The QED Electrical Double Layer in Flow Electrification

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Abstract: **Electrification of low conductivity hydrocarbons in metal pipes is generally thought caused by the electrical double layer (EDL) at the liquid-pipe wall interface. But the origin of the charge in the EDL has remained controversial after a half century of research. Whatever the source of ions, the EDL has a history of widespread use in explaining observed anomalous electrical charge in diverse liquid applications. Here the charge in the EDL is proposed to occur in an evacuated nanoscale gap that forms between the liquid and the pipe wall by cavity quantum electrodynamics (QED). Electromagnetic (EM) radiation at vacuum ultraviolet (VUV) frequencies is produced in the gap by a mechanism called cavity QED induced EM radiation, the origin of which is the thermal kT energy of the atoms in the EDL surfaces that at ambient temperature emit infrared (IR) radiation. The gap is treated as a QED cavity having EM resonance at VUV frequencies and beyond, and therefore the lower frequency IR radiation from atoms in the EDL surfaces is suppressed. Suppressed IR radiation is a loss of EM energy that can only be conserved by an equivalent gain in EM energy at the resonant frequency of the gap, and therefore the suppressed IR radiation is spontaneously up-converted to the VUV. In QED induced flow electrification, the VUV photons by photolysis excite liquid molecules to form electrons and charged molecules, the latter forming the streaming current.**

INTRODUCTION

Over a century ago, Helmholtz [1] considered the EDL to consist of a simple charge distribution in the solution, opposite to that on the solid as depicted in Fig. 1(a). In the solution, ions of the opposite sign predominate over ions of same sign, but the latter are not completely excluded from the surface. The Helmholtz model of the EDL behaves like an electrical capacitor, although absent a gap to separate the positive and negative charged capacitor surfaces. Improvements [1] in the Helmholtz model were made by Guoy and Chapman depicted in Fig. 1(b). Like the Helmholtz model, the Guoy-Chapman model of the EDL is absent a physical gap to separate the charges.

Since Helmholtz and Guoy-Chapman, the electrification of low conductivity hydrocarbons in metal pipes has generally been attributed to the EDL at the liquid-pipe wall interface. Early EDL research [2] suggested that impurity ions in the hydrocarbon liquids produced a streaming current proportional to the potential between the bulk and the liquid adjacent the pipe wall, otherwise called the ζ potential. Later the ζ potential was replaced [3] by the convection of the EDL at the liquid-wall interface by an assumed charge density at the pipe wall. But the sources of charge in the EDL have never identified despite a half-century of research.

The most credible EDL source proposed [4] was the physico-chemical production of ions through a wall corrosion reaction, but over a decade the reaction products that would have verified the corrosion process have never been found.

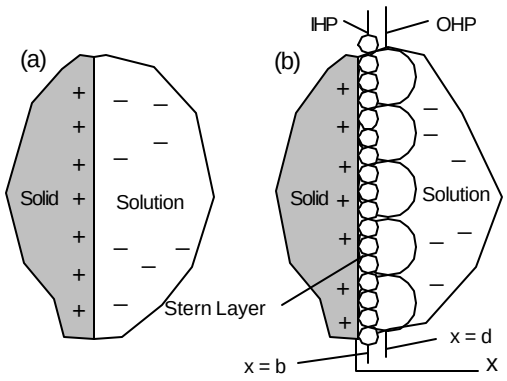

Fig. 1 EDL Models (a) Helmholtz and (b) Guoy-Chapman

Whatever the source of ions, it is axiomatic that the EDL is the source of widespread anomalous electrical charge observed in diverse liquid applications. Here the EDL is proposed charged in an evacuated nanoscale gap that forms between the liquid and the pipe wall. The gap is treated as a QED cavity having an EM resonance at VUV frequencies. The source of charge is the thermal kT energy of the atoms in the EDL surfaces that at ambient temperature emit IR radiation. But in a VUV resonant QED cavity, the lower frequency IR radiation from atoms in the EDL surfaces is suppressed. Suppressed IR radiation is a loss of EM energy that can only be conserved by an equivalent gain in EM energy at the VUV resonant frequency of the gap, and therefore the suppressed IR radiation is spontaneously up-converted to the VUV. In QED induced flow electrification, the VUV photons by photolysis excite liquid molecules to form electrons and charged molecules, the latter forming the streaming current.

Cavity QED induced EM radiation in the EDL is analogous to the frequency up-conversion of suppressed IR radiation to the VUV in the gap between solid surfaces in static electricity [5] and the Casimir effect [6]. Electrons liberated by the photoelectric effect charge the surface in static electricity while the neutral metal plates in the Casimir effect are charged to produce the attractive force.

