding salts. They clearly state that the EZ formation, in their view, does not stem from water structuring effects at the Nafion interface. Other research groups [226-228] are somewhat more positive, although they do not find differences in the EZ generated in Nafion/water interfaces with different types of water (spring water, water treated with magnetic vortexer, etc.). It is, however, of interest to observe that Elton and co-workers admit that phenomena like the expansion of EZ with light, the exclusion of salt and the anomalous flow require further explanation [221,222].

About 14 years have passed since the 2006 paper on "long-range impact of hydrophilic surfaces" and 7 years since the 2013 book by Pollack [2] where he presents in detail the proposed water structure for the EZ. Professor Pollack and co-workers have continuously published evidence for EZ on more surfaces, insisting always on the water structure hypothesis, providing further evidence based on spectroscopic, viscosity and other measurements, but they also published diverse applications of EZ in connection to health, food and biology e.g. Refs. [226–231] but also some applications of EZ related to natural and similar phenomena like gels and persisting water droplets on water surfaces [232-233]. One of the most recent works from Pollack group [224] in a top journal demonstrates in detail and convincingly with extensive experiments a surface-induced flow observed for 5 different hydrogels, all exhibiting significant EZs. The authors show that such flow and EZs are not shown for hydrophobic surfaces. They conclude that this surface-induced flow is quite different from pressure-driven flow and has important and special features: infrared energy increases flow velocity and narrower tunnels generated faster flow. Li and Pollack [224] link in most cases this surface-induced flow to EZ but they also admit that the detailed nature of the hydrogel-water interaction remains an outstanding question in the field. The structured water theory is somewhat underplayed in this recent study [224].

Professor Pollack's book, recently translated into German, is an interesting reading, it has been positively reviewed by several people (e.g. H.H. Bauer, 2014, J. Scientific Exploration, 28(2), 390–394). Professor Pollack is continuously being invited, even in important events (https://bioe.uw.edu/gerald-pollack-to-join-nobel-laureates-to-present-seminar-before-uks-house-of-lords/), and he has given TED and other talks related to EZ and its interpretation as a special structured water phase. He insists on his theory but, as mentioned above, several alternative explanations for the EZ have been proposed. Relatively few researchers outside Pollack's own group are convinced that the EZ is due to some structured water phase, among those supporting a structured-water hypothesis is de Ninno and co-workers [145,137–140,234,235]. She and others from the "Italian school" have put forward the QED (quantum electrodynamics) explanation of EZ, presented in Section 5.4.2. They do find good reasoning between the water structured hypothesis and QED. However, the latter is not widely accepted by the mainstream community either and Philip Ball writes in Nature News (2004) about the "quantum-coherent domains": "… proposed in a paper (Del Giudice et al. [236]) that now seems to be invoked whenever water's weirdness is at issue" (he repeated similar concerns in July 2013 in his article "DNA Waves don't wash, published in Chemistry World). In the latter paper he considers the "coherent domains" to be "a quantum putty to be shaped to order, not a theory to be tested. They haven't yet been clearly detected, nor have they convincingly explained a single problem in chemical physics". Such strong statements have been, as might have been expected, answered by de Ninno and co-workers.

With such debates about the various EZ explanations, we felt that this topic deserved extra attention and a detailed discussion is presented in the next section, of the role the various mechanisms may have in explaining EZ.

5.4. EZ explanations and discussions

There have been several key explanatory mechanisms proposed for EZ. We will now provide a more detailed discussion of the EZ mechanisms proposed, some of which have been mentioned earlier in the manuscript. The three main views are summarized and discussed first, followed by a more extensive discussion.

1. The *structured water* view, advanced by Pollack and others, is based, as mentioned, on a long-range *structure* induced in the water. This implies that EZ water is in a non-equilibrium state, sustaining a *thermodynamic process,* with absorption of light (primarily infra-red) driving charge separation, converting heat energy to electrical potential energy. Pollack and others propose that energy is stored in *novel water bonding structures,* resulting in charge separation. Proposals include Pollack's hexameric water polymer, leading subsequently to the Segarra-Marti et al. [237–239] hypothesis of a water dimer (with a double pair of stacked hexagonal rings), which they show to be viable alternative through advanced *ab initio* modeling. These and other '*structured water*' proposals support the view of EZ as a distinct *liquid crystal phase of water,* between ice and bulk water. As mentioned, the *structured water* view is a somewhat radical departure from the 'traditional' point of view of water in chemistry e.g. as defined by the famous DLVO theory.
2. The conventional *chemotaxis* view, going back to the 1970s, is that the exclusionary force is due to chemical-potential gradients acting on a purely local molecular level. Exclusion effects are explained by essentially local classical electromagnetic forces and interactions among molecules. The classic proposal is *diffusiophoresis*. This explanation was considered by Derraguin in the 1970′s, in the context of specific examples of EZ in biological context, but he rejected it. Supporters of this explanation also typically see it as making other explanations redundant, and reject the idea that any significant 'water structure' can form beyond a few molecular layers of the interface, and reject the idea of a 'liquid crystal' state of water of any magnitude. The *chemotaxis* (diffusiophoresis mechanism) view has good theoretical credentials in the wider context, and at a first glance it is not clear whether it is sufficient to explain all the properties of EZ water and whereas it can explain some transport features convincingly, it may be a part of the full mechanism.
3. The third view is *QED* (quantum electrodynamics, including *'coherence domain'* and 'photonic crystal' theories). This theory proclaims that EZ water depends on non-local quantum field effects. This theory predicts coordination of properties of bulk molecules or atoms over large distances, reflecting quantum entanglement. This type of analysis appears to originate with Elia and Del Guidice as far back as the 1980s [236], and has been developed significantly in recent years, with a growing publication list, and application to the hydrostatic water bridge and other electric field effects in water. These proposals draw on a relativistic quantum effects.

The *QED theory* is perhaps the most intriguing, among all EZ proposals, but it has theoretical foundations. If correct, it means these simple liquid environments display macroscopic *quantum entanglement effects,* at room temperature. It implies that certain macro-structures (in EZ and the water bridge) are formed and stabilised though non-local quantum effects, and have properties that cannot be explained classically. A display of quantum entanglement effects in such a system would be very interesting.

The chemotaxis supporters argue that this theory provides a convincing explanation for the exclusionary force or transport mechanism. This has been analyzed in increasing detail recently, primarily for the case of water-Nafion EZ. They have developed useful and quite successful analytic models. However other theorists argue that chemotaxis is not adequate to explain the full range of observed properties of the exclusion zones, across the full range of water and other liquids, and surface materials that have been observed. They question whether electro-chemical gradients required are present in all cases of the phenomenon, as well as questioning the limitations of chemotaxis to explain properties other than exclusion.

Structured water supporters, especially the Pollack group, have pursued a range of experiments to try to test and establish anomalous properties of anisotropy, absorbance, density, viscosity, charge, etc., that chemotaxis or the conventional DLVO theory should not predict or explain.

The QED theory of "coherence zones" is perhaps the most intriguing alternative. If correct, it means quantum field effects are significant in the chaotic liquid environment of water at room temperature.

Despite considerable research over the last two decades there is still no common agreement on the explanation. In our view, none of these three types of explanatory mechanisms has been ruled out. Moreover, although they may be perceived as competing hypotheses, they may all play a role, and are not necessarily self-exclusive. As it is not entirely evident which of the three approaches (or other or any combination thereof) is the more plausible one, all three views merit more discussion and all three theories are discussed and compared in the remaining of this section.

5.4.1. EZ structured water hypothesis

Is there a special 'EZ structure' formed in the water? There is still no commonly agreed resolution to this question. Given the range of EZ properties that have been studied, it might be thought that the choice should be more evident (and to some researchers it may be). But most properties do not point directly to any unique explanation, or resolve the critical choice of theories. Rather, there is a patchwork of explanatory features.

We consider that the 270 nm absorption property is the most definite feature that seems to show quite directly that there is something in the EZ water that interacts strongly with UV light, something that must be different in structural or material composition to bulk water. The Pollack experiments show its concentration being reduced across the EZ region. We believe that this provides strong direct empirical support for some version of structured water, given the only thing present to produce the structure is water, in some unexpected molecular or structural arrangement. This structure might be explainable in terms of ordinary molecular theory applied to a novel water polymer, or may in turn require some quantum field effects.

We first summarize some conclusions about the hypothesis of some kind of *crystalline water structure* present in EZ. Pollack [2] advanced a model of EZ water structure as hexameric sheets, similar to ice, but with offset layers, and a major disequilibrium: on a large scale, it forms the chemical ratio: $H_3O_2{}^-$ with H^+ excluded. This hexameric lattice structure is an attractive concept, but some quite basic calculations show that his original lattice is unstable. Even just one double-lattice sheet extending across the Nafion surface represents a massive charge displacement and massive local electric fields. Others have reached similar conclusions. Nonetheless it is a good creative scientific intuition, and there is something very important behind the intuition. Neils Bohr's initial models for quantifying atomic electron orbitals in the 1910′s were not ultimately stable either, but revealed a fundamental insight that ultimately proved to be correct.

There is some support for Pollack's water model from the work of Chatzidimtriou-Dreismann and co-workers [31,32] who have, experimentally under certain conditions, advocated a water structure of $H_{1.5}O$, which bears some similarities to Pollack's negatively charged model (−0.5 instead of −1 net charge).

However, even more importantly, Pollack's hexamer model led to the impressive study by Segarra-Martí at al. [237–239], who conducted *ab initio* modeling of smaller water polymer structures, and found what looks like an ideal candidate: a stable molecule, comprised of two pairs of stacked hexagonal rings slightly offset. This represents a disequilibrium: $H_{38}O_{20}{}^{2-}$ and $2H^+$. The first point is that this is theoretically *stable.* This is surprising. The second point, which they consider critical evidence, it that this molecule is predicted to have a distinct UV absorbance peak at 271 nm, consistent with Pollack's experiments. They comment that this peak has been revealed to be a unique characteristic of structured water in solutions of many different substances (salts, amino acids, sugars), similarly to the feature recorded in the EZ by using Nafion 117 solution/film. All experimental studies related to the 270 nm absorption peak refer to Pollack and we have not been able to identify independent experimental studies, outside of Pollack's group, verifying this result.

We have performed some simple calculations that confirm that low molar concentrations (10^{-6}) of this proposed dimer are indeed consistent with both the UV absorption coefficients found by Pollack, and with measured electric field strengths or estimated charge separation. It appears to be a realistic proposition that this novel *water polymer* is in solution in EZ. These results and possible presence of a water polymer appear to support a *structured water model.* This is a surprising and significant result and it is necessary to investigate how this water polymer molecule could be generated by Nafion and other surfaces, through the combination of the surface geometry, electric potential, and incident radiation (required to sustain the EZ). This is presently unknown.

