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LIMITS ON QUANTUM COHERENT DOMAINS IN LIQUID WATER

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A Quantum Field Theoretic analysis has led to the claim that liquid water supports coherent domains of almost millimeter size [E. Del Giudice, G. Preparata, G. Vitiello, *Phys. Rev. Lett.* **61**, 1085 (1988)]. Such domains would be described by one quantum mechanical state function. Further analysis results in new characteristic frequencies and in the claim that a long-range ($> 100\ \mu$m) structure emerges around a molecular size dipole. The quantum-physics-based claim that liquid water supports structures of over 100 micrometer in size at room temperature is irreconcilable with a well-known consensus of condensed matter physics: Brownian collisions make wave functions collapse and hot, wet environments do not allow for quantum entanglements to survive. Simulations, theory, and experiment agree on how a hydration shell of a few layers of directed water dipoles forms around an ion or a polar molecule. Such a shell extends to less than a nanometer. We reexamine the assumptions and theory behind the coherent domain dynamics in water. It appears likely that large, long-lasting coherent domains do not emerge in liquid water.

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1. Introduction

In 1988, a Letter was published with the remarkable title “Water as a Free Electric Dipole Laser” [1]. The guiding idea of the Letter is that a rotating water molecule implies a rotating dipole. Such a rotating dipole emits radiation. With that radiation, stimulated-emission dynamics can occur. The formalism developed for water was similar to one developed earlier for a free electron laser [2]. Thus, the Free Electron Dipole Laser (FEDL).

Working out the idea involves a body of nontrivial Quantum Field Theory. The analysis resulted in a remarkable assertion: "In the study of the dynamics of water, the neglect of the coherent interaction of water molecules with the quantized radiation field is completely unjustified, for we have shown that its coupling to collective quantum states of size $2\pi/\omega_0$ (a few hundreds of microns) is indeed very large". The found long-range interaction was the basis for the claim that "a macroscopic permanent polarization can easily arise in water in the presence of a small electric disturbance such as the local field produced by a macromolecule". New characteristic frequencies in the absorption spectrum of water were also derived.

The statements are all the more remarkable as they contradict what standard physical-chemistry textbooks describe [3, 4]. The consensus picture is that around a dissolved ion or dipole, the water molecules orient their dipoles and form a nanometer-scale hydration shell. Around an ion, there is a stiff 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, the hydration bonds do not have sufficient energy to withstand Brownian motion with its characteristic energy of $k_{\mathrm{B}}T$. Hydration shells around proteins and other biomolecules are the subject of much research. Experimental observation appears to be in a good agreement with the results of theory and molecular dynamics simulation [5, 6]. In Ref. [7], 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 long-range interactions that are claimed in Ref. [1] cover a distance that is more than 10^5 times larger.

Google Scholar lists 434 citations for Ref. [1] (accessed May 7, 2018). The claimed long-range order is regularly used to give plausibility to puzzling phenomena in physics, chemistry, and biology (see *e.g.* Refs. [8–11]). In addition, it has been put forward as the physics that underlies cold fusion [12, 13]. It has been presented as the basic science behind "water memory" and homeopathy [14, 15]. It has also been put forward as the scientific validation behind nonconventional approaches to life and health [16].

At the end of Ref. [1], it is written: "Even though, it must be admitted, our analysis is in many ways at a preliminary, rather rudimentary stage ..." and "Of course much more work is needed in this direction". However, in spite of the spectacular claim about long-range structures in liquid water, little further, independent research has been done into the quantum-field-theoretic analysis that underlies the claim. There is an obvious reason for this. Quantum Field Theory is mostly about interactions between subatomic particles; liquid water is not generally in the realm of interest of quantum field theorists. And while the behavior of water as a solvent *is* central to much of Biochemistry and Biophysics, the standard toolbox in these fields does not contain Quantum Field Theory. In 2007, Philip Ball wrote the following about homeopathy, water memory, and Ref. [1] in his *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” [17]. The abstruseness of the Letter has indeed been an impediment to a good discourse on the methods and results of Ref. [1]. Below, we will summarize and critically reexamine the main line of argument of Ref. [1].

There have been refinements, extensions, and variations of the original quantum-coherent-domain theory of 1988. A longer article of 2006 centers largely around the same equations, but presents a more polished interpretation and discussion [18]. In 2007, the same formalism was applied to the transition of water between the ground state and an excited state at 12.06 eV that is very close to the ionization threshold [19]. In 2009, a similar theory with slightly differently equations was developed [20]. However, as previously stated, Ref. [1] is still the central and most cited source on the subject.