THEORETICAL BACKGROUND

The cavity QED induced EM radiation model of the EDL differs from the Helmholtz and Guoy-Chapman models in that an evacuated gap δ separates the solid surface from the solution as illustrated in Fig. 2. The VUV photon is shown to penetrate the depths ε_p of the solid surface and solution. For clarity, the many VUV photons standing in the gap are omitted and the gap δ is enlarged.

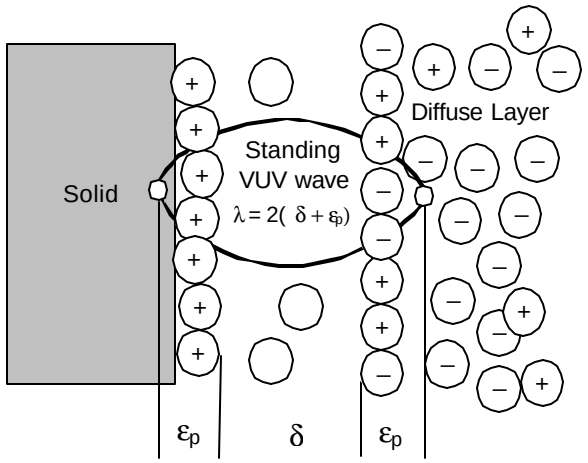

Fig. 2 Cavity QED induced EM radiation - EDL

The VUV photons produce a repulsive force to balance the attractive ES force acting across the gap by the positive charges on the solid and negative charged ions in solution. But not all solution ions in the EDL surface are negative charged. Indeed, a few neutral solvent molecules are allowed to penetrate the otherwise evacuated gap. Positive charged solution ions are repulsed from the positive charged solid and do not need to be compensated by the standing VUV photons.

The source of EM energy that forms the VUV photon is the suppression of IR radiation from the atoms in the surfaces of the EDL as a consequence of the QED confinement in voids or gaps [7] at nanoscale dimensions. For the EDL gap δ, any IR radiation having wavelength λ_{IR}, is suppressed whenever $\lambda_{IR} > \lambda = 2(\delta + 2\varepsilon_p)$. The IR energy U_{IR} suppressed,

$$U_{IR} = 2\frac{A\varepsilon_p}{\Delta^3} N_{dof} \frac{1}{2} kT = 6\frac{A\varepsilon_p}{\Delta^2} kT \qquad (1)$$

where, the factor of 2 accounts for both EDL surfaces, $N_{dof} = 6$ is the number of degrees of freedom of the solvent molecule, A the EDL surface area, Δ the cubical spacing between solvent molecules in the liquid state, k is Boltzmann's constant, and T the absolute temperature.

The thermal kT energy of solution molecules is emitted as EM radiation at IR frequencies depending on temperature T given [8] by the harmonic oscillator. At ambient temperature T = 300 K, the wavelength content is shown in Fig. 3.

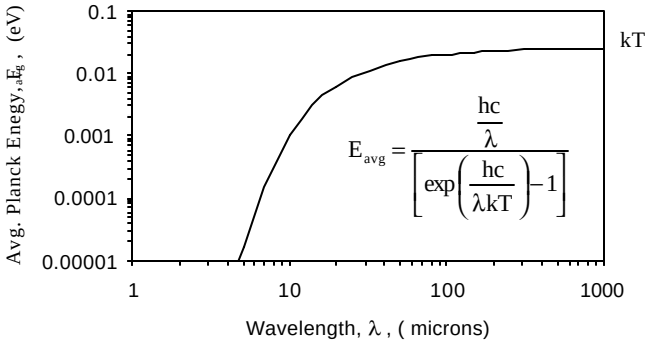

Fig. 3 – Planck Energy of the Harmonic Oscillator at 300 K. In the inset, h is Planck's constant, and c the speed of light.

The Planck energy E_{VUV} of the average VUV photon standing in the penetration depth $\varepsilon_{avg} = \varepsilon_p/2$,

$$E_{VUV} = \frac{hc}{\lambda} = \frac{hc}{2(\delta + 2\varepsilon_{avg})} = \frac{hc}{2(\delta + \varepsilon_p)} \qquad (2)$$

The penetration depth ε_p depends on the absorption coefficient α of the liquid. For the purposes here, water is selected as the representative liquid. The α data [9] is plotted against wavelength in Fig. 4.

