Thermodynamic Evidence for Water as a Quantum Mechanical Liquid

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We consider general theoretical models of water and in particular the nature of the motions of the hydrogen nuclei. If the motion of hydrogen nuclei is classical, then the thermodynamic pressure equation of state for heavy water wherein the hydrogen nuclei are deuterons is identical to the pressure equation of state for light water wherein the hydrogen nuclei are protons. Since the experimental thermodynamic phase diagram for light water is clearly measurably different from the experimental thermodynamic phase diagram for heavy water, one may deduce that the motions of hydrogen nuclei are quantum mechanical in nature. This conclusion is in physical agreement with a recent analysis of X-ray, neutron and deep inelastic neutron scattering data.

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I. INTRODUCTION

The study of the applications of quantum mechanics to water is of long standing interest. Recent important studies\cite{1,2} of the momentum distributions and position correlations\cite{3} in light water H\textsubscript{2}O and in heavy water D\textsubscript{2}O have provided strong evidence that the proton motions in light water and deuteron motions in heavy water are in reality quantum mechanical. The experimental data arises from X-ray and neutron scattering experiments. In particular, from deep inelastic neutron scattering from protons, one may deduce the momentum distribution of protons within water and it is found to differ substantially from the Maxwellian distribution expected from classical proton motions. In fact, quantum fluctuations in the proton velocity dominate the sometimes presumed classical thermal fluctuations.

Our purpose here is to provide experimental thermodynamic evidence that the motions of hydrogen atoms in liquid water cannot be adequately described by classical mechanics. The thermodynamic data is hardly of recent vintage. However, the thermal data has not been previously analyzed in detail for the purpose of assessing the contribution of quantum mechanics to the thermodynamic properties of water. As a theoretical model, we at first presume a Hamiltonian which consists of kinetic energy plus Coulomb potential energy; it is

\[
\mathcal{V} = e^2 \left\{ \sum_{a<b} \frac{z_a z_b}{R_{ab}} - \sum_{i<j} \frac{1}{\alpha_{ij}} \sum_{i,j} \frac{z_a}{|r_j - R_a|} \right\}, \quad (1)
\]

wherein the indices \(a, b, \ldots\) refer to the nuclei of hydrogen and oxygen and the indices \(i, j, \ldots\) refer to the electrons. We also presume that the hydrogen nuclei obey classical mechanics to a sufficient degree of accuracy; i.e.

\[
\langle \frac{P^2}{2M} \rangle = \frac{3}{2} k_B T \quad \text{(Classical Hydrogen Nucleus).} \quad (2)
\]

In Sec.\textbf{III} we prove the following:

\textbf{Theorem:} Under the presumptions of classical motions for the hydrogen nuclei and with the free energy per molecule \(f(v, T)\) obeying

\[
df = -P dv - sdT, \quad (3)
\]

the pressure equation of state \(P(v, T)\) will be identical for light water with proton hydrogen nuclei and heavy water with deuteron hydrogen nuclei. Here, \(v\) represents the volume per molecule. As a consequence, light water and heavy water are predicted to have identical phase diagrams. These conclusions remain valid for more fully quantum electrodynamic microscopic models as shown in Sec.\textbf{III}.

The experimental evidence\cite{4} is that the theorem fails in the laboratory. For example, at atmospheric pressure, the melting temperature of light ice into light water is \(T_{m1} \approx 0^\circ\text{C}\). At atmospheric pressure the melting temperature of heavy ice into heavy water is \(T_{m2} \approx 4^\circ\text{C}\). In the concluding Sec.\textbf{IV} the modifications to the incorrect presumption of classical motion required by thermodynamic experiments is discussed.
II. THERMODYNAMIC EQUATIONS OF STATE

With $N$ molecules in a volume $V$, the free energy of water is found from

$$F = -k_BT \ln T r_{(V,N)} \left\{ e^{-\frac{N}{k_BT}} \right\},$$

d$F$ = $-PdV + \mu dN - SdT.$ \hspace{1cm} (4)

In the thermodynamic limit, the free energy per molecule

$$f(v, T) = \lim_{N \to \infty} \frac{F(V = Nv, N, T)}{N}$$ \hspace{1cm} (5)

obeys Eq.(2).

Consider the kinetic energy of the hydrogen nuclei

$$K_H = \frac{1}{2M} \sum_{c=1}^{N} p_c^2$$ \hspace{1cm} (6)

As an operator, one may consider the Hamiltonian in
Eq.(11) as a function of the hydrogen nuclear mass $M$.

