Flow Electrification by Nanoparticle Impurities

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Abstract- **Flow electrification in power transformers is shown to occur by photochemical reactions initiated in vacuum ultraviolet (VUV) radiation produced in nanoparticle (NP) impurities by quantum electrodynamics (QED). QED confines the thermal kT energy of the NP atoms to vanishing small levels; whereas, the unconfined coolant oil molecules that collide with the NPs have full kT energy. Even though both NPs and oil molecules are at the same temperature, collisions transfer kT energy to the NPs. But QED also prohibits the NP atoms to increase in kT energy, and therefore any excess kT energy in the NP is conserved by the emission of electromagnetic (EM) radiation at its EM confinement frequency - the process called QED induced EM radiation. Typically, EM radiation is emitted at VUV levels that by photochemical reaction with the surrounding oil creates free radicals that electrify the flow. However, NPs comprising oil molecules that cluster during the shearing of the oil in the electrical double layer (EDL) during stick-slip flow may also form. Molecular dynamics (MD) simulations show oil cluster NPs to form in stick-slip flow, but the shear rate in the EDL is orders of magnitude higher than that during flow electrification, and therefore the flow may only be electrified by solid or liquid NP impurities already in the flow. For 100 nm NP impurities, the QED induced current is lower bound by collision transfer to about 3 pA / NP. Extensions are made to chemiluminescence (CL) and aging of hydrocarbon liquids by oxidation.**

I. INTRODUCTION

Traditionally, the EDL is the mechanism by which charges in a flowing liquid are separated. Over the past decade, the source of charge in metal piping is thought to be cations and anions [1] produced by electrochemical reactions that more recently was extended to the flow of coolant oil in power transformers. But pressboard discoloring suggests [2] the oil is undergoing photochemical reactions,

$$A + h\upsilon \rightarrow A^+ + e^- \qquad (1)$$

where, the VUV photon hυ excites oil molecule A to form cation A^+ and electron e^-. Upon relaxation, A^+ recombines with e^- that is indistinguishable from A.

However, this is erroneous. Instead, the VUV photon hυ may form free radicals that are distinguishable from the neutral oil molecule. Consider the following [3] reactions:

$$RH + h\upsilon \rightarrow R* + *H \qquad (2)$$

$$H* + *H \rightarrow H_2 \qquad (3)$$

$$R* + e^- \rightarrow R^- \qquad (4)$$

$$R* + *R \rightarrow RR \qquad (5)$$

Equation (2) shows a hydrocarbon chain RH excited by photon hυ that in the liquid phase forms the chain R∗ and in the gas phase forms hydrogen ∗H fragments. Equation (3) gives the recombination of hydrogen *H fragments to form hydrogen H_2 gas. The recombination of the chain fragment with a free electron to form radical R^- is shown in (4). The formation of an insoluble suspension RR is indicated in (5).

Similarly, dissolved oxygen O_2 excited by VUV leads to the aging of oil by oxidation reactions in (6),

$$H* + O_2 + h\upsilon \rightarrow HO - O* \qquad (6)$$

while premature aging of pressboard insulation by oxidation ∗O-O∗ radicals is shown in (7),

$$R* + O_2 + h\upsilon \rightarrow R* + *O - O* \rightarrow R - O - O* \qquad (7)$$

Upon recombination of R-O-O∗ radicals, a high molecular weight RR molecule is formed that appears as an insoluble suspension of sludge; whereas, the highly reactive hydroxyl radical ∗OH oxidizes the hydrocarbon chain.

In fact, the oxidation of oil in power transformers in terms of the number of free radicals [4] correlates with the size of particle impurities. Indeed, the oxidation of oil is found to increase rapidly as the particle size decreases to submicron levels and is consistent with QED induced EM radiation that only NPs may produce the VUV necessary for photochemical reactions.

II. PURPOSE

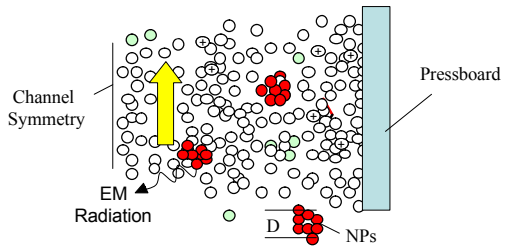
To show NP impurities in coolant oil are the source of flow electrification in power transformers.

III. BACKGROUND

NPs as a source of flow electrification evolved because of difficulties with QED induced EM radiation in bubbles and gaps. Bubbles offer 3D EM confinement, but do not nucleate in pressurized piping systems; whereas, gaps that form in the EDL provide radial, but not lateral and circumferential EM confinement.

