Chapter 2 Sense and Nonsense About Water



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Abstract Water is present in all of its three phases in our natural world. It carves the landscapes on our planet, it is the solvent for biological activity, and it is central in humankind's physical and intellectual existence. We summarize how water's properties as a liquid and as a solvent are a consequence of the molecule being a strong dipole subject to Brownian motion. Short-lived hydrogen bridges between neighboring water molecules set up a flexible tetrahedral network. Convoluted pseudoscientific theories have been formulated about water. Many of these theories involve elaborate forms of higher organization and quantum physics. Some such theories have been used as a basis for scams and quackeries. We discuss of few of these excesses.

Keywords Liquid water \cdot Water as a solvent \cdot Water phase diagram \cdot Brownian motion \cdot Pseudoscience on water

An over-indulgence of anything, even something as pure as water, can intoxicate.

(Jami 2012).

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1 Introduction

Life left the oceans and went terrestrial on a large scale about half a billion years ago. However, even on land water maintained its role as the great enabler. In any terrestrial life-form the vast majority of molecules is water and the intracellular and extracellular solution are aqueous. Water is a volatile enabler as its availability generally fluctuates and overabundance or shortage of water commonly proves calamitous for entire ecosystems. Water thus came to play a prominent role as humans started to develop and formulate world views.

In all of the major, modern-day religions water plays a role as a cleanser and a purifier. As such it is considered to have a symbolic, if not mystical, ability to close the gap between man and the ideal purity of the divine. The Catholic Church prescribes elaborate rituals for the manufacture and disposal of "holy water." Baptism is central in Christianity. Judaism has a similar approach and has its followers achieve purity through immersion in a "mikveh." The Prophet Muhammed said "cleanliness is half the faith" and, consequently, Muslims are to wash with clean water before prayer and before handling the Quran. Both Judaism and Islam have strict rules about the water and the allowable sources of water to be used in the rituals. In Hinduism and in Buddhism it is believed that the sacred waters of the Ganges will wash away the sins of those that bathe in the river. Deities from Poseidon (Homer's *Iliad* 13:26–31) and Jesus (Mark 6:45–52, Matthew 14:22–33, John 6:15–21, *NIV*) up till Kim Il-Sung purportedly walked on water (McNeill 2011) – an act of dominance that would seem to set them metaphysically, as well as literally, above mere water.

With aqueous magic so firmly entrenched in our collective consciousness, it is hard for an individual scientist to keep a rational and empirical outlook when researching water. Below we will describe how seeing liquid water as mere dipoles performing Brownian motion accounts for properties of water as the solvent that facilitates biological activity. No quantum physics is required and no new phases or higher organization need be postulated. We will also tell the tale of a few pseudoscientific mishaps and scams.

2 The Facts on Water

A major pursuit in chemistry is explaining how the bulk properties of a substance result from the characteristics of the constituent molecules. Many of water's bulk properties are consequences of the strong dipole of the molecule and of the intermolecular hydrogen bonds that ensue from the dipoles.

The H-O-H angle in the water molecule is 104.5 degrees, thereby slightly differing from the 109.5 degrees of a perfect tetrahedron. The strong dipole comes about because the oxygen side of the molecule is a stronger attractor of electrons than the side with the two protons. When water is exposed to an electric field, the dipoles will rotate and orient themselves parallel to the electric field. The result is that the field will be reduced. The factor by which the electric field is reduced is the relative dielectric permittivity. For water the value of the relative dielectric permittivity is 80. Dielectric forces arise when the imposed electric field is not uniform and when, for instance, microparticles are dissolved in the water. The system will then lose energy if the material with the highest dielectric constant is forced towards where the electric field is highest. Dielectric forces are commonly used to move and manipulate microparticles (Rousselet et al. 1994).

The consensus picture is that around a dissolved ion or dipole, the water molecules orient their dipoles and form a nanometer-scale hydration shell (Moore 1974; Israelachvili 2011). Around an ion, there is a rigid inner shell of one layer of water molecules. Immediately beyond this, an outer shell consists of one or two more layers that are less rigid. Further away, Brownian collisions (that carry an average energy of about k_BT) overwhelm hydration bonds. Hydration shells around proteins and other biomolecules are the subject of much research. Experimental observation appears to be in good agreement with the results of theory and molecular dynamics simulation (Pettitt et al. 1998; Virtanen et al. 2010). In the references by Ebbinghaus et al. (2007) and Dastidar and Mukhopadhyay (2003) it is shown that the hydration shell around a big protein also extends to no more than about a nanometer away from the protein. The hydration shell effectively screens away the electric field of the underlying ion or dipole. The electric field of an ion in an aqueous solution is already unnoticeable within a nanometer.

