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THE SUPRAMOLECULAR STRUCTURE OF WATER: NMR STUDIES

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ABSTRACT

A total of 174 NMR Proton Relaxation time experiments were performed over a period of 20 years using different instruments in several universities. Namely T_1 and T_2 (the spin-lattice relaxation time and the spin-spin relaxation time, respectively) were measured in different samples of water: distilled, homeopathic, spring water and water treated with electromagnetic fields. All samples were deoxygenated and particular care was devoted to avoid paramagnetic impurities. According to classical magnetic resonance literature $T_1 = T_2 = 3.6$ s. We found surprising results in all the water samples, T_1 being two or three times greater than T_2. The results have been explained in light of recent physical theories such as coherence domains, quantum electrodynamics (QED), thermodynamics of irreversible processes (TIP) and Pollack's water exclusion zone (EZ). The formation of a supramolecular structure of water is suggested. The results are related to the small dimension of the NMR tubes and the role of surfaces.

Keywords: NMR proton relaxation times, QED, thermodynamics of irreversible processes, water, water exclusion zone.

1 INTRODUCTION

It is well known from magnetic resonance literature [1] that the picture of protons in a water molecule being relaxed by a local magnetic field due to the dipolar interaction between the two nuclear moments is a classical one and fails to describe the relaxation effects properly. One reason for this is that the spins obey quantum mechanics rather than classical mechanics.

The theoretical well established, up to now, approach [1] leads to the conclusion that the spin-lattice relaxation time T_1 equals the spin-spin relaxation time T_2: $T_1 = T_2$. If the effects of magnetic fields of the protons on other water molecules are taken into account, again $T_1 = T_2$ under normal conditions. Calculations including the rotational and translational parts lead to a value of $T_1 = 4.4$ s, in agreement with the T_1 experimental results.

Again classical literature [2] claims that the measured T_1 and T_2 values for pure water are $T_1 = T_2 = 3.6$ s.

Of course the classical literature [1, 2] underlines that the calculation is completely different for biological samples or viscous solutions for which other terms must be included (see discussion). At higher viscosity the theoretical curves for T_1 and T_2 diverge.

When $\omega_0\tau_c$, where ω_0 is the frequency and τ_c is the correlation time, is much greater than 1, T_2 becomes much shorter than T_1. A small ratio of T_2/T_1 is common in biological NMR; indeed T_2 values for tissue water tend to be about 10-fold smaller than the T_1 values. Our understanding of water relaxation *in vivo* is far from complete, but it is presumed that there is exchange between free and bound protons, the bound protons having a sufficiently long correlation time to account for the relatively short T_2 values that are observed, as reported in [2].

In the presence of paramagnetic species, T_1 and T_2 decrease drastically. Paramagnetic centres generate very powerful relaxation because the magnetic moment of the electron is about 1000 times greater than the nuclear moments. This leads to an enhancement in relaxation by a factor of about 10^6, so even trace amounts of paramagnetic ions can have a profound effect on relaxation times.

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In this paper we present a research over a period of 20 years, with almost 200 measurements of proton relaxation times, T_1 and T_2, performed on different spectrometers and using different aqueous sources.

Our research is also important for NMR imaging (MRI), the proton relaxation time of H_2O being the main parameter in this case.

Measurements of T_1 and T_2 can also contribute to the characterization and interpretation of imaging findings.

We found surprising results for all water samples, T_1 being two or three times greater than T_2.

We explain these results at light of recent physical theories such as coherence domains, quantum electrodynamics (QED), thermodynamics of irreversible processes (TIP) and Pollack's water exclusion zone (EZ). TIP refers to Prigogine's dissipative structures.

The formation of a supramolecular structure of water is suggested. The results are also related to the small dimension of the NMR tubes and to the role of surfaces.

2 EXPERIMENTAL

A total of 174 NMR Proton Relaxation time experiments were performed over a period of 20 years using different instruments in several universities. These include: Polo Universitario di Colle Val d'Elsa (SI), University of Siena, University of Virginia and University of Sassari. All the relaxation times were measured at different frequencies on various instruments (Table 1).

T_1 and T_2 were measured in different water samples: distilled, homeopathic, spring water and water treated with electromagnetic fields. All samples were deoxygenated and particular care was devoted to avoid paramagnetic impurities. The spin-lattice relaxation rates were measured using the $(180°\text{-}\tau\text{-}90°\text{-}t)_n$ sequence. The maximum experimental error in the relaxation rate measurements was 5% (in a few cases 8–10%).

