Laser Induced Incandescence and Particle Size

THOMAS PREVENSLIK
Foehrenweg 20, Berlin 14195
GERMANY
http://www.geocities.com/thomas_prevenslik

Abstract: - The cooling rate of soot particles after laser induced incandescence (LII) is thought to provide an estimate of the size of nanoparticles (NPs) in the engine exhaust. It is shown that cooling rate is not applicable to NPs, and instead is only a measure of the size of micron-sized particles. The problem is that the conservation of absorbed laser photon energy in NPs is subject to quantum electrodynamics (QED) constraints. Although QED allows the temperature of the NPs to increase during the absorption of the laser photons, QED limits the amount of photon energy that may be absorbed by the NPs to insignificant fractions of the laser photon energy, and therefore the cooling rate of the absorbed laser energy following LII would not be detectable. In effect, the absorption of laser photons in a NP cannot be conserved by an increase in temperature. Instead, the absorbed photon energy is conserved by emission of visible (VIS) radiation in a broadband electromagnetic (EM) spectrum produced during confinement within the NP geometry. The broadband EM emission spectrum is known in LII terminology as the emission signal. Indeed, this paper recommends that the LII emission signal be used as measure of the NPs leaving the cooling rate as a measure of micron sized particles.

Key-Words: - Nanoparticle, heat transfer, suppressed IR, QED, conservation principle

1 Introduction

Historically, LII as a method to determine the size of soot particles was first proposed in 1977 [1]. In the 1980's, analytical derivations of temperatures based on the thermal response of a single NP were developed [2]. Soot in engine exhaust consists of aggregates of NPs [3] ranging from 10 to 1000 nm. Single NP sizes are 5 to 30 nm with most particles in the submicron range from 100 to 250 nm.

The LII analytical procedure in deriving the thermal response of NPs follows the classical laser heating of solids in the bulk, the absorbed laser photon energy conserved by an increase in temperature. Currently, analytical procedures [4-5] do not differ significantly from those developed in the 1980's [2]. Generally, computed temperatures range from 4000-4500 K with the size of the NPs inferred from the rate of cooling.

Nevertheless, LII measurements [2, 4-5] based on cooling rate may be misleading. Unlike the laser heating of solids that follows classical heat transfer theory, consideration must be given to the effects of NP size on the thermal response, e.g., as in thermal conduction at the nanoscale [6]. But the LII literature is silent the effects of NP size because nanoscale heat transfer was not widely known [2] in the 1980's when LII was first introduced.

Indeed, this paper shows the accuracy of LII particle measurement is very sensitive to whether the soot particle is a NP or micron-sized.

The wavelength of infrared (IR) radiation that usually accompanies an increase in temperature in the bulk is larger than the size of NPs. Similar to quantum dots under laser irradiations, the IR radiation in NPs is suppressed because the half-IR wavelength is greater than the NP diameter [7].

Since an increase in NP temperature cannot conserve the absorbed photon energy, EM radiation is emitted in the VIS to conserve the absorbed photon energy. The VIS radiation is produced in a broadband EM spectrum as th e absorbed photon adjusts to the QED constraints imposed by the geometry of the NP. Any chemical species in the NP having quantum states in this spectrum is then excited to produce the respective atomic lines.

Conversely, particles having diameters of tens of microns which are greater than the half-IR wavelength are allowed to absorb the full amount of laser photon energy. Computed LII temperatures of 4000 – 4500 K are reasonable estimates of actual LII temperatures.

The process by which EM emission - not an increase in temperature – conserves the absorption of the laser photon is called cavity QED induced EM radiation [8-9]. Nanovoids (NVs) typify prior applications of QED induced EM radiation, e.g., bubbles in liquids [8] and gaps in solids [9]. With regard to QED confinement, the only difference between NPs and NVs is the index of refraction n_r: for NPs, $n_r > 1$ while for NVs, $n_r = 1$.

2 Problem Formulation

For over 30 years, NP sizes in engine exhausts have been inferred from cooling rates following LII to temperatures from 4000 to 4500 K. The questions posed are:

What size of NPs is accurately known based on the cooling rate of LII temperatures? Are there any alternatives to cooling rate that would improve the measurements of NP size under LII?

3 Problem Solution

3.1 Theoretical Background

In assessing the validity of inferring NP size from cooling rate of particles following LII, it is necessary to explain how an increase in temperature cannot conserve the absorbed laser photon. The NP is taken to be spherical of radius R as shown in Fig. 1.