The molecules in liquid water are colliding repeatedly as they perform Brownian motion. At room temperature, the speed of a water molecule is about 600 m/s (for each translational degree of freedom $\frac{1}{2}mv^2 = \frac{1}{2}k_BT$). For liquid water, the density is such that the mean free path roughly equals the size of the molecule – about 0.25 nm. From these numbers it is readily derived that there are on the order of a trillion (10¹²) collisions per water molecule per second. In other words, there is a collision per picosecond for every individual water molecule.

Much of water's bulk behavior is related to the hydrogen bridges that form between neighboring water molecules (see Fig. 2.1). After fluoride, oxygen is the most electronegative element. The ensuing strong attraction of electrons to oxygen leads to the water molecule's strong dipole. Hydrogen bonds are basically dipoledipole interactions. The strength of the hydrogen bonds in water as well as the large number of hydrogen bonds in a mole of liquid water results in a lot of energy being associated with hydrogen bonds. This energy must be supplied when melting or boiling water and leads to relatively high melting and boiling temperatures. In this context it is instructive to compare water to hydrogen sulfide (H₂S). As a molecule, hydrogen sulfide has an architecture that is almost identical to water. But the electronegativity of sulfur is 2.58, whereas that of oxygen is 3.44. This leads to the H₂S molecule having a smaller dipole than the H₂O molecule. The result is that hydrogen sulfide, in spite of having almost twice the molecular mass of water, is a gas at room temperature. The energy in the hydrogen bridges also leads to liquid water's high specific heat and the high energies associated with melting and evaporation.



Fig. 2.1 The tetrahedral structure of water. The large red dots represent the oxygen atoms and the smaller blue dots represent the hydrogen atoms. The bold segments represent covalent bonds and the dotted segments represent hydrogen bridges. Hydrogen bridges ensue along the dotted segments as the strongly negative electron cloud around an oxygen attracts protons bound to other water molecules. With the tetrahedral structure, a hydrogen-bound electron can transit to the other side of the hydrogen to next be shared with another oxygen. Note that the same structure is obtained upon an inversion where all the dotted segments become bold and all the bold segments become dotted. Such symmetry adds stability to the structure. For liquid water Brownian collisions have sufficient energy to disrupt a hydrogen bond within picoseconds. But upon freezing the tetrahedral structure becomes rigid

Because of the tetrahedral positioning of the oxygen's four electron pairs, the structure depicted in Fig. 2.1 is the favored lattice arrangement. For liquid water, the energy of Brownian collisions (about k_BT) is still such that the hydrogen bond survives for only picoseconds. The tetrahedral structure loses its plasticity upon freezing.

Under atmospheric conditions, water expands by 9% when it freezes. Water has its highest density in its liquid state at 4 °C. This is the reason that ice floats on water. It is also the reason that potholes appear in roads during winter months: water seeps into the cracks in the asphalt when the temperature is above freezing and next fractures the asphalt when it freezes and expands. Expansion upon cooling is counterintuitive as one would think that increased thermal agitation pushes molecules further away from each other. But this behavior is not really anomalous. Silica (SiO₂), the major constituent of sand, also does this and it is the reason that the solid crust of the Earth, with its density of 2750 kg/m³, effectively floats on the liquid mantle that has a density of 3300 kg/m³ (Lowrie 1997). In the case of water, it is again hydrogen bridges that are largely responsible for the shrinking upon melting. When water turns liquid, the organized structure that is depicted in Fig. 2.1 literally collapses (Brini et al. 2017). The Van der Waals forces can next pull water molecules closer together than that they are in the lattice of Fig. 2.1. Only above 4 °C is the situation again such that increasing the energy k_BT of the Brownian collisions increasingly overwhelms the energy of the Van der Waals bonding and leads to driving molecules further apart. Alcohol does not expand upon freezing and the addition of a little alcohol to water leads to a mixture that again expands upon heating. Alcohol (C₂H₅OH) also has intermolecular hydrogen bonds, but less of them per unit of mass.