We consider the work of Segarra-Martí at al. [237-239] to be a very significant and well-documented theoretical study which offers some validation of a structured water model different to Pollack's but with some clear similarities and a theoretical demonstration of the association of the characteristic UV peak to a specific water structure. Somewhat surprisingly, Elton et al. [221,222] in their recent reviews refer to this review as invalidating Pollack's theory (finding that the structure proposed of "bulk-type water aggregates" is unstable).

Anyhow, there are several additional issues we should like to raise. This proposal also suggests a link between hexagonal ice structure and this proposed "EZ water molecule", and supports interest in the So et al. [204] experiments claiming that melting ice produces this molecule in a transitional state of melt water. The evidence for this seems much more tenuous to us. The processes of ice freezing and melting is a related question of interest too, and there is the suggestion that the hexamer ice crystals lead to formation of the proposed hexamer water dimer, but the evidence is not clear to us. The particular challenge to this explanation, however, is that it is based on a *special property of water molecules* (allowing water to form negatively charged supra-molecules); yet EZ also forms in other liquids; so do all these liquids allow the formation of similar large negatively charged molecules? It remains to connect the properties of EZ water, especially the exclusionary 'force', to the presence of the water polymer molecules. This same generic mechanism supposedly applies in other liquids. This indicates it is not specific to the type of charged molecule present, but depends for its possibility only on generic properties, such as dielectric constant, polarity, conductivity.

The next idea from this is that EZ properties are not just a direct result of the specific charged molecules (induced in a low concentration), but of a structural organization induced in the liquid on a larger scale. Such large-scale behavior is commonly observed in some situations (e.g. colloids, cells) where charged bodies in suspension can form long-range structural patterns, sometimes resembling crystal structures. In water, this is subsequently connected to the question of large 'water clusters', and the role of H-bonded networks, i.e. structures formed from weak ionic bonds. This opens another area of interest, which is the production of larger-scale structures from a microscopic *disequilibrium,* as represented in this case by the microscopic charge separation. This is dealt with in non-equilibrium thermodynamics, dissipative systems, chaos theory, etc. It is *not* dealt with in ordinary close-to-equilibrium thermodynamics, and the normal model of liquid water as a thermodynamic equilibrium does *not* provide adequate concepts to analyze this. Sceptical objections that 'structured water' is ruled out by simple thermodynamic theory are not entirely convincing.

In this view, the EZ water system appears to be a little *steady-state non-equilibrium thermodynamic system,* with distinct structures and self-organizing or stabilizing behavior. It appears as a *stable irreversible process*, in a dynamic disequilibrium, sustained by a small energy flow (IR absorption). This makes it an interesting system for thermodynamics. Water is not traditionally considered in this way, i.e. as hosting an irreversible process, generating structure. This change of viewpoint is one of Pollack's fundamental themes. But it still remains to understand in detail how this proposed 'thermodynamic cycle' of EZ water works. It depends on the production and dissolution of structures that we can barely detect.

How the structured water *excludes particles* is not explained in detail. But to summarize, at this stage, we think Pollack's original 'water polymer' proposal, appealing to a direct physical exclusion of particles by an extended *hexameric lattice*, has to be rejected, and may be replaced with the $H_{38}O_{20}{}^{2-}$ *water dimer* as the basis for a secondary structure, creating overall static charge distribution. Note this secondary structure requires a dynamic energy flow to sustain it. It supposedly absorbs IR radiation to power up charge separation, and presumably leaks this energy at boundary interactions (at the EZ interfaces).

In any case, this view is the first main theoretical support for the idea of EZ as a *liquid crystal state.* 'Liquid crystal' behavior results in anisotropic structures, and these have been measured in EZ water, using various spectroscopy/NMR methods. These results are the main experimental evidence for the view of EZ water as a 'liquid crystal' state. They do represent a consistent pattern of behavior, and there does seem to be a viable theoretical mechanism to support this, in the form of the "water dimer" hypotheses. This provides a detailed means of connecting the "structured water" theory and "liquid crystal" theory with empirical observations.

In conclusion, there is no settled answer. We consider that a critical step is the experimental verification by the scientific community of the key spectroscopic prediction, the 270 nm absorption peak including the associated variations of absorbance with distance.

There is, however, the issue of the EZ formation of other (than water) polar liquids close to certain solid surfaces. Such observations may render the connection of the peculiar *water polymer,* $H_{38}O_{20}{}^{2-}$, to the exclusion zone as rather accidental. The former is a curiosity of water chemistry; the latter may be a generic phenomenon, common in several substances (which still need to be confirmed). If there is a common mechanism, and EZ in water requires a thermodynamic cycle, then presumably EZ in other liquids does too, and thus requires some kind of irreversible dynamics, analogous to those inferred for of our water polymer, to support this. But the production of some analogy to the $H_{38}O_{20}{}^{2-}$ in other liquids seems somewhat unlikely. This emphasises the key issue, that the EZ water explanation in terms of 'structured water' seems rather too complex to apply generically to other liquids.

What it suggests to us instead is that there are two distinct processes: the exclusionary force that clears the EZ of particles, which operates in many liquids to create the macroscopic *exclusion zone*; and then secondary structural properties specifically induced in water (or possibly other liquids) by this primary separation. This suggests a primary role for the *chemotaxis* mechanism, discussed later in this section.

Returning now to the 270 nm absorption feature often referred to as established fact by leading EZ researchers, this is not recognised in conventional chemistry literature, or in standard UV spectroscopy databases, as far as we know. It is indeed a primary property that *directly indicates that there is some specific substance or structure generated in the EZ water*, which is not present in bulk water. But there appears to be only one actual experimental study done to measure the UV absorption effect in both EZ and ice [202,203]. Although there are two main papers on the EZ absorption, they are based on only set of experiments.

Considering its importance in the overall concept of theory and link to structured water and the fact that these experiments have not been independently (outside Pollack's group) replicated, we considered the replication of the UV experiments reported by Pollack [202,203], which at first glance could be considered rather straightforward as UV spectroscopy is a rather well-known experimental method. Despite significant efforts, we have not been able to identify clearly the 270 nm peak when considering Nafion as surface. This was unfortunate, of course, as this absorption feature is referred to by most leading proponents of structured water and quantum entanglement theories, and it is often taken as decisive evidence that there is something in the EZ water. Whether the non-reproduction is due to some contamination is not clear to us, as yet. The Pollack et al. experiments are reported carefully, but until successful replication is obtained, the possibility remains that some contamination occurred of water samples with some chemical that absorbs at 270 nm. It is well known that common organic molecules, specifically some amino acids and proteins, have high absorbance in this range. Tiny amounts, also present as microscopic dust motes in the air, can have significant effects. It is discouraging that these UV measurements have not been replicated in literature by any other research group.

5.4.2. *Chemotaxis: the diffusiophoresis hypothesis*

This hypothesis represents the main traditional line of explanation of the exclusionary force, and is argued by some to make *structured water* explanations redundant. Hence evaluating this as the main alternative explanation is important.

This theory is first presented in two studies [143,144] from a research team from the University of Eindhoven and it provides a different, compared to Pollack's structured water, explanation for the observed exclusion zone phenomena. They proposed that the exclusion zone formation is driven by a combination of ion exchange, ion diffusion and diffusiophoresis. The first two processes are common known processes whilst the last is not. Diffusiophoresis is the generation of flow in colloid suspensions due to concentration gradients of other substances.

When the diffusiophoresis phenomena are coupled up with the cation exchange in Nafion-117, the foundations for the formations of an exclusion zone are in place. To test their hypothesis the Dutch research team investigated the formation of exclusion zones in the vicinity to Nafion-117. The selected "solutes" were polystyrene microspheres with a diameter of 1 μm. They were able to generate the large EZ reported by Pollack.

The researchers then constructed, from coupled partial diffusion equations, a mathematical model that can predict the formation of the exclusion zone based on diffusiophoresis variables and the solute concentration and solute species. From their mathematical model, they could predict the EZ as a function of time in agreement with their experimental data (and at different salts and salt concentrations). EZ decreases with increasing salt concentration and is highest for LiCl solution. They summarized their conclusions as follows: *"This so-called exclusion zone (EZ) formation occurs near surfaces such as hydrogels, polymers, or biological tissues. It was recently shown that the underlying physical mechanism leading to this long-range repulsion is a combination of ion-exchange at the interface, diffusion of ions, and diffusiophoresis of colloids in the resulting ion concentration gradient".*

We should at this stage mention a related work by Pollack and coworkers [213] which discusses the dynamic development of exclusion zones on cellulosic surfaces, which, unlike Nafion-117, display no ion exchange properties at all. The authors considered three compounds (cellophane and cellulose acetate with 0.94 or 2.51° of substitution) and investigated their capability to form exclusion zones near their surfaces. The solute used in all the experiments was 2 μm diameter sulfated-polystyrene microspheres. An exclusion zone appeared in all three experiments and a comparison experiment, where Nafion-117 was used, was also conducted. The exclusion zone formation, for all four experiments, is smaller than for Nafion, but still clearly visible (around 50–150 μm depending on the compound, after one hour where the creation of EZ seem to have been stabilized).

It was observed that the two properties responsible for the differences in exclusion zone width are the relative roughness of the surface of the given materials and the hydrophilicity of the material, as it appears that the exclusion zone formation is a consequence of the interactions between the hydrophilic functional groups, in the polymer, and the surrounding water. They also noticed that the cellulosic polymers need to swell (in water) before they can form the exclusion zone. This is interesting as one could expect that a potential exclusion zone would appear while the swelling takes place (if exchange of material is postulated).

In summary from these studies by Pollack, exclusion zones can form in the vicinity to non-ion exchange material and that the width of the exclusion zone depends on functional groups in surface material and the relative roughness of that surface. We should again repeat that these investigations – verifications of EZ for non-Nafion surfaces have not been so far reproduced by other researchers outside Pollack's group.

In conclusion, we can mention that *Diffusiophoresis* helps explain the *exclusion,* but not the other special properties of EZ water (if indeed they are present). Diffusiophoresis is a generic mechanism (like *diffusion* or *osmosis* are generic), and we believe it should operate in interfacial layers to transport colloids or large molecules. But even if it can explain all EZ transport forces, it is not a complete explanation of all the EZ water properties (if they are confirmed). It does not explain the 270 nm absorbance in water particular (assuming it exists). It also does not account for properties like altered density, refractive index, IR absorbance, UV fluorescence, etc. These appear to be properties that are dynamically established as a result of exclusion. If these properties will be completely confirmed, it may be difficult for diffusiophoresis to stand as the sole EZ explanation.