Many samples were measured in regular 5 or 3 mm NMR cells with a capillary inside the cell and $CDCl_3$ in the external part. Other experiments were performed with DMSO inside a capillary and water in the external part. Nevertheless, all these different experimental procedures, including Spin-on and Spin-off, gave the same results.

2.1 Details about the University of Siena experiments

For the NMR experiments a coaxial system formed by a stem coaxial insert (outer diameter of 2 mm) and a 5 mm NMR tube was used. The stem coaxial insert had a capacity of 60 μL, and the external tube contained 530 μL. All the measurements were performed with the deuterated solvent,

Table 1: NMR instruments.

Instrument	Software
Stelar, Spinmaster Ffc-2000 Nmr Relaxometer[1]	
Varian 200 MHz, Gemini[2]	WINNMR 6.1c
Varian 300 MHz, WRX[2]	WINNMR 6.1c
Bruker 400 MHz, AMX[2]	XWINNMR 2.6
Bruker 500 MHz, DRXavance[2]	TOPSPIN 1.3
Bruker 600 MHz, DRX[2]	XWINNMR 2.6
Varian 500 MHz[3]	
Varian 300 MHz[4]	

[1]Polo Universitario di Colle Val d'Elsa (SI), Italy, [2]University of Siena, Italy, [3]University of Virginia, USA, [4]University of Sassari, Italy.

dimethyl sulfoxide (DMSO-d_6) in the external tube and water sample inside the coaxial insert. The tube was positioned so that the whole sample was located within the probe coil. This arrangement gave a well-behaved NMR signal and also facilitated rapid response of the sample to temperature changes, owing to its small volume.

The temperature could be controlled within ±0.1K for the two experimental values of 298 and 313K.

The NMR experiments were repeated more times, using water sample stored either in the NMR tube or in a big flask.

NMR experiments were performed on a Varian WRX 300 spectrometer with a BBO 5 mm probe and a Bruker DRX-600 AVANCE equipped with an *xyz* gradient unit, operating at 300 and 600 MHz for ^{1}H, respectively.

At 600 MHz, 5 mm triple broad-band inverse probe was used for all ^{1}H experiments. Standard ^{1}H NMR spectra were acquired with an FID composed of 16,384 points over a spectral width of 4800 Hz (acquisition time 1.704 s), a 90° pulse of 9.2 μs, a relaxation delay of 10 s and four transients.

The proton spin-lattice relaxation times (T_1) were measured using the 'inversion-recovery' $(\text{RD-}180°\text{-}\tau\text{-}90°\text{-}t)_n$ sequence, where RD = 20 s. In order to avoid the radiation damping phenomenon, the 90° pulse length was determined off-resonance and was of 140 μs. The τ values used for the experiments were: 0.001, 0.01, 0.05, 0.1, 0.4, 0.6, 0.8, 1, 1.4, 2, 2.2, 2.4, 3, 4, 5, 20 s, respectively.

The maximum experimental error in the relaxation rate measurements was estimated to be 5%.

The T_1 values were determined by a three-parameter fit of peak intensities to the following equation:

$$I(\tau) = I_0 + Ae^{(-\tau/T_1)}, \qquad (1)$$

where A is a variable parameter that considers non-ideal magnetization whose value is less than unity [3].

The proton spin-spin relaxation times (T_2) were measured with the CPMG sequence $90°_x\text{-}\tau\text{-}[180°_y\text{-}\tau\text{-echo-}\tau]_n$ [4, 5]. The n values used for the sequence were: 500, 300, 180, 140, 100, 80, 60, 40, 24, 18, 12, 10, 8, 2, respectively. These values led to delays between the first 90° pulse and the start of the acquisition of 20, 12, 7.2, 5.6, 4, 3.2, 2.4, 1.6, 0.96, 0.72, 0.48, 0.40, 0.32, 0.08 s, respectively.