2. The dipole laser

Together with its dipole moment, the water molecule also has moments of inertia. The quantum mechanical treatment of the rigid rotor [3] leads to the discrete energy levels $E_l = l(l+1)\hbar^2/(2I)$, where $l = 0, 1, 2, 3, \ldots$ is the quantum number, I is the moment of inertia, and $\hbar$ is Planck’s constant. The analysis in Ref. [1] focusses on the $l = 0$ and $l = 1$ levels. The energy difference between these levels equals $\Delta E = \hbar^2/I$. With $I \approx 2 \times 10^{-47}$ kg m^2 and $\Delta E = \hbar\omega_0$, it is found that transitions between the $l = 0$ and $l = 1$ levels are associated with photons of $\omega_0 \approx 5 \times 10^{12}$ s^{-1}, *i.e.* the far infrared regime. The corresponding wavelength is about 400 μm.

With room temperature for T, we have $\Delta E \approx 0.1\, k_{\mathrm{B}}T$, where k_{B} is Boltzmann’s constant. As ΔE is apparently an order of magnitude smaller than the basic “$k_{\mathrm{B}}T$ quantum” of Brownian energy, there will be a 50–50 distribution over the $l = 0$ and $l = 1$ levels. Furthermore, to have significance, any dynamics that will be derived should be much faster than the thermal equilibration to the aforementioned 50–50 distribution.

Two problems with the FEDL idea arise at this point. First of all, the moment of inertia of a water molecule depends on the axis of rotation (see Fig. 1). The largest of the three values is about three times the smallest value. The relative width of the range is larger than that of the visible window in the spectrum of light. Lasering generally requires very narrow levels. Secondly, the rotational levels can be seen in the spectra of water vapor [21]. For liquid water, however, they are not observed [22]. This is because hydrogen bonds between neighboring water molecules restrict rotation.

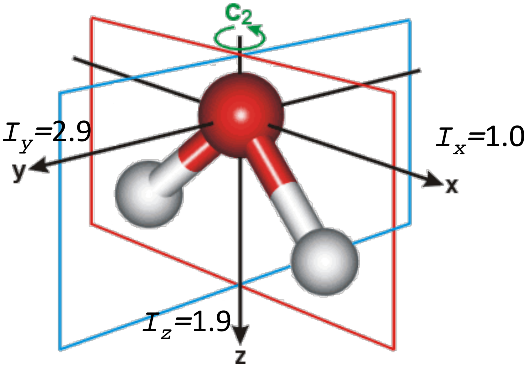

Fig. 1. The moments of inertia of a water molecule around three different axes. The numbers are $\times 10^{47}$ and in units of kg m^2.

The basic idea of Ref. [1] is that the 400 μm wavelength of the radiation would for a very short time (Ref. [1] mentions 10^{-14} s, in that time the wave moves only a few micrometers) act like a laser cavity. In that cavity, the system then forms a "coherent domain". That domain is described by one quantum physical state function. Coherent domains are supposed to come and go very rapidly, but in such a way that, at all times, there is always a significant fraction of the water in the coherent-domain phase.

There is a precedent for this paradigm. In his "two fluid model" Landau explains the superfluid behavior of ^{4}He with a similar rapid coming and going of coherent domains [23]. Superfluidity thus ultimately appears as a macroscopic quantum phenomenon.

3. The dynamical system

In Ref. [1], an inventory is made of the different contributions to the total energy of the system. Next, a Lagrangian is set up and equations that describe the dynamics are derived. Below, we will just present the resulting dynamics and make it intuitive.

The molecules have a ground state (γ_0) and an excited state (γ_1). There is, furthermore, a population of photons (b) that is associated with the traffic between the two states (see Fig. 2). The square norms of the state functions γ_0, γ_1, and b give the population in each state. Two conservation laws are easily inferred. The conservation of the number of molecules gives

$$|\gamma_0|^2 + |\gamma_1|^2 = (\lambda k)^2 \,. \tag{1}$$

For every $\gamma_1 \to \gamma_0$ transition, a photon appears and for every $\gamma_0 \to \gamma_1$, a photon disappears. This leads to

$$|\gamma_1|^2 + |b|^2 = \lambda^2 \,. \tag{2}$$

Later in this section, it will become clear why λ and k are used the way they are in the above conservation laws.