The real possibility arises that these are special properties of water, not generic to EZ as such, but enabled by the conditions set up in EZ water. In this case, diffusiophoresis might well be the primary mechanism for creating EZ, and the creation of 'structured water' may be enabled in this special environment. This question cannot be decisively settled on present evidence, and this illustrates the uncertainty in the explanation. As mentioned, the diffusiophoresis may explain exclusion mechanisms; but it does not explain the peculiar "liquid crystal" properties claimed of EZ water, again assuming such properties exist.

Again this emphasises that these structural properties claimed of EZ water may not be the *cause* of the exclusionary force at all, but a result of an exclusion zone that forms in water through another means. In any case, diffusiophoresis does not seem to help answer the key questions about the properties claimed for the EZ water, which must be investigated in their own right. There are also other theoretical reasons to question the adequacy of a diffusiophoresis mechanism. Note it is a short-range, classical mechanism, which results in long-range order, but some leading researchers have argued for distinctly long-range mechanisms, as discussed by de Florea et al. [143] who mention a wider range of hypotheses for the EZ formation, e.g. the emergence of excited coherent vibration modes of molecules in the membrane or the surrounding water that could create large dipole oscillations [241], long-range forces originating from electromagnetic vibration [242] and the very similar to diffusiophoresis chemotaxis hypothesis [218,219].

5.4.3. The QED theory

In this third hypothesis, a *quantum field effect* is responsible for EZ water. The QED theory appears as interesting or intriguing, if not more, than the water polymer proposal. Among those supporting a structured-water hypothesis are de Ninno and co-workers [145,137–140,234,235]. She and others from the "Italian school" have advanced the QED (quantum electrodynamics) explanation of EZ. However, this is not widely accepted and is contested by those supporting the chemotaxis hypothesis.

First, let us clarify what is meant by a *quantum* effect in this context. All molecular-scale interactions are quantum. Even the simple transmission, reflection and absorption of light in a medium is a quantum effect. But although everything in the molecular-atomic world is intrinsically quantum mechanical, local interactions are normally quasi-classical, and do not illustrate effects of *entanglement, superfluidity, superconductivity.* These effects essentially involve *non-local coordination of complex quantum phase relations across large systems and significant distances* (e.g. $> 10\,\mathrm{nm}$). This is what we refer to as distinctly *quantum field effects* (as opposed to simply the first quantisation of EM forces). These normally take highly sophisticated experiments to produce and measure.

Classical quantum mechanics is good for most molecular-scale interactions, but some phenomena, such as the *Casimir effect* and *van der Waals forces* involve quantum field effects. This is treated in relativistic quantum electrodynamics (QED), not in ordinary quantum mechanics (QM) that we normally use in atomic theory (Schrödinger equations). This concept started from Giuliano Preparata's novel analysis of QED in 1988 [249], best presented in his 1995 book [250]. The important papers by del Giudice, Preparata and Vitello [243,244] apply it to water. This has been investigated and supported as an explanation for EZ by many researchers over the years, e.g. see Elia et al. [234,235], Bunkin et al. [248], Yinnon and Yinnon [246], Wexler et al. [247], and Yinnon et al. [245]. These studies include EZ experiments, modeling and analysis. Their conclusions support the existence of QED coherence domains, or some variants. This also supports the concept of EZ as structured water. Bunkin et al. [248] infer a photonic crystal effect, which is a different kind of quantum effect. They believe that this can explain the light transmittance in the EZ and the reported associated phenomena in the literature such as the UV peak intensity.

The research groups mentioned previously for several years now also claim to produce a *solid form of water at room temperature.* Bizarre as this sounds, they appear to have strong evidence and it has been illustrated in some of Pollack's presentations. They have applied the QED theory to several phenomena, including EZ properties, coherence domains, water clusters, and the water bridge. We consider that this is a coordinated effort of competent researchers, combining experimental studies with theoretical analysis.

Nevertheless, these studies have been ignored by a large part of scientific community, as can be seen in critical reviews by Ball (Nature News, 2004), and others e.g. Yuvan and Bier [251], Bier and Pravica [252] and Elton et al. [221,222]. The reasons for ignoring this theory are not entirely evident.

Still we admit that the problem of evaluating this theory is considerable. It calls on QED quantification of the EM field. The essential QED analysis behind this appears to be valid but it is difficult to visualize what the effects are in a realistic physical way. And while these kinds of effects are certainly real in general (Cassimir effect), the magnitude of the effect on water claimed in this case seems surprisingly large.

5.4.4. Combining the theories

We suggest it is quite possible that all three proposed mechanisms play a role in EZ. The QED/coherence domain theory appears to be consistent with water structure and the chemotaxis mechanism. The QED/coherence domain explanation and the water dimer proposal appear mutually supportive, as also discussed in literature [145,243]. Indeed, the proposed dimer would play a real and essential role in the QED/coherence domain mechanism and this is supported by recent works by Ninno, Germano and co-workers [234,235]. They discuss the range of topics raised here, including spectroscopic and other experimental evidence, QED coherence domain theory, the evidence for two (or three) distinct water molecule populations (but not chemotaxis mechanisms). Of particular interest, Elia et al. [235] had recently discussed the Segarra-Martí et al. [237–239] water dimer model, and how it supports the coherence domain theory. Both researchers refer to the 270 nm absorbance of EZ and melting ice as key established evidence.

EZ creation may involve several mechanisms. There may be a generic *diffusiophoresis mechanism,* that produces an exclusion zone in many liquids, with no further structural features. But in water, some kind of structure is generated, enhancing the EZ size, and contributing additional properties. The Nafion-water EZ grows much larger than other liquid EZs. This picture is significantly different from structured water theories, which take the formation of water structure as the primary driver for EZ creation. The key problems with the structured water explanation are (a) how does it work in other liquids? Why would these other liquids duplicate these very peculiar water structure properties? And (b) why *wouldn't* diffusiophoresis come into play in this process? Especially in the early part of the exclusion process?

6. Discussion and concluding remarks

The discussion about water may seem complex and full of controversies. But this is not new. Ancient greeks and others considered water to be a "fundamental element" of its own value and only during the 19th century (1858) it became clear that water is a substance consisting of O and H, with the exact structure as we know it today being accepted after an important conference in Germany in 1858. But even then it was thought that water was a linear molecule. That this was not the case and there is a 105° angle became clear around 1920. So, it took many centuries to arrive to a more or less correct idea of what water is. Thus, it should not be considered too surprising that the discussion continues, especially in connection to its structure and applications, during the whole of 20th century and within the 21st.

Thus, in the preface of the special volume about water in Chemical Reviews, 2016 ("Water – The Most Anomalous Liquid") L. Pettersson, R. Henchman, A. Nilsson write [60]:

> "One of the most essentials questions to address for a microscopic understanding of water is what are the structure and the dynamics of the hydrogen bonding network in water that give rise to all these unique properties? This question has been discussed intensively for over 100 years and has not yet been solved."

The present review manuscript addressed various aspects of the interplay between water's structure, properties and application concludes with some personal observations.

We have followed the two-state studies by, among others, Pettersson and Nilsson, and we are impressed by the detailed and very promising results obtained, more than just indications that water is a two-state liquid. We have noted that diverse experimental methods used so far cannot as yet provide a definite answer, and neither can molecular simulation models, but there is increasing evidence for a liquid-liquid critical point of water, especially from the work Debenedetti and co-workers.

The comment made the aforementioned Preface [60] by Pettersson and Nilsson may still be valid:

> ”However the interpretation of the experimental results in terms of the structure and the picture of the liquid water is strongly debated. Both Saykally and co-workers and Hamalainen and co-workers examined the intensity of XAS peaks and suggested only minor distortions from the tetrahedral structure”.

We have been involved over 25 years in the thermodynamic analysis, development and validation of advanced association thermodynamic models for water and we have first-hand experienced the inadequacy of even the most advanced thermodynamic models to represent the anomalous properties of water, despite obtaining a good overall representation of phase behavior of many aqueous systems.

We appreciate that there is no definite proof for the two-state theory including the second critical point of water, but we have also seen limited incorporation of the two-state concept in thermodynamics and none – to our knowledge- in the context of the advanced association theories. An issue which we hope will be addressed in the future.

Moreover, it has been unfortunate that spectroscopic data for the hydrogen bonding of water are rather rare, agreement between sources is not very good and we see both disagreements with advanced thermodynamic models and difficulties in the interpretation of the data and the results.

We have noticed recently discovered “anomalies” such as the unusually low dielectric constant of water in confinement and the ortho- and para water isomers, which are affected differently by an electric field and may affect differently chemical reactions. As with many other topics related to water, journalists have commented in different directions. For example, journalists from the Danish press asked “What if alternative people discover different behaviors between para-water and ortho-water?” and “Will we get products with e.g. para-water in the market claimed to have healing effects, as it reacts faster?”.

(https://ing.dk/artikel/kender-du-kemiske-forskel-mellem-ensrettet-modsatrettet-vand-212525 -Article is in Danish)

And this brings us to the “even more” usual properties or applications of water we have seen. In addition to historical references to polywater and water memory, we have presented new experiments and discussions for both the water bridge and the exclusion zone, the latter pioneered by professor Pollack and co-workers. Both phenomena are confirmed by experiments but whether the explanation is directly or indirectly connected to water is still debated. This debate is not always entirely balanced. We noticed a significant discredit of prof. Pollack's work in Chemical & Engineering News 14.12.2009 article with statements like ”claiming macrostructures of water that extend pas the picosecond domain is absurd”, ”this is the cold fusion of physical chemistry” and a comment by Prof. Pavel Jungwirth (Academy of Sciences, Czech Republic):

> ”The primary problem with Pollack's research is that it employs macroscopic experiments to draw conclusions about water structure. Instead, microscopic tools such as spectroscopy and molecular simulations are the proper tools for investigating the molecular structure of water”.

(https://cen.acs.org/articles/87/i50/Watering-Down-Science.html)

But, in our view, there is nothing wrong with doing “macroscopic” experiments, or drawing conclusions from general observations.

In the meantime, we note that neither molecular simulations nor spectroscopic methods have provided a definite answer and the very wide range of techniques used by many researchers (conventional IR and Raman spectroscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy (XAS), X-ray emission spectroscopy (XES), X-ray Raman spectroscopy, Resonant inelastic X-ray scattering, Small Angle X-ray scattering (SAXS), Femtosecond pump-probe spectroscopy, 2D & 3D IR spectroscopy and 2D Raman-THz spectroscopy) are of course useful, but the scientific community is still debating how the experimental data should be interpreted.