In contrast, NPs of impurities offer full 3D EM confinement. NPs are similar to solid state quantum dots (QDs) under near IR (NIR) laser irradiation. Visible (VIS) light is produced as the low frequency NIR photon under EM confinement [5] in the QD only to be promptly frequency up-converted by QED to VIS frequencies. Unlike QDs, there are no NIR lasers in the coolant oil to irradiate the NPs. But this is of no consequence because the NPs maintained at ambient temperature by direct contact with the coolant emit EM radiation. Impurity NPs of diameter D producing EM radiation are depicted in Fig. 1.

Figure 1 Flow Electrification by QED induced EM radiation.



V ANALYSIS

Flow electrification by QED finds basis in the EM confinement of IR radiation from the NP atoms. Although the EM confined NP atoms are at the same temperature as the adjacent EM unconfined oil molecules, the NP atoms have only a fraction of the thermal kT energy of the oil molecules. EM energy is therefore transferred to the NP atoms by collisions of oil molecules. Since any kT energy in excess of that allowed by QED is prohibited, the excess is conserved by the emission of EM radiation at the VUV confinement frequency of the NP, the VUV exciting the oil to form the free radicals that electrify the flow.

A. EM Confinement

In NPs, the EM confinement frequency f and wavelength λ of the QED induced photons are,

$$f = \frac{c}{\lambda} \quad \text{and} \quad \lambda = 2Dn_r \tag{8}$$

where, c is the speed of light and n_r is the refractive index of the NP. The Planck energy E_p QED photons,

$$E_p = \frac{hc}{2Dn_r} \tag{9}$$

where, h is Planck's constant.

B. Thermal kT Energy of the NP Atoms

NP atoms are treated as harmonic oscillators [6] having the dispersion of kT energy shown in Fig. 2.

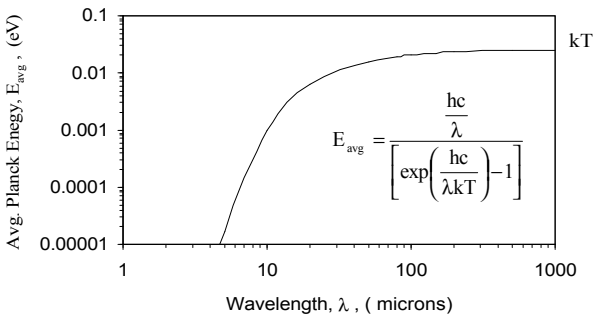


Figure 2. Harmonic Oscillator at 300 K
In the inset, k is Boltzmann's constant and T is absolute temperature.

Most of the thermal kT energy of the atom resides at wavelengths longer then about 100 microns. Fig. 2 shows NP atoms under VUV confinement; say a D = 0.1 micron NP with a wavelength λ = 0.2 micron for n_r = 1 has kT energy << $1x10^{-5}$ eV, although the temperature is the same for the unconfined oil molecules having full kT = 0.0258 eV. EM energy then transfers into the NP by oil molecule collisions. Heat transfer induced by QED is not by a temperature difference, but by the difference in kT energies.

C. Collisional Heating

The QED effect of a NP immersed in the coolant conserving collisional heat Q_C from the kT energy of oil molecules by EM emission is illustrated in Fig. 3.

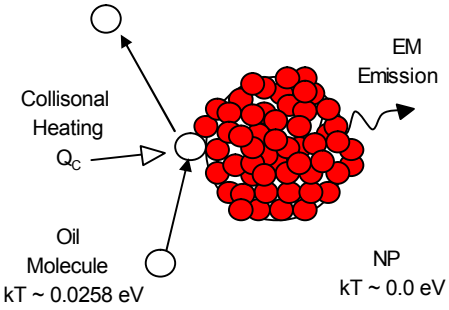


Figure 3. NP Conserving Collisional Heating by EM Emission

The collisional heat Q_C transferred [7] to the NP is,

$$Q_C = \frac{\pi}{2\sqrt{3}} pPD^2 \sqrt{\frac{kT}{m}} \tag{10}$$

where, p is the probability of energy transfer, and P is the ambient pressure. The mass m of oil molecules is, m = MW/N_{avag} where MW is molecular weight and N_{avag} is Avagadro's number.