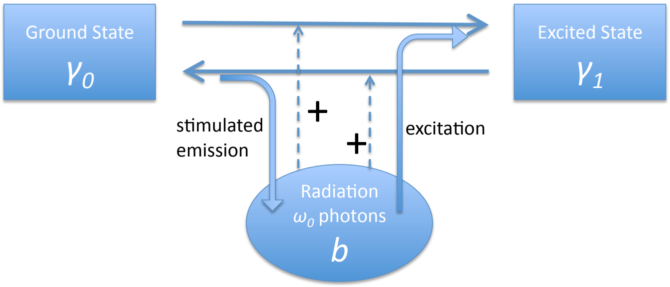

Fig. 2. The dynamics in a coherent domain as proposed in Ref. [1]. Water molecules can be in two rotational states, $l = 0$ and $l = 1$. The wave functions corresponding to these states are γ_0 and γ_1. The photons that are associated with the transitions between these states constitute state b.

In a classical context, Eq. (2) could be seen as a conservation of energy. However, in Quantum Field Theory, the picture is more complex because of an added energy term. The system also loses energy through the coupling between the photons and the molecular dipoles. If there are N molecules in the coherence domain, then we have $E_{\gamma_1} \propto N$ and $E_b \propto N$, where E_{γ_1} is the energy in the excited state molecules and E_b is the energy in the photons. It turns out that the energy in the aforementioned coupling amounts to $E_{\gamma_0,\gamma_1,b} \propto -N\sqrt{N}$. The coupling term essentially says that the system loses energy whenever a photon interacts with a dipole, whether it is through excitation or through stimulated emission. Because of the different proportionalities, "$\propto N$" *vs.* "$\propto -N\sqrt{N}$", the coupling becomes relatively more significant for a larger system. With a large enough N, and the $(N\sqrt{N})$-term thus being sufficiently dominant, the system will keep oscillating. In a "normal" chemical reaction with no energy input from the outside, one would never see a sustained oscillation. The oscillations that we analyze below are like Landau's superfluidity in that they are a macroscopic quantum effect. However, paradoxically, our quantum effect actually only appears if the system is large enough.

The dynamics in the phase space that is spanned by γ_0, γ_1, and b is restricted to the curves that constitute the intersections of the cylinders described by Eqs. (1) and (2) (see Fig. 3). The following autonomous system describes the $(\gamma_0(t), \gamma_1(t), b(t))$-dynamics:

$$\begin{aligned}\dot{\gamma_0} &= b^*\gamma_1\,,\\ \dot{\gamma_1} &= -b\gamma_0\,,\\ \dot{b} &= \gamma_0^*\gamma_1\,,\end{aligned} \tag{3}$$

where $\dot{} \equiv \frac{\mathrm{d}}{\mathrm{d}t}$. These equations are derived in Ref. [1], but it can be easily intuited how the schematic in Fig. 2 leads to these equations. Equations (3) represent the bare bone dynamics of the system. Constants have been scaled away. Time is dimensionless — it is the real time multiplied by ω_0 (the frequency of the involved radiation) and by a dimensionless combination of parameters G, that equals about 17. The asterisks denote complex conjugation. It is easily verified that Eqs. (3) imply the conservation laws (1) and (2).

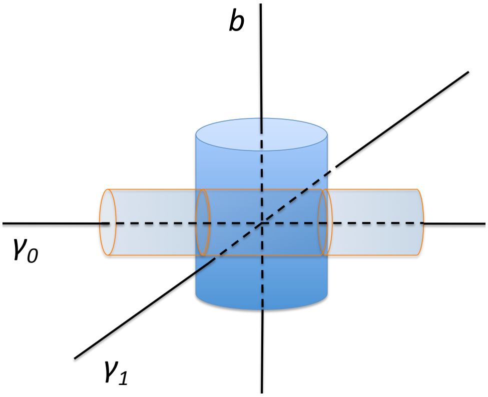

Fig. 3. The dynamics of the system described in Fig. 2 leads to two conservation laws given by Eqs. (1) and (2). These conservation laws describe cylinders in the 3D space that is spanned by the ground state γ_0, the excited state γ_1, and the radiation b. The allowed trajectories are constituted by the intersections of the cylinders.

Through substitution, the authors of Ref. [1] identify a periodic solution of Eqs. (3). They claim this to be a limit cycle solution. However, this cannot be the case. The existence of conservation laws makes clear that Eqs. (3) cannot be a system where dissipation makes a phase space contract to an eventual single limit cycle.