Four scans were recorded for each n by applying a 20 s recycle delay between sequences to avoid saturation, and using phase cycling to improve the signal-to-noise ratio. CPMG echo envelopes were fitted to an exponential function with a nonlinear regression method based on the Levenberg-Marquardt algorithm. The relative error in T_2 was <2%. The decays were always found to be single exponential, indicating that the self-diffusion of water and exchange of protons between bulk water and solute were sufficiently rapid for the water response to be characterized by a single averaged relaxation time. The T_2 values were obtained by a fit of peak intensities using the following exponential decay function:

$$y = y_0 + Ae^{-\tau/T}. \qquad (2)$$

The echo amplitude, in the CPMG sequence, at time $t = 2\tau$ (the top of the echo) contains a number of factors due to such diverse phenomena as transverse relaxation, self-diffusion, homonuclear couplings and chemical exchange, none of which affects its RF phase. On the other hand, spin echo eliminates (refocuses) the effects of field/RF offset, field inhomogeneity, chemical shifts and heteronuclear couplings. Any spin-echo instability therefore arises from imperfections in one or more of the refocusing phenomena. In particular, the instabilities due to field inhomogeneity fluctuations that affect both echo phase and echo magnitude (in extreme cases, they may completely prevent echo formation) have been eliminated using the spinning of sample. Since most modern NMR instruments employ quadrature phase detection, the echo phase and all its statistical characteristics are experimentally accessible and are taken into consideration in our analysis.

The CPMG sequence is remarkable in producing a long train of echo signals that enables efficient measurements of spin-spin relaxation and the diffusion constant, as well as maximizing signal-to-noise ratio in various challenging experimental conditions [6, 7].

All NMR data were processed with XWINNMR software (version 2.5) on Silicon Graphics O2 equipped with RISC R5000 processors, working under the IRIX 6.3 operating system.

3 RESULTS

Some of the 174 experiments are reported in the following tables and figures: T_1, T_2, $\Delta(T_1 - T_2)$.

Table 2: Data recorded at the University of Virginia (USA) at 500 MHz and $T = 298$K.

	Bidistilled H_2O	Spring H_2O	H_2O tap
T_1 ± Ea	4.383 ± 0.228	5.144 ± 0.209	4.569 ± 0.066
T_2 ± Ea	2.743 ± 0.066	2.199 ± 0.027	2.671 ± 0.055
$\Delta(T_1 - T_2)$ ± Ea	1.640 ± 0.294	2.945 ± 0.236	1.898 ± 0.121

This table is related to Fig. 1. The second part refers to the errors. All the other experiments showed similar errors.

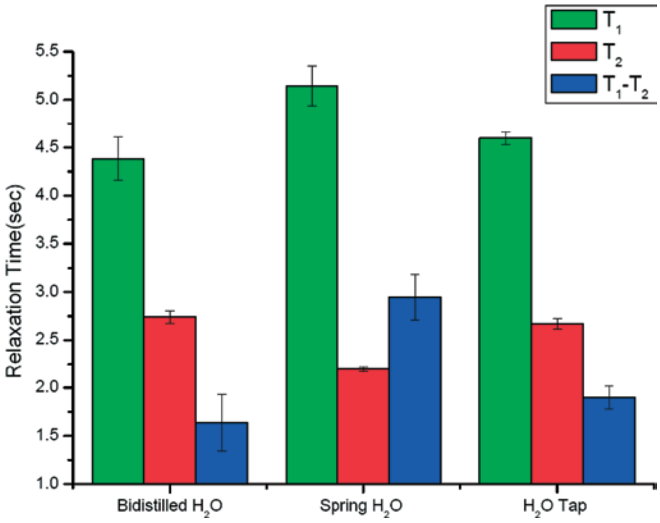

Figure 1: Related to Table 2.

Table 3: Water treated with an electromagnetic field (January 2006).

	Not treated	Not treated degassed	Treated	Treated degassed
$T_{1(600\text{ MHz})}$	3.897	3.500	3.608	3.890
$T_{2(600\text{ MHz})}$	1.020	1.444	1.108	1.542
$\Delta(T_1 - T_2)$	2.877	2.056	2.500	2.348

This table is related to Fig. 2.

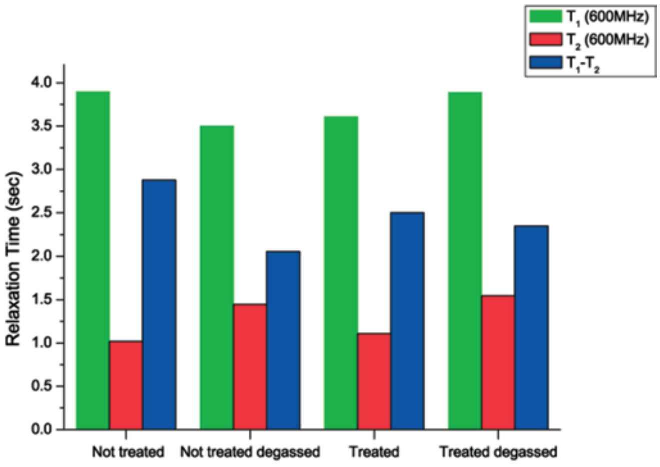

Figure 2: Related to Table 3.

