Anomalies in H$_2$O-D$_2$O Mixtures: Evidence for the Two-Fluid Structure of Water

M. Buzzacchi, E. Del Giudice and G. Preparata

Dipartimento di Fisica dell’Università di Milano
and I.N.F.N. - Section of Milan
Via Celoria 16, 20133 Milan, Italy

Abstract

Recent probing of H$_2$O-D$_2$O mixtures by various means (neutron deep inelastic scattering, Raman absorption, electrical H$^+/D^+$ conductivity) revealed an unexpected dependence of the relevant physical quantities on the isotopic composition of the mixture. We show that these observations can find their physical rationale in the context of an approach to the physics of liquid water which takes into account the non-negligible interaction of the molecules with the electromagnetic field, from which a two-fluid microscopical picture of water naturally emerges.

5 February 1998
1 Introduction

It is not unusual, and rather fortunate, that a seemingly eccentric research programme is vigorously and ably pursued by some scientists, based upon motivations that turn out to have poor foundations, but whose outcome unveils some subtle and far reaching property of nature. Thus demonstrating once more that in science creative error, unlike common-sense prejudice, proves often a blessing.

The research programme we have in mind focusses on some remarkably anomalous behaviours of \( \text{H}_2\text{O}-\text{D}_2\text{O} \) mixtures, when probed by a variety of means: deep-inelastic neutron scattering [1], vibron excitation in Raman scattering [2] and \( \text{H}^+ / \text{D}^+ \) conductivity [3]. The original motivation of the above experiments [1] is, apparently, the expectation that the possible quantum coherence of the pure states (\( \text{H}_2\text{O} \) or \( \text{D}_2\text{O} \)), or Quantum Entanglement (QE), would be disrupted in the mixture of the fluids, thus modifying the scattering mechanisms (through the modification of quantum interference) at work in the pure liquids. As a result, one would thus expect some peculiar dependence on \( x_D \) (the molar fraction of \( \text{D}_2\text{O} \) in the mixture, \( 0 \leq x_D \leq 1 \)) of the observable cross sections.

As we shall review below, such expectations have been indeed confirmed by the experiments [1,2,3]. Have we then found, as the authors of Refs. [1,2,3] claim, a strong evidence for QE? In a recent comment [5] to the Letter of Ref. [1] we have argued against the conclusions of the authors on the basis of two facts:

- the large size of the effects: up to 30% in deep inelastic neutron scattering [1];
- the neutron wavelengths involved in the experiment are smaller than \( 0.1\text{Å} \), more than an order of magnitude smaller than the separations between the H (D) nuclei. As well known, in this physical situation
(barring some very unusual interaction which, however, is not explicitly mentioned) the scattering process is necessarily incoherent, excluding that any spatial coherence in the initial multi-hydrogen wave function may affect the scattering process. And the experimental validity of the "impulse approximation", based on the incoherence of the scattering process, bears witness to the untenability of the idea that QE may explain the stunning results of Ref. [1].

In the same comment [5], we also ask the question: if not QE what else could explain the anomalous effects in H₂O-D₂O mixtures? And we argue that some good description of the data arises from the assumption that water consists of two interpenetrating fluids, one consisting of Coherence Domains (CD’s), in which the water molecules oscillate in phase with a macroscopic, classical configuration of the electromagnetic field trapped within them, while the other comprises a dense gas of incoherent molecules that fill the interstices among the CD’s and is generated by the "evaporation" of the outer parts of the CD’s due to thermal fluctuations.

The above theory of water has been fully developed and described in Ref. [6], and its foundations in QED have been thoroughly discussed in a recent, readily accessible book [7]. Thus, in this paper, we shall only briefly recall the main aspect of the new theory of water [6], based on QED coherence, whose validity appears further corroborated, as we shall argue in the following, by the anomalous properties of H₂O-D₂O mixtures.