Widespread is the misconception that a microwave oven is generating heat by emitting at a resonance frequency of water. The actual fact is that it is possible to quantitatively account for the operation of a microwave oven with great accuracy by modeling the water molecule as a sphere with an electric dipole that is rotating in a viscous, overdamped medium. Because of the dipole, the microwave oven's GHz radiation applies a torque to the water molecule and makes it rotate. The generated heat is due to the friction with the medium. Imagine a water molecule with its dipole in an arbitrary direction and no electric field present. If an electric field is suddenly applied, the dipole will align. However, there is a characteristic time associated with the relaxation to the new alignment. Peter Debye derived $\tau = 4\pi \eta R^3/k_B T$ for this relaxation time (Debye 1945; Elton 2017). Here η represents the shear viscosity (about 10^{-3} N × s/m² for liquid water). With R = 0.14 nm for the radius of the water molecule, this equation leads to a remarkably accurate estimate: $\tau \approx 10$ ps. It is obvious that the rotating dipole will keep up with an applied AC field if that field is not changing too fast, i.e. if $\omega \leq \tau^{-1}$, where ω is the angular frequency of the applied AC field. For $\omega \gg \tau^{-1}$ the field cycles so fast that the dipole will effectively "feel" the zero-average of the field. No rotation and generation of heat will occur in that case. With the 2.45 GHz of an ordinary microwave oven, we are well below the τ^{-1} cutoff.

There are small discrepancies between Debye's predictions and measured spectra. However, these discrepancies have been resolved by taking the tetrahedral geometry (cf. Fig. 2.1) into account and realizing that much of the molecular motion consists of "hopping" from one such structure to another (Elton 2017). It is not through an invocation of quantum resonances or higher organization that discrepancies have been resolved, but through a more precise assessment of hydrogen bonds and intermolecular geometry.

3 Mishaps

3.1 Polywater

In 1962 the Russian physicists Nikolay Fedyakin and Boris Deryagin reported the discovery of a new type of water (Deryagin and Fedyakin 1962). In narrow capillaries they claimed to have found water that was more dense and more viscous than normal. It was thought to be a polymerized form of water and it therefore came to

be called "polywater." Deryagin, who was the head of a prestigious research center in Moscow, showed his results in the West in 1966 and the paranoia of the Cold War soon led to large scale research efforts in the United States and Western Europe. It was suggested that with the proper catalyst, rivers, lakes, and oceans could be turned into molasses. Newspapers frequently reported about polywater in a hysteric and apocalyptic tone. Nevertheless, the international scientific community kept experimenting and theorizing in a free and open manner.

Within a few years it became clear that it had all been a delusion. Polywater was nothing but ordinary water that had been slightly contaminated. The first skeptical voices were heard in 1970 and by 1974 scientists generally agreed that there was no such thing as polywater. Research into the subject died out. Figure 2.2 shows the accumulated number of scientific articles on the subject of Polywater.

Where scientists have left polywater behind and moved on to new subjects, historians and philosophers of science have subsequently written a lot about the polywater affair. Was it a hypothesis that did not survive the testing, i.e., was it science the way it ought to be conducted? Or was it science led astray? Much cited is the book *Polywater* by Felix Franks (1981). Franks takes the latter viewpoint and describes the episode as "pathological science."

Ultimately, 299 papers about polywater were published. After 1974 no more scientific articles on the subject appeared (Ackermann 2006). Figure 2.2 shows the accumulated number of papers as a function of time. What is remarkable is that the logistic curve is an almost perfect fit. The curve is mindful of an epidemic and in the reference by Ackermann (2006) the author indeed characterizes the polywater episode as a "false information epidemic."



Fig. 2.2 The accumulated number of scientific articles on the subject of polywater as time evolves. Data were taken from the reference by Ackermann (2006). The number of papers that were ultimately published on the subject is $N_0 = 299$. The red curve represents a best fit of the logistic function $n(t) = N_0/(1 + \exp[-\alpha(t - t_0)])$

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The logistic function, $n(t) = N_0/(1 + \exp[-\alpha(t - t_0)])$, is the solution of the Verhulst Equation: $\dot{n}(t) = \alpha n(t)(1-n(t)/N_0)$. The equation describes how for small n(t) there is an exponential increase that is characterized by a rate α . For larger n(t) the solution approaches a horizontal asymptote, i.e. $n(t \to \infty) = N_0$. The free parameter in the solution of the differential equation can be identified with setting the initial time constant t_0 . The Verhulst Equation was first formulated for a population of animals that initially increases exponentially but flattens when the carrying capacity of the environment is approached. Half a century ago Bass described how the Verhulst Model also applies to durable goods like lawn mowers, televisions, or clothes dryers (Bass 1969). Sales of such products increase exponentially as the products first enter the market and word about usefulness spreads. But later, as the market approaches its saturation level, sales come to a halt. Ideas and fashions appear to follow a similar dynamic. In the reference by Coulmont et al. (2016) it is shown how Verhulst dynamics also applies to baby names: logistic curves are fitted to data that show how "Diane" and "Seymour" first rose in popularity, but ultimately became outdated.

