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PPPL- 5209

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October 2015

PRINCETON PLASMA PHYSICS LABORATORY

Prepared for the U.S. Department of Energy under Contract DE-AC02-09CH11466.

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Modeling thermionic emission from laser-heated nanoparticles

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(Dated: 27 October 2015)

An adjusted form of thermionic emission is applied to calculate emitted current from laser-heated nanoparticles, and to interpret time-resolved laser-induced incandescence (TR-LII) signals. This adjusted form of thermionic emission predicts significantly lower values of emitted current compared to the commonly-used Richardson-Dushman equation, since the buildup of positive charge in a laser-heated nanoparticle increases the energy barrier for further emission of electrons. Thermionic emission inlfuences the particle's energy balance equation, which can affect TR-LII signals. Additionally, reports suggest that thermionic emission can induce disintegration of soot aggregates when the electrostatic Coulomb repulsion energy between two positively charged primary particles is greater than the van der Waals bond energy. Since the presence of aggregates strongly influences the particle's energy balance equation, using an appropriate form of thermionic emission to calculate emitted current is essential for interpreting TR-LII signals.

Keywords: thermionic emission, laser-induced incandescence, soot, aggregate

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The laser-induced incandescence (LII) diagnostic has been extensively applied[1] (and references therein) as a combustion diagnostic for non-invasive, *in situ* characterization of soot particles in background flame environments. The LII diagnostic has also been used to characterize carbon black[2], and non-carbonaceous nanoparticles[3–5]. For time-resolved LII (TR-LII), particles are heated with a short-pulsed laser, and the induced incandescence signals are subsequently recorded. Since incandescence is a function of particle temperature, $T(t)$, interpreting TR-LII signals involves calculating $T(t)$ by numerically solving the particles' mass and energy balance equations during and after the laser pulse. The mass and energy balance equations describe the influence of various heat transfer processes on $T(t)$.

One of the heat transfer processes is thermionic emission, which describes the release of electrons from hot cathodes. Owen W. Richardson first proposed[6] that the relationship between thermionic emission current and cathode temperature follow an Arrhenius equation. Subsequent research led to the well-known Richardson-Dushman equation,

$$J_{RD} = A_0 T^2 \exp\left(-\frac{\phi}{k_B T}\right) \tag{1}$$

where J_{RD} is the emitted current density (A/cm^2), T is the cathode temperature (K), ϕ is the cathode work function (J), and $A_0 = 4\pi m_e k_B^2 e/h^3 \sim 120$ A/cm^{2}K^2 is the Richardson constant, where m_e, k_B, e, and h are the electron mass, Boltzmann's constant, electron charge, and Planck's constant, respectively. Although thermionic emission has traditionally been applied[7] (and references therein) to characterize current emitted from hot metal filaments (e.g., gas discharge lamps), thermionic emission can also describe current emitted from any hot conducting particles, such as laser-heated soot particles. Consequently thermionic emission will influence interpretation of results from the LII diagnostic.

Thermionic emission can influence the soot particle's energy balance equation by directly cooling the soot particle[8,9], and by inducing disintegration of soot aggregates[10]. The particle cooling rate due to thermionic emission has previously[8,9] been described by a modified form of the Richardson-Dushman equation,

$$Q_{RD} = \pi D^2 \frac{\phi}{e} J_{RD}, \tag{2}$$

where Q_{RD} (J/s) is the particle cooling rate, and D is the soot primary particle diameter. Filippov *et al.*[10] described a model where thermionic emission of electrons results in a positive charge buildup in the primary particles, which in turn, can induce disintegration of soot aggregates when the electrostatic Coulomb repulsion energy between positively charged particles is greater than the van der Waals bond energy. This phenomenon of laser-induced aggregate disintegration is qualitatively similar to a Coulomb explosion[11], where ultrafast picosecond or femtosecond lasers with high instantaneous intensities (typically greater than 10^{14} W/cm^2) are used to irradiate atomic or molecular clusters. The high laser intensities quickly ionize the cluster, which subsequently "explodes" when the ions rapidly separate. Production of X-rays[12,13] and high-velocity (> 100 keV) ions[14–16] has been observed from heating noble gas clusters with intense pulses from femtosecond lasers. Since recent results[17–21] show that aggregation significantly influences TR-LII signals by reducing the conductive cooling rate, appropriately modeling thermionic emission is crucial for interpreting TR-LII signals.