When looked from a quantum-field theoretical point of view, an ensemble of water molecules is a matter quantum field, which in its "Perturbative" Ground State (PGS) performs zero-point fluctuations, as dictated by the Heisenberg Principle. The same happens to the modes of the quantized electromagnetic field. For
$T=0$, there exists a critical density $\rho_C \simeq 0.3 \, \text{g/cm}^3$, at which the PGS becomes unstable, and the combined system, matter plus electromagnetic field, gains energy by condensing a classical electromagnetic field, whose oscillations are in phase with those of the matter molecules between their molecular ground state and a peculiar excited state, whose energy is $E = 12.06 \, \text{eV}$. In this way the new ground state, the Coherent Ground State (CGS), consists of a highly coherent configuration of matter and radiation, which gets successively eroded by the disordering effects of temperature, until one reaches the boiling temperature when all molecules leave the CGS. It has been shown [6,7] that many of the fundamental thermodynamic properties of water can be accurately and naturally described by this simple and powerful theory, rigorously based on the fundamental laws of Quantum Electrodynamics. In particular, theory shows that the fraction $\xi(T)$ of incoherent molecules as a function of $T$ is given by the graph in Fig.1, showing that for $T=300 \, \text{K}$, $\xi \approx 0.7$.

But let us see now how these ideas can capture the fascinating physics behind the surprising experimental observations of Refs.[1,2,3].

2 Anomalous neutron deep-inelastic scattering

An analysis of the anomalous neutron deep-inelastic scattering off nuclei of H$_2$O and D$_2$O molecules starting from the two-fluid picture of water that QED coherence implies can be performed as follows: due to the phase coherence which allows a sharing of the recoil momentum among the large number ($N \simeq 10^7$) of molecules clustered in a CD, the coherent fraction is less effective in the scattering.

\footnote{For an independent assessment of the latter statement please consult [8].}
of neutrons than the incoherent, vapour-like fraction. We can write:

$$\sigma_{H,D}^{(i)} = \sigma_{H,D}^{(c)} \left( \epsilon_{H,D} \frac{N_{H,D}^{(c)}}{N_{H,D}} + \frac{N_{H,D}^{(i)}}{N_{H,D}} \right),$$  \hspace{1cm} (1)

where $N_{H,D}^{(i)}$, $N_{H,D}^{(c)}$ and $N_{H,D} = N_{H,D}^{(i)} + N_{H,D}^{(c)}$ are the numbers of incoherent, coherent and total $H_2O$ and $D_2O$ molecules respectively, $\sigma_{H,D}^{(i)}$ the deep-inelastic cross sections off the H, D nuclei of the incoherent molecules and $\epsilon_{H,D} < 1$ is introduced to account for the different cross-sections in the two phases of water.

Due to the two-fluid nature of both $H_2O$ and $D_2O$, the fraction $\xi_{H,D} = \frac{N_{H,D}^{(i)}}{N_{H,D}}$ of incoherent molecules, will in general depend on the molar fraction $x_D$ (see below). Anyway, from thermodynamic equilibrium one can fix unambiguously the two limiting values:

$$\frac{N_{H}^{(i)}}{N_{H}} \to 1 \quad (x_D \to 0),$$  \hspace{1cm} (2)

$$\frac{N_{D}^{(i)}}{N_{D}} \to 1 \quad (x_D \to 1).$$  \hspace{1cm} (3)

As a result, if $Q^{(0)} = \left( \frac{\sigma_{H}}{\sigma_{D}} \right)_{pure} \simeq 10.7$ denotes the ratio between the cross sections in the pure liquids [1], i.e.

$$Q^{(0)} = \frac{\sigma_{H}^{(i)} [\epsilon_H (1 - \xi_H) + \xi_H]}{\sigma_{D}^{(i)} [\epsilon_D (1 - \xi_D) + \xi_D]}$$  \hspace{1cm} (4)

one obtains the limits:

$$\frac{\sigma_{H}}{\sigma_{D}} \to Q^{(0)} \left[ \epsilon_D (1 - \xi_D) + \xi_D \right] \quad (x_D \to 0),$$  \hspace{1cm} (5)

$$\frac{\sigma_{H}}{\sigma_{D}} \to Q^{(0)} \left[ \frac{1}{\epsilon_H (1 - \xi_H) + \xi_H} \right] \quad (x_D \to 1).$$  \hspace{1cm} (6)