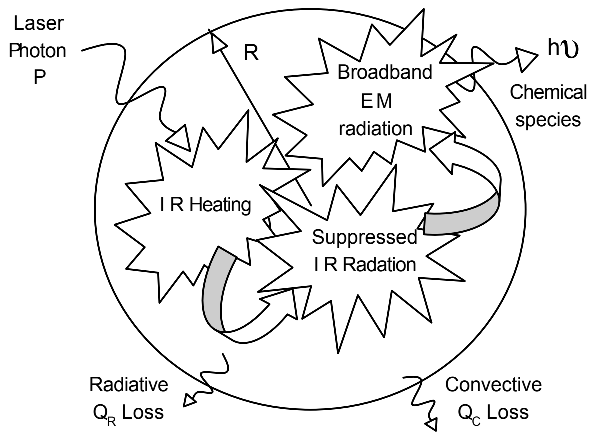


Figure 1. LII of NP

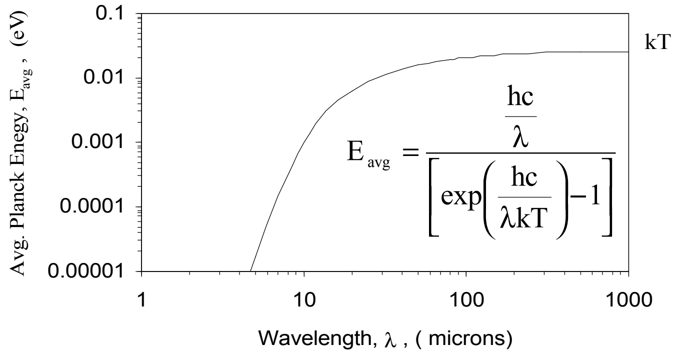
The laser photon P at wavelength λ_P is shown absorbed by the NP according to the Rayleigh limit [4, 5]. In classical heat transfer, the absorption of P is conserved by an increase in temperature T.

However, the amount of photon energy absorbed by the NP is only significant if the principal IR wavelength λ is less than the resonant EM wavelength λ_{EM} of the particle, i.e., $\lambda < \lambda_{EM}$.

$$\lambda < \lambda_{EM} = 4n_r R = 2n_r D \qquad (1)$$

where, D is the particle diameter, D = 2R, and λ_{EM} is enlarged by the refractive index n_r to correct for the speed of light c in solid NPs.

The principal IR wavelength is defined through the Einstein-Hopf relation for the harmonic oscillator [10]. The dispersion of average Planck energy E_{avg} with wavelength λ at T ~ 300 K is shown in Fig. 2.



$$E_{avg} = \frac{\frac{hc}{\lambda}}{\left[\exp\left(\frac{hc}{\lambda kT}\right) - 1\right]}$$

Figure 2 Harmonic Oscillators at T ~ 300K
In the inset, *h* and *k* are Planck's and Boltzmann's constants, and *c* is the speed of light in vacuum

At ambient temperature, Fig. 2 shows the atoms in NPs have insignificant thermal kT energy at submicron wavelengths, i.e., $E_{avg} \rightarrow 0$ as $\lambda \rightarrow 0$. For example, a 10 nm diameter soot NP with $n_r \sim 2$ has $\lambda_{EM} \sim 40$ nm. At 3800 K, $E_{avg} = 2.23\text{x}10^{-42}$ eV, and is many orders of magnitude smaller at 300 K. Thus, even if the NP temperature increases from 300 to 3800 K, the typical LII laser photon P having Planck energy 2-4 eV cannot be conserved by an increase in NP temperature.

For the NP atom as a harmonic oscillator, most of the thermal kT energy at ambient temperature resides at wavelengths $\lambda > 100$ microns, the lower bound of which is defined as the principal IR wavelength, i.e., $\lambda \sim 100$ microns. Thus, soot particles having D < $\lambda/2n_r \sim 25$ microns cannot conserve the absorbed photon by an increase in temperature. Conversely, for particles having D > 25 microns, QED allows the absorbed photon to be conserved with a temperature increase, say to 4000-4500 K as reported for LII.

With regard to NPs, the fact that that QED limits the thermal kT energy in NPs requires the laser photon to be conserved in another way, say by prompt VIS emission in a broadband EM spectrum.