It is remarkable that the simple Verhulst Equation leads to such a perfect fit to the data shown in Fig. 2.2. It appears as if it were a completely deterministic evolution of half a decade and 299 papers that turned an illusion into a generally-recognized delusion. In the remainder of this section we will see that polywater is the exception rather than the rule. Many of the misapprehensions about water have turned out more long-lasting. Such misapprehensions have also become gratefully adopted and exploited by quacks and scammers.

3.2 Homeopathy and "Water Memory"

Homeopathy was developed about 200 years ago and it was most likely inspired by the proliferating practice of smallpox inoculation. Smallpox used to be fatal in about 25% of all cases. In an inoculation a very small amount of pus or scabs from someone infected with smallpox would be administered. It would generally lead to mild symptoms, but upon recovery the inoculated individual would have immunity against the disease. Homeopathy extrapolated the idea: a strong cup of coffee may lead to sleeplessness but give someone a very diluted caffeine solution and it will work as a *remedy* against sleeplessness. However, once Avogadro's number was established, it became obvious that the dilutions that are used in homeopathic practice are so extreme that no molecule of the original substance is ultimately left.

In an attempt to take their practice out of the realm of quackery and obtain scientific credibility, advocates of homeopathy have concocted a number of theories as to why a substance can have an effect even after it has been completely diluted away. The issue came to a head in June of 1988. In that year Jacques Benveniste and his group published a paper in *Nature* (Davenas et al. 1988). The paper reported the results of a simple bench experiment. Basophils are the white blood cells that are responsible for much of the immune response. The *Nature* article reported how homeopathic dilutions of antibody triggered a response in such basophils. At the end of the article the authors briefly address the fundamental ontological problem of a molecule having an effect without being physically present. In the abstract it writes: "Since dilutions need to be accompanied by vigorous shaking for the effects to be observed, transmission of the biological information could be related to the molecular organization of water." The earliest use of the word "memory" that we found in this context was in a news column in *Nature* that was written in August of 1988 in the midst of the uproar that followed the publication of the article of Benveniste's group (Coles 1988).

After the publication of the article by Davenas et al., *Nature* set up a team to oversee replications. These replications failed. However, Benveniste passionately stood by his results. In the polemics that ensued, he often backed up the "water memory" claim with an article that, also in 1988, had appeared in *Physical Review Letters*. The article was by Del Giudice, Preparata, and Vitiello and it was titled "Water as a Free Electric Dipole Laser" (Del Giudice et al. 1988).

One of the basic outcomes of Quantum Mechanics is that action, the product of energy and time, comes in packages of $\hbar = 1.05 \times 10^{-34}$ J × s. The \hbar is also known as the Reduced Planck's Constant. Angular momentum has the same Joule×seconddimension as action and this means that rotation can only occur with an angular momentum, |L|, that is an integer multiple of \hbar (Merzbacher 1970). Del Giudice et al. consider water molecules as dipoles that are rotating around their own center of mass and going back and forth between the ground state $(|\mathbf{L}| = 0)$ and the first excited state ($|\mathbf{L}| = \hbar$). A photon is emitted when a water molecule falls back to the ground state. But that same photon can next make another water molecule jump to the first excited state. It can also, through so-called stimulated emission, induce another molecule in the excited state to drop to the ground state and emit. Quantum Field Theory is the appropriate framework to describe the interaction between photons and dipoles (Merzbacher 1970). This theory has a much higher level of complexity than the ordinary quantum mechanics that is basic to much of chemistry. After a short introduction the authors set up a quantum-field Lagrangian. Next a dynamical system for the evolution of the three relevant populations (ground state water, excited state water, and photons) is derived from the Lagrangian. The authors do not realize that the derived dynamical system is actually the well-known Euler System to describe rigid body rotation (Goldstein et al. 2002; Shnir 2005). Next, their analysis of the dynamical system is littered with errors (Bier and Pravica 2018).

However, already the setup of the paper is mistaken. The Lagrangian in the reference by Del Giudice et al. (1988) would be legitimate if the water molecules were standing still and if the exchanged photons were the only "contact." But as was mentioned in the previous section, in liquid water an average molecule collides every picosecond with another molecule. Energy is exchanged in these collisions and a realistic Lagrangian has to include terms to this effect.

Brownian collisions underlie friction and let a system relax towards a Boltzmann equilibrium. In the previous section we saw that treating water as spheres that interact through electrostatic forces and perform overdamped motion leads to quantitatively accurate descriptions. The reference by Elton (2017) shows how such descriptions apply until well into far-infrared frequencies.

