Tribochemistry by Quantum Mechanics

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ABSTRACT: Tribochemistry is shown to find origin in the nanoparticles (NPs) that form in the rubbing and scratching of surfaces. Atoms in surfaces are not under electromagnetic (EM) confinement and have full thermal kT energy. But in NPs, the atoms are under EM confinement at vacuum ultraviolet (VUV) frequencies that by quantum mechanics (QM) are restricted to vanishing kT energy. Therefore, in the transient as NPs form, the atoms have excess kT energy beyond that allowed by QM. Also in excess of that allowed by QM is the steady kT energy accumulated in the NPs from subsequent collisions with molecules in the surroundings. But the specific heat of NPs at VUV frequencies also vanishes, and therefore both transient and steady excesses in kT energy cannot be conserved by an increase in temperature. Instead, the excess kT energies are conserved by the quantum electrodynamics (QED) induced up-conversion of kT energy to the VUV confinement frequency of the NP. The VUV radiation then leaks from the NPs to provide tribochemistry with a high frequency source of EM radiation that allows chemical reactions to proceed by photolysis.

KEYWORDS: Tribochemistry, quantum mechanics

I. BACKGROUND

Tribochemistry may be defined [1] as the emission of photons and electrons from the rubbing of surfaces, although scratching [2] significantly enhances emissions. In 1948, exo-emission of electrons was first reported [3] by Kramer who attributed the energy necessary to produce electrons to surface re-crystallization following frictional heating. Since then, many mechanisms including nascent surfaces [4-5] and dangling bonds [6] have been proposed to explain tribochemistry.

Traditional tribo charging teaches rubbing or scratching provides the mechanical energy necessary to overcome the work function (WF) of the material, usually about 5-7 eV. However, it is unlikely that the WF of a material is lowered by any form of mechanical energy. By the photoelectric effect, Einstein showed EM and not mechanical energy is required to remove electrons from a material. Therefore, the Fermi distribution implicit in the WF is not expected to change by mechanical energy. Fundamentally, electrons are bound to atoms far greater than atoms are bound to each other, and therefore rubbing or scratching in tribochemistry may only remove particles of atoms rather than electrons.

Tribochemistry finds similarity with the rubbing of surfaces in static electricity. Over 2000 years ago, the Greeks found amber rods electrify upon rubbing with a cloth. Given that particles may only form because of the tight binding of electrons to atoms, it is difficult to reconcile the static electricity observed since the early Greeks unless the particles somehow produce EM radiation.

In this paper, QED induced EM radiation [7] as the mechanism by which charge is produced in static electricity is extended to tribochemistry. Like static electricity, not all particles produce EM radiation at VUV levels. Only the EM radiation from NPs having EM confinement frequencies in the VUV may initiate chemical reactions. Micron particles (MPs) emit QED induced EM radiation in the infrared (IR). But this is of no consequence because chemical reactions are not likely initiated with IR radiation.

By QED induced EM radiation, NPs from nascent surfaces formed by rubbing and scratching are the source of EM radiation that decomposes hydrocarbons [4] and not the surface itself. Similarly, organic gases [5] decompose by EM radiation from NPs that form as larger MPs rub against each other under ultrasonic vibration. Moreover, electron emission thought [6] to occur from bond disruption is caused by EM radiation from NPs that form from rubbing and scratching.

Generally, electron emission from EM radiation at VUV levels is restricted to energies > WF. Electron energies < WF are usually explained by the lowering of the WF by local stresses caused by defects and impurities in the lattice [3] or surface damage [8] in rubbing. QED induced EM radiation differs in that only the NP diameter D matters. Using static electricity [7] estimates, the QED induced electron energies for D < 50 nm range from the WF to the far higher 1 keV soft X-rays. But for D > 50 nm, the EM radiation is emitted at electron energies < WF.