VIS emission occurs as the absorbed photon is absorbed in the NP. The QED confinement constrains the P photon wavelength λ_P to the resonant EM wavelength λ_{EM} of the NP, the broadband EM emission spectrum produced as the wavelength λ_P of the absorbed P photon adjusts to the resonant EM wavelength λ_{EM} of the NP. For $\lambda_P > \lambda_{EM}$, the P photon undergoes frequency up-conversion, while undergoing down-conversion for $\lambda_P < \lambda_{EM}$. A broadband EM emission spectrum scan typical of the LII signal (Figs. 2 and 3 of [11]) is depicted in Fig. 3.

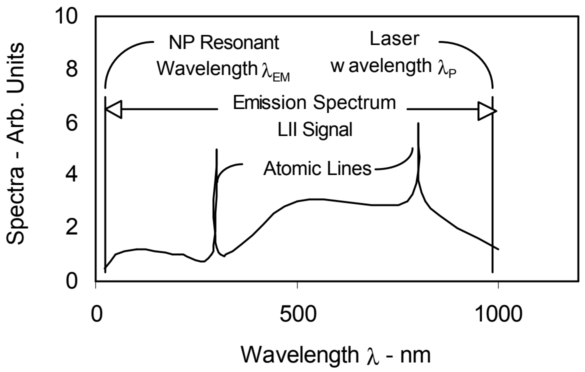


Figure 3. Emission Spectrum of LII Signal Induced by Laser Photon confinement in NPs.

Since the EM broadband spectrum is continuous, *all* quantum states of chemical species in the NP over the wavelength interval [λ_{EM},λ_P] are excited. Fig. 1 depicts a chemical excitation by photon hυ.

3.2 Results

The validity of LII in measuring the size of NPs depends on the temperature T prior to the absorption of the P photon. By similarity, the harmonic oscillator response at T ~ 300 K and principal IR wavelength λ ~ 100 microns may be extended to principal wavelength λ_T and initial temperature T_T,

$$\lambda_T = \lambda\left(\frac{T}{T_T}\right) \tag{2}$$

The range of valid soot particle measurements may be extended by increasing the initial temperature, say by heating the NPs with an IR laser prior to exciting the particles with the laser P photon. The particle diameter D in relation to the initial temperature T_T is shown in Fig. 4.

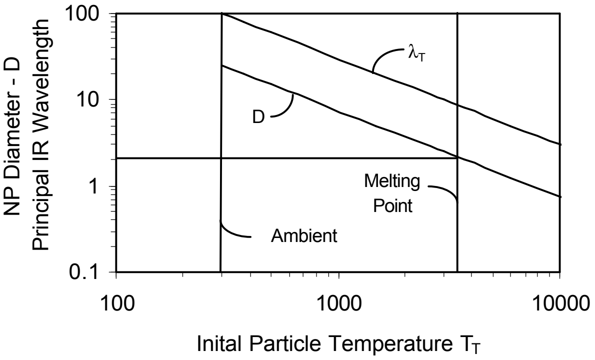


Figure 4. Particle Diameter D and Principal IR Wavelength λ_T vs. Initial Temperature T_T.

Indeed, Fig. 4 shows by increasing the initial temperature to the ~ 3800 K melting point of graphite, the measurement of the smallest soot particle that can accurately measured with a subsequent photon P improves from 25 to about 2 microns. But this is not in NP range.

The Planck energy E induced in the NP by the QED confinement,

$$E = \frac{hc}{4Rn_r} = \frac{hc}{2Dn_r} \tag{3}$$

Planck energy E in terms of the particle diameter D is shown in Fig. 5. Particle size > 2 microns may be inferred from cooling rate for initial temperatures from 3800 to 300 K. In contrast, NPs having D < 250 nm and E > 1 eV produce VIS emission. The C_2 line of carbon is excited by NPs having diameters D < 0.062 microns and E > 5 eV.

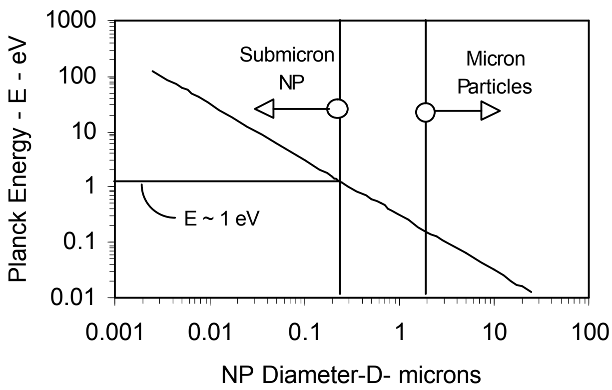


Figure 5. Planck Energy E vs. NP Diameter 2R

3.2 Discussion

Cavity QED induced EM radiation based on the confinement of the absorbed photon P is consistent with the emission scans in LII signals of soot [(Figs. 2 and 3 of [11]) as depicted here in Fig. 3. Indeed, the LII signals are produced by VIS emission - not thermal IR emission. In fact, wavelength resolved emission scans of LII emissions were shown not to fit the thermal (blackbody) emission curve [11].