We cannot be sure but as “well-defined” water systems are rare in many experimental methods, “impurities” of diverse type may have played a role in many of the observations, including EZ, polywater and water memory experiments. After all, as we discussed, even the effect of well-defined compounds (e.g. hydrocarbons and salts) on water is complex and the hydrophobic effect nature and effect of ions on water structure (beyond its first solvation layer) continue to be debated.

To the above controversies we should add further (even more) intense debates related to the link of water (if indeed any) to homeopathy (via water memory), athletic performance and healthy life, and the notion that the source of water can have very significant effects on human health. Even well-established scientists have promoted such notions e.g. the late professor Mu-Shik Jhon, who has claimed the importance of the so-called hexagonal water, as a water structure of particular positive characteristics for health, etc. In that context, he promoted the use of water with structure-making ions like Calcium, etc., as they convert – he claims- water to hexagonal water, while other ions like Potassium destroy the hexagonal structuring of water.

We do not see such arguments having found any widespread accept in the scientific community, but we cannot be sure they can be entirely dismissed. After all, water's constitution due to e.g. minerals is different depending on the source. Looking at the hydrochemical constitution of water in Europe from the European Geological survey, we see in fresh water differences of pH: 6.1–9.8 and electrical conductivity: 3–1700 mS/m and similar large differences in mineral – bottled water.

Another area of significant debate is how water is affected by diverse electromagnetic fields. We have been in contact with entrepreneurs in Denmark who have developed devices claiming some structuring of water e.g. PowerPack, AMTech, Lagur and other devices. We have seen clear evidence of performance of these devices in some practical applications e.g. in removing limescale. We have done and continue to do engineering studies with them e.g.

(https://www.cere.dtu.dk/research-and-projects/framework-research-projects/electro-magnetic-processing-of-fuel-and-water-in-processes-in-the-maritime-industry; https://www.cere.dtu.dk/research-and-projects/specific-research-projects/karakalk)

However, we should state that, with the exception of Lagur and Vi-Aqua, and possibly a few other products, where patents are available or careful performance testing has been done, there is generally limited information, in the form of patents, publications or other scientific information about most of these so-called “structured water” devices. Limited information on how water is structured and whether these phenomena can be reproduced, under which conditions, and how they can be explained.

This is regrettable, but in as much as it is a black-box approach, we do not agree with statements which we have seen in literature (e.g. by Søren Keiding in https://videnskab.dk/25-soforklaringer/vand-vand-og-atter-vand and others [240]) that e.g. Grander water, presence of extensive water clusters and similar statements belong to Irving Langmuir's “pathological science field” and thus they should not be trusted or studied. We hope that a detailed scientific investigation can one day take place for some of these proposed devices claiming “structured water” with practical applications. Such claims and associated devices and their effects should either be scientifically verified or discarded. To the best of our knowledge, this has not happened as yet.

In conclusion, we find it rather regrettable that the discussions on the above phenomena about water structure, properties and applications are limited typically in "specialized" conferences, where mostly attendees agreeing with each other rather than in conferences where all views, no matter how far they may be, are debated. We close this review manuscript with a statement by professor Søren Keiding (translated from the Danish journal AKTUEL NATURVIDENSKAB, 2016, nr. 3) about another aspect which may play an important role in future water studies:

> ”Research in the last 200 years have given numerous suggestions for new ”structures” of water: polywater, rings of water molecules, high density and low density water, homeopathic water and the ”4th phase”. None of these both the serious and more colourful suggestions to new structures of water have seriously moved our understanding of water forward. Maybe we could learn more about water molecules if instead we became better in the study of dynamics, how water molecules move in between each other and not always search for the determining structure”.

Finally, we would like to summarize our views, our personal reflections about this review.

It is a review about water structure, properties and (some) applications written for a rather general audience. It may appear long but this is vast topic and the details are in the references. We have made a choice of topics, not everything is covered. Water science has developed enormously over the recent years, and in diverse disciplines e.g. chemistry, physics and biology. The biological aspects are not covered here. We wanted to have a balance between controversial aspects in –what some call- the "mainstream" science (Sections 2 and 3), emphasis on anomalous properties, link to thermodynamics and two-state theory and the less well-accepted areas discussed in Sections 4 and 5, with emphasis on water bridge and exclusion zone phenomena. Most of the claims, both in sections 2&3 and 4&5, have not been proven as yet. We have summarized mostly literature studies in this review, presenting also our views, but also included some of our own investigations. We do not attempt to convince anybody but present an unbiased discussion, as we understand it, about the difficult topic of water structure and properties from various angles. Our emphasis is to cover topics and angles very rarely seen together in reviews of water. We have attempted to differentiate experimental evidence from theories, whenever this was possible. In the case of exclusion zone, we summarized in some detail three mechanisms, all of which may play a role in explaining experimental observations. This remains to be seen whether it is true, along with several of the other hypotheses and claims reviewed in this work, especially for the two-state water theory. While the emphasis in this review in on water structure-properties interplay, some applications are also mentioned. An improved understanding of water structure and properties will be of pivotal importance in both science and engineering. It is also for this reason we would like to cover a wider range of aspects of water science and technology**.** The communities as presented in Sections 2–5 appear as almost not talking to each other, despite both working on this very important topic. Whether our manuscript can contribute a bit in bridging this gap remains to be seen, but we do recognize it may be difficult.

Acknowledgements

The authors wish to thank the European Research Council (ERC) for funding this research under the European Union's Horizon 2020 research and innovation program (grant agreement No 832460), ERC Advanced Grant project "New Paradigm in Electrolyte Thermodynamics".

The authors would also like to thank the VILLUM Foundation for funding of this research as part of the grants 17449 (Direwaves) and 23323 (WaterStruc). Georgios M. Kontogeorgis and Xiaodong Liang thank Professor Michael L. Michelsen (1944–2020) for many exciting discussions about water over the years.

References

[1] P. Ball, H_2O. A Biography of Water, Phoenix, 1999.
[2] G.H. Pollack, The Fourth Phase of water. Beyond Solid, Liquid, and Vapor, Ebner and Sons Publishers, Seattle WA, USA, 2013.
[3] P. Ball, Water – an enduring mystery, Nature 452 (2008) 291–292.
[4] F. Mallamace, C. Corsaro, H. Stanley, A singular thermodynamically consistent temperature at the origin of the anomalous behavior of liquid water, Sci. Rep. 2 (2012) 1–5 993.
[5] F. Mallamace, C. Corsaro, D. Mallamace, C. Vasi, H. Stanley, The thermodynamical response functions and the origin of the anomalous behavior of liquid water, Farad. Discuss. 167 (2013) 95–108.
[6] P.S Debenedetti, G. Water, J. Phys. Condens. Matter 15 (2003) R1669–R1726.
[7] V. Holten, C.E. Bertrand, M.A. Anisimov, J.V. Sengers, Thermodynamics of supercooled water, J. Chem. Phys. 136 (9) (2012) 094507.
[8] G.M. Kontogeorgis, G. Folas, Thermodynamic Models For Industrial applications. From classical and Advanced Mixing Rules to Association Theories, Wiley, 2010.
[9] *IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). Online version (2019-) created by S. J. Chalk. ISBN 0-9678550-9-8.* https://doi.org/10.1351/goldbook
[10] van der Lubbe, S.C.C.; Fonseca Guerra, C. The Nature of Hydrogen bonds: a delineation of the role of different energy components on hydrogen bond strengths and lengths. Chem. An Asian J. 2019, *14* (16), 2760–2769. doi:10.1002/asia.201900717.
[11] G.M. Kontogeorgis, Association theories for complex thermodynamics, Chem. Eng. Res. Des. 91 (2013) 1840–1858.
[12] de Hemptinne, J.C., Lebanois, J.M., Mougin, P., Barreau, A. 2012. Select thermodynamic models for process simulation. Ed. Technip.
[13] C. McCabe, A. Galindo, Chapter 8. SAFT Associating fluids and fluid mixtures in Applied Thermodynamics of Fluids, edited by A.R.H. Goodwin, J.V.Sengers, C.J.Peters, (RSC Publishing, 2010).
[14] Y. Tao, W. Zou, J. Jia, W. Li, D. Cremer, Different ways of hydrogen bonding in water – why does warm water freeze faster than cold water? J. Chem. Theory Comput 13 (1) (2017) 55–76.
[15] J. Wu, J.M. Prausnitz, Phase equilibria for systems containing hydrocarbons, water, and salt: an extended peng-robinson equation of state, Ind. Eng. Chem. Res. 37 (1998) 1634–1643.
[16] E. Tsochantaris, X. Liang, G.M. Kontogeorgis, Evaluating the performance of the PC-SAFT and CPA equations of state on water's anomalous properties, J. Chem. Eng. Data 65 (12) (2020) 5718–5734.
[17] M. Kleiner, G. Sadowski, Modeling of polar systems using PCP-SAFT: an approach to account for induced-association interactions, J. Phys. Chem. C 111 (43) (2007) 15544–15553.
[18] A.M. Palma, A.J. Queimada, J.A.P. Coutinho, Improved prediction of water properties and phase equilibria with a modified cubic plus Association equation of state, Ind. Eng. Chem. Res. 56 (2017) 15163–15176.
[19] B.D. Marshall, A second order thermodynamic perturbation theory for hydrogen bond cooperativity in water, J. Chem. Phys. 146 (2017) 174104.
[20] B.D. Marshall, Perturbation theory for water with an associating reference fluid, Phys. Rev. E 96 (2017) 052602.
[21] B.D. Marshall, On the Cooperativity of association and reference energy scales in thermodynamic perturbation theory, J. Chem. Phys. 145 (2016) 204104.
[22] B.D. Marshall, Mixture equation of state for water with an associating reference fluid, Ind. Eng. Chem. Res. 57 (2018) 4070–4080.
[23] B.D. Marshall, A doubly associated perturbation theory for water, Fluid Ph. Equilib. 500 (2019) 112252.
[24] B.D. Marshall, A resummed thermodynamic perturbation theory for positive and negative hydrogen bond cooperativity in water, J. Phys. Condens. Matter 31 (2019) 184001.
[25] B.D. Marshall, A simple second order thermodynamic perturbation theory for associating fluids, Condens. Matter Phys. 24 (3) (2021) 33602.
[26] B.D. Marshall, A modified perturbed chain-statistical associating fluid theory equation of state for water which includes an association dependent hard sphere diameter, AlChE J. 67 (10) (2021) e17342.
[27] X. Liang, B. Maribo-Mogensen, I. Tsivintzelis, G. Kontogeorgis, A comment on water's structure using monomer fraction data and theories, Fluid Ph. Equilib. 407 (2016) 2–6.
[28] W. Luck, A model of hydrogen-bonded liquids, Angew. Chem. Int. Ed. Engl. 19 (1980) 28–41.
[29] J. Town, X. Liang, G.M. Kontogeorgis, Application of quantum chemistry insights to the prediction of phase equilibria in associating systems, Ind. Eng. Chem. Res. 60 (16) (2021) 5992–6005.
[30] S. Dixit, J. Crain, W.C.K. Poon, J.L. Finney, A.K. Soper, Molecular segregation observed in a concentrated alcohol-water solution, Nature 416 (2002) 829.
[31] C.A. Chatzidimitriou-Dreismann, Nachr. Chem. 52 (2004) 773.
[32] C.A. Chatzidimitriou-Dreismann, T.A. Redah, R.M.F. Streffer, J. Mayers, Anomalous deep inelastic neutron scattering from liquid H2O-D2O: evidence of nuclear quantum entanglement, Phys. Rev. Letters 79 (15) (1997) 2839–2842.
[33] J.-.H. Guo, Y. Luo, A. Augustsson, S. Kashtanov, J.-.E. Rubensson, D.K. Shuh, H. Ågren, Nordgren, J. Phys. Rev. Lett 91 (2003) 157401.
[34] G. Kontogeorgis, I. Tsivintzelis, N. von Solms, A. Grenner, D. Bøgh, M. Frost, A. Knage-Rasmussen, I. Economou, Use of monomer fraction data in the parametrization of association theories, Fluid Ph. Equilib. 296 (2010) 219–229.

