Flow electrification by cavity QED

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Abstract

Over the past 50 years, the electrification of hydrocarbon liquids and oils flowing in metal pipes has been studied extensively. Today, the mechanism by which the charges are produced is thought caused by corrosion of the pipe surface, the corrosion producing a flow of electrons from the oxidation of the metal, the electron flow balanced by streaming currents in the liquid along the pipe length. But the lack of corrosion products to confirm the electrochemical process in combination with the proportionality of streaming current to surface shear stress suggests that other flow electrification mechanisms may be at play, specifically electromagnetic (EM) mechanisms. To this end, a cavity quantum electrodynamic (QED) induced photoelectric effect mechanism is proposed. But air bubbles are precluded as QED cavities because surface tension and system pressures collapse the bubbles to dissolve the air in the oil as individual or clusters of nitrogen and oxygen molecules. Rather, the QED cavities are formed in the process of tearing of the oil from itself or the pipe wall, the process described as one of rupture, the QED cavities comprising oil clusters in microscopic vacuum spaces. Tearing occurs as the tensile stress at a point in the flow of high shear stress exceeds a critical stress dependent on the oil and the amount of air entrained in the oil. At ambient temperature, every molecule in the oil clusters usually radiates low frequency infrared (IR) energy of magnitude 6 x $\frac{1}{2}$ kT, where k is Boltzmann's constant and T is absolute temperature. But during tearing while the QED cavities still sufficiently small and have high EM resonant frequencies, the low frequency IR radiation from the oil clusters is momentarily suppressed. To conserve energy, the suppressed IR energy is promptly released as coherent multi-IR photons that combine to vacuum ultraviolet (VUV) levels at the surfaces of the QED cavity. Flow electrification occurs as the VUV light liberates electrons by the photoelectric effect. Whether the oil or pipe wall loses electrons depends on the respective optical bandgaps, but usually the oil loses electrons and acquires a positive charge, the metal pipe gaining electrons acquiring a negative charge.

Keywords: laminar flow, bubbles, charge, electrification, inhibited cavity QED

1. Introduction

Over 50 years ago, the electrification of flowing insulating liquids was thought [1] caused by impurity ions, the streaming current directly proportional to the ζ - potential between the bulk and the liquid adjacent to the wall. In the 1980's, the electrification mechanism was found [2] to depend on the charge density of impurity ions at the wall interface as characterized by the convection of the equilibrium double-layer of these ions at the wall liquid interface. Instead of the ζ - potential, the streaming current was quantified [3] by the charge density at the wall, but the source of the charge was not identified.

Recently, a physicochemical explanation [4,5] was proposed for flow electrification, the source of charge being the electrons produced by the corrosive oxidation of the metal by chemical reaction, the corrosion producing a flow of electrons balanced by streaming currents in the liquid along the pipe length. However, corrosion products in the liquid that would confirm the corrosion process as the source of flow electrification have not been found. That corrosion may not be the source of flow electrification is further evidenced by recent experiments [6,7] in flow against pressboard walls that shows the streaming currents are proportional to the wall shearing stress.

In the search for the mechanism underlying flow electrification, it is instructive to briefly review contact electrification mechanisms, the latter also having avoided detection despite extensive study.

1.1 Review of contact electrification

Electrons in metals occupy all states up to the Fermi level. Upon contact of dissimilar metals, electrons move across the interface until thermodynamic equilibrium is reached where the contact potential balances the difference in Fermi levels. In the contact of insulators by metals, electrons also move from the metal to the insulator but only if the Fermi level of the metal is higher than the conduction band of the insulator. However, there is a problem. Thermodynamic equilibrium requires only one contact for the Fermi levels to equilibrate and is independent of the type of materials in contact. But experiments show that thermodynamic equilibrium is reached in a single contact only for metals - many contacts are necessary to achieve equilibrium between metals and insulators. This means a mechanism in addition to the balancing of Fermi levels is at play in contact electrification.