Table 4: Bidistilled water containing different chemicals:

	3 October 2005 (300 MHz)		27 December 2005 (600MHz)	
	T_1	T_2	T_1	T_2
Sample 1	3.19 ± 0.04	2.05 ± 0.01	3.60 ± 0.27	1.41 ± 0.03
Sample 2	2.91 ± 0.06	1.61 ± 0.09	3.57 ± 0.24	1.32 ± 0.05
Sample 3	2.89 ± 0.03	1.48 ± 0.08	3.10 ± 0.30	1.66 ± 0.01
Bidistilled H_2O			3.82 ± 0.22	2.74 ± 0.07

Sample 1: $NaHCO_3$ 5×10^{-5}M.
Sample 2: $NaHCO_3$ homeopathic solution.
Sample 3: 5CH 57 *Arnica Montana* 1642 (homeopathic solution).
This table is related to Fig. 3.

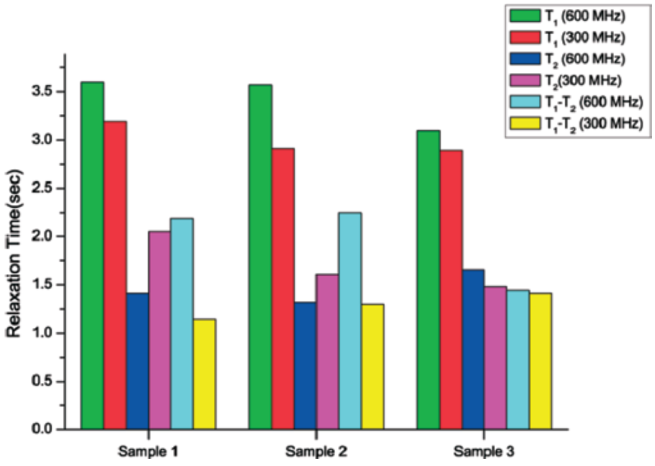

Figure 3: Related to Table 4.

Table 5: Bidistilled water (May 2006).

		s
	T_1	3.203
	T_1 SPIN ON	3.185
d 20* = 20 ms	T_2	1.623
	T_2 SPIN ON	1.507
d 20* = 10 ms	T_2	1.425
	T_2 SPIN ON	1.410
d 20* = 2 ms	T_2	0.949
	T_2 SPIN ON	0.946

This table is related to Fig. 4.
*Fixed echo time to allow elimination of diffusion.

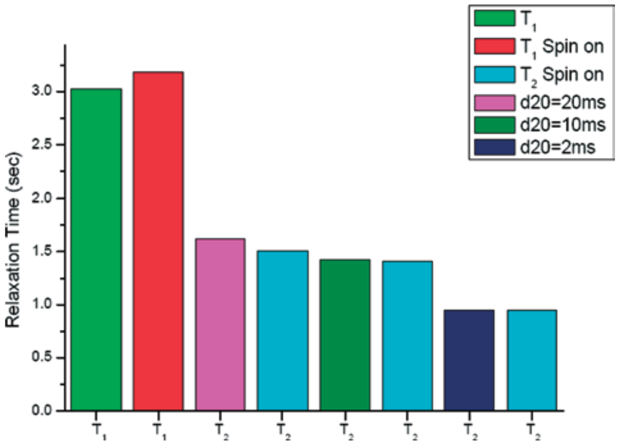

Figure 4: Related to Table 5.

The experimental data reported in Tables 2–5 and in Figs 1–4 highlight a very surprising result: the nuclear spin relaxation time T_1 is not equal to T_2 as accepted for a long time in classical magnetic resonance literature [1, 2] and more recent references, which always refer to [1, 2]. T_1 was almost double and in some cases was 2.5–3 times greater than T_2.

These results were common to all the water samples examined (174 experiments) and do not depend on magnetic field frequencies, which, obviously, change the values in the correlation times equation (see discussion), but not the general trend.

In particular, the homeopathic solutions gave very similar values. It is important to underline that in the case of the homeopathic solutions we deal with *extremely diluted* ones, which means that the samples are pure water, except that they had initially contact with different active principles that affect the *ontic evolution* of samples [8–10]. As pointed out by Louis Rey [11, 12] the thermoluminescence of *extremely diluted solutions* has been studied and it was found that, despite their dilutions beyond the Avogadro numbers, the emitted light was specific of the original salts dissolved initially.