NPs having a wide range of NP sizes therefore emit electrons over a wide spectrum of energies consistent with observations. Indeed, electrons emitted in the diamond scratching of alumina [9] have energies lower than the WF of 5-7 eV including electron spectra in excess of 48 eV. Observations of electron emissions [2] from a few eV to 1 keV have prompted

the proposal of a tribomicroplasma produced during rubbing and diamond scratching of surfaces. Again, QED induced EM radiation differs in that a wide range of particles from NPs to MPs inherently provide a broadband electron energy spectrum.

Since the 1940's, frictional temperature at asperities [3,6] has been thought [2] the source of electron emission. However, experiments of lubricants [2] applied to diamondlike carbon (DLC) films show dry sliding to produce high friction, but the steady charging potential was found to be greatest with perfluoropolyether (PFPE) lubricated surfaces. Frictional temperature rise [3] and subsequent re-crystallization therefore cannot be the electron emission mechanism.

Because frictional heating cannot explain why the charging potential in PFPE lubricated DLC films is higher than for dry films, a tribomicroplasma [2] by an electron transfer mechanism was proposed. In this regard, QED induced EM radiation once again differs and asserts the charging potential is higher with lubrication because the NPs removed from the DLC acquire a steady source of kT energy in collisions with the PFPE lubricant molecules not present with dry films in evacuated surroundings.

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II. PROBLEM STATEMENT

To provide a QM basis to tribochemistry based on QED induced EM radiation from NPs that form during the rubbing and scratching of surfaces. Most data in the literature is for electron emission, and therefore photon emission is not considered here. Nevertheless, the QM basis is required to explain bursts of electron emission from a few eV to 48 eV, yet provide steady charging potentials under PFPE lubrication to as high as 1 keV.

III. INTRODUCTION

Tribochemistry by QED induced EM radiation relies on the NPs to conserve transient and steady excess kT energy by EM emission as shown in Fig. 1.

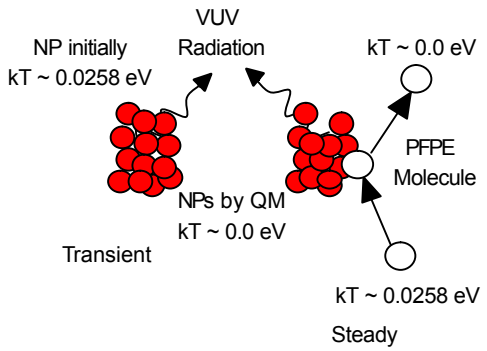

Fig. 1 Tribochemistry
Transient and Steady EM Emission from NPs

A. Transient EM Emission

Transient VUV emission occurs from kT energy available from atoms in the NPs that form at the instant surfaces are rubbed or scratched. Prior to NP formation, the full kT energy of the atoms is emitted as IR radiation. But QM restricts atoms in isolated NPs under EM confinement at VUV levels to have vanishing specific heat. Upon formation, the NP atoms therefore cannot conserve the excess kT energy by an increase in temperature. Instead, the excess kT energy is conserved by a burst of VUV radiation at the EM confinement frequency of the NP.

B. Steady EM Emission

Steady VUV radiation follows the transient VUV emission until the NPs coalesce to larger MPs. Over this time, the NPs absorb kT energy from collisions with molecules in the surroundings.

Indeed, collisions far more efficiently transfer EM energy to NPs than lasers. Laser radiation scatters to reduce the Mie absorption [10] efficiency. But collisions between NPs and the smaller surrounding molecules are inelastic so the full kT energy of the colliding PFPE molecules is transferred to NPs.

IV. THEORY

A. QM Restrictions

QM confines the EM wavelength λ of photons in NPs. At 300 K, the Einstein-Hopf relation [11] for the harmonic oscillator as a function of NP wavelength λ is shown in Fig. 2.