Almost as an afterthought it is stated at the end of the reference by Del Giudice et al. (1988) that a permanent electrical polarization can form around an "impurity that carries a sizable electric dipole" from, for instance, a macromolecule. Again there is mention of "ordered structures in macroscopic domains." The possibility of such a polarization rolls out of long and complicated formulae and it is presented on the last page of the paper. The convoluted mathematics, however, disguise how the authors are essentially already assuming what they are proving. They postulate that the impurity or macromolecule causes a constant and homogeneous electric field that extends over hundreds of micrometers. That an electric field causes a polarization in a polarizable medium is almost a tautology. Debye's formulae are already successful in establishing a quantitatively accurate relationship between an electric field and its ensuing polarization (Moore 1974; Israelachvili 2011). The problem is, of course, that no ion or polymer in an aqueous solution will ever give rise to a constant, homogeneous electric field that extends over macroscopic distances. As was mentioned before, fields are screened away within nanometers. Moreover, macromolecules are subject to Brownian fluctuations and the electric fields that they exude will not be constant.

The reference by Del Giudice et al. (1988) ends with an appeal to further develop the ideas of water as a free electric dipole laser. But not much subsequent fundamental work has been undertaken in that direction. Most of the citations of this article simply invoke the alleged long-range order as a possible explanation for otherwise inexplicable phenomena (see e.g. Liu et al. 2011). The Journal of Alternative and Complementary Medicine is responsible for a very significant part of the citations. As was mentioned before, especially homeopathic medicine has gratefully picked up on the claimed long-range order. Google Scholar indicates that the article has been cited 480 times (accessed May 2020). Over the last 15 years the paper has received uncritical citations at a steady rate of about 20 per year. More than a "false information epidemic" it looks like we are dealing here with a genetic disorder that is transferred from one generation to the next without serious threat of proliferation.

In the immediate aftermath of the "cold fusion" uproar of 1989, "water as a free electric dipole laser" was advanced as an explanation for the alleged phenomenon (Bressani et al. 1989). Even after cold fusion was discredited (Miskelly et al. 1989; Price et al. 1989), work to this effect continued (Fleischmann et al. 1994).

A brief Google search furthermore reveals how there is a large number of more popularly oriented books and websites where the reference by Del Giudice et al. (1988) is invoked as providing the scientific legitimacy behind a variety of unconventional approaches to life, science, and health (e.g. McTaggart 2002). The reference by Del Giudice et al. (1988) has also featured in advertisements to purportedly explain the efficacy of products with names like "Reverse Aging" and "Divine Alignment" (Trinfinity8 2018).

It is especially the "permanent electric polarization around an impurity"-suggestion in the reference by Del Giudice et al. (1988) that has been cited in the last few decades in order to support claims that liquid water could keep and carry a "memory." Structures in liquid water, it is purported, would be able to retain a "memory" of an originally dissolved compound even if the dilutions are such that no molecule of the original compound is left in the water. But in actual fact, none of the conclusions of the reference by Del Giudice et al. (1988) justifies the idea of "water memory." The reference by Del Giudice et al. (1988) makes no statements about what happens when the macromolecules are diluted away. There is nothing in this reference that suggests an "imprint" that is left by a substance that is no longer there. Even if coherent domains were real, it is impossible to see how they would create a "memory" and constitute a validation for homeopathic practices.

Liquid water is generally not in the realm of interest of physicists working in Quantum Field Theory. It is therefore that those most qualified have not pursued the Quantum Coherent Domains in liquid water. Water, of course, is all-important in Condensed Matter Physics and in the Biosciences. But researchers in these field are generally unfamiliar with Quantum Fields. It is the enigmatic nature of the reference by Del Giudice et al. (1988) that has been most instrumental in building its popularity. Quantum Coherent Domains carry the respectability of basic physics research on matter at its most fundamental level. They thus constitute the ultimate argumentum ab auctoritate. Those that are most zealously invoking the reference by Del Giudice et al. (1988) and "water memory" in the peddling of pseudoscience and quackery are generally the least qualified to assess the underlying validity. Writing about homeopathy, water memory, and the reference by Del Giudice et al. (1988), Philip Ball formulated it as follows in a 2007 *Nature News* column: "This 'field' has acquired its own *deus ex machina*, an unsubstantiated theory of 'quantum coherent domains' in water proposed in 1988 that is vague enough to fit anything demanded of it" (Ball 2007).

