Water as a Free Electric Dipole Laser

Emilio Del Giudice
Istituto Nazionale di Fisica Nucleare, Sezione di Milano, Milano, Italy

Giuliano Preparata
Dipartimento di Fisica, Università di Milano, Milano, Italy, and
Sezione di Milano,
Istituto Nazionale di Fisica Nucleare, Milano, Italy

and

Giuseppe Vitiello
Dipartimento di Fisica, Università di Salerno, Salerno, Italy, and
Sezione di Napoli, Istituto Nazionale di Fisica Nucleare, Napoli, Italy
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We show that the usually neglected interaction between the electric dipole of the water molecule and the quantized electromagnetic radiation field can be treated in the context of a recent quantum field theoretical formulation of collective dynamics. We find the emergence of collective modes and the appearance of permanent electric polarization around any electrically polarized impurity.

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It is well known that liquid water is a very complicated system,[1,2] and that it may show significant departures from its average bulk behavior in the presence of macromolecules,[3] colloidal particles,[4] and polarized impurities.[5] In addition, there are some experimental indications of its important role in the dynamics of macromolecules.[6]

In recent times very remarkable progress has been made through detailed dynamical calculations in the framework of a model which describes water as a network of H-bonded molecules.[7] However, it seems legitimate to us to wonder what effect on the structure of liquid water could the quantized electromagnetic field have, which is usually neglected. That our question might be totally nontrivial is suggested by the surprisingly close analogy that one can establish with the free-electron laser.[8] There the undulator field induces on a bunch of free electrons an oscillating electric dipole, transverse to their motion, which gets coherently coupled to the appropriate modes of the electromagnetic radiation. On the other hand, it is well known that the water molecules possess a considerable electric dipole.

The aim of this paper is to investigate whether under suitable conditions the electric dipoles of water molecules can interact coherently with selected modes of the radiation field, as it just happens in the free-electron laser. We shall employ a theoretical approach that has already been applied to describe successfully some important aspects of free-electron-laser dynamics.[9] Thus our model for liquid water in a volume V is defined by the following Hamiltonian ($\mathbf{A}$ denotes the electromagnetic field in the radiation gauge):

$$H=\sum_{j=1}^{N} H_j, \tag{1}$$

$$H_j=\frac{1}{2I}\mathbf{L}_j^2+\mathbf{A}\cdot\dot{\mathbf{d}}_{ej}, \tag{2}$$

where the sum runs over the N molecules of the volume V, and $\mathbf{L}_j$ is the total angular momentum of the single molecule, I its (average) momentum of inertia, and $\mathbf{d}_e$ its electric dipole vector. We set

$$I=2md_g^2 \quad (d_g \simeq 0.82\ \text{Å}) \tag{3}$$

(Ref. 10) and

$$|\mathbf{d}_e|=2ed_e \quad (d_e \simeq 0.2\ \text{Å}), \tag{4}$$

where m is the proton mass and e its charge.

As we are interested in the collective aspects of the interaction of the electric dipoles with the quantized electromagnetic field, we concentrate our attention only on those electromagnetic modes whose wavelength is either larger than or comparable with the size L of the system, so that the plane-wave factor $e^{i\mathbf{k}\cdot\mathbf{x}}$ shall always be dropped out.

Following the development of Ref. 9, we can cast our problem [Eqs. (1) and (2)] in the framework of a quantum field theory of a complex scalar field $\psi(\mathbf{u},t)$, the wave field, in interaction with the quantized electromagnetic field $\mathbf{A}$.

By standard quantum-field-theory methods it is straightforward to write down the relevant path integral that describes the dynamics of our system (we use the natural units $\hbar = c = 1$),

$$Z=\int[d\psi\, d\psi^*][da_r\, da_r^*]\exp(iW[\psi,\psi^*,a,a^*]), \tag{5}$$

where the action integral ($\mathbf{u}$ is the unit vector in the dipole direction) is given by

$$W=\int d\Omega_{\mathbf{u}}\, dt\, L(\mathbf{u},t); \tag{6}$$

$$L(\mathbf{u},t)=\frac{i}{4\pi}\sum_{r,\mathbf{k}}a_r^*(\mathbf{k},t)\dot{a}_r(\mathbf{k},t)+\psi^*(\mathbf{u},t)i\frac{\partial\psi}{\partial t}(\mathbf{u},t)-\psi^*(\mathbf{u},t)\frac{\mathbf{L}^2}{4md_g^2}\psi(\mathbf{u},t)$$
$$+\frac{2ed_e}{V^{1/2}}i\sum_{r,\mathbf{k}}\left(\frac{k}{2}\right)^{1/2}(\epsilon_r\cdot\mathbf{u})\psi^*(\mathbf{u},t)\psi(\mathbf{u},t)\{a_r(\mathbf{k},t)e^{-ikt}-a_r^*(\mathbf{k},t)e^{ikt}\}, \tag{7}$$

$\mathbf{L}^2$ is the square of the angular momentum operator

$$\mathbf{L}^2=-\frac{1}{\sin\theta}\left[\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}+\frac{\partial^2}{\partial\phi^2}\right], \tag{8}$$

and $a_r(\mathbf{k},t)$ is the amplitude of the mode $\mathbf{k}$ with polarization r [$\mathbf{k}\cdot\epsilon_r(\mathbf{k})=0$, from the transversality condition].