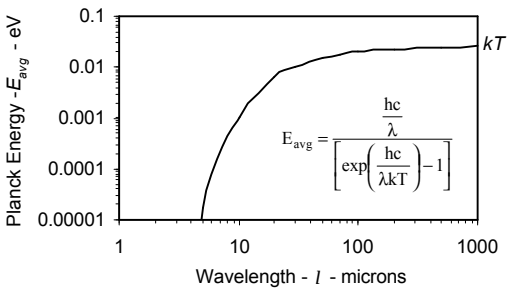

Fig. 2 Harmonic Oscillator at 300 K
In the inset, h is Planck's constant, and c the speed of light.

Gas or liquid molecules in the surroundings colliding with the NPs are not under EM confinement and have full kT energy; whereas, the NP atoms under EM confinement have small kT energy. Fig. 2 shows full kT energy ~ 0.0258 eV for λ > 100 microns in the FIR and kT ~ $1x10^{-5}$ eV at EM confinement of λ ~ 5 microns. Hence, NPs under EM confinement at VUV wavelengths λ < 0.050 microns have vanishing small kT << $1x10^{-5}$ eV.

B. EM Confinement Frequencies

NPs absorbing EM radiation in collisions with surrounding molecules is similar to that for quantum dots [12] under laser irradiation.

For NPs having D << λ, the EM confinement is analogous to the QM analogy of creating photons of wavelength λ by supplying EM energy to a QM box with walls separated by λ/2. For NPs of diameter D and refractive index n_r, the EM confinement frequency f and Planck energy E_P,

$$f = \frac{c}{\lambda}, \quad \lambda = 2n_r D, \text{ and } \quad E_P = \frac{hc}{\lambda} = \frac{hc}{2n_r D} \qquad (1)$$

C. Vanishing Specific Heat

Classical heat transfer conserves absorbed EM energy by an increase in temperature, but is not applicable to NPs because of QM restrictions on thermal kT energy. Equivalently, the specific heat of NPs may be said to vanish. To show this, the Einstein specific heat for the NP atoms as harmonic oscillators is modified to that for the vibration of thermal photons in EM confinement.

Einstein assumed the atoms in solids are harmonic oscillators vibrating independent of each other. But the thermal photons as oscillators vibrate not only coherently at the EM confinement frequency having the shape of a spherical box of photons, but at optical instead of atomic frequencies. Taking one thermal photon for each degree of freedom, the energy U of a NP with N atoms,

$$U = 3N \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]} \qquad (2)$$

For the specific heat C given by ∂U/∂T, the dimensionless specific heat C* is,

$$C^* = \frac{C}{3Nk} = \frac{\left(\frac{hc}{\lambda kT}\right)^2 \exp\left[\frac{hc}{\lambda kT}\right]}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]^2} \qquad (3)$$

At 300 K, C* vanishes for $\lambda = 2n_r D < 5$ microns [7]. Absorbed EM energy is therefore conserved by a temperature increase for λ > 5 microns while EM emission occurs for λ < 5 microns.

V. ANALYSIS

A. Transient EM Emission

The atoms in the NP have the same kT energy as those in the solid or liquid prior to fragmentation. The energy U of the NP is,

$$U = \frac{\pi}{6}\left(\frac{D}{\Delta}\right)^3 3kT = \frac{\pi}{2}\left(\frac{D}{\Delta}\right)^3 kT \qquad (4)$$

where, Δ is the cubic spacing between NP atoms at solid density, Δ ~ 0.3 nm. Lacking specific heat, the NP conserves the energy U in a burst of VUV radiation that by Einstein's photoelectric effect electrifies the surroundings.

The charge q is,

$$q = N_P Ye = \frac{U}{E_P} Ye = \pi kT\left(\frac{D}{\Delta}\right)^3 \frac{n_r D}{hc} Ye \qquad (5)$$

where, N_P is the number of QED photons induced in the NPs at Planck energy E_P. For NPs having $n_r < 2$ and D < 50 nm, $E_P > 6$ eV where most materials have yields Y ~ 0.1 electrons/VUV photon. The charge q produced is, q ~ 0.5 fC / NP.