There is currently an almost universal consensus that a liquid water environment is too hot and too wet for quantum entanglement to play any role of significance (Tegmark 2000). A collision between two water molecules localizes these molecules and implies that the involved quantum mechanical wave functions collapse onto position eigenfunctions (Unruh and Zurek 1989). As was already discussed, molecules in liquid water collide with terahertz frequency. A cubic micrometer of liquid water contains about 10¹⁰ molecules. As a coherent domain, such a cubic micrometer will therefore not last beyond an insignificant 10⁻²² s. Most importantly, until today science has needed no recourse to quantum mechanics or quantum field theory in order to explain the bulk behavior of water (Brini et al. 2017; Elton 2017).

3.3 Polywater Reiterated

It was already mentioned in the Introduction that the intracellular and extracellular solution are aqueous. The first living cells evolved in the oceans and it is therefore that, even in terrestrial multicellular organisms, the extracellular fluid has an ionic composition that is similar to that of seawater. Blood, sweat, and sperm taste salty.

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For sodium and chloride ions, the concentration in the extracellular liquid is generally larger than 10^2 mM. The extracellular potassium concentration is about 10 mM. Inside the cell it is reversed: concentrations of sodium and chloride are about 10 mM and the potassium concentration is about 10^2 mM. The inside of a living cell is, furthermore, negatively charged relative to the outside. The potential difference is about 100 mV (Alberts et al. 1994; Hille 1992; Läuger 1991).

In the years after World War 2, the intricate system of pumps, transporters, and channels that control the electrochemical potentials was slowly getting unraveled (Alberts et al. 1994, Hille 1992, Läuger 1991). Na⁺,K⁺-ATPase was discovered in 1957 (Skou 1957). This is the ion pump that maintains the electrochemical gradients for sodium and potassium. It derives its energy from the hydrolysis of ATP (adenosine triphosphate) (Alberts et al. 1994). ATP is the currency of energy in a living cell and it is where the energy that is released in the breakdown of glucose is initially stored.

The transmembrane electrochemical potential of sodium is high, and it is used in a cell as an energy source for transmembrane transport. The sodium-glucose cotransporter (Alberts et al. 1994) is a membrane-spanning protein that was first identified in 1960 (Crane et al. 1961). It binds a glucose molecule on the extracellular side, goes through a number conformational states, and in the end lets that glucose molecule detach on the intracellular side. The scheme works even when the intracellular glucose concentration is larger than the extracellular one. This is because the cotransporter, concurrently with the glucose transport, also transports a sodium ion from the outside to the inside of the cell. The electrochemical gradient of sodium thus provides the driving force for the energetically-uphill transport of glucose.

The genes that are associated with the different proteins that carry out the transmembrane transport have been identified. Also identified have been many mutations in these genes and the malfunctions that these mutations can lead to. Cystic fibrosis, for instance, is caused by a mutation that leads to a defective chloride channel. The 3D atomic structure of most pumps, transporters, and channels is currently known. Nowadays, the knowledge of such 3D structures is often the starting point for drug design. The challenge in such design is to construct a molecule that will bind to the intended membrane protein and elicit the desired effect on that protein's activity. Much of the search for drugs against obesity and diabetes, for instance, is focused on the aforementioned glucose-sodium cotransporter.

In 1947 Gilbert Ling (1919–2019) was prominently involved in the development of a type of microelectrode that facilitated the measurement of transmembrane potentials. The microelectrode greatly helped the advance of our understanding of the cell's electrochemistry. But Ling took issue with the developing consensus in the scientific community. He proposed that a mixture of crosslinked proteins and water ultimately formed a gel inside the living cell. Polarized layers of this gel would give the cell its electrical properties. That there is more potassium than sodium or chloride inside the cell would be a result of the affinities of involved proteins. Consumption of energy to maintain the transmembrane electrochemical potentials would not be necessary. Starting in the 1950s, Ling published books and articles to promote his model. However, as molecular biology developed rapidly, his ideas became ever more marginal. Electron microscopy made cell membranes and embedded proteins visible. With radioactive and fluorescent markers, with atomic force microscopy, with patch clamp, and with optical tweezers the movement and activity of biomolecules could be probed and followed (Barkai et al. 2012). Ling's model lacked evidence and became a sideshow.