A satisfactory agreement with the experimental data is obtained by choosing $\epsilon_D \approx 0$, $\epsilon_H \approx 0.5$. For the intermediate dilution range, let $\eta$ be the ratio between the number of incoherent $H_2O$ and $D_2O$ molecules:

$$N_{H}^{(i)} = \eta N_{D}^{(i)},$$  \hspace{1cm} (7)
then, assuming for simplicity $\epsilon_D = \epsilon_H = 0$,

$$\frac{\sigma_H}{\sigma_D} \simeq Q^{(0)} \eta(x_D) \frac{x_D}{1 - x_D}.$$ \hspace{1cm} (8)

The experimental dependence of $\frac{\sigma_H}{\sigma_D}$ on $x_D$ (see Fig.2) in the range $0.3 \leq x_D \leq 0.7$ can be easily fitted by a straight line:

$$\left( \frac{\sigma_H}{\sigma_D} \right)_{exp} \simeq 4 + 6.7 \, x_D :$$ \hspace{1cm} (9)

this can be used to derive an estimate for $\eta$ at equal H$_2$O-D$_2$O concentration ($x_D = 0.5$):

$$\eta(x_D = 0.5) = 0.83.$$ \hspace{1cm} (10)

This result will be rederived and substantiated in the following sections.

3 Anomalous Raman absorption cross sections

The same line of thought can lead to an explanation of the anomalous absorption cross sections of the OH and OD stretching modes observed in mixtures. The experimental results are reported in Fig.3, where the ratio $Q = \frac{\sigma_{OH}}{\sigma_{OD}}$ is plotted for several values of the concentration $x_D$.

In order to understand these "unreasonable" results, we shall rely on the two-fluid picture of water, described in the Introduction. We need, of course a scattering mechanism which is substantially different in the two phases. While in the incoherent fluid Raman scattering proceeds "as usual", in the coherent phase we notice at least two essential differences: the first is the energy gap ($\delta = 0.26$ eV per molecule) [6] that separates the initial, coherent molecular state from the incoherent one, which will lower the energy of the relevant intermediate (incoherent) states excited by the initial photon beam; while the second is that the final excited stretching mode, being incoherent, will lead to an outgoing photon
whose energy is lower by the gap $\delta$. This line, however, will be of very difficult detection, due to its extremely short lifetime to decay back to the coherent ensemble. So, under the hypothesis that only incoherent molecules can absorb the incident probing radiation, one has for $x_D \simeq 0.5$:

$$\sigma_{OH} = \frac{N_H^i(x_D)}{N_H^i(0)} \sigma_{OH}^{pure} = \frac{\xi(1-x_D) - \lambda}{\xi} \sigma_{OH}^{pure}$$  \hspace{1cm} (11)

and

$$\sigma_{OD} = \frac{N_D^i(x_D)}{N_H^i(1)} \sigma_{OD}^{pure} = \frac{\xi x_D + \lambda}{\xi} \sigma_{OD}^{pure}$$  \hspace{1cm} (12)

where $\lambda$ is defined by the relation (see Eq.10):

$$\eta(x_D = 0.5) = \frac{\xi (1-x_D) - \lambda}{\xi x_D + \lambda} \simeq 0.83$$  \hspace{1cm} (13)

So one obtains:

$$Q \simeq \frac{\xi (1-x_D) - \lambda}{\xi x_D + \lambda} \left( \frac{\sigma_{OH}}{\sigma_{OD}} \right)_{pure}$$  \hspace{1cm} (14)

Using the previous values ($\xi=0.7; \lambda=0.03$) and setting $x_D=0.5$ one gets:

$$Q_{th} \simeq 0.84 Q^{(0)}$$  \hspace{1cm} (15)

whose agreement with experiment is good.