B. Steady EM Emission

The power Q_C transferred [13] in collisions of lubricant PFPE molecules with NPs,

$$Q_C = \frac{\pi}{2\sqrt{3}} pPD^2 \sqrt{\frac{kT}{m}} \qquad (6)$$

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

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

$$E_P \frac{dN_P}{dt} = Q_C \qquad (7)$$

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

$$I = \frac{dN_P}{dt} Ye = \frac{\pi}{2\sqrt{3}} \frac{pPD^2}{E_P} \sqrt{\frac{kT}{m}} Ye \qquad (8)$$

where, Y is the electron yield / VUV photon, and e is the electron charge. For PFPE lubricant [2] having MW = 6000, the QED induced current I for probability p = 1 with index $n_r = 2$ is shown in Fig. 3.

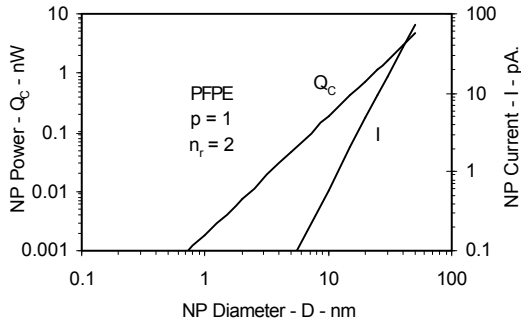

Fig. 3 QED Induced Power Q_C and Current I / NP

The peak NP power Q_C and current I for PFPE is a lower bound for lower molecular weight lubricants. Fig. 3 shows for PFPE at D = 50 nm the power Q_c = 4.6 nW produces current I = 75 pA. For D > 50 nm, E_p < WF = 6 eV and the current I vanishes because the yield Y << 1.

C. Summary

Transient bursts produce charge of about 0.5 fC / NP. Current in lubricants is lower bound by PFPE at about 75 pA / NP.

V. DISCUSSION

A. Transient Charge

QED induced EM radiation produces Planck energies E_P and number $N_e=N_PY$ of electrons that depend on the diameter D of the NPs. Fig. 4 shows the peak $N_e \sim 3000$ occurs at D = 45 nm. The charge $q = eN_e = 0.5$ fC / NP as found in Section IV.A and C. For D < 45 nm, $E_P >$ WF; whereas, for D > 45 nm, $E_P <$ WF.

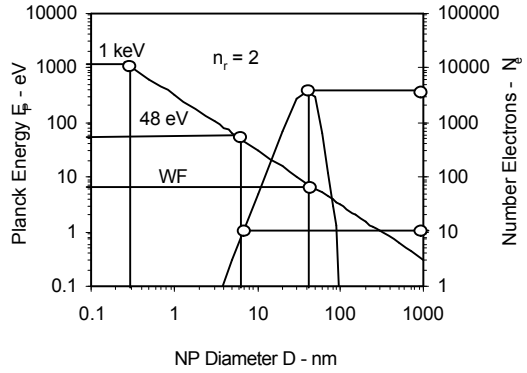

Fig. 4 QED Induced EM Radiation
Planck Energy E_P and number N_e of electrons / NP

The surroundings were assumed to have a WF = 6 eV and electron yield Y = 0.1 at E_P = 6.21 eV with Y vanishing for E_P < 6.21 eV. Superposed on Fig. 4 are the observed [2] electron energies of 1 keV and 48 eV. Electrons $N_e \sim 3000$ emitted near the WF occur at D = 45 nm; whereas, for E_P = 48 eV, D = 7 nm and $N_e \sim 10$. Bursts are unlikely to produce 1 keV electrons for D = 0.3 nm because the number N_e of electrons < 1 for D < 4 microns.

