

Flow Electrification by Photochemical Reaction

Thomas V. Prevenslik

Abstract— The electrification of coolant oil in power transformers is generally thought caused by electrochemical reaction of the oil with the pressboard flow channels. Because measurements of charge products at low levels are difficult, the electrochemical reaction process has yet to be confirmed. In contrast, photochemical processes are clearly evident because the pressboard discolors during operation. This means electromagnetic (EM) radiation having Planck energy beyond the vacuum ultraviolet (VUV) is somehow produced in the flow. The VUV radiation herein is produced in nanoscale gaps in the oil slip-flow at the pressboard surfaces. When the gaps are closed, van der Waals (vdW) bonds form between the oil and the pressboard atoms, but break upon opening. The gaps are treated as quantum electrodynamics (QED) cavities having EM resonances at VUV frequencies, and therefore the lower frequency EM radiation emitted from breaking vdW bonds is suppressed. Suppressed EM radiation is energy loss that in a QED cavity is conserved by an equivalent gain at its resonant frequency, and therefore the suppressed EM radiation is frequency up-converted to produce the necessary VUV radiation that discolors the pressboard while emitting electrons that electrify the flow.

I. INTRODUCTION

Half of a century ago, the electrification in the flow of hydrocarbons through metal pipes received considerable attention [1] because of explosions [2] in the petroleum refining and transportation industry. At that time, the electrical double layer (EDL) was proposed as the mechanism by which cations separate from the anions in the flow. The ions were assumed dispersed in the hydrocarbon, but how they were produced in the flow was not defined. Since then, electrochemical reactions have been proposed to explain the source of electrification in the flow of hydrocarbons [3] [4] in piping and more recently in the flow of oil in power transformers [5].

But there is a problem with electrochemical reactions as the source of ions in flow electrification. Although positive charge streaming currents are generally measured, the charged reaction products have never been found [3] supposedly because of difficulty in detecting the low-levels of charges. Indeed, considerable effort [6] to identify the electrochemical reaction products in the charging of the oil coolant has proved frustrating. Even so, the electrification of transformer oil continues on the basis of electrochemical reactions [3] [4] formulated over a decade ago.

Surface charges [7] from the direct ionization of surface groups and specific ion adsorption are required to initiate electrochemical reactions with the pressboard. But a source of VUV radiation is required to form the ionized groups

and radicals in the coolant oil, e.g., from entrained water to form hydrogen $[H]^+$ and hydroxyl $[OH]^-$ radicals.

Recently, flow electrification in power transformers has been proposed [8] caused by differences in work function between the oil and pressboard. But the difference in work functions between oil and various metals including insulators was shown < 1 eV. Since the Planck energy to ionize common oils [9] requires VUV potentials from 6-10 eV, it is unlikely that differences in work function are the source of charge in flow electrification.

Photochemical processes at VUV levels readily produce cations and electrons from the oil including hydrogen $[H]^+$ and hydroxyl $[OH]^-$ radicals from traces of entrained water. However, the strongest argument for photochemical processes in power transformers is that the pressboard discolors during operation near ambient temperature. Recent effort [10] to provide an experimental basis for the source of flow electrification in power transformers focused on why the pressboards changed color in service.

Further support of photochemical processes is that major constituents of pressboards are wood based cellulose with small quantities of hemicellulose and lignin known [11] to undergo color change under VUV radiation. Indeed, VUV radiation readily produces the singlet state of oxygen known to be a strong oxidant of wood suggesting the color change of pressboard occurred by photochemical reactions.

II. PURPOSE

To show the flow of coolant oil in power transformers is electrified by photochemical reactions, the necessary VUV radiation produced from the breaking of vdW bonds in nanoscale gaps that form in slip-flow at the pressboard surfaces.