Recently, the Two-step model [8] was proposed for contact electrification, the model asserting charge accumulation occurs by the combined sequence of contact and separation, the electron energy levels raised by a jacking operation during separation. But the mechanism by which the electrons are raised to higher energy states during separation was not identified. To this end, a cavity QED induced photoelectric mechanism [9] was proposed. The photoelectric process relies on the interface as a high frequency QED cavity to inhibit low frequency EM radiation corresponding to thermal kT energy inherent in atomic clusters, the clusters forming in the interface during separation. The inhibited EM energy concentrates as Planck energy in the surfaces of the metal and insulator, and if the Planck energy reaches VUV levels, electrons are produced by the photoelectric effect. The Two-step model for a solid metal and insulator is illustrated in Fig. 1.



Fig. 1 Contact electrification - Solid metal and insulator. Two-step model including cavity QED induced photoelectric effect

Solid insulators in repetitive contact with solid metals break down to form a layer of fine powder that may be described by a composite of atomic and molecular clusters. Each atom in the clusters has $3 \times \frac{1}{2} kT$ of low frequency EM energy. During separation, the EM radiation from atoms in the suspended powder is inhibited because the interface between metal and insulator is briefly a high frequency QED cavity. The EM radiation inhibited from the interface is compensated by the absorption of Planck energy by the metal and insulator surfaces, the photoelectric effect of which occurring in the VUV, thereby givng a high quantum yield of electrons. Metals acquire a positive charge upon electron loss while the insulator is charged negative upon electron gain. Subsequent contact transfers free electrons to the solid insulator.

1.2 Purpose

The purpose of this paper is to extend the cavity QED induced photoelectric mechanism in the Two-step model of contact electrification to flow electrification.

2. Theoretical background

2.1 Piping system and laminar flow

The cavity QED induced photoelectric process requires the formation of microscopic spaces during laminar pipe flow of hydraulic oil, but laminar oil flow is usually considered absent of microscopic spaces. Bubbles are known to be present in flowing liquids and on that basis the spaces necessary to complement the cavity QED effect may at least initially thought to be caused by bubbles. Both vaporous or air bubbles are present in hydraulic systems. Vaporous bubbles nucleate as the pressure P in the system is lowered below the vapor pressure P_{vap} of the fluid, $P < P_{vap}$. Air bubbles nucleate from air that enters the system. If the air is dissolved at pressure P_{air} , bubbles are thought to nucleate in the system where the pressure is lower than the pressure at which the air was dissolved, $P < P_{air}$. Of interest is the piping system [5] comprising a straight piece of pipe shown in Fig. 2.



Fig. 2. Flow electrification - (a) Piping system (b) Pipe nomenclature

The piping system is shown in Fig. 2(a). A horizontal pipe discharges fluid to the atmosphere and falls into a receiving tank. Pumping the fluid back to the pipe entrance closes the loop. Air enters the piping system through the open receiving tank, and even if the receiving tank is sealed the air may readily enter the system through the pump. Entrained air in hydraulic systems leads to cavitation [10,11] and is usually removed with de-foaming agents. Fig. 2(b) shows the pump supplying the pipe with fluid at pressure P_S , the highest pressure in the system. The flow velocity increases in the vena contracta at the pipe entrance at point A with a lowering of the pressure, $P_A < P_S$. The flow is laminar over the pipe length *L* from point A to the exhaust at point B, the pressure *P* dropping linearly from P_A to P_B . From point B, the fluid exhausts to the atmosphere at pressure P_{atm} , the lowest pressure in the system. In the laminar flow region, a circular pipe of radius R develops a parabolic velocity, the velocity V_x at position x from the exit a function of radius r is,

$$V_x = 2V_M \left(1 - \frac{r^2}{R^2} \right) \tag{1}$$

where, V_M is the average axial velocity. The frictional stress τ between the liquid and wall surface depends on the viscosity μ of the liquid,

$$\tau = \mu \frac{dV}{dr} = -4\mu \frac{V_M}{R} \tag{2}$$

As the pipe radius vanishes, the frictional stress τ rapidly increases and the supply pressure P_s increases to maintain the flow. At *x*, the pressure P_x ,

$$P_x = P_{atm} + 8\mu V_M \frac{x}{R^2} = 4\frac{\mu^2 x}{\rho R^3} \text{Re}$$
 (3)

where, Re is the Reynold's number, Re = $2\rho V_M R/\mu$. In terms of the flow Q,

$$Q = AV_{M} = \frac{\left(P_{x} - P_{atm}\right)}{x} \left(\frac{\pi R^{4}}{8\mu}\right)$$
(4)

and is more commonly known as the Poiseuille equation.