When applied to laser-heated nanoparticles, the Richardson-Dushman equation (Equation (1)) significantly overestimates the emitted current, and consequently, the particle cooling rate. Thermionic emission from a laser heated particle results in a positive charge buildup, which increases the barrier for subsequent emission of electrons. (The positive charge buildup in a traditional case of thermionic emission from a metal filament in a gas discharge lamp is negligible as long as current is being supplied to the filament.) Therefore, the Richardson-Dushman equation should be adjusted to include the effects of the positive charge buildup, resulting in the following expression[22],

$$J_{Therm} = A_0 T^2 \exp\left(-\frac{(\phi + \Delta\phi)}{k_B T}\right), \tag{3}$$

where J_{Therm} describes the adjusted current density (A/cm^2) for thermionic emission from laser-heated particles, and $\Delta\phi$ describes the increased barrier (eV) for further electron emission due to the positive charge buildup. For a spherical particle with diameter D and charge $Q_P > 0$, $\Delta\phi$ has the following form,

$$\Delta\phi = e{\cdot}V_P = k_E \frac{eQ_P}{R}, \tag{4}$$

where $V_P = Q_P/C_P$ is the electric potential, $C_P = (4\pi\epsilon_0)R$ is the capacitance, $R \equiv D/2$ is the radius, and $k_E \equiv 1/(4\pi\epsilon_0)$ is the Coulomb constant. Equation (4) reflects the electrostatic Coulomb barrier at the particle surface for emitted electrons. The particle charge, Q_P, is equal to the outgoing charge of emitted electrons, and can be calculated by integrating

Experimental parameters			
D	70 nm	F	0.2 J/cm^2
T_{Gas}	300 K	ϕ	4.7 eV
p_{Gas}	1 atm	λ_{MFP}	70 nm

TABLE I. Experimental parameters used for this study. Temporal temperature profiles were modeled from soot particles with a 70 nm diameter, with room temperature (300 K) atmospheric pressure (1 atm) air as the background gas. A monodisperse diameter distribution was assumed for the purposes of this study. The laser fluence was set to $F = 0.2$ J/cm^2, and the work function, ϕ of graphite is 4.7 eV. Electrons traveling in air have a mean free path of $\lambda_{MFP} \sim 70$ nm.

current (Equation (3)) with respect to time,

$$Q_P(t) = eN_{Emit}(t) = \pi D^2 \int_0^t J_{Therm}(s)\mathrm{d}s, \tag{5}$$

assuming isotropic current emission, where $N_{Emit}(t)$ is the number of emitted electrons.

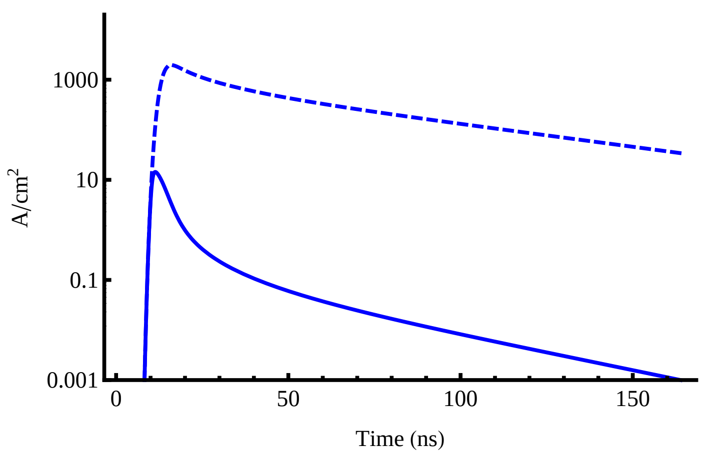

FIG. 1. Predicted current density using the standard (Equation (1), dashed line) and adjusted (Equation (3), solid line) form of the Richardson-Dushman equation. The adjusted form includes the effects of positive charge buildup in soot, resulting in a sharp decrease in predicted current density.