Hence, the identity

$$K_H = -M \left( \frac{\partial H}{\partial M} \right).$$ \hspace{1cm} (7)

By a general theorem of statistical mechanics\(^\text{7}\), one has

$$\langle K_H \rangle = -M \left( \frac{\partial F}{\partial M} \right)_{V,N,T} = \frac{3}{2} N k_BT,$$ \hspace{1cm} (8)

wherein Eq.(2) has been invoked. Regarding the proton or
the deuteron as the nucleus of the hydrogen atom, it is
important to note that the proton is a Fermion and the
deuteron is a Boson. If the nucleus undergoes classical
motion, then the whole notion of quantum statistics plays
no role in the thermal equations of state. The free energy
difference between light water and heavy water then can
be found by integrating Eq.(5) from the proton mass to
the deuteron mass; In detail,

$$\Delta F = \int_{M_1}^{M_2} \left( \frac{\partial F}{\partial M} \right)_{V,N,T} dM,$$

$$\Delta F = \frac{3}{2} N k_BT \int_{M_1}^{M_2} \frac{dM}{M} = -\frac{3}{2} N k_BT \ln \left( \frac{M_2}{M_1} \right),$$

$$\Delta F = -\frac{3}{2} N k_BT \ln 2 = -(3 \ln 2) N k_BT.$$ \hspace{1cm} (9)

The difference between light water and heavy water thereby amounts to

$$\Delta f = -(3 \ln 2) k_BT.$$ \hspace{1cm} (10)

If the hydrogen nucleus moves via classical mechanics,
then the only thermodynamic difference between light
and heavy water is the entropy change per molecule

$$\Delta s = -\left( \frac{\partial \Delta f}{\partial T} \right)_v = (3 \ln 2) k_B.$$ \hspace{1cm} (11)

Eq.(11) in no way changes the pressure equation of state
$P(v, T)$,

$$\Delta P = -\left( \frac{\partial \Delta f}{\partial v} \right)_T = 0,$$ \hspace{1cm} (12)

so that the theorem in Sec.II holds true. On the other
hand, the difference between light water and heavy water is measurable in the laboratory. The question then arises
as to which presumptions of the theory are incorrect.

III. MORE DETAILED INTERACTIONS

In order to consider quantum electrodynamic interactions,
one may include the vector potential in the Coulomb gauge,

$$A(r) = \nabla \times A(r) \text{ and } div A(r) = 0.$$ \hspace{1cm} (13)

Eq.(11) must be replaced by

$$H = K + V + H_{\text{rad}},$$

$$K = \sum_a \left( \frac{p_a^2}{2M_a} \right)^2 + \sum_j \left( \frac{p_j + (e/c)A(r_j)}{2m} \right)^2,$$

$$V = e^2 \left\{ \sum_{a<b} \frac{z_a z_b}{R_{ab}} + \sum_{i<j} \frac{1}{r_{ij}} - \sum_{aj} \frac{z_a}{\mid r_j - R_{a} \mid} \right\},$$

$$H_{\text{rad}} = \frac{1}{8\pi} \int (E(\mathbf{r})^2 + B(\mathbf{r})^2) d^3 \mathbf{r},$$ \hspace{1cm} (14)

wherein the transverse field equal time commutation relations read

$$\frac{i}{\hbar c} [A_k(r), E_l(r')] = 4\pi \Delta_\delta (r-r'),$$

$$\Delta(r) = \int \left( 1 - \frac{kk}{k^2} \right) e^{ikr} \left( \frac{d^3k}{(2\pi)^3} \right).$$ \hspace{1cm} (15)

The hydrogen nuclear velocity $V$ is now given by

$$M V = P - \frac{e}{c} A(R),$$ \hspace{1cm} (16)

yielding a mean kinetic energy

$$\frac{1}{2} M \langle V^2 \rangle \geq \frac{3}{2} k_BT,$$

$$-M \left( \frac{\partial F}{\partial M} \right)_{V,N,T} \geq \frac{3}{2} N k_BT.$$ \hspace{1cm} (17)

In Eq.(17) for the hydrogen nuclear kinetic energy, equality
holds true when the hydrogen nuclear motions are
classical and the inequality holds true when the hydrogen
nuclear motions are quantum mechanical. The inequality
in Eq.(17) is proved in Appendix A.
Only in the classical case will heavy water have the same pressure equation of state \( P(v, T) \) as light water. It is experimentally
\[ \text{clearly the case that the phase diagram for heavy water differs from that of light water providing strong evidence for quantum mechanical hydrogen nuclear motions.} \]

IV. CONCLUSIONS

For quantum electrodynamics general theoretical models of water we have shown that the notion of classically moving Hydrogen nuclei is in conflict with the experimental differences in the thermodynamic phase diagrams of light and heavy water. This conclusion is in physical agreement with recent results based on deep inelastic neutron scattering[4] and on neutron and X-ray scattering[5]. The central point is that for a typical motion frequency \( \Omega \), as given in Eq. (A3) below, a necessary condition for classical motion is that
\[
\beta \Omega \equiv \frac{\hbar \Omega}{k_BT} \ll 1 \quad \text{(Classical Motion)} \quad (18)
\]
which fails by a large margin for proton and/or deuterium motion in water.