The Noether theorem leads to the following conserved quantity:

$$N=\int d\Omega_{\mathbf{u}}\psi^\dagger(\mathbf{u},t)\psi(\mathbf{u},t), \tag{9}$$

where N is just the number of dipoles contained in the volume V.

As emphasized in Ref. 9, Eq. (9), implying that the paths contributing to Z must have the "macroscopic" size $N^{1/2}$, suggests the relevance of the following rescalings:

$$\psi(\mathbf{u},t)=N^{1/2}\xi(\mathbf{u},t),$$
$$a_r(\mathbf{k},t)=N^{1/2}b_r(\mathbf{k},t). \tag{10}$$

In terms of the new functions ξ and b_r, the Lagrangian (7) scales as

$$L(\mathbf{u},t)=N\bar{L}(\mathbf{u},t), \tag{11}$$

where $\bar{L}(\mathbf{u},t)$ has, in terms of ξ and b_r, precisely the same form as L but for the extremely important difference that the coupling strength $2ed_e/V^{1/2}$ now gets multiplied by the very large number $N^{1/2}$; furthermore, Eq. (9) can now be rewritten as

$$\int d\Omega_{\mathbf{u}}\xi^*(\mathbf{u},t)\xi(\mathbf{u},t)=1. \tag{12}$$

By changing variables in the path integral (5), we clearly see that the solution of our quantum field theory consists simply of the "classical" solution of the variational problem

$$\delta\int\bar{L}\, d\Omega_{\mathbf{u}}\, dt=0, \tag{13}$$

modulo "quantum fluctuations" whose size is $O(1/N^{1/2})$.[9] The variational problem (13) yields the following Euler-Lagrange equations:

$$i\frac{\partial\xi(\mathbf{u},t)}{\partial t}=\frac{\mathbf{L}^2}{4md_g^2}\xi(\mathbf{u},t)-i2ed_e\left(\frac{N}{V}\right)^{1/2}\sum_{\mathbf{k},r}(\epsilon_r\cdot\mathbf{u})\left(\frac{k}{2}\right)^{1/2}\{b_r(\mathbf{k},t)e^{-ikt}-b_r^*(\mathbf{k},t)e^{ikt}\}\xi(\mathbf{u},t), \tag{14}$$

$$i\frac{\partial b_r(\mathbf{k},t)}{\partial t}=ie^{ikt}\left(\frac{Nk}{2V}\right)^{1/2}2ed_e\epsilon_r(\mathbf{k})\cdot\int d\Omega_{\mathbf{u}}\mathbf{u}\xi^*(\mathbf{u},t)\xi(\mathbf{u},t). \tag{15}$$

In order to proceed any further we must get back to the meaning of the complex functions $\xi(\mathbf{u},t)$ and $b_r(\mathbf{k},t)$. It is clear that $N|\xi(\mathbf{u},t)|^2$ represents the average number of dipoles in the volume V that are polarized in the $\mathbf{u}$ direction, while $N|b_r(\mathbf{k},t)|^2$ is the average number of photons in the mode $\mathbf{k},r$. By expansion of $\xi(\mathbf{u},t)$ in spherical harmonics, i.e., writing

$$\xi(\mathbf{u},t)=\sum_{lm}C_{lm}(t)Y_l^m(\mathbf{u}), \tag{16}$$

$N|C_{lm}(t)|^2$ denotes the number of molecules that populate the rotational state $|l,m\rangle$ of our rigid rotator, which, neglecting all interactions, at thermal equilibrium should follow a Boltzmann distribution with $E_l=l(l+1)/4md_g^2$. Under normal conditions (unpolarized bulk water) the levels $l=0$ and $l=1$ have comparable populations. To simplify our problem,[11] from now on we shall work in the subspace spanned by the four states $|0,0\rangle$ and $|l,m\rangle$, and restrict the electromagnetic modes to the resonating ones, i.e., those for which $k=\omega_0=1/2md_g^2$.[12] Setting