An even more intriguing outcome of this experiment is shown in Fig.4, where the relative deviations:

$$\Delta \sigma_{OD} = \frac{\sigma_{OD}(x_D) - \sigma_{OD}^{(0)}}{\sigma_{OD}^{(0)}}$$  \hspace{1cm} \hspace{1cm} \hspace{1cm} (16)

$$\Delta \sigma_{OH} = \frac{\sigma_{OH}(x_D) - \sigma_{OH}^{(0)}}{\sigma_{OH}^{(0)}}$$

are given for various mixtures. One sees that $\Delta \sigma_{OH} < 0$, but $\Delta \sigma_{OD} > 0$. If the anomaly in the behaviour of $Q$ were due to the lack of formation of the coherent dissipative structures in mixtures [1,2,3,4], one should observe $\Delta \sigma_{OH} < 0$ and $\Delta \sigma_{OD} < 0$, since the postulated ”defective” cooperativity in $\text{H}_2\text{O}-\text{D}_2\text{O}$ mixtures should affect both species. An interpretation of this effect is possible if one thinks
that the scattered intensities are not strictly proportional to the number of OH
and OD oscillators. Indeed, the two-fluid structure of water implies that, since
only the incoherent molecules are involved in the interaction with the external
electromagnetic probe, $\Delta \sigma_{OD} > 0$ means that $N_{D_2O}^{(i)} > \xi x_D$ and $\Delta \sigma_{OH} < 0$
means that $N_{H_2O}^{(i)} < \xi (1 - x_D)$. In fact, one has:

$$\Delta \sigma_{OD}(0.5) \simeq \frac{\lambda}{\xi x_D} = +0.09, \quad \Delta \sigma_{OH}(0.5) \simeq \frac{-\lambda}{\xi (1 - x_D)} = -0.09, \quad (17)$$

which compare well with the results of Fig.4.

In the next section, where we analyse the anomalous $H^+/D^+$ conductivity in
$H_2O-D_2O$ mixtures, this effect will be clarified and its relation to the two-fluid
structure of water physically further motivated.

4 Anomalous $H^+/D^+$ conductivity

An earlier experiment [3] was performed in order to test the idea that thermal
fluctuations could induce a continuous formation of short-lived coherent struc-
tures. According to this view, the non-factorizability of the wave wave function
of the particles involved in such processes could result in the quantum delocal-
ization of $H^+ (OH^-)$ ions and their tunnelling through clusters of water molecules
($H_2O)_n$, thus enhancing the ionic conductivity. The chance of formation of these
coherent dissipative structures would be largely suppressed if we replaced some
fraction of the $H_2O$ molecules with $D_2O$ molecules, as in $H_2O-D_2O$ mixtures,
since the most favourable environment is clearly one of identical molecules. As
a consequence, one should observe a decrease in the ionic $H^+$ conductivity of
mixtures.

This was indeed confirmed experimentally, as we shall briefly review: the
conductivity of $D^+$ (from DCl) in pure $D_2O$ and that of $H^+$ (from HCl) in pure
H$_2$O were first measured. Subsequently, samples of HCl-H$_2$O and DCl-D$_2$O with equal molarity were mixed at various $x_D$ concentrations. The experiment measured the combined H$^+$/D$^+$ conductivity $\Lambda$ of the mixtures. Standard electrochemistry predicts that $\Lambda$ should depend linearly on $x_D$:

$$\Lambda = \Lambda_{D^+}x_D + \Lambda_{H^+}(1 - x_D),$$

(18)

where $\Lambda_{D^+}=312.7$ S cm$^2$ mol$^{-1}$ and $\Lambda_{H^+}=426.3$ S cm$^2$ mol$^{-1}$ are the conductivities of the pure samples\[3\].

The data revealed an unambiguous deviation from (18), with a maximum deviation -5.1 % at $x_D=0.5$. K$^+$ conductivity in H$_2$O-D$_2$O mixtures was also measured and only a tiny deviation from linearity (-0.8 % at $x_D=0.5$) was observed. These facts gave substance to the expectation that the above mentioned quantum effects might play a role in H$^+$ dynamics in water.

In the following we shall argue that the analysis of water presented in Refs.[6,7] provides an alternative explanation of the above effect. As we sketched in the Introduction, pure normal and heavy water at thermal equilibrium ($T=300$ K) comprise a coherent and an incoherent fraction of molecules with relative populations $(1 - \xi) \simeq 0.3$ and $\xi \simeq 0.73$\[3\]. The stability of the ”islands” of coherent matter is ensured by the formation of an energy gap, while matter and radiation in the incoherent phase retain their uncoupled, perturbative dynamics, which renders the incoherent molecules a very dense vapour.