III. BACKGROUND

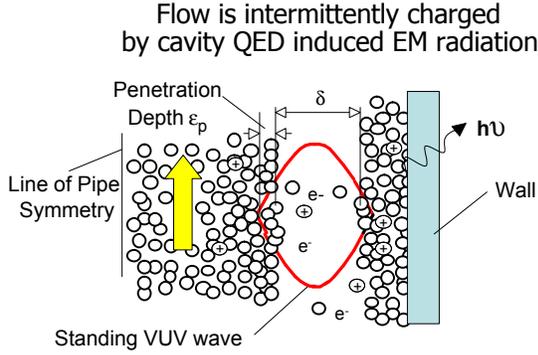
In 2003, flow electrification by QED induced EM radiation relied on the nucleation of nanoscale bubbles [12] to explain charging. But bubble nucleation requires the local pressure to be lowered in eddies by high velocities that is not likely in typical flow systems, especially if the flow is pressurized.

QED induced EM radiation in 2004 was applied [13] to microporous filters. The nucleation of nanoscale bubbles in the inlet to the filter was found to be the source of electrification – not the EDL inside the pores.

In 2005, QED induced EM radiation was applied [14] to a QED double layer comprising a nanoscale gap that forms in slip-flow [15] at solid boundaries. It is important to note the QED double layer, herein called the QED gap, is not the traditional EDL that separates ions by the zeta potential in that the gap, but rather the source of cations and

electrons that electrify the flow. The QED gap is shown in figure 1.

Fig. 1 Flow Electrification Mechanism



EM radiation at VUV levels produced as the QED gaps momentarily open and close depends on the wettability of the flow boundary. For hydrocarbons and oils, QED gaps readily form for oleophobic walls that resist wetting, e.g., plastics, polytetrafluoroethylene (Teflon[®]), and fluorinated graphite. Oleophobic walls are absent the liquid film coating the pipe wall. QED gaps do not readily form on oleophilic surfaces, e.g., metals and mica. Oleophilic surfaces are depicted in figure 1.

The VUV radiation [14] was produced by the suppression of IR radiation from the atoms in the gap surfaces during opening. Since the loss of EM energy from the suppression of IR radiation in a QED cavity may only be conserved by an equivalent gain at its resonant frequency, the suppressed IR radiation was spontaneously frequency up-converted to beyond the VUV. The full thermal kT energy at ambient temperature was assumed suppressed in the calculation of the number of VUV photons on gap opening. Here, k is Boltzmann's constant and T is absolute temperature.

However, the assumption [14] that the full kT energy was suppressed upon gap opening is erroneous. Figure 2 shows the IR radiation from atoms in the surface of the QED cavity given by the harmonic oscillator [16] at temperature $T = 300$ K. Here the wavelength $l = 2d$, where d is the dimension of the QED gap. Indeed, the full kT energy ~ 0.0258 eV is not suppressed on closure unless $l > 100 \mu\text{m}$, i.e., the QED cavity gap d is required to close from gaps $d = l/2 > 50 \mu\text{m}$. But for closed gaps having resonant QED cavity wavelength $l \sim d \sim 0$, the kT energy $\ll 0.00001$ eV, and therefore an insignificant amount of IR radiation is suppressed so that few, if any VUV photons are produced as the gap opens.

Although the closed gap is absent kT energy, the vdW bonds between atoms in the condensed state have EM energy. Usually the kT energy of the atom in the condensed state is conserved with its kinetic energy. But this takes time, and suppressed IR radiation may be more promptly conserved by the atom forming vdW bonds with neighbor atoms. For the purposes here, the suppressed IR radiation from the thermal kT energy is assumed equivalent to the EM radiation from the breaking of vdW bonds.