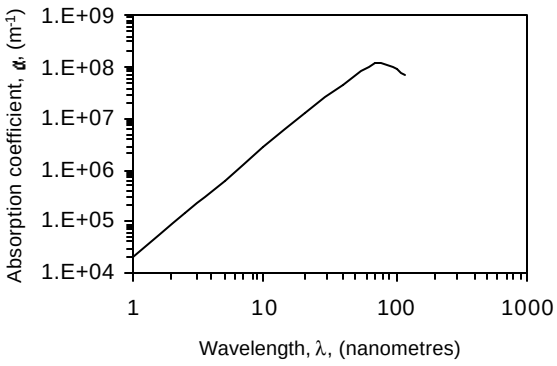

Fig. 4 – Absorption coefficient α for water

The Beer-Lambert law gives the depth ε_p by the absorption coefficient α of the cavity wall at the EM resonant wavelength $\lambda = 4R$ of the QED cavity. The EM radiation intensity I at depth ε_p is related to the intensity I_o at the QED cavity surface by,

$$I / I_o = \exp(-\alpha\varepsilon_p) \quad (3)$$

For $\alpha\varepsilon_p = 5.15$, over 99 % of the surface intensity is absorbed. In this paper, the penetration depth $\varepsilon_p = 5.15 / \alpha$.

Conservation of EM energy gives the surface number density N_{VUV} /A density of VUV photons having Planck energy E_{VUV} standing in the gap.

$$\frac{N_{VUV}}{A} = \frac{U_{IR}}{AE_{VUV}} = 6\frac{\varepsilon_p}{\Delta^3}\left(\frac{kT}{E_{VUV}}\right) = 12kT\frac{\varepsilon_p}{\Delta^3}\left(\frac{\delta+\varepsilon_p}{hc}\right) \quad (4)$$

The Planck energy E_{VUV} and number N_{VUV} of VUV photons are shown in Fig. 5.

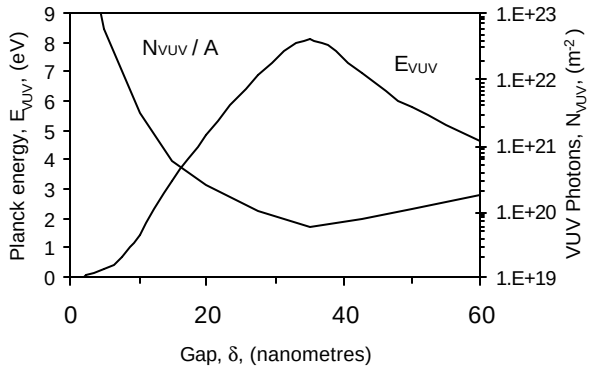

Fig. 5 Planck energy and Number of VUV photons

The QED force of each VUV photon,

$$f_{VUV} = -\frac{\partial E_{VUV}}{\partial\delta} = \frac{hc}{2(\delta+\varepsilon_p)^2} \quad (5)$$

The total QED force developed by all N_{VUV} photons,

$$F_{QED} = f_{VUV}N_{VUV} = 6\frac{kT}{(\delta+\varepsilon_p)}\frac{\varepsilon_p A}{\Delta^3} \quad (6)$$

The ES attractive force f_{ES} between the charges q of each atom in the opposing pair of surfaces,

$$f_{ES} = \frac{q^2}{4\pi\varepsilon_o\delta^2} \quad (7)$$

The total ES force developed by charges q on the lateral atomic spacing Δ between surface atoms,

$$F_{ES} = f_{ES}\frac{A}{\Delta^2} = \frac{q^2 A}{4\pi\varepsilon_o\delta^2\Delta^2} \quad (8)$$

The equilibration of QED and ES forces,

$$q = \delta\sqrt{\frac{24\pi\varepsilon_o\varepsilon_p kT}{(\delta+\varepsilon_p)\Delta}} \quad (9)$$

Typically, Δ ~ 0.3 nm. Fig. 6 shows the unit electron charge q = e corresponds to a gap δ of about 3 nm, the charge q increasing as the gap δ increases.