Now, what will happen when we mix H$_2$O and D$_2$O? A thermodynamical argument guarantees that a slight ”unbalancement” in the coherent (incoherent) H$_2$O populations with respect to $1-\xi$ ($\xi$) in pure H$_2$O must occur in the mixture.

\[2\]The data can be extrapolated to obtain the ionic conductivity in the limit of zero ionic concentration

\[3\]We shall neglect small differences in the QED-coherence properties of H$_2$O and D$_2$O.
The same holds for D$_2$O, but the unbalancement is in the opposite direction. For thermodynamical equilibrium demands the transfer of some D$_2$O coherent molecules into the incoherent phase, while an equal number of H$_2$O incoherent molecules gets reabsorbed in the coherent phase. Indeed, let us approximate the partition function for incoherent molecules:

$$Z_i = \frac{V T^3}{N \pi^{5/2}} m^{3/2} (I_1 I_2 I_3)^{1/2}, \quad (19)$$

where $m$ denotes the mass and the $I_k$’s the principal axes of inertia of a molecule. If we ignore rotational degrees of freedom (water molecules perform only hindered rotations), we have:

$$\frac{Z_D^{D_2O}}{Z_H^{H_2O}} \simeq \left(\frac{m_D}{m_H}\right)^{3/2} = 1.17, \quad (20)$$

while coherence guarantees that the partition functions for coherent H$_2$O and D$_2$O molecules are equal:

$$\frac{Z_c^{D_2O}}{Z_c^{H_2O}} = 1. \quad (21)$$

Equilibrium is reached when the chemical potential is constant everywhere and this can be achieved through the described transfer mechanism: at equal H$_2$O-D$_2$O concentration ($x_D = 0.5$) the incoherent fraction gets enriched in heavy water by about 15%. With this in mind, and the consideration that the scattering processes responsible for resistivity (or its inverse, conductivity) take place essentially within the incoherent fraction, we can provide a different picture of the anomalous proton/deuteron conductivity in mixtures: as a first approximation one has for the scattering cross sections:

$$\sigma_D(x_D) = x_D \sigma_{D,D_2O} + (1 - x_D) \sigma_{D,H_2O}, \quad (22)$$

$$\sigma_H(x_D) = x_D \sigma_{H,D_2O} + (1 - x_D) \sigma_{H,H_2O}. \quad (23)$$
This holds when the number of $H_2O$ and $D_2O$ molecules involved in the scattering are exactly proportional to their concentrations, but according to the previous considerations one has:

$$N^{(i)}_{H_2O} = [(1 - x_D)\xi - \lambda]N, \quad N^{(i)}_{D_2O} = (x_D\xi + \lambda)N,$$

(24)

where $\lambda$ has the value 0.03. As a consequence, at least for dilutions not too different from 0.5, one must change (22),(23) into:

$$\sigma_D(x_D) = \frac{\xi x_D + \lambda}{\xi} \sigma_{D,D_2O} + \frac{(1 - x_D)\xi - \lambda}{\xi} \sigma_{D,H_2O},$$

(25)

$$\sigma_H(x_D) = \frac{\xi x_D + \lambda}{\xi} \sigma_{H,D_2O} + \frac{(1 - x_D)\xi - \lambda}{\xi} \sigma_{H,H_2O},$$

(26)

and we choose $\sigma_{D,D_2O} = 1.364$ [3], $\sigma_{D,H_2O} = \sigma_{H,D_2O} \simeq 1.364^{1/2}$ relative to $\sigma_{H,H_2O} = 1$ [3]. The conductivity of the mixtures is then given by:

$$\Lambda(x_D) = x_D \frac{\sigma_D(x_D = 1)}{\sigma_D(x_D)} \Lambda_D + (1 - x_D) \frac{\sigma_H(x_D = 0)}{\sigma_H(x_D)} \Lambda,\Lambda_H,$$

(27)

whose behaviour as a function of $x_D$ is plotted in Fig.5. This simple calculation, which is a rather straightforward consequence of the ideas developed in Refs. [6,7] gives a remarkable agreement with the experimental data [3], thus providing a further corroboration of the two-fluid structure of water.