2.2 Air clusters in flowing hydrocarbon liquids

If bubbles as QED cavities are the source of flow electrification, the pressure P_x in the piping system must be lowered to nucleate vaporous or air bubbles, i.e., $P_x < P_{vap}$ or $P_x < P_{air}$. But hydrocarbon liquids and oils have very low vapor pressure, the vapor pressure [10] of heptane at ambient temperature $P_{vap} \sim 45$ mbar. Since the lowest system pressure is P_{atm} , and since $P_{vap} << P_{atm}$, the nucleation of air bubbles is far more likely than vaporous bubbles. The solubility of air in petroleum based fuels [10] is characterized by the Ostwald coefficient defined as the ratio of the volume of air dissolved to the volume of fluid. Data on heptane is not available, but hydraulic systems are known [11] to absorb significant amounts of air, reaching ~ 10 % by volume at atmospheric pressure and temperature. On this basis, a large amount of air may be considered entrained in hydrocarbon fluids including heptane, but how the air is dispersed throughout the system depends on surface tension.

Indeed, surface tension tends to produce air clusters rather than bubbles. Hereinafter, air clusters are understood to be clusters of nitrogen and oxygen molecules, the molecules clustering on the scale of nanometers. In contrast, the scale of bubbles may vary from a few microns to those visible of millimeter size, surface tension prohibiting the formation of bubbles less than a radius R_0 ,

$$R_0 = \frac{2S}{P_{ST}} \tag{5}$$

where, *S* is the surface tension and P_{ST} is the surface tension pressure. In heptane having $S \sim 0.02$ Nt/m [10] at atmospheric pressure with $P_{ST} = P_{atm}$, the smallest bubble has a radius $R_0 \sim 0.4 \,\mu\text{m}$. Not only are bubbles having a radius $R < R_0$ not found in hydraulic systems, but bubbles having a radius $R > R_0$ are also not found, the latter because the bubble under pressure is unstable. If the air bubble is subjected to higher pressures in the piping system, say at the pump, the higher system

pressure in combination with surface tension pressure always collapses the bubble and dissolves the air into the oil. Air bubbles as such do not exist in hydrocarbon liquids and oils. Nevertheless, the air is still dissolved in the oil as individual or nano-scale clusters of air molecules homogeneously dispersed throughout the system. But air clusters as QED spaces not only are not evacuated, but are too small to be QED cavities - a mechanism other than vaporous or air bubbles is required to produce micron sized evacuated spaces.

2.3 Tearing of hydraulic liquids during flow and QED cavities

Traditionally, it is generally accepted that evacuated spaces form in flowing liquids [12] by the presence of microscopic bubble nuclei that grow very rapidly if exposed to low-pressure regions in the system. However, recent studies [13] with oil placed in tension by pulling on an acrylic hydraulic cylinder show that bubbles do not grow from the microscopic nuclei that are usually assumed to be present, but rather the oil column suddenly ruptures or tears. On this basis, the oil column at least until rupture may be viewed as a continuum solid with rupture defined by the state of tensile stress in the liquid, rather than by hydrostatic tension alone. Consistent with QED cavities, the spaces may be considered evacuated as the rapidity of the rupture process precludes the diffusion of air or oil vapor which occur on far longer time scales.

Recently, a theory of cavitation for liquids in motion was proposed [14] based on the maximum tensile stress. If QED cavities are crucial in flow electrification, a tension stress theory that permits evacuated cavities to form in laminar flow [2-7,13] is important. In laminar pipe flow, viscous shearing stresses act on the pipe surface in the direction of flow. Hence, the liquid may be expected to rupture in tension during laminar flow, as the maximum tensile stress in the liquid under pure shear occurs at 45° to the wall surface. Indeed, flow tests [6] show electrification in flow against pressboard walls to be proportional to shear stress.