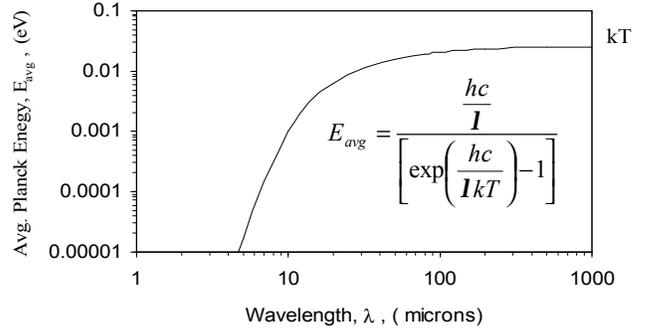


Figure 2 – Planck Energy of the Harmonic Oscillator at 300K. In the inset, h is Planck's constant, and c the speed of light.

Upon gap opening, the EM radiation released as vdW bonds break is QED induced to VUV levels. By the photoelectric effect, the VUV produces cations and electrons in the gap surfaces, the charge difference across the gap giving the vdW attraction an electrostatic origin. Thus, the Planck energy E_{vdW} of the vdW bonds is estimated by equivalence with the Hamaker [17] energy/unit area,

$$\frac{A_{Ham}}{12pd^2} = \frac{1}{d^2} E_{vdW} \quad (1)$$

where, A_{Ham} is the Hamaker coefficient, d is the gap separation, d^{-2} is the number of E_{vdW} photons/unit area standing across the gap. Since $A_{Ham} = n kT$,

$$E_{vdW} = \frac{nkT}{12p} \quad (2)$$

where, $n = 1, 2, \dots, m$, and $m = 100$. Thus, $E_{vdW} \sim kT$ is a reasonable estimate [7] of vdW bond energy.

IV. THEORY

Flow electrification in a circular pipe of diameter D and length L depending on the suppressed vdW bond energy U_{vdW} considers the atoms along the slip-flow line,

$$U_{vdW} = \left(\frac{pD}{D} \right) \left(\frac{L}{D} \right) E_{vdW} = \left(\frac{A}{D^2} \right) E_{vdW} \quad (3)$$

where, $A = pDL$, and D is the cubical spacing between atoms in the hydrocarbon or oil molecules at liquid density, typically $D \sim 0.3$ nm.

The Planck energy E_{VUV} of the VUV photon standing in the gap d ,

$$E_{VUV} = \frac{hc}{l} = \frac{hc}{2(d + 2e_p)} \quad (4)$$

where, the penetration depth e_p depends on the absorption coefficient a of the hydrocarbon or oil. Here, E_{VUV} is treated as an independent variable from 0 to 20 eV.

Conservation of EM energy gives the number N_{VUV}/A of VUV photons having Planck energy E_{VUV} in the gap,

$$\frac{N_{VUV}}{A} = \left(\frac{1}{D^2} \right) \frac{E_{vdW}}{E_{VUV}} \quad (5)$$

For $E_{vdW} \sim kT$, N_{VUV}/A is shown in figure 3.

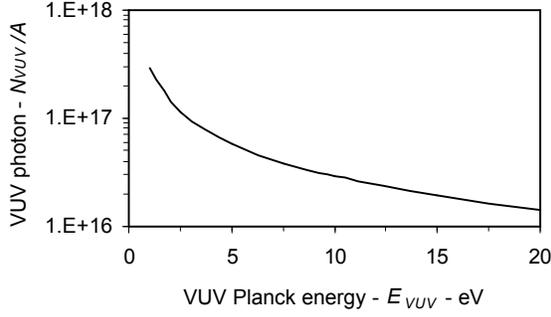


Figure 3 Area Density of VUV Photons

Cavity QED induced EM radiation continually charges the oil coolant flow by the photoelectric effect. Electron loss leaves a cation that until contacting an electrical ground in the piping system forms the streaming current. The surface charge density \mathbf{s} is given by,

$$\mathbf{s} = \frac{N_{VUV}}{A} Y e \quad (6)$$

where, Y is the yield / VUV photon, and $e = 1.6 \times 10^{-19}$ C/electron.