$$\gamma_0(t)=C_{00}(t),\quad \gamma_m(t)=C_{1m}(t)e^{-i\omega_0 t},$$

and calling $b(t)$ the amplitude of the electromagnetic mode coupled to transition $|l,m\rangle\leftrightarrow|0,0\rangle$, one can cast the system (14) and (15) in the form

$$\dot{\gamma}_0(t)=\Omega\sum_m b_m^*(t)\gamma_m(t),$$
$$\dot{\gamma}_m(t)=-\Omega b_m(t)\gamma_0(t), \tag{17}$$
$$\dot{b}_m(t)=2\Omega\gamma_0^*(t)\gamma_m(t),$$

where

$$\Omega = \frac{4ed_e}{\sqrt{3}} \left(\frac{N}{2\omega_0 V} \right)^{1/2} \omega_0 = G\omega_0. \tag{18}$$

Note that in pure water (H_2O), $G \cong 17$. Taking advantage of the rotational symmetry of the problem, our system can be further simplified by setting $\gamma_m(t) = \gamma_1(t)$ and $b_m(t) = b(t)$. One thus obtains

$$\begin{aligned} \dot{\gamma}_0(t) &= 3\Omega b^*(t)\gamma_1(t), \\ \dot{\gamma}_1(t) &= -\Omega b(t)\gamma_0(t), \\ \dot{b}(t) &= 2\Omega \gamma_0^*(t)\gamma_1(t), \end{aligned} \tag{19}$$

which admits the following constants of motion:

$$|\gamma_0|^2 + 3|\gamma_1|^2 = 1, \tag{20}$$

$$2|\gamma_1|^2 + |b|^2 = \tfrac{2}{3}\sin^2\theta_0, \tag{21}$$

where the angle θ_0 $(0 \le \theta_0 \le \pi/2)$ specifies the initial conditions as

$$\begin{aligned} |\gamma_0(0)|^2 &= \cos^2\theta_0, \\ |\gamma_1(0)|^2 &= \tfrac{1}{3}\sin^2\theta_0, \\ |b(0)|^2 &= 0. \end{aligned} \tag{22}$$

If we call Γ_0, Γ_1, B and ϕ_0, ϕ_1, ψ the modulus and the phase of γ_0, γ_1, b, respectively, the system (19) admits a limit cycle:

$$\beta = \phi_1 - \phi_0 - \psi = \pi/2, \tag{23}$$

$$\begin{aligned} \Gamma_0(t) &= \bar{\Gamma}_0 \\ &= (1/\sqrt{3})[1 + \cos^2\theta_0 + (1 - \tfrac{1}{4}\sin^2 2\theta_0)^{1/2}]^{1/2}, \\ \Gamma_1(t) &= \bar{\Gamma}_1 = (1/\sqrt{3})(1 - \bar{\Gamma}_0^2)^{1/2}, \\ B(t) &= \bar{B} = (\tfrac{2}{3})^{1/2}(\bar{\Gamma}_0^2 - \cos^2\theta_0)^{1/2}, \end{aligned} \tag{24}$$

and

$$\dot{\phi}_1 - \dot{\phi}_0 = \omega_2 = (2\bar{\Gamma}_0\bar{\Gamma}_1/\bar{B})\Omega, \tag{25}$$

and the small oscillations around it are controlled by the pulsation

$$\omega_1 = 2\sqrt{2}[1 - \tfrac{1}{4}\sin^2 2\theta_0]^{1/4}\Omega. \tag{26}$$

It is easy to see that access to the limit cycle can be obtained only for $\theta_0 \gtrsim \pi/4$. Note that the "thermal start" [Boltzmann distribution, in normal conditions $\Gamma_0(0) \cong \Gamma_1(0)$] corresponds to $\theta_0 = \pi/3$. On the other hand, for $\theta_0 < \pi/4$ the system (19) goes through a quasiperiodic motion with average pulsation

$$\bar{\omega} = (2\cos 2\theta_0)^{1/2}\Omega. \tag{27}$$

From our definitions it is straightforward to calculate the polarization along any direction $\mathbf{n}$; one finds

$$\begin{aligned} P_{\mathbf{n}} &= \langle \xi | \mathbf{n} \cdot \mathbf{u} | \xi \rangle \\ &= (2/\sqrt{3})\Gamma_0(t)\Gamma_1(t)\cos(\omega_2 - \omega_0)t. \end{aligned} \tag{28}$$