Tearing occurs upon oil rupture, the oil rupture taking place by the maximum tension theory as the nominal tensile stress is raised above a limiting stress because of the stress concentration produced by the air clusters, the limiting stress depending on the oil and entrained air content. On this basis, the Tearing Hypothesis [13] was formulated and may be described by the separation of oil from itself or walls of the flow boundary leaving an evacuated space, the tearing process also producing oil clusters within the evacuated spaces. Typical laminar pipe flow having microscopic QED cavities adjacent the pipe wall and in the flow stream is illustrated in Fig. 3.



Fig. 3 Laminar pipe flow with QED cavities as evacuated spaces and oil clusters

In this paper, the evacuated spaces are treated as QED cavities, the oil clusters providing the thermal kT energy necessary to produce the light and electron emission by the cavity QED induced photoelectric effect.

2.4 Source of EM energy

In the cavity QED induced photoelectric effect, the source of EM energy is the thermal kT energy of the oil molecules in the clusters that form from the surfaces of the QED cavities. The EM source may be quantified by the energy density Ψ of the liquid molecules contained in the cluster. For a spherical oil cluster of radius R_0 , the EM energy U_{EM} is,

$$U_{EM} = \frac{4\pi}{3} R_0^3 \Psi$$
 (6)

where, the EM energy density is, $\Psi \sim N_{dof} \times \frac{1}{2} kT / \Delta^3$. N_{dof} is the number of degrees of freedom of the oil molecule, and Δ is the spacing between oil molecules at liquid density, $\Delta \sim 0.3$ nm.

The thermal kT energy of the oil molecule as a harmonic oscillator at ambient temperature T is emitted as IR radiation as shown in Fig. 4. The Planck energy E is observed to saturate at 0.025 eV at a wavelength λ of about 100 µm. Of interest to the suppression of IR energy is that most of the Planck energy is contained at $\lambda > 20$ µm. Since a spherical cavity of radius R has a resonant EM wavelength $\lambda \sim 4R$, most of the IR radiation from an oil cluster in a spherical QED cavity having a radius $R \sim 5$ µm is momentarily suppressed. To conserve EM energy, the suppressed IR radiation is promptly emitted as coherent multi-IR photons that combine on adjacent oil and wall surfaces to VUV levels, the electrons produced by the photoelectric effect, thereby producing the cavity QED induced photoelectric effect.



Fig. 4 Planck energy and wavelength Average harmonic oscillator at ambient temperature

2.5 IR to VUV conversion

The momentary suppression of IR radiation from molecules within the oil clusters formed by surface tension is a loss of EM energy that is conserved by a gain in EM energy in the surrounding space. The EM energy release is in the form of multi-IR photons that collectively combine to VUV levels. Fig. 5 shows a oil cluster of radius R_0 in an evacuated space between the flow and the

wall. The EM radiation having Planck energy E is shown to illuminate both the wall and oil. The optical band-gap of the oil is assumed lower than that of the pipe, and therefore the oil is depicted to lose electrons and acquire positive charge while the pipe gains electrons and acquires negative charge. VIS photons are shown to be emitted from the air clusters in the oil, the blue color observed [13] most likely that of nitrogen.



Fig. 5 Oil Cluster adjacent pipe wall

The Planck energy *E* at a distance *R* from the center of the cluster over the adjacent oil or wall surfaces comprised of molecules of dimension Δ is,

$$E = \frac{U_{EM}}{4\pi \left(\frac{R}{\Delta}\right)^2} = \frac{1}{6} N_{dof} \left(\frac{R_0}{R}\right)^2 \left(\frac{R_0}{\Delta}\right) kT$$
(7)

2.6 Photoelectric effect

In the cavity QED induced photoelectric effect, the number N_e of electrons produced depends on the number N_p of photons and the photoelectric yield γ_P of electrons per photon,

$$N_e = N_p \gamma_P \tag{8}$$

Since the released EM radiation is coherent and comprised of multi-IR photons, the number N_p of VUV photons having Planck energy E_{VUV} may be written,

$$N_{p} = \frac{U_{EM}}{E_{VUV}} = \frac{2\pi}{3} N_{dof} \left(\frac{R_{0}}{\Delta}\right)^{3} \left(\frac{kT}{E_{VUV}}\right)$$
(9)