Nevertheless, Ling's ideas did find a small following. Prominent is the work of Gerald Pollack. Pollack has focused on a more basic surface effect. When water with dissolved molecules or microspheres has an interface with a hydrophilic surface, a so-called exclusion zone (EZ) forms (Zheng and Pollack 2003). The solutes or microspheres move away from the interface. The EZ can measure a few hundred micrometers. Pollack has proposed that the water in the exclusion zone has polymerized and entered another phase: planar sheets of hexagonal lattices with $(H_3O_2)^-$ as the basic unit (see Fig. 2.3) (Pollack 2013). This would explain the observed negative charge near the interface. The membrane of a living cell consists of phospholipids. These molecules consist of strongly hydrophilic phosphate headgroups and apolar hydrocarbon tails. The cell membrane is a bilayer in which the apolar hydrophobic tails point toward one another and the hydrophilic phosphate headgroups stick out into the aqueous solutions. Living cells would thus consist in large part of water in the EZ phase. This would in Pollack's view also explain why living cells are negatively charged.

The major problem with the theory is that the configuration depicted in Fig. 2.3 has never been observed. Because it concentrates so much negative charge, the structure would be very unstable if it were to exist. Postulating a new phase to explain the observed EZ breaches the spirit of Occam's Razor. Surface effects can be very complex (Israelachvili 2011), but it is the appropriate direction to look into



Fig. 2.3 The planar sheet of hexagons that was proposed as a polymeric form of water by Pollack. Water would presumably go to this phase in the close vicinity of a hydrophilic surface. The basic unit is $(H_3O_2)^-$. However, because of the net negative charge the phase would be highly unstable and it is actually unlikely to ever materialize

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for an explanation of the exclusion zone. It is likely because of a "polywater déjà vu" that not many researchers have paid serious attention to Pollack's theory. However, there is no reason to *a priori* mistrust the published EZ measurements. These measurements moreover, have been replicated (see, e.g., Elton et al. 2020) and it is a matter of scientific integrity to get to understand the phenomenon. Furthermore, the EZ can be important in understanding biological phenomena and it can possibly find technological applications in microfluidics and filtration.

The EZ effect has also been observed when polar liquids other than water have been used (Chai and Pollack 2010). This is already an indication that the explanation may not lie in specific molecular structures and rearrangements thereof, but instead in more generally applying dynamics of solutes and solvents.

The observed negative charge of the EZ could be explained as follows. Because of the excluded solutes or microparticles, water has an effectively higher concentration in the EZ layer. Water molecules are perpetually dissociating into hydrogen and hydroxide and then again re-associating, i.e., $H_2O \leftrightarrow H^+ + OH^-$. The diffusivities of water, hydrogen, and hydroxide have been well-studied. Hydrogen has a higher diffusion coefficient than hydroxide (Lee and Rasaiah 2011). If the water concentration is higher in the EZ layer, then more H^+ and OH^- will be formed there. As the H^+ will more rapidly diffuse away into the bulk outside the EZ layer, a net negative charge will remain behind.

3.4 Spin-off

"Water" with adjectives like "EZ," "hexagonal," "structured," etc., is the snake oil of the twenty-first century. A small Google search suffices to recognize that. Special mention in this context should be made of Shui-Yin Lo.

Soon after publishing two papers in *Modern Physics Letters B* on a newly discovered form of ice (I_E crystals) in 1996 (Lo 1996; Lo et al. 1996), Shui-Yin Lo was involved in dubious marketing operations involving the I_E crystals. A blue laundry ball of the size of a tennis ball was supposed to make detergent unnecessary. The 75-dollar laundry ball would create I_E crystals outside the ball and the "nanotricity" of these crystals would remove dirt from cloth. State attorneys general and the Federal Trade Commission were very quick to recognize this for the fraud that it was and put a stop to it. The same company also sold a device to be put into a car's air filter. There the I_E -technology would improve gas mileage and engine performance. Also this product was taken of the market through interference of the criminal justice system.

Lo, however, persevered in spite of these setbacks. In 2009 he published another article in a scientific journal on stable water clusters at room temperature (Lo et al. 2009). Doubts about this article were later expressed in a comment in the same journal (Kožíšek et al. 2013). Next Lo and his co-workers discovered that a double helix shape was common among these clusters. They then went on to focus on the "immunological and enzymatic effects" and moved into the health care business. A

paper was published in *Forum on Immunopathological Diseases and Therapeutics* (Lo et al. 2012) and a website "www.doublehelixwater.com" was set up. Many forms of questionable science coalesce in the 2012 article of Lo et al. as both the EZ water of Pollack and the Quantum Coherent Domains of Del Giudice are proposed as possible explanations of "Double Helix Water." On the website the "Double Helix Water" is offered for sale and many health benefits are described. "Promising and startling" preliminary results are reported in curing autism, but it appears to also work as an antibiotic and as a remedy for ailments like shoulder pain and arthritis. At the bottom of every page on the website it writes: "These statements have not been evaluated by the Food and Drug Administration. This product is not intended to diagnose, treat, cure, or prevent any disease." The website has been active for almost a decade and it is sad to have to conclude that the disclaimer makes it possible to indefinitely peddle the same rip-off as a health care product after it was almost immediately terminated as a laundry-ball or fuel-additive.