[35] L.F. Vega, F. Llovell, Review and new insights into the application of molecular-based equations of state to water and aqueous solutions, Fluid Ph. Equilib. 416 (2016) 150–173.

[36] Y. Marcus, Effect of ions on the structure of water: structure making and breaking, Chem. Rev. 109 (2009) 1346–1370.

[37] Rastogi, A., Ghosh, A.K., Suresh, S.J., 2011. Hydrogen bond interactions between water molecules in bulk liquid, near electrode surfaces and around ions. Chapter in “Thermodynamics-Physical Chemistry of Aqueous Systems”, Edited by Dr. Juan Carlos Moreno, InTech.

[38] A.V. Muthachikavil, B. Peng, G.M. Kontogeorgis, X. Liang, Distinguishing weak and strong hydrogen bonds in liquid water – a potential of the mean force-based approach, J. Phys. Chem. B 125 (26) (2021) 7187–7198.

[39] Y.E. Gorbaty, R.B. Gupta, The structural features of liquid and supercritical water, Ind. Eng. Chem. Res. 37 (8) (1998) 3026.

[40] Y.E. Gorbaty, A.G. Kalinichev, Hydrogen bonding in supercritical water. 1. Experimental results, J. Phys. Chem. 99 (1995) 5536-5340.

[41] Y.E. Gorbaty, Y.E. Demianets, An X-ray study of the effect of pressure on the structure of liquid water, Mol. Phys. 55 (3) (1985) 571–588.

[42] A.G. Kalinichev, J.D. Bass, Hydrogen bonding in supercritical water. 2. Computer simulations, J. Phys. Chem. A 101 (1997) 9720–9727.

[43] A.G. Kalinichev, Y.E. Gorbaty, A.V. Okhulkov, Structure and hydrogen bonding of liquid water at high hydrostatic pressures: monte Carlo NPT-ensemble simulations up to 10 kbar, J. Mole. Liq. 82 (1999) 57–72.

[44] A.G. Kalinichev, Universality of hydrogen bond distributions in liquid and supercritical water, J. Mole. Liq. 241 (2017) 1038–1043.

[45] P.J. Smits, I.G. Economou, C.J. Peters, J. de Swaan Arons, Equation of state description of thermodynamic properties of near-critical and supercritical water, J. Phys. Chem. 98 (46) (1994) 12080–12085.

[46] G.K. Folas, G.M. Kontogeorgis, M.L. Michelsen, E.H. Stenby, Vapor-liquid, liquid-liquid and vapor-liquid-liquid equilibrium of binary and multicomponent systems with MEG. Modeling with the CPA EoS and an EoS/G^E model, Fluid Ph. Equilib. 249 (2006) 67–74.

[47] S. Dufal, T. Lafitte, A. Haslam, A. Galindo, G. Clark, C. Vega, G. Jackson, The A in SAFT: developing the contribution of association to the helmholtz free energy within a Wertheim TPT1 treatment of generic mie fluids, Mol. Phys. 113 (2015) 948–984.

[48] B. Maribo-Mogensen, G. Kontogeorgis, K. Thomsen, Modeling of dielectric properties of complex fluids with an equation of state, J. Phys. Chem. B 117 (2013) 3389–3397.

[49] F. Mallamace, C. Branca, M. Broccio, C. Corsaro, C. Mou, S. Chen, The anomalous behavior of the density of water in the range $30K < T < 373K$, Proc. Natl. Acad. Sci. 104 (2007) 18387–18391.

[50] E. Müller, K. Gubbins, An equation of state for water from a simplified intermolecular potential, Ind. Eng Chem. Res. 34 (1995) 3662–3673.

[51] S. Aparicio-Martínez, K. Hall, Phase equilibria in water containing binary systems from molecular based equations of state, Fluid Phase Equilib 254 (2007) 112–125.

[52] G. Clark, A. Haslam, A. Galindo, G. Jackson, Developing optimal wertheim-like models of water for use in statistical associating fluid theory (SAFT) and related approaches, Mol. Phys. 104 (2006) 3561–3581.

[53] N. von Solms, M. Michelsen, C. Passos, S. Derawi, G. Kontogeorgis, Investigating models for associating fluids using spectroscopy, Ind. Eng. Chem. Res. 45 (2006) 5368–5374.

[54] A. Grenner, G.M. Kontogeorgis, M.L. Michelsen, G.K. Folas, On the estimation of water pure compound parameters in association theories, Mol. Phys. 105 (2007) 1797–1801.

[55] I. Tsivintzelis, D. Bøgh, E. Karakatsani, G.M. Kontogeorgis, The role of monomer fraction data in association theories – can we improve the performance for phase equilibrium calculations? Fluid Ph. Equilib. 365 (2014) 112–122.

[56] X. Liang, I. Tsivintzelis, G. Kontogeorgis, Modeling water containing systems with the simplified PC-SAFT and CPA equations of state, Ind. Eng. Chem. Res. 53 (2014) 14493–14507.

[57] F. Stillinger, Water revisited, Science 209 (1980) 451–457.

[58] H. Frank, The structure of ordinary water: new data and interpretations are yielding new insights into this fascinating substance, Science 169 (1970) 635–641.

[59] Barbosa M., The weirdness of water could be the answer. https://www.youtube.com/watch?v=-OLFwkfPxCg

[60] L. Pettersson, R. Henchman, A. Nilsson, Water–the most anomalous liquid, Chem. Rev. 116 (2016) 7459–7462.

[61] W.C. Röntgen, Ueber die constitution des flüssigen wassers, Ann Phys 281 (1892) 91–97, doi:10.1002/andp.18922810108.

[62] H.E. Armstrong, Problems of hydrone and water: the origin of electricity in thunderstorms, Nature 113 (2830) (1924) 124–126 And other articles from that period. See also reference [2]for a discussion of Armstrong theory.

[63] O.Y. Samoilov, Structures of certain liquids .2. the structure of water and of aqueous solutions, Zh. Fiz. Khim. 31 (3) (1957) 537–553.

[64] G.W. Robinson, C.H. Cho, G.I. Gellene, Refractive index mysteries of water, J. Phys. Chem. B 104 (2000) 7179–7182.

[65] S.M. Baschenko, L.S. Marchenko, On Raman spectra of water, its structure and dependence on temperature. Semiconductor Physics, Quant. Electron. Optoelectron. 14 (2011) 77–79 V.

[66] C.E. Walrafen, Raman spectral studies of the effects of temperature on water and electrolyte solutions, J. Chem. Phys. 44 (4) (1966) 1546–1558.

[67] G. D’Arrigo, G. Maisano, F. Mallamace, P. Migliardo, Wanderlingh, Raman scattering and structure of normal and supercooled water, J. Chem. Phys. 75 (9) (1981) 4264–4270.

[68] D.E. Hare, C.M. Sorensen, Raman spectroscopic study of dilute HOD in liquid H_2O in the temperature range -31.5 to 160 °C, J. Chem. Phys. 93 (1990) 6954–6961.

[69] S. Woutersen, B. Ensing, M. Hilbers, Z. Zhao, C.A. Angell, A liquid-liquid transition in supercooled aqueous solution related to the HDA-LDA transition, Science 359 (2018) 1127–1131.

[70] P. Wernet, D. Nordlund, U. Bergmann, M. Cavalleri, N. Odelius, H. Ogasawara, L.Å. Näslund, T.K. Hirsch, L. Ojamäe, P. Glatzel, L.G.M. Pettersson, A. Nilsson, The structure of the first coordination shell in liquid water, Science 304 (2004) 995–999.

[71] F. Perakis, K. Amann-Winkel, F. Lehmkühler, M. Sprung, D. Mariedahl, J. Sellberg, H. Pathak, A. Späh, F. Cavalca, D. Schlesinger, et al., Diffusive dynamics during the high-to-low density transition in amorphous ice, Proc. Natl. Acad. Sci. U. S. A. 114 (2017) 8193–8198.

[72] K. Kim, A. Späh, H. Pathak, F. Perakis, D. Mariedahl, K. Amann-Winkel, J. Sellberg, J. Lee, S. Kim, J. Park, et al., Maxima in the Thermodynamic Response and Correlation Functions of Deeply Supercooled Water, Science 358 (2017) 1589–1593.

[73] K.W. Kim, P.H. Poole, … A. Nilsson, Experimental observation of the liquid-liquid transition in bulk supercooled water under pressure, Science 370 (2020) 978–982.

[74] G. Camisasca, D. Schlesinger, I. Zhovtobriukh, G. Pitsevich, L.G.M. Pettersson, A proposal for the structure of high- and low-density fluctuations in liquid water, J. Chem. Phys. 151 (2019) 034508.

[75] V. Holten, M.A. Anisimov, Entropy-driven liquid-liquid separation in supercooled water, Sci. Rep. 2 (713) (2012) 1–7.

[76] F. Caupin, M.A. Anisimov, Thermodynamics of supercooled and stretched water: unifying two-structure description and liquid-vapor spinodal, J. Chem. Phys. 151 (2019) 034503.

[77] V. Holten, J.V. Sengers, M.A. Anisimov, Equation of state for supercooled water at pressures up to 400MPa, J. Phys. Chem. Ref. Data 43 (2014) 043101.