Most metals in the visible and ultraviolet [15] have low electron yields ($\gamma_p < 10^{-3}$) while reasonable yields ($\gamma_p < 10^{-1}$) are only obtained at VUV frequencies. Similarly, photoconductivity studies of dielectric liquids [16] are normally performed with VUV photons as the valence and conduction bands are usually separated by about 5-6 eV. Fig. 6 shows the number N_e of electron charges produced by a single oil cluster with the multi-IR photons combining to a Planck energy $E_{VUV} \sim 4.9$ eV. The radius R_0 is limited to 5 µm because if the evacuated space of thickness *D* is treated as a 1D QED cavity, the EM resonant wavelength is, $\lambda \sim 2D$. To suppress most of the EM energy, Fig. 4 shows $\lambda < 20$ µm, and therefore D < 10 µm, i.e., the largest oil cluster that can fit in the 1D cavity has a radius $R_0 < 5$ µm.



Fig. 6 Flow electrification - Electronic charge and oil cluster radius

2.7 Comparison with data

At atmospheric pressure, a typical oil cluster in heptane formed by surface tension has a radius $R_0 \sim 0.4 \,\mu\text{m}$ giving a charge of about 24 pC at unity electron yield as shown in Fig. 6. The data [5] for the 0.24, 0.58, and 1.25 mm pipes shows the flow Q at a Re number of 2000 as 4.24, 10.25, and 22.1x10⁻⁷ m³/s and streaming currents I of 3.1, 2.7, and 2.2x10⁻¹¹A. The respective I / Q are 7.3, 2.6, and 1 x10⁻⁵C m⁻³. Hence, the oil cluster number N_{OC} densities in the respective pipes are 3, 1.1, and 0.4x10⁶ m⁻³, although more clusters are required at lower electron yields.

Perhaps of more relevance is a comparison of the amount of charge in oil clusters in flow electrification with common experience. For example, the charge collected by a person per step by walking across a carpet [17] is about 30 nC, and would be comparable to the charge on a single oil cluster in heptane having a radius of $R_0 \sim 4 \mu m$ and a unity electron yield.

3. Flow Analysis

In the QED induced photoelectric effect, electrons and positive charge molecules are produced from the oil on a volumetric basis depending on the number N_{OC} of oil clusters in microscopic cavities. The electrons migrate to the pipe wall; whereas, the charged molecules move at the fluid velocity V_M to form the streaming current *I*. Consider the pipe cross-section at a distance *x* upstream from the exit in Fig. 2. Flow electrification experiments [18] show for a given pipe radius *R* the streaming current *I* is proportional to the product of pipe length *x* and Re number. Equivalently by the Poiseuille equation, Eqn. 4, the proportionality may be also written as the products of flow *Q* and pipe length *x*, or the pipe area *A* and the pressure ($P_x - P_{atm}$) difference,

$$I \propto \frac{4\mu^2}{R^3} (\operatorname{Re} x) = 8\mu \left(\frac{Qx}{R^2}\right) = A(P_x - P_{atm})$$
(10)

The streaming currents *I* in pipe flow find analogy with the flow of electrical current in an conductor. For a given length *x* of the pipe or conductor, the pipe area *A* is analogous to the conductor area and the pressure difference ($P_x - P_{atm}$) analogous to the voltage ($V_x - V_0$) difference. If flow electrification is a volume effect, the term $N_e Q$ replaces the flow *Q*, where N_e is the electron density. But the number of electrons is proportional to the number N_{OC} of oil clusters, $N_e \propto N_{OC}$. Since N_{OC} is inversely proportional to P_x , $N_{OC} \propto P_x^{-1}$. Hence,

$$I \propto A \left(P_x - P_{atm} \right) \propto N_e Q \left(\frac{x}{R^2} \right) \propto N_{oC} Y \left(\frac{Qx}{R^2} \right) \propto \frac{1}{P_x} \left(\frac{Qx}{R^2} \right)$$
(11)

or,

$$I \propto \frac{\left(\frac{x \operatorname{Re}}{R}\right)}{P_{atm} + 4 \frac{\mu^2 x}{\rho R^3} \operatorname{Re}}$$
(12)

and the volume current density I / Q,

$$\frac{I}{Q} \propto \frac{\frac{x}{R^2}}{P_{atm} + 4\frac{\mu^2 x}{\rho R^3} \text{Re}}$$
(13)