Thermionic emission current is significantly reduced (Figure (1)) when effects of the particle's positive charge buildup, $\Delta\phi$ (Equation (4)), are included. Thermionic emission is calculated with experimental conditions shown in Table (I). Soot temperature, $T(t)$, was calculated (Figure (2)) by numerically solving standard mass and energy balance equations[8],

$$\frac{\mathrm{d}U_{Int}}{\mathrm{dt}} = Q_{Abs} - Q_{Rad} - Q_{Cond} - Q_{Sub} - Q_{Therm}, \tag{6a}$$

$$\frac{\mathrm{d}M}{\mathrm{dt}} = \dot{M}_{Sub}, \tag{6b}$$

where the U_{Int} is the particle's internal energy, and is proportional to particle temperature, $T(t)$. The Q_i (J/s) terms describe the rate of energy gained or lost by: absorption of laser energy, Q_{Abs}; blackbody radiation, Q_{Rad}; conductive cooling[23], Q_{Cond}; sublimation (evaporative cooling), Q_{Sub}; and thermionic emission, $Q_{Therm} = (\pi D^2 \cdot \phi / e) J_{Therm}$ (Equation (3)). Particle mass loss, $\dot{M}$ (g/s), is caused by sublimation, $\dot{M}_{Sub}$. Further details about these terms can be found elsewhere[1,8,9,17,24–26]. The number of emitted electrons was calculated from Equation (5), and is shown in Figure (2). The predicted electric potential (Equation (4)) at the soot particle surface is 2.5 V (Equation (5)). For comparison, the work function of graphite is 4.7 eV (Table (I)).

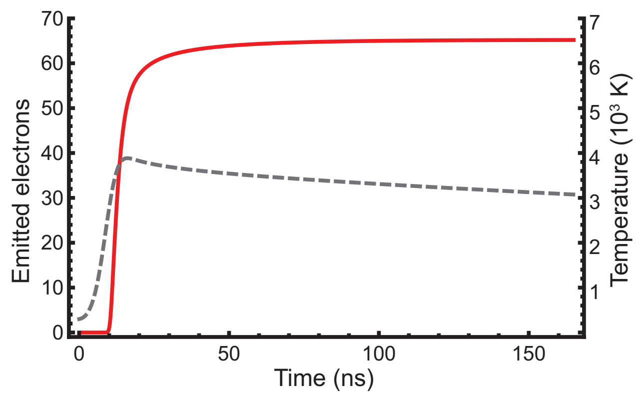

FIG. 2. Predicted temporal profiles for cumulative number of emitted electrons, $\mathrm{N}_{Emit}(\mathrm{t})$ (red, solid line), and particle temperature, $T_P(\mathrm{t})$ (gray, dashed line). Equation (5) was used to predict $\mathrm{N}_{Emit}(\mathrm{t})$, and the mass and energy balance equations (Equation (6)) were numerically solved, to predict $T_P(\mathrm{t})$. The timescale for emission of current is $\sim$ 10-20 ns.

Figure (3) shows that thermionic emission has a negligible influence on the particles' mass and energy balance equations when effects of the positive charge buildup, $\Delta\phi$, are included. At $\sim$3500 K, for given experimental parameters, the particle cooling rate calculated with the adjusted form of thermionic emission (Equation (3)) is $4 \cdot 10^{-11}$ J/s. The particle cooling rate calculated with the Richardson-Dushman equation (Equation (1)) is $3 \cdot 10^{-7}$ J/s. For comparison, the cooling rates due to conduction and sublimation are approximately 10^{-6}

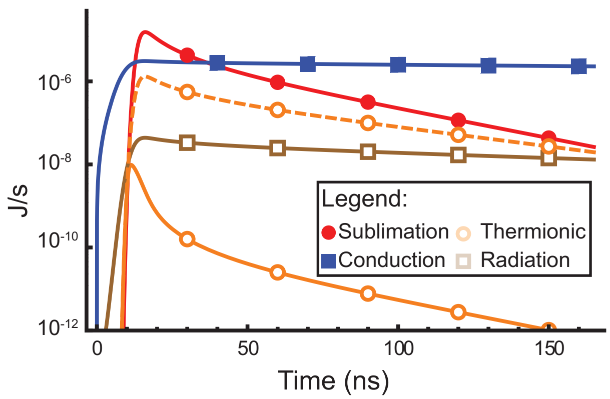

FIG. 3. Relative magnitudes of the modeled heat transfer processes: sublimation, Q_{Sub} (solid red circles), thermal conduction, Q_{Cond} (solid blue squares), thermionic emission, Q_{Therm} (hollow orange circles) and radiation, Q_{Rad} (hollow brown squares). Thermionic emission was calculated with (Equation (3), solid line) and without (Equation (1), dashed line) including the influence of the positive charge buildup, $\Delta\phi$. Including $\Delta\phi$ results in Q_{Therm} having an insignificant effect on the energy balance equation, compared to other heat transfer processes shown above.