4 DISCUSSION

In order to explain the experimental results, we refer to the classical equations of nuclear spin relaxation times, for slow motion (e.g. viscous solutions). This is not our case, but it is useful to understand how these equations can be modified.

All relaxation effects depend on the frequency spectrum of local fields at the nucleus and there is almost always a definite characteristic time scale for the fluctuations, i.e. a *correlation time* τ_c.

The calculation of T_1 for the spin-lattice relaxation time leads to:

$$\frac{1}{T_1} = \frac{3}{20}\left(\frac{g_N^2 \beta_N^2}{\eta^2 r^6}\right)\left\{\frac{2\tau_c}{1+\omega_0^2\tau_c^2} + \frac{8\tau_c}{1+4\omega_0^2\tau_c^2}\right\}. \tag{3}$$

The calculation of T_2 is considerably more complicated than the one we have just performed for T_1. We merely quote the result:

$$\frac{1}{T_2} = \frac{3}{40}\left(\frac{g_N^2 \beta_N^2}{\eta^2 r^6}\right)\left\{6\tau_c + \frac{10\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right\}. \tag{4}$$

We have neglected the magnetic fields of the protons on other water molecules that diffuse by, but also produce, relaxation. The theoretical expression must therefore be supplemented by a further term, which is:

$$\left(\frac{1}{T_1}\right)_{\text{trans}} = \frac{\pi}{5}\left(\frac{g_N^2 \beta_n^2}{\eta^2}\right)\frac{N}{Db}. \tag{5}$$

Here D is the coefficient of self diffusion, N the concentration of spins and b the distance of closest approach between spins on different molecules. Taking $D = 1.85 \times 10^{-5}$, $N = 6.75 \times 10^{22}$, b = 1.74Å for water, we estimate $(T_1)_{\text{trans}} = 12.6$ s. The total relaxation rate is the sum of the rotational and translational parts:

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_{\text{rot}} + \left(\frac{1}{T_2}\right)_{\text{trans}}. \tag{6}$$

As long as τ_c is short, so that $\omega_0\tau_c = 1$, T_1 and T_2 remain equal. Both contributions to $(1/T_1)$ should be proportional to (η/T), since the first depends on the correlation time $\tau_c = 4\pi\alpha^3\eta/3kT$ and the second on the diffusion coefficient, whose value calculated for a spherical molecule is $1/D = 6\pi\eta\alpha/kT$. This prediction is well tested by the experiments of Bloembergen on proton relaxation times in glycerin, a liquid whose viscosity varies very strongly with temperature [1].

As the liquid becomes more viscous and the correlation time increases, the component of the local field fluctuations at the resonance frequency ω_0 decreases, tending to zero when $\omega_0\tau_c$? 1. The result is that the value of T_2 decreases, being still proportional to $1/2\tau_c$ but the spin-lattice relaxation time T_1 now becomes very long, as it is proportional to $2\tau_c/(1 + \omega_0^2\tau_c^2)$.

Hence in the limit of long correlation times, T_1 is proportional to τ_c instead of $1/\tau_c$ and begins to increase again. In the region between long and short correlation times, T_1 goes through a minimum at the point $\omega_0\tau_c = 1$. The line width $1/T_2$ continues to increase linearly with τ_c until the molecular motion slows down so much that it is completely frozen. At this stage we have a randomly oriented solid.

This conceptual behavior vs. the value of the correlation time is reported, together with some of our experimental data, in Fig. 5 and is in agreement with formation of a low-entropy dissipative structure,

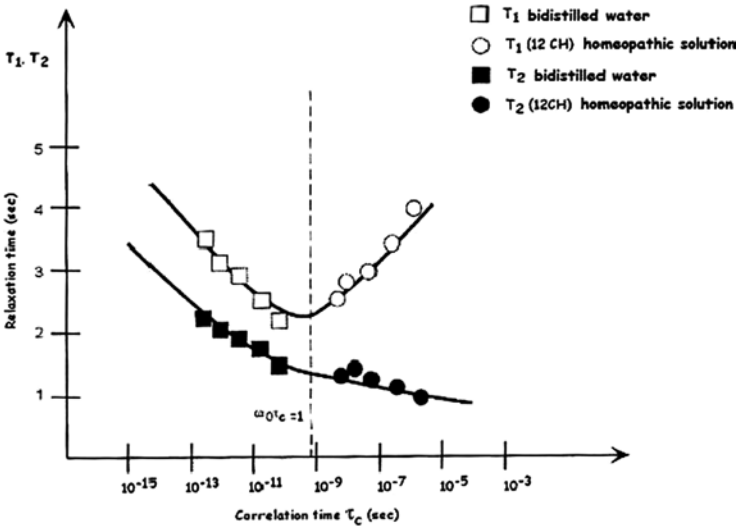

Figure 5: H_2O proton relaxation times at 200 Mc/s (experimental) compared with the conceptual behavior.