In a 532 nm laser excitation of engine exhaust, none of the abundant diatomic radicals OH, CH, and C_2 absorb 532 nm radiations, yet the respective atomic lines appear in the emission spectrum and are explained by multi-photon excitation processes [11]. But the unlikely possibility of photons combining to form photons of higher Planck energy at exactly the correct frequency suggests another mechanism is at play in NPs to excite OH, CH, and C_2.

In contrast, QED induced EM radiation producing a continuous emission EM spectrum upon the absorption of the laser P photon excites the quantum states of all chemical species in the interval [λ_{EM},λ_P]. Unlike the usual explanation of multi-photon processes whereby a number of photons somehow "add-up" to form higher energy photons, QED induced EM radiation finds firm basis in the partition of the EM energy of the absorbed laser P photon into all quantum states below the EM resonant frequency of the NP confinement. In effect, the NP upon the absorption of the laser P photon becomes a momentary continuous broadband laser.

Beyond LII of soot NPs, QED induced EM radiation explains how high energy quantum states in molecules are excited by IR photons without invoking the strained classical arguments usually given to explain multi-photon processes.

4 Conclusions

QED confinement of the absorbed laser photon drastically alters the LII literature to date. But the argument that a NP is unable to conserve the absorbed laser photon by an increase in temperature is based on the simple and undeniable physics.

Nevertheless, why absorbed laser photons cannot be conserved in NPs by a temperature increase may be difficult to understand. LII researchers accustomed to heat transfer in the bulk need to reconsider the effects of the nanoscale in the thermal response of NPs. Based on the analysis in this paper, the following answers are given to the questions posed in the Problem Formulation.

4.1 Particle Size Measurements

The size of NPs cannot be determined from cooling rates following LII. Only larger particles > 25 microns are accurately measured at ambient temperature. Increasing the soot temperature to the melting point 3800 K of soot extends the validity of LII to particles of about 2 microns.

4.2 Alternatives to Cooling Rate

The objective of LII is to determine the size of NPs – not micron sized particles. The following are recommended:

(1) Consider alternatives to the LII procedure of inferring NP size from the cooling rate, and.

(2) Investigate the emission scans of the LII signals as a measure of NPs, e.g., computing the area under the emission scans as proportional to the number of NPs in the engine exhaust.

References:

[1] A. C. Eckbreth, Effects of Laser-Modulated Particulate Incandescence on Raman Scattering Diagnostics, *J. Appl. Phys.*, Vol. 48, 1977, pp. 4473-9

[2] L. A. Melton, Soot Diagnostics Based on Laser Heating, *Appl. Optics*, Vol. 23, 1984, pp. 2201- 2208.

[3] D. F. Dolan, D. V. Kittelson, and D. Y. H. Pui, Diesel Exhaust Particle Size Distribution Measurement Techniques, SAE Paper No. l 800187, 1980.

[4] D. R. Snelling, et al., Particulate Matter Measurements in a Diesel Engine Exhaust by Laser-Induced Incandescence and the Standard Gravimetric Procedure, SAE Technical Paper 1999-01-3653.

[5] F. Liu, G. J. Smallwood, and D. R. Snelling, Effects of primary particle diameter and aggregate size distribution on the temperature of soot particles heated by pulsed lasers, *J. Quant. Spectr. Rad. Tran.*, Vol. 93, 2005, pp. 301-312.

[6] G. Chen, Particularities of heat conduction in nanostructures, *J. Nanoparticle Research*, Vol. 2, 2000, pp. 199-204.

[7] T. V. Prevenslik, Quantum Dots by QED, 2007, To be published.

[8] T. V. Prevenslik, Flow Electrification by Photochemical Reaction, Proceedings of the Int. Symp.on Electrohydrodynamics, 2006, Buenos Aires, pp. 197-200.

[9] T. V. Prevenslik, The Casimir force and the conservation of EM energy, 2005, presented at 10th National Congress on Theoretical and Applied Mechanics, 13-16 September, Varna.

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

[11] L. Vander Wal and K. J. Weiland, Laser-induced incandescence: Development and characterization towards a measurement of soot-volume fraction, *Phys. Rev. B*, Vol. 59, 1994, pp. 445-52.