The quantum yield for n-Heptane and transformer oils is not available. Figure 4 shows the yield Y for silicone oil [18] that shows as the vdW bonds break, the QED gaps produce $E_{VUV} \sim 12 - 20$ eV with $Y \sim 0.01$.

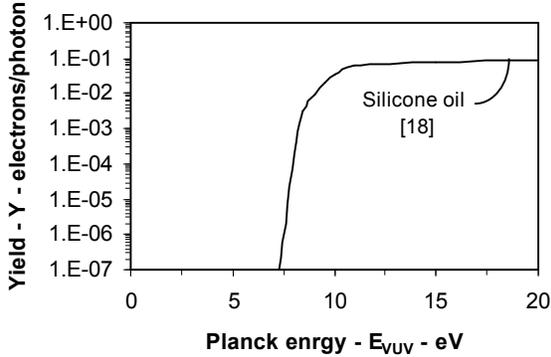


Figure 4 Quantum Yield [18] for Silicone Oil.

For area charge density \mathbf{s} (C/m²) and flow velocity V (m/s), the streaming current I (C/s) and volume flow Q rate (m³/s) are presented [3] as the ratio I/Q (C/m³) as a function of Reynolds number Re . In pipes of diameter D having flow velocity V ,

$$\frac{I}{Q} = \frac{\mathbf{p} D \mathbf{h} V \mathbf{s}}{\mathbf{p} D^2 V / 4} = 4 \frac{\mathbf{h} \mathbf{s}}{D} = \left(\frac{4e}{D D^2} \right) \left(\frac{E_{vdW}}{E_{VUV}} \right) \mathbf{h} Y \quad (7)$$

where, \mathbf{h} is the fraction of the pipe circumference $\mathbf{p} D$ producing charge.

For laminar flow at $Re = 2000$, diameters of 0.24, 0.58, and 1.25 mm were found [3] to have I/Q ratios of 6×10^{-5} , 2.2×10^{-5} , and 1×10^{-5} C/m³, respectively. Figure 5 shows the experimental data for I/Q ratios at various diameters D to be closely fitted by (7) for $\mathbf{h} Y \sim 5 \times 10^{-7}$.

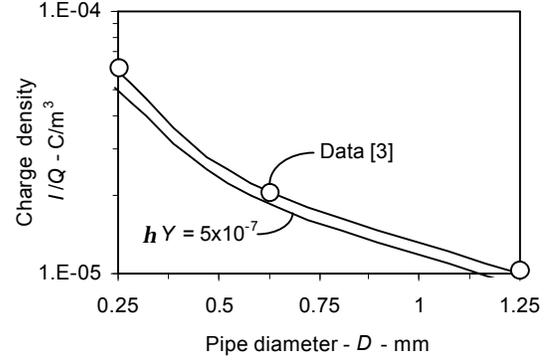


Figure 5 Charge Density for $\mathbf{h} \sim 5 \times 10^{-5}$ and $Y \sim 0.01$

V. DISCUSSION

A. Photochemical Reactions

Evidence for photochemical reactions in the degradation of power transformers has always been present, but absent a credible source of VUV radiation in the oil coolant channels has been dismissed. Indeed, the life of a transformer is thought [19] limited by the degradation of cellulose insulation through electrochemical reactions in the presence of water and oxygen at high temperature. But only photochemical processes may explain the rapid increase of static electrification in controlled injection [20] of oxygen simulating air intrusions during maintenance.

Moreover, accumulated charge in common pressboard [UK1 in Fig. 6d of Ref. 10] does not increase over temperatures from 15 to 80 C. In contrast, VUV radiation at ambient of temperature is sufficient to excite the singlet state of oxygen [11] that readily degrades the pressboard.

Similarly, the acetylene detected [20] after BTA was introduced in the oil was most likely formed by VUV radiation from QED induced photochemical reactions. Further, the pressboard discoloring thought [21] caused by electrical discharges with the possibility of triggering chain reactions is most likely caused by the QED induced VUV irradiation of cellulose.