in the form of the supramolecular structure of water. The values of τ_c in the right part of the figure are typical of a supramolecular structure similar to a liquid crystal. A liquid crystal or liquid cluster can be defined as a substance that flows as a liquid but has some order in its arrangement of molecules and a phase of matter whose order is intermediate between that of a liquid and a crystalline solid. Water possesses features of solid state substances rather than statistical liquids [13–16].

As pointed out by Nobel laureate in chemistry professor Ilya Prigogine, low-entropy dissipative structures manifest a coherent, supramolecular character that leads to new, quite spectacular manifestations, such as biochemical cycle involving oscillations. These spatio-temporal structures arise from the nonlinear dynamics of these phenomena.

All our experimental NMR data suggest the existence of a long range correlation involving a large number of water molecules, much larger than values compatible with the customary electrostatic theories. This correlation is long-lasting as shown by the value of τ_c. However, no evidence of this lasting correlation can be found in bulk water; as a matter of fact, this lack of evidence has convinced many physicists in recent decades that liquid water is a homogeneous monophasic liquid. Only recently, evidence has been reported [17] that liquid bulk water is a mixture of two phases, in which each molecule is continuously crossing between the two, giving rise to flickering liquid structure. Why does this flickering situation get stabilized in the NMR experiments? A reasonable answer should take into account that water subjected to NMR measurements is confined into narrow capillaries or small cells, where the water molecules are close to a wall. This circumstance has already been mentioned in our previous studies as the root of the explanation of the surprising NMR results [18, 19]. One should therefore admit that water near walls acquires physical properties different to those of bulk water. This conclusion is supported by findings of the group led by G. Pollack [20, 21]. They found that water on a hydrophilic surface forms layers of ‘anomalous’ water up to 500 μm thick. The anomalies are:

1. higher viscosity,
2. a strong negative redox potential (this water is able to release electrons quite easily),

3. the loss of the property of being solvent (hence the name exclusion zones or EZ coined by Pollack for these regions),
4. its local temperature is lower than that of bulk water.

All these findings point to the existence of a highly correlated water at interfaces [20, 21].

The Pollack data matches our data quite well, providing a consistent picture of interfacial water. This picture recently obtained theoretical support from QED [22, 23]. Moreover the QED findings appear to be a dynamical implementation of the thermodynamic requirements provided by the TIP [24].

The main points of this unified QED–TIP approach are:

1. Above a density threshold and below a temperature threshold, water molecules are simultaneously subject to collective electrodynamical attraction and disruptive thermal dynamics based on collisions.
2. Under electrodynamical attraction, molecules form coherence domains (CD) oscillate in unison between two electron cloud configurations in tune with a self-trapped electromagnetic (e.m.) field. The wavelength of the e.m. field coincides with the size of the CD.
3. The energy of each component of the CD is smaller than the energy of the same molecule when it is free. This energy difference is the ‘energy gap’ and determines how the CD is protected against external assaults. When the thermal noise kT competes with the energy gap, we obtain the flickering situation observed in bulk water.
4. When some further attraction is added, for instance the attraction between molecules and the wall, the CD is more protected against thermal noise and water therefore becomes more coherent. In the case of water, this attraction acquires a quite long range (several hundred micrometers) because another coherent mechanism is at work. This mechanism [25] provides coherent coupling of the electric dipoles of water molecules, up to a distance of several hundred microns, when a polarization field, such as the field produced by the wall, is present. This electric dipole coherence adds to the electron cloud coherence and stabilizes it, giving rise to the observed thick layer of EZ–water.

The combined QED–TIP approach (elsewhere [26] we termed it the CDDS approach in the framework of COOS, i.e. Confined Ontic Open Sytems) therefore sheds some light on the peculiar properties of interfacial water. Notice that all the water in living organisms is interfacial because it is always closer than a fraction of a micron to some interface. An example of the application of this new conceptual framework appears in an analysis of the Belousov–Zhabotinsky system and of the role of water in it [27].

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