D. QED Induced Current

Absent an increase in NP temperature, the collisional Q_C heat is conserved by the emission of EM radiation,

$$E_P \frac{dN_P}{dt} = Q_C \tag{11}$$

where, dN_P/dt is the rate of QED photons produced having Planck energy E_P. The QED induced current I is,

$$I = \frac{dN_P}{dt} Ye = \frac{\pi}{2\sqrt{3}} \frac{pPD^2}{E_P} \sqrt{\frac{kT}{m}} Ye \tag{12}$$

where, Y is the electron yield / VUV photon, and e is the electron charge. For NPs having D < 100 nm, E_P > 6.21 eV and the EM radiation is emitted in the VUV where fuel-oils have typical yields Y ~ 0.1 electrons/VUV photon. For n-Hexane with MW = 86, the QED induced current I for transfer probability p = 0.001 and D < 100 nm is shown in Fig. 3.

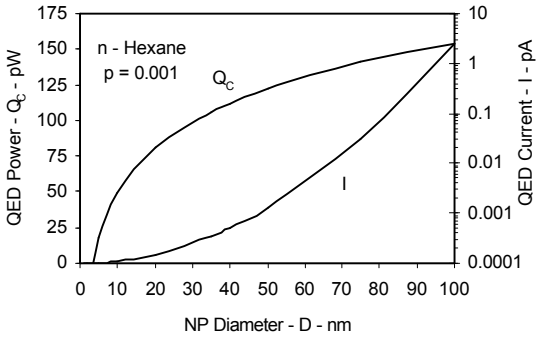


Figure 3. QED Induced Power Q_C and Current I / NP

Under collisional Q_C heating, the NP is induced by QED to produce electrical current I depending on its diameter D. Fig. 3 shows the heat Q_C ~150 pW produces a current I ~ 3 pA in a D = 100 nm diameter NP. For D > 100 nm, the current I tends to vanish because at $E_P < 5$ eV, the electron yield Y is very small.

VI DISCUSSION

Typically, flow electrification occurs at shear rates $\gamma < 2.4x10^4/s$. MD simulations showing oil molecules to cluster during stick-slip flow are given in Appendix A. But the strain rate in the simulations is about 4 orders of magnitude higher than in flow electrification, and therefore NPs formed by clustering of oil molecules are not the reason for flow electrification.

What this means is flow electrification by NPs is caused by NP metal and metal oxide impurities in the size range D < 0.10 micron. Since jet fuel filters are held to the higher API 1581 standard than that for power transformer oil filters, and since API 1581 limits [8] filtering only to about 0.3 microns, transformer electrification by NPs cannot be reduced by filtering.

Electrification of oil by NP impurities is similar to the CL observed [9] upon adding gold NPs to luminol in that the QED induced EM radiation that charges the oil produces VIS light in luminol. The oxidation of fuel-oil in underground storage tanks shielded from UV radiation [10] may be explained by NP impurities and QED induced EM radiation.

The similarity of coolant oil oxidation to aging [11] in solid polyethylene cables suggests breakdown in power transformers may be reduced by adding liquid UV blockers, such as Tinuvin®, that blend homogeneously with the oil coolant.

VII CONCLUSIONS

In flow electrification, liquid NPs formed by clustering of oil molecules in the EDL by shearing of oil is extremely unlikely.

Instead, solid NP impurities having diameters < 0.1 microns in coolant oil are shown to be the source of VUV radiation that by photochemical reaction electrifies the flow in power transformers.

Both photochemical and electrochemical reactions leave distinguishable reaction products, although after relaxation the gaseous and sludge products from photochemical reactions tend to neutrality.

Flow electrification by the photochemical formation of free radicals in NPs is consistent with the oxidation of gasoline and diesel fuel in underground storage tanks not exposed to environmental UV radiation.

Free radicals from NP impurities in coolant oil are similar to VIS light from gold NPs in luminol.

The dramatic increase in oxidation of oil in power transformers for NP impurities is consistent with QED induced EM radiation not producing VUV unless the NP diameters < 0.1 micron.

Flow electrification may only be reduced by liquid UV blocker additives such as Tinuvin® that homogeneously blend into the coolant oil. UV blockers in NP form such as TiO_2 may actually increase and not reduce flow electrification.

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APPENDIX A

Historically, MD simulations [A1] considered thin liquid films confined between solid walls, one wall fixed and the other moving. The moving wall carried a weight allowing it to move under pressure developed during shear in the film. A spring attached to the weight provided restraint in the direction of motion. The MD simulation contained 288 wall and 144 fluid atoms. Stick-slip was induced by imposing a velocity to the end of the spring. The pressure induced from the shearing of a

liquid periodically lifted the weight to form momentary gaps at the interface with solid walls.