B. Steady Current

Steady collisions produce current I as lubricant PFPE molecules collide with NPs. Fig. 5 gives the corresponding electron rate $dN_e/dt = I / e$ of electrons, where I is taken from Fig. 3. For D = 45 nm and unity collision probability, per NP electron rates dN_e/dt excluding recombination are of order 10^9/s and consistent with reported [2] data. Near the WF at D = 45 nm, the electron rate is high at 4.6×10^8 / s. Unlike bursts, steady collisions of PFPE molecules with NPs having D = 0.3 nm produce 1 keV electrons at rate $dN_e/dt \sim 100$ / s.

C. Tribomicroplasma

Tribomicroplasma [2] having the number of electrons balanced by the positive charged ions is consistent with QED induced EM radiation in that the removal of an electron by a VUV photon leaves the atom or molecule with a positive charge.

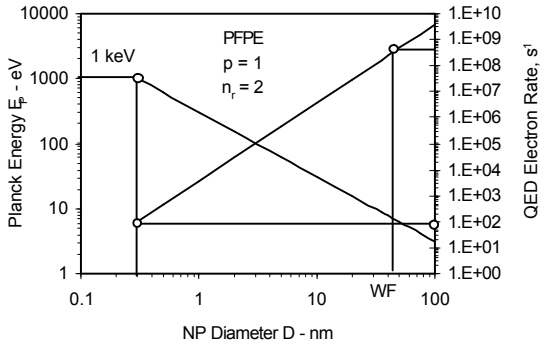

Fig. 5 Energy E_P and per NP Electron Rate dN_e/dt

REFERENCES

[1] Molina, G.J., Furey, J., and Kajdas, C., 2007, "A Deterministic-Chaos Study of Electron Triboemission Outputs," *J. Tribology*, 129, pp. 679-683.

[2] Nakayama, K., 1992, "Triboemission of electrons, ions, and photons from diamondlike carbon films and generation of tribomicroplasma," *Surf. Coat. Tech.*, 188-189, pp 599-604.

[3] Simoi, C., Hrianca, I., and Cracium, P., 1968, "Exoemission of Electrons without Photostimulation," *Phys. Stat. Sol*. 29, pp. 761-766.

[4] Morecroft, D.W., *Wear*, 1971, "Reactions of octadecane and decoic acid with clean iron surfaces," 18, pp. 333-339.

[5] Mori, S. and Imaizumi, Y., 1988, "Adsorption of model compounds of Lubricant on Nascent Surfaces of Mild and Stainless Steels under Dynamic Conditions," *STLE Trans*., 31, pp. 449-453.

[6] Hsu, S.M., Zhang, J., and Yin, Z., 2002, "The nature and origin of tribochemistry," 2002, *Trib. Lett.*, 13, pp.131-139.

[7] Prevenslik, T., 2008, "A Unified Theory of Natural Electrification", Proc. of 6th Int. Conf. App. Electrostatics, Shanghai Maritime University, November 3-7, pp. 60-63.

[8] Dickinson, J.T., Jensen, L.C., and Jahan-Latibari, A., 1983, "Fractoemission: The Role of Charge Separation," *J. Vac. Technol. A.*, A2, pp. 1112-1116.

[9] Molina, G.J., Furey, M.J., Ritter, A.L., and Kajdas, C., 2001, "Triboemission from Alumina, Single Crystal Sapphire, and Aluminum," *Wear*, 249, pp.214-219.

[10] Bohren, C.F. and Huffman, D.R. *Absorption and Scattering of Light by Small Particles*, J. Wiley & Sons, 1983.

[11] Christy, R.W. and Pytte, A. *The Structure of Matter: Introduction to Modern Physics*, Benjamin, New York, 1965.

[12] Prevenslik, T.V. "Quantum Dots by QED," International Conference on Materials for Advanced Technologies (ICMAT), July 2-6, Singapore, 2007.

[13] Das, K.K., Rostovtsev, Y.V., Lehmann, K. and Scully, M.O. Thermodynamic and noise considerations for the detection of microscopic particles in a gas by acoustic Raman spectroscopy, *Optics Comm.*, 2005, 246, 551-9.