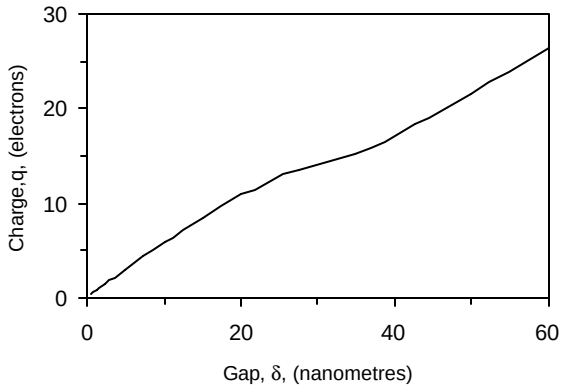

Fig. 6 Equilibrating Charge in EDL gap

APPLICATION

Half of a century ago, EDL theory [2] based on the ζ-potential were proposed to explain flow electrification. In hydrocarbon liquids, ionizing solute impurities treated as weak electrolytes were assumed to dissociate into cations and anions. If the anions adsorb on the wall of the metal pipes, the presence of the ζ-potential forms a diffuse layer of cations that spreads into the liquid, and if so, pipe flow sweeps the cations away to produce the positive charged streaming current. The fundamental problem with the EDL is the same now as it was then – that to produce steady streaming current, the EDL must be continually recharged, or supplied with an external source of cations, the mechanism of which has remained controversial.

Cavity QED induced EM radiation continually recharges the EDL by the photolysis of fluid molecules at the interface of the liquid and the pipe wall depicted in Fig. 1. The density σ of electrons and charged molecules produced by the surface number density N_{VUV} /A of VUV photons is,

$$\sigma = \frac{N_{VUV}}{A}\,Ye \quad (10)$$

where, σ is surface charge density in C/m^2 and Y is the electron yield / VUV photon. For most liquids, $E_{VUV} > 5$ eV and $Y > 10^{-6}$. The charge σ density is illustrated for various yields Y in Fig. 7.

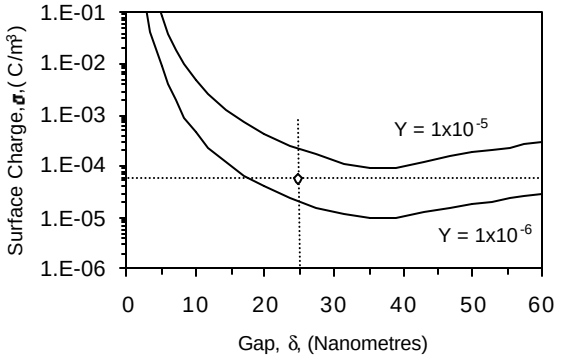

Fig. 7. Surface charge and photolysis yields.

Typically, the streaming current I at flow velocity V (m/s) and volume flow Q rate (m^3/s) are presented [4] as the ratio I/Q (C/m^3) as a function of Reynolds number Re. In straight pipes of length L and diameter d having flow velocity V,

$$\frac{I}{Q} = \frac{\pi d V \sigma}{\pi d^2 V / 4}\left(\frac{d}{V\tau_o}\right) = 4\frac{\sigma}{V\tau_o} \qquad (11)$$

The streaming current I leaks to the pipe wall depending on the relaxation time τ_o of the fluid, i.e., $\tau_o = \varepsilon\varepsilon_o / \kappa$, where ε is permittivity of the fluid and κ is the electrical conductivity. The ratio $d / V\tau_o$ may be understood as the probability of a charged ion leaving the pipe or not leaking to the pipe wall is proportional to the diameter d and inversely proportional to the product $V\tau_o$, where if $V\tau_o > L$, $Vt_o = L$.

In laminar flow at Re = 2000, pipes with length L = 4 m and diameters of 0.24, 0.58, and 1.25 mm were found [4] to have I/Q ratios of $6x10^{-5}$, $2.2 10^{-5}$, and $1x10^{-5}$ C/m^3, respectively. Over a wide range of gaps d from 20 to 60 nm, Fig. 7 shows an average surface charge $\sigma \sim 6x10^{-5}$ C / m^2 at an electron yield $Y \sim 5x10^{-6}$. For $V\tau_o > L$, the corresponding I/Q ratios $6x10^{-5}$, $2.5x10^{-5}$, and $1.1x10^{-5}$ C/m^3 are reasonable estimates of the flow electrification.

DISCUSSION

Prior applications of QED induced flow electrification [10,11] were based on the nucleation of bubbles in cavitation. However, bubble nucleation requires lowering of the flow pressure by eddies that cannot be justified under typical flow conditions, especially if the flow is pressurized. Conversely, cavity QED induced EM radiation allows nanoscale gaps to form at the pipe wall even under high pressure, and therefore enables the flow to electrify more readily than by bubbles. Moreover, the evacuated gap may change during flow conditions. Indeed, intermittent gaps at the pipe wall are likely under turbulent flow conditions. Regardless, QED induced EM radiation produced in the gaps whether steady or intermittent electrify the flow by photolysis.

CONCLUSIONS

In flow electrification, the EDL is continually recharged by the photolysis of liquid molecules by cavity QED induced EM radiation.

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