3.5 "Magnetic Water"

Water is not a magnetic material. Nevertheless, there are many claims surrounding "magnetic water" – water that has merely been passed through a strong magnetic field. A variety of devices for household and industrial use is for sale. According to the advertisements, routing the water along a series of magnets leads to benefits such as: reduced corrosion and mineral deposition, increased or decreased pH, increased bioavailability of dissolved compounds, improved kidney and digestive health, increased crop yields, and enhanced setting of concrete.

The inspiration for these devices appears to derive from a nebulous industrial technique for reducing mineral buildup in pipes and tanks. There is some evidence of magnetism being investigated to this end even as early as the 1880s for use in steam boilers (Ambashta and Sillanpää 2010). From an engineering perspective, the process is straightforward. Passing supersaturated solution through a strong magnetic field supposedly facilitates precipitation or growth of suspended particles. Particles can then settle at the bottom of reservoirs and be flushed out, rather than adhering to interior surfaces and requiring more costly chemical removal.

Several reviews have been published, yet there is no agreed upon mechanism for how and why a magnetic field would possibly enhance precipitation. The rate of chemical precipitation is sensitive to a variety of factors (temperature, pH, contaminants, etc.). Most studies have not been rigorous in this regard and this is probably why results have been inconsistent (Chibowski and Szcześ 2018). In industrial practice, bulk precipitation is commonly induced by simply cooling a saturated solution (Keister 2008). Even if magnetic fields were to trigger bulk precipitation, any such application to household tap-water pipes is undermined by the fact that any precipitant simply remains suspended all the way to the drinking glass.

In the marketing of the devices, claims of altered structures and memory are once again common in order to produce an appealing mystique. Magnets supposedly possess the ability to induce a distinct "North" or "South" character into molecules or reduce the size of water "clusters" surrounding ions (see, for example, *Magnetized Water* 2020). We have already discussed Brownian motion, the short duration of hydrogen bonds, and the limited reach of hydration shells. In this context it is obvious that even if there were magnetically induced alterations in order, they would disappear again once the magnetic field is gone. Water itself is actually weakly diamagnetic, a property owed precisely to the molecule's lack of an intrinsic magnetic moment. But the effect is so weak as to make water practically immune to magnetic effects. Long-lasting, extremely large field gradients (to the order of 100 T²/m) are needed to produce any significant effects (Ueno and Iwasaka 1994), requiring expensive superconductor-based magnets. Here we are reminded of a more direct application of strong magnetic fields to ingested water: Magnetic Resonance Imaging (MRI). Yet despite the hundreds of millions of exams performed yearly (OECD 2020), we are still left wanting for tales of their miraculous effects on human health.

The "polywater outbreak" lasted less than a decade (cf. Figure 2.2). But for coherent-domain-water, hexagonal water, and magnetic water the dynamics have been a lot slower. Figure 2.4 shows the number of accumulated publications on the subject of "magnetic water treatment" up to the year 2019. If a Verhulstian course is again going to be followed, then there is still a long way to go. So far, even the inflection point is not in sight.



Fig. 2.4 The accumulated number of scientific articles on the subject of "Magnetic Water Treatment" as time evolves. Data was retrieved from Elsevier's Scopus (http://www.scopus.com/). The red curve represents the best fit of an exponential $n(t) = \exp[\alpha(t - t_0)]$

4 Conclusions

The Career of Nikodem Dyzma was first published in 1932. It was the debut novel of the Polish author Tadeusz Dołęga-Mostowicz (2014). The entertaining story describes how a former postal clerk from a small rural town catches a lucky break as he is struggling to make a living in Warsaw. He finds an envelope containing an invitation to an exclusive upper-class party. He goes there in the hope to finally eat a decent meal. In a confrontation with other guests, his cluelessness and coarseness are taken as signs of profound insight and aphoristic wisdom. Next the protagonist does not have to take a lot of initiative to become a rising star in Warsaw high-society. He is seen as a wish-come-true in spite of indications to the contrary. He is made the head of a national bank and, ultimately, he is offered the prime-ministership.

There is a community of researchers for whom water has become an inanimate Nikodem Dyzma. Guided by a desire for Transcendence and Redemption and in search of a Theory-of-Everything, they have turned a simple, common, stable and small molecule into something that it is not.

Sometimes a solvent is just a solvent.

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