[78] J. Russo, H. Tanaka, Understanding water’s anomalies with locally favoured structured, Nat. Commun. 5 (3556) (2014) 1–11.

[79] T.E. Gartner, L. Zhang, P.M. Piaggi, R. Car, A.Z. Panagiotopoulos, P.G. Debenedetti, Signatures of a liquid-liquid transition in an ab initio deep neural network model for water, Proc. Natl Acad. Sci. *U. S. A.* 117 (42) (2020) 26040–26046.

[80] C. Huang, K.T. Wikfeldt, L.G.M. Pettersson, … A. Nilsson, The inhomogeneous structure of water at ambient conditions, Proc. Natl Acad. Sci. U. S. A. 106 (36) (2009) 15214–15218.

[81] T. Tokushima, Y. Harada, O. Takahashi, Y. Senba, H. Ohashi, L.G.M. Pettersson, A. Nilsson, S. Shin, High resolution X-ray emission spectroscopy of liquid water: the observation of two structural motifs, Chem. Phys. Lett. 460 (2008) 387–400.

[82] S. Woutersen, U. Emmerichs, H.J. Bakker, Femtosecond mid-IR pump-probe spectroscopy of liquid water: evidence for a two-component structure, Science 278 (1997) 658–660.

[83] K. Sanderson, H2Oh! water is actually two liquids disguised as one, NewScientist (2018) 26–29.

[84] Y. Zubavicus, M. Grunze, New insights into the structure of water with ultrafast probes, Science 304 (2004) 974–976.

[85] J.D. Smith, C.D. Cappa, K.R. Wilson, B.M. Messer, R.C. Cohen, R.J. Saykally, Energetics of hydrogen bond network rearrangements in liquid water, Science 306 (2004) 851–853.

[86] J.D. Smith, C.D. Cappa, B.M. Messer, R.C. Cohen, R.J. Saykally, Response to comment on “energetics of hydrogen bond network rearrangements in liquid water, Science 308 (2004) 793b.

[87] Schirber, M. The new mystery of water https://www.livescience.com/3724-mystery-water.html (accessed May 26, 2020).

[88] Ball, P. Evidence mounts that water has two liquid forms https://www.chemistryworld.com/news/evidence-mounts-that-water-has-two-liquid-forms/3008766.article (accessed May 26, 2020).

[89] R. Shi, H. Tanaka, Direct evidence in the scattering function for the coexistence of two types of local structures in liquid water, J. Am. Chem. Soc. 142 (2020) 2868–2875.

[90] P. Poole, F. Sciortino, U. Essmann, H. Stanley, Phase behaviour of metastable water, Nature 360 (1992) 324–328.

[91] A.G. Smart, The war over supercooled water, Phys Today (2018).

[92] P.G. Debenedetti, F. Sciortino, G.H. Zerze, Second critical point in two realistic models for water, Science 369 (2020) 289–292.

[93] P.G. Debenedetti, One substance, two liquids? Nature 392 (1998) 127–129.

[94] A.K. Soper, Is water one liquid or two ? J. Chem. Physics 150 (2019) 234503.

[95] J. Teixeira, The puzzling problem of water properties at low temperature. An experimentalist view, Substantia 3 (2) (2019) 57–63 Suppl. 3.

[96] L.G.M. Pettersson, Y. Harada, A. Nilsson, Do X-ray spectroscopies provide evidence for continuous distribution models of water at ambient conditions? Proc. Natl Acad. Sci. U. S. A. 116 (35) (2019) 17156–17157.

[97] V.I. Tikhonov, A.A. Volkov, Separation of water into its Ortho and Para isomers, Science 296 (2002) 2363-2363.

[98] A. Kilaj, H. Gao, D. Rösch, U. Rivero, J. Küpper, S. Willitsch, Observation of different reactivities of para and ortho-water towards trapped diazenylium ions, Nat Commun (2018) 9.

[99] L. Fumagalli, A. Esfandiar, R. Fabregas, S. Hu, P. Ares, A. Janardanan, Q. Yang, B. Radha, T. Taniguchi, K. Watanabe, G. Gomila, K.S. Novoselov, A.K. Geim, Anomalously low dielectric constant of confined water, Science 360 (2018) 1339–1342.

[100] J. Errington, P. Debenedetti, Relationship between structural order and the anomalies of liquid water, Nature 409 (2001) 318–321.

[101] P. Debenedetti, H. Stanley, Supercooled and glassy water, Phys Today 56 (2003) 40–46.

[102] A. Nilsson, L.G.M. Pettersson, The structural origin of anomalous properties of liquid water, Nature Comm 6 (2015) 8998 1-11.

[103] P. Gallo, K. Amann-Winkel, C. Angell, M. Anisimov, F. Caupin, C. Chakravarty, E. Lascaris, T. Loerting, A. Panagiotopoulos, J. Russo, J.A. Sellberg, H.E. Stanley, H. Tanaka, C. Vega, L. Xu, L.G.M. Pettersson, Water: a tale of two liquids, Chem. Rev. 116 (2016) 7463–7500.

[104] J.C. Palmer, F. Martelli, Y. Liu, B. Car, A.Z. Panagiotopoulos, P.G. Debenedetti, Metastable liquid-liquid transition in a molecular model of water, Nature 510 (2014) 385.

[105] D.A. Fuentevilla, M.A. Anisimov, Scaled equation of state for supercooled water near the liquid-liquid critical point, Phys. Rev. Lett. 97 (19) (2006) 8–11, doi:10.1103/PhysRevLett.97.195702.

[106] C.E. Bertrand, M.A. Anisimov, Peculiar thermodynamics of the second critical point in supercooled water, J. Phys. Chem. B 115 (48) (2011) 14099–14111.

[107] O. Mishima, J. Chem. Phys. 123 (2005) 154506.

[108] edited by M.A. Anisimov, J.V. Sengers, J.V. Sengers, R.F. Kayser, C.J. Peters, J.J. White, Equations of State for Fluids and Fluid Mixtures Elsevier, Amsterdam, 2000, p. 381. edited by.

[109] O. Mishima, Volume of supercooled water under pressureand the liquid-liquid critical point, J Chem. Phys. 133 (2010) 144503.

[110] H. Pathak, J.C. Palmer, D. Schlesinger, K.T. Wikfeldt, J.A. Sellberg, L.G.M. Pettersson, A. Nilsson, The structural validity of various thermodynamical models of supercooled water, J. Chem. Phys. (13) (2016) 145.

[111] E.B. Moore, V. Molinero, Growing correlation length in supercooled water, J. Chem. Phys. (24) (2009) 130, doi:10.1063/1.3158470.

[112] Q. Sun, Local statistical interpretation for water structure, Chem. Phys. Lett. 568–569 (2013) 90–94.

[113] J. Troncoso, The isobaric heat capacity of liquid water at low temperatures and high pressures, J. Chem. Phys. 147 (8) (2017) 084501.

[114] R. Shi, J. Russo, H. Tanaka, Common microscopic structural origin for water's thermodynamic and dynamic anomalies, J. Chem. Phys. 149 (22) (2018) 224502 G.

[115] G.M. Kontogeorgis, S. Kiil, Introduction to Applied Colloid and Surface Chemistry, 1st ed., Wiley, 2016.

[116] J.H. Hildebrand, Is there a "hydrophobic effect"? Proc. Nat. Acad. Sci. U. S. A. 76 (1) (1979) 194.

[117] K.A. Dill, The meaning of hydrophobicity, Science 250 (478) (1990) 297–298 response by Privalov, P.L., Gill, S.J., Murphy, K.P.

[118] J.N. Israelachvili, Intermolecular and Surface Forces, 3rd ed., Academic Press, Elsevier, 2011.

[119] S.J. Gill, I. Wadso, An equation of state describing hydrophobic interaction, Proc. Natl Acad. Sci. U. S. A. 73 (9) (1976) 2955–2958.

[120] B. Kronberg, The hydrophobic effect, Curr. Opin. Colloid Interface Sci. 22 (2016) 14–22.

[121] J. Wu, J.M. Prausnitz, Pairwise-additive hydrophobic effect for alkanes in water, Proc. Natl. Acad. Sci. U. S. A. 105 (28) (2008) 9512–9515.

[122] R. Leberman, A.K. Soper, Effect of high salt concentrations on water structure, Nature 378 (1995) 364–366.

[123] U. von Stockar, Biothermodynamics. The role of thermodynamics in biochemical engineering, Chapter 5 – Water Written by Willem Norde, EPFL Press, 2013.

[124] K.A. Dill, Dominant forces in protein folding, Biochemistry 29 (31) (1990) 7133–7155.

[125] D. Chandler, Interfaces and the driving force of hydrophobic assembly, Nature 437 (2005) 640–646.

[126] J.M. Prausnitz, R.N. Lichtenthaler, E.G. de Azevedo, Molecular Thermodynamics of Fluid-Phase Equilibria (1999).

[127] C.J. van Oss, R.J. Good, Hydrogen bonding, interfacial tension and the aqueous solubility of organic compounds, J. Dispersion Sci. Technol. 17 (4) (1996) 433–449.

[128] R. Buchner, G.T. Hefter, P. May, Dielectric relaxation of aqueous NaCl solutions, J. Phys. Chem. A 103 (1) (1999) 1–9.

[129] J.B. Hubbard, L. Onsager, W.M. van Beek, M. Mandel, Proc. Natl. Acad. Sci. U.S.A. 74 (2) (1977) 401–404.

[130] J.B. Hubbard, Dielectric dispersion and dielectric friction in electrolyte solutions, J. Chem. Phys. 68 (1978) 1649–1664.

[131] B. Maribo-Mogensen, G. Kontogeorgis, K. Thomsen, Modeling of dielectric properties of aqueous salt solutions with an equation of state, J. Phys. Chem. B 117 (36) (2013) 10523–10533.

[132] A.W. Omta, M.F. Kropman, S. Woutersen, H.J. Bakker, Negligible effect of ions on the hydrogen-bond structure in liquid water, Science 301 (2003) 347–349.

[133] Y. Zhang, P. Cremer, Curr. Opin. Chem. Biol. 10 (2006) 658.

[134] K.J. Tielrooij, N. Garcia-Araez, M. Bonn, H.J. Bakker, Cooperativity in ion hydration, Science 328 (2010) 1006–1009.

[135] R. Leberman, A.K. Soper, Effect of high salt concentrations on water structure, Nature 378 (1995) 364–366.

[136] M. Frosch, M. Bilde, O.F. Nielsen, From water clustering to osmotic coefficients, J. Phys. Chem. A. 114 (2010) 11933–11942.

[137] A. De Ninno, M. De Francesco, Water molecules ordering in strong electrolyte solutions, Chem. Phys. Lett. 705 (2018) 7–11.