In more quantitative detail, suppose one defines a proton quantum noise temperature \( \tilde{T} \) in terms of the mean proton kinetic energy
\[
\frac{1}{2} M \langle |\mathbf{V}|^2 \rangle = \frac{3}{2} k_B \tilde{T}. \quad (19)
\]
In general, \( \tilde{T} > T \) as proved in Appendix A. If the quantum noise temperature is equal (to a sufficient degree of accuracy) to the thermal temperature, \( \tilde{T} \approx T \), then the proton motion may be presumed to be classical. The experimental number[2, 3] for light water in the neighborhood of room temperature is
\[
\tilde{T} \approx 3.7 \ T \quad \text{at} \quad T \approx 300 \ ^\circ \text{K}. \quad (20)
\]
Thus, the quantum noise in the proton velocity dominates the purely classical thermal fluctuations in the proton velocity for normal laboratory water samples. The large quantum mechanical contribution to the mean kinetic energy is due to the quantum uncertainty principle localization of the proton.

Appendix A: Inequalities

The mobility of a hydrogen nucleus may be expressed via the Kubo formula[8] as
\[
\mu(\zeta) = \frac{1}{3\hbar} \int_0^\beta d\lambda \int_0^\infty dt \, e^{i\lambda t} \langle \mathbf{V}(-i\lambda) \cdot \mathbf{V}(t) \rangle, \quad (A1)
\]
wherein
\[
\mathbf{V} \equiv \mathbf{\dot{R}} = \frac{i}{\hbar} [\mathcal{H}, \mathbf{R}], \quad \beta = \frac{\hbar}{k_BT} \quad \text{and} \quad 3m \zeta > 0. \quad (A2)
\]
The mobility obeys the sum rules
\[
2M \pi \int_0^{\infty} \operatorname{Re} \{\mu(\omega + i0^+)\} d\omega = 1,
\]
\[
2M \pi \int_0^{\infty} \omega^2 \operatorname{Re} \{\mu(\omega + i0^+)\} d\omega = \Omega^2 \equiv 4\pi ne^2/3M,
\]
\[
\Omega = \left\langle \sum_j \delta(\mathbf{R} - \mathbf{r}_j) \right\rangle. \quad (A3)
\]
The self diffusion coefficient obeys the Einstein relations
\[
D_{\text{self}} = \frac{1}{k_BT} \lim_{\omega \to 0} \operatorname{Re} \{\mu(\omega + i0^+)\},
\]
\[
D_{\text{self}} = \lim_{t \to \infty} \left\langle \left( \mathbf{R}(t) - \mathbf{R}(0) \right)^2 \right\rangle / (6t). \quad (A4)
\]
The fluctuation-response theorem[8] implies a rigorous expression for the kinetic energy of the hydrogen nucleus
\[
\frac{1}{2} M \langle |\mathbf{V}|^2 \rangle = \frac{3}{2} \left\{ \frac{2M}{\pi} \int_0^{\infty} E_T(\omega) \operatorname{Re} \{\mu(\omega + i0^+)\} d\omega \right\},
\]
\[
E_T(\omega) = \left( n(\omega) + \frac{1}{2} \right) \hbar \omega ,
\]
\[
E_T(\omega) = \left( \frac{\hbar \omega}{\frac{2}{k_BT}} \right) \coth \left( \frac{\hbar \omega}{2k_BT} \right). \quad (A5)
\]
wherein \( E_T(\omega) \) is the mean energy of a thermal oscillor of frequency \( \omega \). The inequality
\[
E_T(\omega) \geq k_BT \quad (A6)
\]
together with Eqs. (A3) and (A5) imply
\[
\frac{1}{2} M \langle |\mathbf{V}|^2 \rangle \equiv \frac{3}{2} k_BT \tilde{T} , \quad \tilde{T} \geq T. \quad (A7)
\]
For a particle obeying classical mechanics to a sufficient degree of accuracy, equality \( \tilde{T} = T \) in Eq. (A7) holds true. For a particle obeying quantum mechanics, the quantum fluctuations yield kinetic energies over and above the classical thermal value \( \tilde{T} > T \).
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