Photochemical reactions under VUV eject electrons from the coolant oil molecules leaving cations [18] with only partial polarization. But the cations become fully polarized as they drift into the bulk where they produce streaming currents until they discharge at electrical grounds. It follows that chemical analysis of the oil after relaxation would not detect the cations in the products of the photochemical reaction. This is not the case with electrochemical reactions because after relaxation the ions remaining are [7] identifiable. Thus, the lack of ionic products [3] [6] in the oil suggest photochemical reactions are the source of charge in flow electrification.

B. Wettability of Surfaces

Flow electrification by cavity QED induced EM radiation depends on the breaking of vdW bonds in an evacuated gap, at least momentarily at solid boundary surfaces. The analysis here shows that that vdW bonds between n-Heptane and the pipe wall [3] need only break

over $h \sim 5 \times 10^{-5}$ of the pipe circumference pD . For D from 0.25 to 1.25 mm, hpD is 40 to 200 nm, i.e., the width hpD along the pipe length L produces the charging.

The importance of wetting is evidenced in the electrification of insulating oil in power transformers [8] of commercial pressboard. Metals and plastics are oleophilic to oil and accumulate little, if any charge. Teflon[®] having a work function of 6.5 eV is unlikely to produce 10x higher charge than that found for metals and other plastics having work functions from 4-5 eV. Rather, the significant increase in charge occurs because the slip-flow of oil against oleophobic Teflon[®] electrifies the flow more than against oleophilic metals and other plastics.

Similarly, the higher charge found [Figure 5d of Ref.10] in fluorine treated pressboard compared to oxygen treated and untreated pressboard is likely related to oil wetting. Indeed, the $CF_4 - O_2$ plasma treatment of most polymers [22] show wettability increases with surface oxidation and decreases with fluorination consistent with [Figure 6d of Ref. 10].

C. EDL and the QED Gap

In flow electrification of transformer oils, traditional arguments [8] that the charge is produced in the EDL by differences in work function < 1 eV between the oil and the solid boundary must be dismissed because the VUV ionization energies $> 6-10$ eV of the oil or pressboard far exceed the work function differences.

Cavity QED induced EM radiation produces VUV radiation as vdW bonds break in QED gaps that form in slip-flow at solid boundaries. Bubbles are not necessary to produce VUV radiation. Indeed, the intermittent breaking of vdW bonds as the fluid undergoes slip-flow at the solid boundaries is a far easier way of electrifying the flow.

VI. CONCLUSIONS

Historically, the EDL was proposed as the source of charge in flow electrification based on the fact that charge was transferred in contact electrification of solid bodies depending on the difference in work functions. In flow electrification, however, charging does not correlate with work function differences between the coolant oil and solid materials including both metals and insulators. Hence, the EDL has nothing to do with flow electrification.

Moreover, the EDL is limited by the zeta function to thermal kT energy of ~ 0.0258 eV, and therefore cannot provide the 6-10 eV Planck energy to produce the surface charge necessary for electrochemical reactions to proceed by direct ionization and adsorption. Thus, electrochemical reactions cannot be the source of flow electrification.

In contrast, the discoloring of pressboard at temperatures near ambient is proof positive that photochemical reactions are occurring in the flow of oil coolant, the reactions producing a positive streaming current of cations with the companion electrons providing the negative charge. Unlike electrochemical reactions based on both cations and anions, photochemical reactions form cations and electrons that after relaxation are indistinguishable from bulk transformer oil, and in this way may explain why charged ions have never been found in flow electrification experiments.

In summary, flow electrification is caused by photochemical reactions induced by VUV radiation from the breaking of vdW bonds in nanoscale gaps that intermittently open and close under slip-flow at flow boundaries, the VUV radiation produced by cavity QED induced EM radiation.

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