[138] P. Renati, Z. Kovacs, A. De Ninno, R. Tsenkova, Temperature dependence analysis of the NIR spectra of liquid water confirms the existence of two phases, one of which is in a coherent state, J. Mol. Liq. 292 (11149) (2019) 1–10.

[139] A. De Ninno, M. Francesco, ATR-FTIR study of the isosbestic point in water solutions of electrolytes, Chem. Phys. 513 (2018) 266–272.

[140] A. de Ninno, M. Francesco, An equation for the isosbestic wavelength in aqueous solutions of electrolytes, J. Mole. Struct. 1200 (2020) 127125.

[141] J. Henniker, The depth of the surface zone of a liquid, Rev. Mod. Phys. 21 (1949) 322–341.

[142] E.K. Wilson, Watering down science? Chem. Eng. News 87 (2009) 32–33.

[143] D. Florea, S. Musa, J. Huyghe, H. Wyss, Long-Range Repulsion of Colloids driven by Ion Exchange and Diffusiophoresis, Proc. Natl. Acad. Sci. U. S. A. 111 (2014) 6554–6559.

[144] S. Musa, D. Florea, H.M. Wyss, J.M. Huyghe, Convection associated with exclusion zone formation in colloidal suspensions, Soft Matter 12 (2016) 1127–1132.

[145] A. De Ninno, Dynamics of formation of the exclusion zone near hydrophilic surfaces, Chem. Phys. Lett. 667 (2017) 322–326.

[146] S. Bai, P. Huang, Y. Meng, S. Wen, Modeling and analysis of interfacial electro-kinetic effects on thin film lubrication, Tribol. Int. 39 (2006) 1405–1412.

[147] S. Musa, D. Florea, S. van Loon, H. Wyss, J.M. Huyghe, Interfacial water: unexplained phenomena, Poromechanics (2013) 2086–2092 V © ASCE 2013.

[148] G. Di Bonaventura, A. Pompilio, V. Crocetta, S. De Nicola, F. Barbaro, L. Giuliani, E. D'Emilia, E. Fiscarelli, R.G. Bellomo, R. Saggini, Exposure to extremely low-frequency magnetic field affects biofilm formation by cystic fibrosis pathogens, Fut. Microbiol. 9 (12) (2014) 1303–1317.

[149] J.A.J. Haagensen, M. Bache, L. Giuliani, N.S. Blom, Effects of resonant electromagnetic fields on biofilim formataion in *pseudomonas aeruginosa*, Appl. Sci. 11 (2021) 7760.

[150] https://en.wikipedia.org/wiki/Water_thread_experiment

[151] E. Fuchs, K. Gatterer, G. Holler, J. Woisetschläger, Dynamics of the floating water bridge, J. Phys. D App.l Phys. 41 (2008) 185502.

[152] L. Skinner, C. Benmore, B. Shyam, J. Weber, J. Parise, Structure of the floating water bridge and water in an electric field, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 16463–16468.

[153] E. Davenas, F. Beauvais, J. Amara, M. Oberbaum, B. Robinzon, A. Miadonnai, A. Tedeschi, B. Pomeranz, P. Fortner, P. Belon, et al., Human basophil degranulation triggered by very dilute antiserum against Ige, Nature 333 (1988) 816–818.

[154] J. Benveniste, Memory of water revisited, Nature 370 (1994) 6488.

[155] L. Rey, Thermoluminescence of ultra-high dilutions of lithium chloride and sodium chloride, Physica A 323 (2003) 67–74.

[156] L. Rey, Can low-temperature thermoluminescence cast light on the nature of ultra--high dilutions? Homeopathy 96 (2007) 170–174.

[157] H. Walach, W.B. Jonas, J. Ives, R. van Wijk, O. Weingartner, Research on homeopathy: state of the art, J. Altern. Complement. Res. 11 (5) (2005) 813–829.

[158] Biotech innovation ApS – Ventilation, emhætte, slamsuger, fedtudskiller, statisk elektricitet. https://biotech-i.dk/ (accessed May 26, 2020).

[159] Kalk i vandet | Undgå kalkaflejring med Kalkknuseren til privat & erhverv https://www.kalkknuser.dk/ (accessed May 26, 2020).

[160] https://lagur.dk/

[161] https://videnskab.dk/25-soforklaringer/vand-vand-og-atter-vand (article –in Danish- by professor Søren Rud Keiding)

[162] https://samvirke.dk/artikler/maaske-kan-vand-huske-og-forandre-sig-naar-man-spiller-musik-for-det (article –in Danish- by Lyv Mygind)

[163] Morse, D., et al., U.S. Patent 5, 606,273 (1997).

[164] E. Chibowski, L. Holysz, Effect of a radiofrequency electric field on the zeta potential of some oxides, Colloids Surf. A 101 (1995) 99.

[165] M. Colic, D. Morse, Effects of amplitude of the radiofrequency electromagnetic radiation on aqueous suspensions and solutions, J. Colloid Interface Sci. 200 (1998) 265–272.

[166] K. Higashitani, J. Oshitani, Magnetic effects on thickness of adsorbed layer in aqueous solutions evaluated directly by atomic force microscope, J. Colloid Interface Sci. 204 (1998) 363–368.

[167] J.J. Leahy, C. Macken, M. Ryan, The effects of radiofrequency electromagnetic radiation on the adhesion behavior of aqueous suspensions, J. Colloid Interface Sci. 225 (2000) 209–213.

[168] P. Ball, Memory of water' biologist dies after heart surgery, Nature 431 (2004) 729.

[169] S. Pincock, Jacques benveniste, Lancet North Am. Ed. 364 (9446) (2004) 1660.

[170] L. Montagnier, J. Aisa, S. Ferris, J.L. Montagnier, C. Lavallee, Electromagnetic signals are produced by aqueous nanostructures derived from bacterial DNA sequences, Interdiscip Sci. Comput. Life Sci. 1 (2009) 81–90.

[171] V.L. Voeikov, The possible role of active oxygen in the memory of water, Homeopathy 96 (2007) 196–201.

[172] L.R. Milgrom, Conspicuous by its absence: the memory of water, macro-entanglement and the possibility of homeopathy, Homeopathy 96 (2007) 209–219.

[173] M.F. Chaplin, The memory of water: an overview, Homeopathy 96 (2007) 143–150.

[174] Y. Thomas, The history of the memory of water, Homeopathy 96 (2007) 151–157.

[175] V. Elia, E. Napoli, R. Germano, The 'memory of water": an almost deciphered enigma. Dissipative structures in extremely dilute aqueous solutions, Homeopathy 96 (2007) 163–169.

[176] J. Teixeira, Can water possibly have a memory? A skeptical view, Homeopathy 96 (2007) 158–162 [aDepartment of Radiation Oncology, National Cancer Center / National Clinical Research Center for Cancer, Cancer Hospital, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing, China].

[177] E.R. Lippincott, R.R. Stromberg, W.H. Grant, G.L. Cessac, Polywater. Vibrational spectra indicate unique stable polymeric structure, Science 164 (3887) (1969) 1482–1487.

[178] E.R. Lippincott, G.L. Cessac, R.R. Stromberg, W.H. Grant, Polywater – a search for alternative explanations, J. Colloid Interface Sci. 36 (4) (1971) 443–460.

[179] D.L. Rousseau, S.P.S. Porto, Polywater: polymer or artifact? Science 167 (1970) 1715–1719.

[180] D.L. Rousseau, Polywater" and sweat: similarities between infrared spectra, Science 171 (3967) (1971) 170–172.

[181] R.E. Davis, D.L. Rousseau, R.D. Board, Polywater": evidence from electron spectroscopy for chemical analysis (ESCA) of a complex salt mixture, Science 171 (3967) (1971) 167–170.

[182] N. Daraboina, C. Malmos, N. von Solms, Synergistic kinetic inhibition of natural gas hydrate formation, Fuel 108 (2013) 749–757.

[183] N. Daraboina, C. Malmos, N. von Solms, Investigation of kinetic hydrate inhibition using a high pressure micro differential scanning calorimeter, Energy Fuels 27 (2013) 5779–5786.

[184] S. Mazloum, J. Yang, A. Chapoy, B. Tohidi, A new method for hydrate early warning system based on hydrate memory, in: Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011), Edinburgh, Scotland, United Kingdom, July 17-21, 2011.

[185] E.C. Fuchs, J. Woisetschläger, K. Gatterer, E. Maier, R. Pecnik, G. Holler, H. Eisenkölbl, The floating water bridge, J. Phys. D Appl. Phys. (2007) 6112–6114.

[186] J. Woisetschläger, K. Gatterer, E.C. Fuchs, Experiments in a floating bridge, Exp. Fluids (2009) 121–131.

[187] G.H. Pollack, Cells, gels and the engine of life, Toxicol. Pathol. (2001) 617–618.

[188] L. Piatkowski, A.D. Wexler, E.C. Fuchs, H. Schoenmaker, H.J. Bakker, Ultrafast vibrational energy relaxation of the water bridge, Phys. Chem. Chem. Phys. (2012) 6160–6164.

[189] E.C. Fuchs, B. Bitshnau, J. Woisetshläger, E. Maier, B. Beuneu, J. Teixeira, Neutron scattering of a floating heavy water bridge, J. Phys. D Appl. Phys. (2009) 065502.

[190] E.C. Fuchs, L.F. Agostino, A. Wexler, R.M. Wagterveld, J. Tuinstra, J. Woisetschläger, The behavior of a floating water bridge under reduced gravity conditions, J. Phys. D Appl. Phys. (2010) 25501.

[191] E.C. Fuchs, P. Baroni, B. Bitschnau, L. Noirez, Two-dimensional neutron scattering in a floating heavy water bridge, J. Phys. D Appl. Phys. (2010) 105502.

[192] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature (2008) 301–310.

[193] M. Napoli, J.C.T. Eijkel, S. Pennathur, Nanofluidic technology for biomolecule applications: a critical review, Lab Chip (2010) 957–985.

[194] K. Kostarelos, L. Lacerda, C.D. Partidos, M. Prato, A. Bianco, Carbon nanotube–mediated delivery of peptides and genes to cells: translating nanobiotechnology to therapeutics, J. Drug Deliv. Sci. Technol. (2005) 41–47.

[195] Namin R.M., Karimi Z., (2013) Dynamics of a vertical water bridge.

[196] AD. Wexler, M.L. Sáenz, O. Schreer, J. Woisetschläger, EC. Fuchs, The preparation of electrohydrodynamic bridges from polar dielectric liquids, J. Vis. Exp. (2014).

[197] M. Eisenhut, X. Guo, A.H. Paulitsch-Fuchs, E.C. Fuchs, Aqueous phenol and ethylene glycol solutions in electrohydrodynamic liquid bridging, Open Chem. 3 (9) (2011) 391–403.

