A QFT Water Model for Surface Nanobubbles

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Basic Facts

1. Surface Nanobubbles have diameters in the range 25 to 1000nm
2. They are stable
3. Their stability is not changed by surfactants
4. Their surface shapes are irregular [1]
Problems

1. Difficult to understand stability
2. Difficult to understand why they are formed
3. Difficult to understand surface distortions
4. Different theories proposed with different set of assumptions [2][4][3][5]
QFT Model: Ideas 1

A Quantum Field Theory (QFT) based Water Model predicts that water has two phases. One of which is a spontaneously created coherent domain (CD). [6]. We can explain the properties of nanobubbles by assuming that these CD, with their volume fixed by the excitation spectrum of water, forms the boundary of surface nanobubbles. We sketch the basic idea.

1. Quantum Mechanics tells us that a classical oscillator of frequency $\omega$ has zero point energy $\frac{1}{2} \hbar \omega$.

2. A free electromagnetic field $E(x, t)$ can be expanded as a Fourier transform as a collection of classical oscillators with frequencies ranging between 0 and $\infty$.

3. The em field then must have zero point energy $E = \int d\nu \frac{E \cdot E}{8\pi} = \int d\omega \rho(\omega) \hbar \omega$, where $\rho(\omega)$ is the density.

4. But $E = \partial_t A$ where $A$ is the vector potential. Thus the vector potential is always present, has long range, is time dependence and interacts with currents.
QFT Model Ideas 2

1. The presence of the radiation vector potential is well known to lead to physically observed effects. It gives rise to the Casimir Effect [11] and explains the Lamb shift [10][12] in the spectrum of hydrogen.

2. The effect of this fluctuating radiation field is very small. It can cause atomic transitions with a probability of \( \approx 10^{-5} \) and is thus usually ignored.

3. Insight of Preparata and collaborators was that this need not be true for condensed matter systems.[6]
QFT Model Ideas 3

Let us explain why

1. Start with a Lagrangian $L$ of water molecules, $\Psi(x, t)$ interacting with the radiation part of the electromagnetic field $A(x, t)$ in a volume set by a electronic transition wavelength $\lambda \approx 100$ nm. The key physical point is that there are over $10^7$ molecules present in this volume.

2. Suppose there are $N$ electrons and $N$ photons in the volume set by $\lambda$. In this small region we ignore $x$ dependence and scale all fields by $\sqrt{N}$. This gives $L \rightarrow NL$ and the action $S \rightarrow N \int L$.

3. For large $N (\approx 10^7)$ in volume $10^6$ cubic nm a path integral formulation of the model tells us that the dominant paths for action $NS$ are solutions of the classical Euler Lagrange equations for which $\delta S = 0$. 
QFT Model Ideas 4

The Lagrangian used is (short range force terms ignored):

\[ L = L_{\text{matter}} + L_{\text{em}} \]

where

\[ L_{\text{matter}} = \int \psi^*(\vec{x}, \alpha, t) \frac{\delta}{\delta t} \psi(\vec{x}, \alpha, t) - H_{\text{matter}} \]

\[ H_{\text{matter}} = \int \psi^*(\vec{x}, \alpha, t) H_{\alpha} \psi(\vec{x}, \alpha, t) + H_{\text{rad}}^1 + H_{\text{rad}}^2 + H_{\text{SR}} \]

\[ H_{\text{rad}}^1 = e \int A(\vec{x}, t) \psi^*(\vec{x}, \alpha, t) J(\alpha) \psi(\vec{x}, t) \]

\[ H_{\text{rad}}^2 = e^2 \hbar \int A(\vec{x}, t) \psi^*(\vec{x}, t) \psi(\vec{x}, t) \]

\[ A(\vec{x}, t) = \sum_{\vec{k}} \frac{1}{\sqrt{2\omega_{\vec{k}} V}} [a_{\vec{k}}(t) e^{-i\omega_{\vec{k}} t} e^{i\vec{k} \cdot \vec{x}} + hc] \]

\[ L_{\text{em}} = \sum_{\vec{k}} \left[ -\frac{i}{2} a_{\vec{k}}^*(t) \frac{\delta}{\delta t} a_{\vec{k}}(t) + hc \right] \]
QFT Model Ideas 5

The Euler Lagrange equations obtained from this Lagrangian are non linear. They have the form, after some work, (g is a coupling constant that depends on N and the dipole moment)

\[
\frac{d\psi_1}{dt} = -ig\psi_2A^* \\
\frac{d\psi_2}{dt} = -ig\psi_1A \\
\frac{i}{2} \frac{d^3A}{dt^3} + \frac{d^2A}{dt^2} + i\mu \frac{dA}{dt} + g^2A = 0
\]

The vector potential equation has a run away mode if \( g^2 \geq g_c^2 \). \( g_c \) depends on N, \( \mu \) is a mass term which comes from the \( e^2\hbar A^2 \) term present in the Lagrangian. The runaway solution implies that if we start with \( A \) small it rapidly becomes big and makes \( \psi_i \) big as well. When this happens the frequency of \( A \), orginally set by the transition wavelength and the velocity of light can be shown to become smaller by a factor of \( 10^{-2} \). Hence the oscillating photons and water molecules spontaneously form a coherent optical cavity like domain.[7][6]
Consequences

1. The coherent domains are stable only when surfaces are present. Otherwise they have a lifetime of femtoseconds.[8][9]

2. The coherent domains expell gases from them and do not allow surfactants to enter.

3. The domains form the shell of nanobubbles. As the volume allowed for a coherent domain is known (it is fixed by the allowed photon wavelength $\lambda$), thus the allowed sizes of nanobubbles are fixed by the thickness of the shell that can be stabilised by surface effects.

4. The boundary of the shell is expected to be charged. This possibility has been suggested by a number of people but is a consequence of the QFT Water model.[14][4][15][13]

Thus the model explains the stability, size and basic features of surface nanobubbles. It suggests that water molecules have a tendency to form coherent structures if its higher electronic states can be stablised. Surfaces and biomolecules do this. This talk is based on work in progress. An incomplete set of references are included. An interesting recent paper explains how a single nanobubble
of $H_2$ is created by electrochemical methods and explains its stability using ideas of chemistry. [5]. This case is not the one we discuss.
References


[9] Private communication S. Adhikari