5 Conclusions

The main aim of this paper, as explained in the Introduction, was two-fold. On one hand to emphasize the importance of the experimental observations of unexpected effects in $H_2O-D_2O$ mixtures [1,2,3] for our understanding of a fundamental physical system, such as water; and on the other to show that their explanation does not involve the rather arcane (and definitely “untenable”) mechanisms of Quantum Entanglement (QE) but provides a strong and convincing evidence of
the two-fluid nature of water, and of the theory of QED coherence [6,7,8] which lies at its roots.

We believe (and the unconvinced reader is invited to strongly object) that both goals have been attained. For we have brought to focus, and together, three "anomalies" of the H$_2$O-D$_2$O mixtures that should (we don’t know whether they will) cause more than one sleepless night to the molecular dynamicists who assert that through Montecarlo simulations they understand water, both light and heavy. In addition we have argued, we hope convincingly, that at least for deep-inelastic neutron scattering [1] and the vibron excitation in Raman scattering [2] QE cannot be the explanation due to basic theoretical reasons for the former and to experimental discrepancies for the latter. On the other hand, the simple and well defined two-fluid picture of water, both light and heavy, that naturally arises from a theory of condensed matter that has finally been able to include among the relevant interactions the electrodynamic one (and this in a full quantum field theoretical framework) has been shown to remarkably account in a quantitative fashion for the subtle and strange phenomena we have analysed in this paper.

In conclusion, the main lesson we think can be learned from the present analysis is that, even though the vast majority of the physics literature is today devoted to "normal" (in the sense of T. Kuhn) science, where the generally accepted "paradigm" cannot but be corroborated in an atmosphere of collective accomplishment and self-satisfaction, some unexpected progress may arise from the little "anomalies" that get readily accepted on the basis of some more or less obscure (and modern quantum mechanics proves prodigious at that) arguments that do not seem to jeopardize the "paradigm". And the progress we have in mind is the shift from the defective electrostatic paradigm of today’s condensed matter (the "Electrostatic Meccano", as we like to call it) to electrodynamic co-
herence, that takes full account of the neglected, but very real and deeply rooted in QED, long range interaction between matter and the electromagnetic field.

How many more far reaching "anomalies" shall we be able to observe when this shift will be accomplished? It is a question on whose answer we can at present only dream.

References

[1] C.A. Chatzdimitrou-Dreismann, T. Abdul Redah, R.M.F. Streffer, J. Mayers, Phys. Rev. Lett. 79, 2839 (1997).

[2] C.A. Chatzdimitrou-Dreismann, U.K. Krieger, A. Möller, M. Stern, Phys. Rev. Lett. 75, 3008 (1995).

[3] H. Weingärtner, C.A. Chatzdimitrou-Dreismann, Nature 346, 548 (1990).

[4] C.A. Chatzdimitrou-Dreismann, E.J. Brändas, Int. J. Quant. Chem. 37, 155 (1990).

[5] M. Buzzacchi, E. Del Giudice, G. Preparata (comment submitted to Phys. Rev. Lett.)

[6] R. Arani, I. Bono, E. Del Giudice, G. Preparata, Int. J. Mod. Phys. B 9, 1813 (1995).

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

[8] C.P. Enz, On Preparata’s Theory of a Superradiant Phase Transition, Helv. Phys. Acta 70 (1997) 141-153.
FIGURE CAPTIONS

**Fig.1:** The incoherent fraction of water molecules as a function of \( T \).

**Fig.2:** (o) Anomalous n-DIS in H\(_2\)O-D\(_2\)O mixtures: no dependence of \( Q \) on \( x_D \) was expected; (*) our prediction for \( x_D=0.5 \)

**Fig.3:** (o) Anomalous Raman absorption in H\(_2\)O-D\(_2\)O mixtures: no dependence of \( Q \) on \( x_D \) was expected; (*) our prediction for \( x_D=0.5 \)

**Fig.4:** \( \Delta \sigma_{OD} \) and \( \Delta \sigma_{OH} \) as a function of \( x_D \); (*) our predictions for \( x_D=0.5 \)

**Fig.5:** H\(^+\)/D\(^+\) conductivity in H\(_2\)O-D\(_2\)O mixtures. Solid line: our calculation. Circles: experimental data [3]. Dashed line: theoretically expected conductivity.