For γ_0, γ_1, and b being real, Eqs. (3) are actually the Euler equations for rigid body rotation [24]. The Euler equations describe standard anharmonic oscillations and they are solved in terms of elliptic functions. In the 1980s, a complex generalization exactly like Eqs. (3) was derived in the context of magnetic monopole dynamics. This generalization is known as the Nahm equations [25].

The following solution is readily derived:

$$\begin{aligned}
\gamma_0(t) &= \lambda k e^{i\phi_{\gamma 0}} \mathrm{cn}\left[\lambda(t-t_0), k\right] , \\
\gamma_1(t) &= \lambda k e^{i\phi_{\gamma 1}} \mathrm{sn}\left[\lambda(t-t_0), k\right] , \\
b(t) &= \lambda e^{i\phi_b} \mathrm{dn}\left[\lambda(t-t_0), k\right] .
\end{aligned} \tag{4}$$

Here, the dn, sn, and cn denote the standard elliptic functions [26, 27]. As Eqs. (3) constitute an autonomous system (no explicit time dependence on the right-hand sides), the "starting time" t_0 is a free parameter. Next, it is easily verified that there is a scaling invariance in Eqs. (3): if any $(f_1(t), f_2(t), f_3(t))$ solves the system, then so does $(\lambda f_1(\lambda t), \lambda f_2(\lambda t), \lambda f_3(\lambda t))$. We thus have λ as a next free parameter. The parameter k is a real number between 0 and 1 that characterizes the elliptic function. For $k = 0$, the elliptic functions are ordinary sines and cosines again. For $k = 1$, they are hyperbolic secants (sech) and a hyperbolic tangent (tanh). If γ_0, γ_1, and b are real, then the free parameters t_0, λ, and k are all that is necessary to match the initial conditions.

We took unusual symbols for the conserved quantities on the right-hand sides in Eqs. (1) and (2). However, at this point, our choice conveys the straightforward relation between the conserved quantities and the parameters λ and k of solution (4).

For the parameter k, we have $0 < k < 1$. This means that solution (4) has to be rearranged in case the initial conditions are such that $|\gamma_0|^2 > |b|^2$. In that case, we take for the conservation laws

$$|\gamma_0|^2 + |\gamma_1|^2 = \lambda^2 \qquad \text{and} \qquad |\gamma_1|^2 + |b|^2 = (\lambda k)^2\,, \tag{5}$$

and formulate the solution as

$$\begin{aligned} \gamma_0(t) &= \lambda e^{i\phi_{\gamma 0}} \mathrm{dn}\left[\lambda(t - t_0), k\right]\,, \\ \gamma_1(t) &= \lambda k e^{i\phi_{\gamma 1}} \mathrm{sn}\left[\lambda(t - t_0), k\right]\,, \\ b(t) &= \lambda k e^{i\phi_b} \mathrm{cn}\left[\lambda(t - t_0), k\right]\,. \end{aligned} \tag{6}$$

The period T of the elliptic functions $\mathrm{sn}(u, k)$, $\mathrm{cn}(u, k)$, and $\mathrm{dn}(u, k)$ is given by the complete elliptic integral of the first kind [26]: $T = 4K(k) = 4\int_0^{\pi/2} (\sqrt{1 - k^2 \sin^2\theta}\,)^{-1}\, d\theta$. After some algebra, we can straightforwardly express our period T in terms of initial conditions $\gamma_0(0), \gamma_1(0), b(0)$. With

$$\begin{aligned} k^2 &= \min\left\{ \frac{|\gamma_0(0)|^2 + |\gamma_1(0)|^2}{|\gamma_1(0)|^2 + |b(0)|^2}, \frac{|\gamma_1(0)|^2 + |b(0)|^2}{|\gamma_0(0)|^2 + |\gamma_1(0)|^2} \right\} \qquad \text{and} \\ \lambda^2 &= \max\left\{ |\gamma_0(0)|^2 + |\gamma_1(0)|^2, |\gamma_1(0)|^2 + |b(0)|^2 \right\}\,, \end{aligned} \tag{7}$$

we have for the period $T(k, \lambda)$,

$$T(k, \lambda) = 4K(k)/\lambda\,. \tag{8}$$

Linear dynamical systems, like the harmonic oscillator $\ddot{x} = -\omega^2 x$, have a characteristic frequency. Limit cycles, as commonly occurring in nonlinear dynamical systems, also have a characteristic frequency. Equations (3), however, have *no* characteristic frequency. Like in the case of the pendulum ($\ddot{x} = -\sin x$) or other anharmonic oscillators (like $\ddot{x} = -x^3$), the oscillations described by Eqs. (3) have frequencies that are related to the amplitude. The solutions of Eqs. (3) are closed curves (see Figs. 3 and 4). Together, these curves fill the entire phase space. Different curves correspond to different frequencies.