[198] L.B. Skinner, C.J. Benmore, B. Shyam, J.K.R. Weber, J.B. Parise, Structure of the floating water bridge and water in an electric field, in: Proceedings of the National Academy of Sciences of the United States of America, 2012, pp. 16463–16468.

[199] https://en.wikipedia.org/wiki/Pockels_effect#cite_ref-1

[200] E.C. Fuchs, A.D. Wexler, L.L.F. Agostinho, M. Ramek, J. Woisetschläger, Methanol, ethanol and propanol in EHD liquid bridging, J. Phys. Conf. Ser. 329 (2011) 012003.

[201] J.M. Zheng, G.H. Pollack, Long range forces extending from polymer surfaces, *Phys Rev* E 68 (2003) 031408.

[202] J. Zheng, W.C. Chin, E. Khijniak, G.H. Pollack, Surfaces and interfacial water: evidence that hydrophilic surfaces have long-range impact, Adv. Colloid Interface Sci. 19–27 (2006).

[203] B.H. Chai, J.-m. Zheng, G.H. Pollack, Spectroscopic studies of solutes in aqueous solution, J. Phys. Chem. A 112 (2008) 2242–2247.

[204] E. So, R. Stahlberg, G. Pollack, Exclusion zone as intermediate between ice and water, WIT Trans. Ecol. Environ. 153 (2011) 1.

[205] H. Yoo, R. Paranji, G.H. Pollack, Hydrophilic surfaces on interfacial water dynamics probed with NMR spectroscopy, J. Phys. Chem. Lett. 18 (6) (2011) 532–536 2.

[206] M.J. Esplandiu, D. Reguera, J. Fraxedas, Electrophoretic origin of long-range repulsion of colloids near water/Nafion interfaces, Soft Matter 16 (2020) 3717–3726.

[207] I. Klyuzhin, A. Symonds, J. Magula, G.H. Pollack, New method of water purification based on the particle-exclusion phenomenon, Environ. Sci. Technol. 42 (2008) 6160–6166.

[208] K. Ovchinnikov, G.H. Pollack, Can water store charge? Langmuir 25 (2009) 542–547 And Reply to Comment on Can Water Store Charge, Langmuir, 2009, 25, 11202.

[209] B. Chai, G.H. Pollack, Solute-free zones in polar liquids, J. Phys. Chem. B. 114 (2010) 5371–5375.

[210] S.A. Skopinov, M.V. Bodrova, M.P.R. Jablon, G.H. Pollack, F.A. Blyakhman, Exclusion Zone" formation in mixtures of ethanol and water, J. Solut. Chem. 46 (2017) 626–632.

[211] G.H. Pollack, Comment on "A theory of Macromolecular Chemotaxis" and "Phenomena associated with gel-water interfaces. Analyses and alternatives to the long-range ordered water hypothesis", J. Phys. Chem. B (2013) 7843–7846.

[212] Frank, H.S., Wen, WY. Ion-solvent interaction. Structural aspects of ion-solvent interaction in aqueous solutions: a suggested picture of water structure.

[213] B. Sulbarán, G. Toriz, G. Allan, G.H. Graham; Pollack, E. Delgado, The dynamic development of exclusion zones on cellulosic surfaces, Cellulose 21 (3) (2014) 1143–1148.

[214] L. Shu, L. Jegatheesan, V. Jegatheesan, C.Q. Li, The structure of water, Fluid Ph. Equilib. 511 (2020) 112514.

[215] R. Roy, W.A. Tiller, I. Bell, M.R. Hoover, The structure of liquid water; novel insights from material research; potential relevance to homeopathy, Mater. Res. Innovat. 9-4 (2005) 93–124.

[216] M.A. Henderson, The interaction of water with solid surfaces: fundamental aspects revisited, Surf. Sci. Rep. 46 (2002) 1–308.

[217] O. Björneholm, … H. Bluhm, Water at interfaces, Chem. Rev. 116 (2016) 7698–7726.

[218] J.M. Schurr, B.S. Fujimoto, L. Huynh, D.T. Chiu, A theory of macromolecular chemotaxis, J. Phys. Chem. B 117 (25) (2013) 7626–7652 12.

[219] J.M. Schurr, Phenomena associated with gel-water interfaces. Analyses and alternatives to the long-range ordered water hypothesis, J. Phys. Chem. B 117 (25) (2013) 7653–7674.

[220] G.H. Pollack, Comment on "A theory of Macromolecular Chemotaxis" and "Phenomena associated with gel-water interfaces. Analyses and alternatives to the long-range ordered water hypothesis, J. Phys. Chem. B (2013) 7843–7846.

[221] D.C. Elton, P.D. Spencer, J.D. Riches, E.D. Williams, Exclusion zone phenomena in water – a critical review of experimental findings and theories, Int. J. Mol. Sci. 21 (2020) 5041.

[222] D.C. Elton, P.D. Spencer, A. Gadomski, Pathological water science – four examples and what they have in Common, Water in Biomechanical and Related Systems, 17, Biologically-Inspired Systems, 2021.

[223] P.D. Spencer, J.D. Riches, E.D. Williams, Exclusion Zone water is associated with material that exhibits proton diffusion but not birefringent properties, Fluid Ph. Equilib. 466 (2018) 103–109.

[224] Z. Li, G.H. Pollack, Surface-induced flow: a natural microscopic engine using infrared energy as fuel, Sci. Adv. 6 (2020) eaba9041.

[225] P. Spencer, Examining Claims of Long-Range Molecular Order in water Molecules, Queensland University of Technology, 2018 MSc Thesis.

[226] H. Jabs, B. Rubik, Self-organization at aqueous colloid-membrane interfaces and an optical method to measure the kinetics of exclusion zone formation, Entropy 16 (2014) 5954–5975.

[227] A. Sharma, … G.H. Pollack, Effect of health-promoting agenda on exclusion-zone size, Dose Response (2018) 1–8.

[228] A. Sharma, G.H. Pollack, Healthy fats and exclusion-zone size, Food Chem. 316 (2020) 126305.

[229] N. Kundacina, M. Shi, G.H. Pollack, Effect of local and general anesthetics on interfacial water, PLoS One (2016) 0152127.

[230] M. Kowacz, G.H. Pollack, Propolis-induced exclusion of colloids: possible new mechanism of biological action, Colloid Interface Sci. Commun. 38 (2020) 100307.

[231] R. Pedregal-Cortes, … G.H. Pollack, Interfacial water and its potential role in the function of sericin against biofouling, Biofouling 35 (7) (2019) 732–741.

[232] G.H. Pollack, Why hydrogels don't dribble water, Gels 3 (43) (2017) 3390 10.

[233] I.S. Klyuzhin, … G.H. Pollack, Persisting water droplets on water surfaces, J. Phys. Chem. B 114 (2010) 14020–14027.

[234] V. Elia, G. Ausanio, A. De Ninno, R. Germano, E. Napoli, M. Niccoli, Experimental evidences of stable water nanostructures at standard pressure and temperature obtained by iterative filtration, Water 5 (2014) 2014 (Basel).

[235] V. Elia, G. Ausanio, A. De Ninno, R. Germano, E. Napoli, M. Niccoli, Electrically induced liquid–liquid phase transition in water at room temperature, Phys. Chem. Chem. Phys. (2019).

[236] E. Del Giudice, G. Preparata, G. Vitiello, Phys. Rev. Lett. 61 (1988) 1085–1088.

[237] J. Segarra-Martí, D. Roca-Sanjuan, M. Merchan, Can the hexagonal ice-like model render the spectroscopic fingerprints of structured water? Feedback from quantum-chemical computations, Entropy 16 (2014) 4101–4120 **2014**.

[238] J. Segarra-Martí, D. Roca-Sanjuán, M. Merchán, On the hexagonal ice-like model of structured water: theoretical analysis of the low-lying excited states, Comput. Theor. Chem. (2014) 266–273.

[239] J. Segarra-Martí, P.B. Coto, R. Mercedes, D. Roca-Sanjuán, M. Merchán, Towards the understanding at the molecular level of the structured-water absorption and fluorescence spectra: a fingerprint of pi-stacked water, Mol. Phys. 111 (9–11) (2013) 1308–1315.

[240] B.C. Gibb, Weird and wonderful water, Nat. Chem. 8 (2016) 733–734.

[241] H. Fröhlich, Long range coherence and the action of enzymes, Nature 228 (5276) (1970) 1093.

[242] B.V. Deryagin, M.V. Golovanov, Electromagnetic nature of forces of repulsion forming aureoles around cells, Colloid J. USSR 48 (2) (1986) 209–211.

[243] E. Del Giudice, A. Tedeschi, G. Vitiello, V. Voeikov, Coherent structures in liquid water close to hydrophilic surfaces, J. Phys. Conf. Ser. 442 (2013) 1–5 012028.

[244] R. Arani, I. Bono, E. del Giudice, G. Preparata, QED coherence and the thermodynamics of water, Int. J. Modern Phys. B 9 (15) (1995) 1813–1841.

[245] T.A. Yinnon, V. Elia, E. Napoli, R. Germano, Z.Q Liu, Water ordering induced by interfaces: an experimental and theoretical study, Water 7 (2016) 96–128 (Basel)2016.

[246] C.A. Yinnon, T.A. Yinnon, Domains in aqueous solutions: theory and experimental evidence, Mod. Phys. Lett. B 23 (16) (2009) 1959–1972.

[247] A.D. Wexler, E.C. Fuchs, J. Woisetschäger, G. Vitiello, Electrically induced liquid-liquid phase transition in water at room temperature, Phys. Chem. Chem. Phys. (2019).

[248] N.F. Bunkin, V.S. Gorelik, V.A. Kozlov, AV. Shkirin, N.V. Suyazov, Colloidal crystal formation at the "Nafion−Water" interface, J. Phys. Chem. B 118 (2014) 3372–3377 2014, doi:10.1021/jp4100729.

[249] G. Preparata, Phys. Rev. A 38 (1988) 233.

[250] G. Preparata, QED, Coherence in Matter, World Scientific, Singapore, 1995.

[251] S. Yuvan, M. Bier, Sense and Nonsense About Water, in: A. Gadomski (Ed.), Water in Biomechanical and Related Systems, 17, Biologically-Inspired Systems, 2021.

[252] M. Bier, D. Pravica, Limits on quantum coherent domains in liquid water, Acta Phys. Pol. B 49 (2018) 1717 2018.

[253] M.W. Ho, Large supramolecular water clusters caught on camera - a review, Water J. 6 (2014) http://www.waterjournal.org/volume-6/ho.