The MD simulations presented here were obtained with a Fortran 77 program based on the "Leap-frog" algorithm given in Allen-Tildesley [A2]. The oil was taken to be n-Hexane having molecular weight 86 and density 680 kg/m^3. The Lennard – Jones parameters [A3] were $\varepsilon/k = 339.3$ and $\sigma = 0.593$ nm. A total of 500 n-Hexane molecules comprise the simulation box having sides $\delta = 4.71$ nm.

Instead of the fixed and moving walls [A1] simulation, the EDL was sheared by prescribing the steady Lees-Edwards [A4] linear velocity gradient across the simulation box in the direction normal to the flow. Periodic boundary conditions were imposed in the direction of and lateral to the flow. Plug flow at velocity V ~ 1 m/s was effectively separated from the boundary by a gap δ giving a shear rate $\gamma \sim V/\delta \sim 2x10^8$/s.

Typically, flow electrification in piping of diameter D occurs at shear rate $\gamma \sim 6V/D$. For Re = 2000, the data [A5] is upper bound by $\gamma \sim 2.4x10^4$/s at V ~ 1 m/s and D ~ 0.25 mm. Hence, the MD simulation is 4 orders of magnitude higher in shear rate than found in flow electrifications. The MD simulation began with a FCC configuration of molecules that were equilibrated at atmospheric pressure and temperature as shown in Fig. A1. Initially, large negative pressures typical of the FCC configuration are observed, but rapidly converge to ambient pressure conditions..

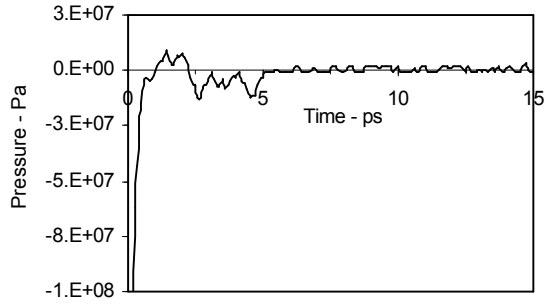

Figure A1. MD Simulation – Equilibration

Both pressure and temperature increase during stick and recover during slip as illustrated in Fig. A2. Peak pressure is about 2000 bar at a temperature of 900 K.

NPs of oil molecules were found to cluster during the EDL shearing process. The Allen-Tildesley [A2] algorithm (F34) was used to sort the molecules into clusters defined by a critical cluster radius and count the number of molecules in the cluster. The cluster radius was taken as 1.05 σ which means the molecules are in contact. The cluster size time history is shown in Fig. A3. Of the 500 molecules in the simulation, large fractions are observed to form and fragment on the order ~ 10 ps. Each such cluster formation being distinct from the surroundings may be considered a NP producing a burst of VUV radiation.

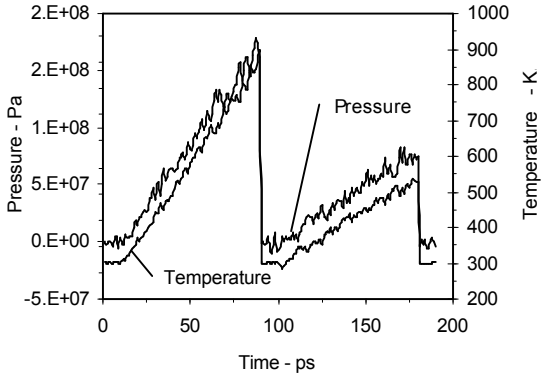

Figure A2. MD Simulation – EDL Pressure and Temperature

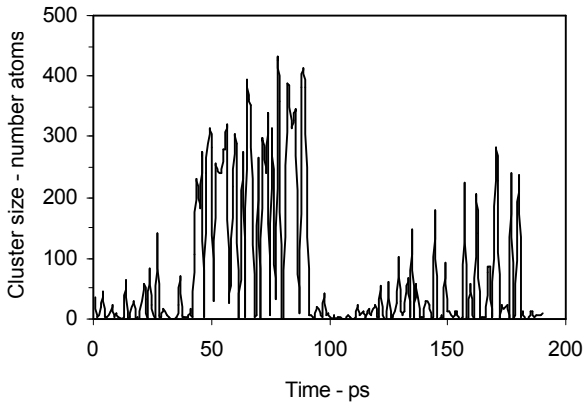

Figure A3 MD Simulation – Cluster size in EDL

However, MD simulations at shear rates $\gamma < 2x10^4$/s common to flow electrification did not show pressure and temperature increases or clustering. The MD results here are consistent with [A1] in that the stick-slip process produces high pressures during shear, but only at far higher shear rates than occur [A5] in flow electrification. Indeed, clustering only occurs at high shear rates [A6] beyond that usually accessed by experiments.

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