If γ_0, γ_1, and b are complex valued, then the solution should contain 6 free parameters. Equations (4), therefore, contain the imaginary powers of e. These terms represent constant phase factors. It is easily deduced through substitution that, in order to satisfy Eqs. (3), the phases have to satisfy the relation: $\phi_{\gamma 0} - \phi_{\gamma 1} + \phi_b = \pi$. Thus, Eqs. (4) constitute a 5-free-parameter solution. In Section 5, it will be illustrated that this solution does exhibit the required gauge invariance, *i.e.*, a mere phase shift does not affect the relevant physics.

Though not trivial, it is ultimately feasible to write down a general 6-free-parameter solution of Eqs. (3) [28]. For each of the variables $\gamma_0(t)$, $\gamma_1(t)$, and $b(t)$, a 2^{nd} order nonlinear ordinary differential equation can be formulated. For γ_1, the equation is $\ddot{\gamma}_1 = -(A - 2|\gamma_1|^2)\gamma_1$, where $A = \lambda^2 + (\lambda k)^2$ is a constant. Next, we separate out γ_1 into its real and imaginary part, *i.e.*, $\gamma_1(t) = x(t) + iy(t)$. The resulting differential equations for $\ddot{x}$ and $\ddot{y}$ are $\ddot{x}(t) = -\left(A - 2r^2(t)\right)x(t)$ and $\ddot{y}(t) = -\left(A - 2r^2(t)\right)y(t)$, where $r^2(t) = x^2(t) + y^2(t)$. It is easily ascertained that these equations describe a motion in the xy-plane that is ruled by a central force that derives from a potential $V(r) = \left(Ar^2 - r^4\right)/2$. With such a motion, the total energy and the angular momentum are conserved, thus giving two free constants. It is interesting to note that the solutions that we identified in Eqs. (4) and (6) have a constant phase. That means that in the complex xy-plane, they stay on one and the same line through the origin and thus have a zero angular momentum. Two-dimensional motion in a central force field is a much studied problem and our $V(r) = \left(Ar^2 - r^4\right)/2$ leads to general solutions for $x(t)$ and $y(t)$ in terms of elliptic functions [29], though the forms are more complicated than Eqs. (4) and (6).

In Ref. [1], harmonic oscillations are substituted into the dynamical system. Indeed, upon substitution of $\gamma_0 = \Gamma_0 \exp\left[i(\Omega_0 t + \theta_0)\right]$, $\gamma_1 = \Gamma_1$ $\exp\left[i(\Omega_1 t + \theta_1)\right]$, and $b = B_0 \exp\left[i(\Omega_b t + \theta_b)\right]$ into Eqs. (3), five independent algebraic equations relating the Γs, the B_0, the Ωs, and the θs are derived. However, the obtained 4-parameter family of solutions is ultimately not dynamic in nature. In this family of solutions, the phase factors change, but the pertinent quantities $|\gamma_0|^2$, $|\gamma_1|^2$, and $|b|^2$ do not change. Any solution in this family is characterized by a point in Fig. 3 that remains stationary. In the context of the motion in the central force field that was discussed in the previous paragraph, this family of solutions corresponds to circular motion and a nonzero angular momentum. There are no small oscillations around the solutions in this family; if a solution is not represented by a stationary point in Fig. 3, then the only way it can move is around on the curve that is constituted by the intersection of the two cylinders.

4. The effect of Brownian collisions

For liquid water, the size of the molecule roughly equals the mean free path — it is about 0.25 nm. At room temperature, the speed of a water molecule is about 600 m/s. It is readily evaluated that this implies about a trillion (10^{12}) collisions per water molecule per second. A coherent domain of 400 μm × 400 μm × 400 μm would contain about 10^{18} molecules. In Ref. [1], the lifetime of a coherence domain is identified with approximately one period of an oscillation described by Eqs. (3). If we take this to be the 10^{-14} s that is mentioned in Ref. [1], then we find that there are about 10^{16} collisions in the coherent domain during its lifetime. There is also a smaller number of collisions between "domain molecules" and molecules from the bath outside the domain.