Let us now suppose that within the volume V we have an impurity with a sizable electric dipole, which generates an electric field $\mathbf{E}_d$ oriented in the z direction. The static part of the Hamiltonian H_j [Eqs. (1) and (2)] will acquire a new term

$$V_d = -\mathbf{d}_{ej} \cdot \mathbf{E}_d, \tag{29}$$

which will mix the states $|0,0\rangle$ and $|1,0\rangle$, to produce the new eigenstates

$$\begin{aligned} |\tilde{0}\rangle &= \cos\alpha |0,0\rangle + \sin\alpha |1,0\rangle, \\ |\tilde{1}\rangle &= -\sin\alpha |0,0\rangle + \cos\alpha |1,0\rangle, \end{aligned} \tag{30}$$

with eigenvalues

$$\lambda_{0,1} = (\omega_0/2)[1 \mp (1 + 4V_d^2/\omega_0^2)^{1/2}], \tag{31}$$

and

$$tg\alpha = [\omega_0 - (\omega_0^2 + 4V_d^2)^{1/2}]/2V_d. \tag{32}$$

For V_d not too strong $(\alpha < \pi/8)$ the dynamics of our system is practically unchanged, except for the rotation (30), induced by the electrostatic mixing, which modifies the form (28) of the polarization P_3 as

$$P_3(t) = (1/\sqrt{3})\{\sin 2\alpha\,(\Gamma_0^2 - \Gamma_1^2) + \cos 2\alpha\, 2\Gamma_0(t)\Gamma_1(t)\cos([\omega_2 - (\omega_0^2 + 4V_d^2)^{1/2}]t)\}. \tag{33}$$

Equations (24) to (28) and (31) to (33) display the essence of this work. Let us see what their physical meaning is. For different initial conditions (θ_0), the system will exhibit different dynamical behaviors; however, for $\theta_0 < \pi/4$ the frequencies involved will fall in the interval [see (27)] $0 < \nu < 500$ cm^{-1}; while for $\pi/3 > \theta_0 > \pi/4$ the frequencies populate three distinct bands around 1600, 750, and 400 cm^{-1}. It should be recalled that in our frequency range the main absorption bands of pure water are located at 1640, 580, and 180 cm^{-1}.[13]

But the most intriguing result of this work is the prediction (33) of the emergence of a *permanent* electric polarization around an impurity that carries a sizeable electric dipole (organic macromolecules are known to have this property). The amount of such polarization turns out to be

$$\langle P_3(t) \rangle = (1/\sqrt{3})\sin 2\alpha\,(\bar{\Gamma}_0^2 - \bar{\Gamma}_1^2), \tag{34}$$

which in the region where $2V_d/\omega_0$ is ~ 1 attains very respectable values. Note that in the absence of the collective interaction analyzed in this paper, one must have $\bar{\Gamma}_0^2 = \bar{\Gamma}_1^2$, as prescribed by thermal equilibrium, and no significant electric polarization can emerge even for rather strong electric fields.

So far no account has been made for the radiative energy losses from the volume V, which clearly is not an electromagnetic cavity. By taking such losses into account one can easily see that the lifetimes of our collective modes are of the order of $2\pi/\omega_0$, and thus considerably larger than the periods $2\pi/\omega_1$, $2\pi/\omega_2$, and $2\pi/\bar{\omega}$ of the collective dynamics. For $\theta_0 > \pi/4$ the energy losses will bring the Γ_0 and Γ_1 to their limit-cycle values, and the system will resume "lasering" in such a regime only when the thermal processes will have brought θ_0 above $\pi/4$.

Even though, it must be admitted, our analysis is in many ways at a preliminary, rather rudimentary stage, nevertheless, we believe that we can draw a number of relevant conclusions: (i) 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 ($G \simeq 17$); (ii) because of the latter fact, the time scale associated with the coherent interaction is much shorter ($\simeq 10^{-14}$ s) than those connected with short-range interactions. In such coherent dynamics, our analysis has also recognized the relevance of frequency bands which can be related to the observed absorption bands of pure water; (iii) 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, or the field at the surface of a colloid grain or within clays.

As a result, one can envisage the possibility that the coherent interaction between the water electric dipoles and the radiation field fulfills the very important task of generating ordered structures in macroscopic domains (i.e., within a few hundred microns) which could then have a fundamental role in the organization of inanimate as well as living matter[14] in the wonderful ways that physical analysis is incessantly revealing. Of course much more work is needed in this direction.

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[10] This value refers to the highest moment of inertia of the water molecule. See Ref. 1.

[11] One can see that in thermal equilibrium the ratios R_l between the populations of the state $|l,m\rangle$ and the state $|0,0\rangle$ are $R_1 = 0.887$, $R_2 = 0.698$, $R_3 = 0.487$, $R_4 = 0.301$, $R_5 = 0.165$, etc. For heavy water D_2O, the same ratios are 0.942, 0.835, 0.698, 0.549, 0.406, . . ., respectively.

[12] This obviously implies that the size L of our V is now constrained to be less than $2\pi/\omega_0 = 4.3 \times 10^{-2}$ cm.

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