J/s. Therefore, the particle cooling rate calculated from the adjusted form of thermionic emission has a negligible influence on the particle's energy balance equation.

Following the approach by Filippov *et al.*, laser-induced disintegration of soot aggregates is still predicted to occur given the experimental conditions in Table (I), even with the lower values of emitted current calculated from the adjusted form of thermionic emission. Thermionic emission of electrons results in positively charged soot particles. When the electrostatic Coulomb repulsion energy between positively charged particles is greater than the van der Waals bond energy, the soot aggregate can disintegrate into primary particles. Assuming a monodisperse diameter distribution within an aggregate, the repulsion energy between two charged spheres is,

$$U_{Rep} = k_E \frac{(eN_{Emit})^2}{D+d}, \tag{7}$$

where $U_{Rep} = \sim 75$ eV, N_{Emit} was calculated from Figure (2), and $d = 0.7$ nm was assumed to be the van der Waals bond distance. The van der Waals bond energy between two spheres with diameters much greater than the van der Waals bond length, $D \gg d$, is[27],

$$U_{VDW} = \frac{A_H D}{24d}, \tag{8}$$

where $U_{VDW} = 12$ eV is the van der Waals bond energy, and $A_H = 2.9$ eV is the Hamaker constant for graphite[28,29]. For comparison, similarly-sized soot aggregates are predicted to disintegrate when $N_{Emit} = 24$ electrons, well under the predicted values for N_{Emit} shown in Figure (2). Note, that this approach assumes uniform aggregate heating, consistent with Rayleigh-Debye-Gans polyfractal aggregate (RDG/PFA) theory[30–32], and uniform thermionic emission within an aggregate. For simplicity, disintegration of soot aggregates was assumed to be a binary process; partial disintegration of soot aggregates into smaller clusters was not considered for the purposes of this study. Additionally, effects of laser-induced annealing[25,33–35] on particle charging and on the mass and energy balance equations were not considered for the purposes of this study.

If emitted electrons rapidly return to positively charged soot particles, then laser-induced aggregate disintegration will not be predicted to occur. Figure (2) shows that the timescale for current emission is $\sim$ 10-20 ns. The timescale for electrons attachment to molecular oxygen (forming O_2^-) in room temperature, atmospheric pressure air was measured to be $\sim$12 ns[36], which is similar to the predicted emission time. Under this assumption, almost all emitted electrons will attach to O_2 molecules, and will not return to partially positively charged soot particles. Without the presence of oxygen, the emitted electrons are predicted to return to the partially positively charged soot particles. Although not considered for the purposes of this study, the presence of a background plasma, strong external electric fields or intense laser electric fields can also prevent electrons from returning to soot particles. (Additionally, since particles are typically acquire negative charge in a background plasma, the cooling rate due to thermionic emission is predicted to be more significant.) The ponderomotive energy of electrons in the laser-generated electric field is trivial for laser fluences (< 1 J/cm^2) and pulse durations ($\sim$10 ns) typically used for LII experiments. If the emitted electrons do not return to the soot aggregate, then the soot particles will remain positively charged, which can lead to aggregate disintegration.

In summary, an adjusted form of thermionic emission (Equation (3)) for laser-heated soot particles, which incorporates the effects of the particles' positive charge buildup, is presented. The buildup of positive charge results in significantly lower values of the thermionic emission current and the particles' cooling rate. Nevertheless, even with the lower values of current calculated from the adjusted form of thermionic emission (Equation (3)), the electrostatic Coulomb repulsion energy is still predicted to overcome the van der Waals bond energy, which can lead to disintegration of soot aggregates. Appropriately modeling thermionic emission from laser heated soot particles is crucial for predicting the likelihood of laser-induced disintegration of soot aggregates, and for interpreting TR-LII signals.

ACKNOWLEDGMENTS

The authors thank Alex Merzhevskiy and Yao-Wen Yeh for assistance. This work was supported by the U.S. Department of Energy, office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. James M. Mitrani acknowledges support through the Program in Plasma Science and Technology, at the Princeton Plasma Physics Laboratory.

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