Such Brownian collisions are not without consequence. Energy is exchanged in these collisions. For our system, the collisions cause added traffic between the ground state, the excited state, and the radiation (*cf.* Fig. 2). They also cause traffic between others energies (translational, vibrational, *etc.*) and the rotational energies that are the focus of our analysis. Brownian collisions are the underlying mechanism behind thermal equilibration. The Brownian collisions add a noise-term and a dissipation-term to the coherent domain dynamics of Eqs. (3). The dissipation coefficient is related to the amplitude of the noise through the Fluctuation–Dissipation Theorem [30].

Brownian collisions and the ensuing fluctuation-dissipation are the molecular mechanism that underlies the Second Law of Thermodynamics. In a system without energy input from the outside (the system in Fig. 2 indeed has no such input), Brownian collisions will bring the system to a thermodynamic equilibrium, *i.e.* a stationary state in which the energy is equally distributed over the available degrees of freedom. It is in violation of the Second Law if a closed system with 10^{18} densely packed water molecules in the liquid state exhibits a sustained oscillation between the $\ell = 0$ and $\ell = 1$ state.

The anharmonic oscillator with just an added noise term has been studied recently [31, 32] and it is at the limit of mathematical analyzability. However, even without detailed mathematical analysis, it can be readily understood and intuited that even a small amount of noise and dissipation will disrupt the nested-closed-curves topology that is depicted in Fig. 4. Brownian motion will cause the curves in Fig. 4 to *not* close upon themselves.

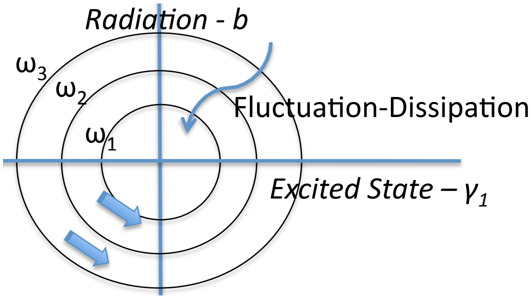

Fig. 4. The solutions of Eqs. (3) that are depicted in Fig. 3 are circles when projected on the (γ_0, γ_1) or (γ_1, b) plane. Unlike for the harmonic oscillator, these circular trajectories have a frequency that changes with the radius. Brownian collisions between molecules add noise and dissipation to the system. The addition of noise and dissipation will result in the trajectories not closing upon themselves anymore.

Brownian noise would not destroy a limit-cycle topology. Limit cycles are robust and structurally stable. With added noise, a limit-cycle system would move in a narrow band around the limit cycle. It would still exhibit the characteristic frequency. Limit cycles, however, only occur in open nonequilibrium systems, *i.e.* systems that transport or convert incoming energy before they put it out again.

In the previous section, it was shown how the different closed curves correspond to different frequencies. Without Brownian noise, the frequency of the oscillation depends on the initial conditions. The effect of Brownian noise is that that frequency is not maintained (see Fig. 4).

5. The permanent polarization

The most spectacular claim in Ref. [1] is that the coherent domain dynamics describes how a "sizable electric dipole" from a "macromolecule" can lead to a polarization across the entire almost millimeter-magnitude coherent domain. This claim has commonly been put forward as the theoretical underpinning when anomalies in liquid water, with or without small concentrations of solute, are observed and examined (see, for instance, Refs. [33, 34]). Below, we show how the pertinent derivation is done and assess the veracity of the claim.

For the state functions $\gamma_l(t)$, with $l = 0$ for the ground state and $l = 1$ for the excited state, we take

$$\gamma_0(t) = \lambda e^{i\phi_0}\mathrm{cn}\left[\lambda(t-t_0), k\right] , \qquad \gamma_1(t) = \lambda e^{i\phi_1}\mathrm{sn}\left[\lambda(t-t_0), k\right] . \tag{9}$$

The orientation of the water dipole is given by the spherical harmonics Y_l^m. These spherical harmonics are generally known from their use in describing the wave function of the electron in the hydrogen atom for the different energy levels l [3]. For $l = 0$, there is one harmonic ($m = 0$) and for $l = 1$, there are three ($m = -1$, $m = 0$, and $m = 1$)

$$\begin{aligned} Y_0^0(\theta,\varphi) &= \frac{1}{2}\sqrt{\frac{1}{\pi}}\,, \\ Y_1^{-1}(\theta,\varphi) &= \sqrt{\frac{3}{8\pi}}\sin\theta\; e^{-i\varphi}\,, \\ Y_1^0(\theta,\varphi) &= \sqrt{\frac{3}{4\pi}}\cos\theta\,, \\ Y_1^1(\theta,\varphi) &= -\sqrt{\frac{3}{8\pi}}\sin\theta\; e^{i\varphi}\,. \end{aligned} \tag{10}$$