Flow electrification data [5] in terms of the volumetric current density I / Q is illustrated in Appendix A, Fig. A-1(a). The 0.24 mm pipe gives a variable response that decreases with Re, while the 0.58 and 1.25 mm pipe response remain constant with Re. Fig. 7(a) shows the I / Q relation given by Eqn. 14 to reasonably approximate the data. The I / Q relation was normalized to the zero Reynolds intercepts from Fig. A-1(a). For the 0.24, 0.58, and 1.25 mm pipe, the pipe locations *x* were found to be 0.75, 0.9, and 1.6 m, respectively.



Fig. 7. QED photoelectric effect (a) Charge density I/Q (b) Current I.

The I/Q data [5] transformed to current *I* as a function of Re number is shown in Fig. A-1(b). Fig. 7(b) shows the current *I* - relation in Eqn. 12 to reasonably approximate the data. The *x* pipe locations were obtained by fitting the *I* - relation to the data at Re = 2000. The *x* locations were then used to obtain the I/Q relations shown in Figs. 7(a) and (b). At low Re numbers, Fig. 8 shows the current density I/Q varies inversely with the square of the radius *R* consistent with the data [19]. Exponents less than 2 are indicated at higher Re numbers.



Fig. 8. QED photoelectric effect - I/Q vs. pipe radius

4. Conclusions

The overall conclusions are:

Flow electrification of hydrocarbon liquids is similar to contact electrification of insulators with metals, as both rely on thermal kT energy at ambient temperature to produce IR radiation from clusters of atoms and molecules in microscopic evacuated spaces that is momentarily suppressed by cavity QED. To conserve EM energy, the suppressed IR energy is promptly released as coherent multi-IR photons that combine to the VUV levels necessary for liberating electrons from the surfaces of the QED cavity by the photoelectric effect.

The analytical I and I / Q relations derived are reasonable approximations of flow electrification data for a volume charge relation. An area charge relation does not correlate with the data.

In flow electrification, the conclusions are:

Entrained air in hydrocarbon liquids and hydraulic oils is not likely to exist in the form of microscopic bubbles, but rather as individual or clusters of nitrogen and oxygen molecules. Vapor bubbles are not likely to form because of low vapor pressure.

The QED cavities comprising microscopic evacuated spaces containing oil clusters are formed as the oil ruptures and tears.

Electrons and charged oil molecules are produced from VUV light. But the VUV light may also produce VIS photons, the blue light from the excitation of nitrogen from entrained air in the oil.

Tearing and rupture caused by the tensile stresses at a point in the moving liquid exceeding the stress limit of the liquid oil in the presence of entrained air is consistent with the maximum tension theory of cavitation.

Adding air into the system is expected to increase electrification while de-foaming agents should decrease electrification. However, other impurities in the oil may replace air as the singularity in the liquid by which the tensile stress is raised to the stress limit for rupture.

The proportionality of flow electrification to wall shear stress in flow against pressboard walls is consistent with the maximum tension theory of cavitation and the QED process.

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Appendix A

Flow electrification data

Generally, flow electrification is quantified in terms of the ratio of current *I* to the volume flow rate *Q*, the I/Q ratio having units of C / m³. For heptane flowing in pipes having radii *R* of 0.24, 0.58, and 1.25 mm, the experimental data [5] in terms of the I/Q ratio as a function of Re number is presented in Fig. A-1(a).



Fig. A-1 Flow electrification - Heptane (a) Charge density I/Q (b) Current I

The current *I* in the flow electrification data [5] may be recovered by the transformation,

$$I = (Q)\frac{I}{Q} = (AV_{M})\frac{I}{Q} = \left(\frac{\pi R\mu}{2\rho} \operatorname{Re}\right)\frac{I}{Q}$$
(B.1)

For heptane, $\mu \sim 0.387 \times 10^{-3}$ Pa-s and $\rho \sim 684$ kg/m³. For $L \sim 4$ m, the current *I* as a function of Re is shown in Fig. A-1(b).