Here, θ is the angle of the dipole with the z-axis and φ is the angle with the x-axis of the projection of the dipole on the xy-plane. As we saw before, the energy difference between the ground state and the excited state is small (about $0.1\,k_\mathrm{B}T$). Thus, the four available states are taken to be equally populated. For the not-normalized state function $\chi(t,\theta,\varphi)$ of the entire system, one then has

$$\chi(t,\theta,\varphi) = \gamma_0(t)Y_0^0(\theta,\varphi) + \gamma_1(t)\left\{Y_1^{-1}(\theta,\varphi) + Y_1^0(\theta,\varphi) + Y_1^1(\theta,\varphi)\right\}e^{-i\omega t}\,. \tag{11}$$

Here, ω is the angular velocity associated with the $l = 1$ level as explained in the first paragraph of Section 2 (though it should be realized that the time "t" in Eq. (11) is the new dimensionless unit). To evaluate the polarization P_z in the z-direction, we take the projection of the dipole on the z-axis and average over the entire unit sphere, *i.e.* $P_z \propto \langle\chi|(\boldsymbol{u}\cdot\boldsymbol{e_z})|\chi\rangle$. Here, $\boldsymbol{u}$ denotes a vector in the direction of the dipole. The problem reduces to an integration over the unit sphere, $P_z \propto \int \chi(\cos\theta)\chi^*\,\mathrm{d}\Omega_{\boldsymbol{u}}$, that can be evaluated to yield

$$P_z \propto \cos\left[\phi_0 - \phi_1 + \omega t\right]\mathrm{sn}\left[\lambda(t-t_0), k\right]\mathrm{cn}\left[\lambda(t-t_0), k\right] . \tag{12}$$

The original physical setup is isotropic, *i.e.*, the directions are not physically distinguishable. So there should be no polarization. Equation (12) indeed shows that P_z has a zero average. The cosine term has a zero average and so does the product of the sn and the cn. The latter can be easily seen after realizing that $\int \mathrm{sn}\, u\ \mathrm{cn}\, u\, \mathrm{d}\, u \propto \mathrm{dn}\, u$ and that $\mathrm{dn}\, u$ oscillates symmetrically around its average.

It can also be ascertained from Eq. (12) how the ϕ_0 and ϕ_1 represent gauge freedoms. These factors can produce a phase shift of the cosine, but they will leave the physically relevant zero-average unaffected.

Next, we add the "sizable electric dipole" of Ref. [1]. Reference [1] models the presence of the "sizable electric dipole" with the presence of a constant, homogeneous electric field $\boldsymbol{E}$ that extends over the entire coherent domain. The reality of such modeling is questionable. First of all, it is hard to imagine how even a polymer of micrometer order length could give rise to an electric field that is constant and homogeneous over several hundreds of micrometers. Secondly, the movable water dipoles screen the fields of dissolved dipoles and mitigate them. In biological solutions, there is the added effect of dissolved small ions like sodium, potassium, and chloride. The so-called Debye–Hückel screening (chapter 10 in Ref. [3] and chapter 12 in Ref. [4]) that results from the presence of these ions is very effective and essentially eliminates any field within nanometers. Thirdly, a macromolecule is also subject to Brownian fluctuations. The individual charged groups twist and turn, and it is hard to imagine them giving rise to a constant homogeneous electric field.

A constant homogeneous field that extends over the entire coherent domain breaks the isotropy of the system. With Curie's Principle (a symmetry or asymmetry of a cause is always preserved in its effects [35]) in mind, it is no surprise that a constant homogeneous electric field in a medium of dipoles will give rise to a net polarization. It would actually have been a surprising violation if there had been no ensuing polarization. By postulating a macroscopic constant homogeneous electric field, the authors of Ref. [1] are already assuming what they are trying to prove.

It does not require Quantum Field Theory, or even quantum physics or any form of quantum entanglement, to have dipoles align themselves with a constant homogeneous electric field. Already a century ago, Peter Debye considered dipoles making up a classical gas or liquid. His dipoles are subject only to Brownian motion. He derived analytical formulae for the polarization in such a medium when a constant homogeneous electric field is imposed. These formulae have been successful in accounting for experimental results and are now a standard feature in many authoritative textbooks (chapter 15 of [3], chapter 5 of [4], and Appendix 13 of [36]). We will, nevertheless, follow the idea of Ref. [1] and derive a formula for the polarization but we will enter the solutions that we derived in Section 3.

The eventual polarization is calculated with a perturbation approach. The presence of an electric field $\boldsymbol{E}$ adds a term $H = -\boldsymbol{d} \cdot \boldsymbol{E}$ to the Hamiltonian, where $\boldsymbol{d}$ is the dipole of a water molecule. Without loss of generality, the field $\boldsymbol{E}$ is assumed to be in the z-direction. The perturbation leads to a "mixing" of the $l = 0$ state and the $l = 1$ state,

$$\begin{pmatrix} Y_0^0 \\ Y_1^0 \end{pmatrix}_{\text{new}} = \begin{pmatrix} \cos\tau & \sin\tau \\ -\sin\tau & \cos\tau \end{pmatrix} \begin{pmatrix} Y_0^0 \\ Y_1^0 \end{pmatrix} ,$$

where the parameter τ depends on the dipole strength $\boldsymbol{d}$, the electric field $\boldsymbol{E}$, and the frequency ω. A good explanation of this "state mixing" is found in Ref. [37]. It is a perturbation treatment and one is looking at the effect of the perturbing Hamiltonian on the unperturbed state. Doing again the integral $P_z \propto \int \chi(\cos\theta)\chi^* \, \mathrm{d}\Omega_{\boldsymbol{u}}$, but now with the "new" Y_0^0 and Y_1^0 substituted in Eq. (11), it is found that

$$\begin{aligned} P_z \ \propto\ & \cos(2\tau)\cos(\phi_0 - \phi_1 + \omega t)\ \mathrm{sn}\left[\lambda(t - t_0), k\right]\ \mathrm{cn}\left[\lambda(t - t_0), k\right] \\ & + \sin(2\tau)\left\{1 - 2\ \mathrm{sn}^2\left[\lambda(t - t_0), k\right]\right\} . \end{aligned} \tag{13}$$

The expression from Eq. (12) now comes with a prefactor $\cos(2\tau)$. There is a new term that goes with a $\sin(2\tau)$ prefactor and that does not involve the ω-oscillation. The long-time average of the term in curly brackets is nonzero if $k \neq 0$. By evaluating the integral of this term over one period and dividing by this period, the long-time average can be obtained. This can be done with standard methods [26, 27] and yields

$$\langle P_z \rangle \propto \sin(2\tau)\left[1 - \left(2/k^2\right)\left\{1 - E(k)/K(k)\right\}\right] . \tag{14}$$

Here, $K(k)$ is again the elliptic integral of the first kind that we encountered before, and $E(k)$ is the elliptic integral of the second kind ($E(k) = \int_0^{\pi/2} \sqrt{1 - k^2 \sin^2\theta} \, \mathrm{d}\theta$).

6. Discussion

The claim by way of quantum physics that liquid water supports structures of almost millimeter size at room temperature appears to be at odds with a well-known fact of condensed matter physics: Brownian collisions destroy quantum entanglement and make wave functions collapse. The issue became particularly salient when, in the 1990s, Penrose and Hameroff proposed that the units in a long biopolymer could be the binary units in a quantum computer that produces "consciousness" [38]. In 2000, Max Tegmark took issue with this idea and derived how collisions with water and ions from the medium terminate any quantum entanglements between the units of a biopolymer within 10^{-13} s [39]. There is currently a widespread consensus among biophysicists that the aqueous environment in a living cell is simply too hot and too wet to allow for quantum entanglement to play a role in intermolecular interactions. This is because a collision localizes the colliding particles and thus makes state functions collapse onto position eigenfunctions (see *e.g.* Ref. [40]). In the first paragraph of Section 4, we saw that, in liquid water, there are 10^{12} collisions per molecule per second and that there are about 10^{18} molecules in a coherent domain. This implies that, inside a coherent domain, there is a collision every 10^{-30} s. If the decoherence timescale is the collision timescale, then a coherent domain does not survive beyond this completely inconsequential 10^{-30} s.

None of the conclusions of Ref. [1] warrants the idea of a "water memory". Reference [1] is silent about what happens when the macromolecules are diluted away. There is nothing in Ref. [1] that hints at an "imprint" 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".

All in all, there are good grounds to doubt the coherent domains that Ref. [1] proposes. The theory is built on questionable premises. Next, there are errors in the mathematical analysis. And finally, even if they are real, the coherent domains do not give rise to the claimed characteristic frequencies and to the long-range order.

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