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Calculation of Heating by CW Laser of Metal Nanoparticles Suspended in a Droplet of Liquid Fuel

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EXECUTIVE SUMMARY

Formulae are developed to calculate the temperature reached by metal particles suspended in liquid fuel or other electromagnetically absorptive medium and we apply them to aluminum and aluminum oxide nanoparticles suspended in JP-10 under a 10.6 μm , 25 Watt continuous wave laser. We used three different models for the distribution of laser intensity: as a cylindrical beam of uniform intensity, as a Gaussian beam, and as an Airy diffraction pattern. The average and maximum temperatures were found to be fairly consistent between the three models but were the highest for the Airy diffraction pattern. Mie theory predicts that aluminum nanoparticles at 80 nm are approximately 100 times as absorptive as aluminum oxide nanoparticles of a similar size and therefore reach significantly higher temperatures. Although JP-10 is highly absorptive in the infrared region, it boils at 460 K, and the resulting vapor at one atmosphere of pressure is several hundred times less absorptive than the liquid. According to our calculations, aluminum nanoparticles could be heated above their ignition temperature under these conditions even when shielded by a millimeter of JP-10 vapor, but only by a few microns of JP-10 liquid.

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CALCULATION OF HEATING BY CW LASER OF METAL NANOPARTICLES SUSPENDED IN A DROPLET OF LIQUID FUEL

1. INTRODUCTION

Several different experimental techniques exist that involve using a laser to heat microparticles or nanoparticles to extremely high temperatures. For example, in laser induced incandescence, a laser is used to heat absorptive particles (typically from soot) to temperatures around 4000 K so that their black-body radiation can be measured for characterization purposes. While laser induced incandescence was originally used only to study carbon particles, it has more recently been applied to other materials as well, such as metal nanostructures [1] and can be performed either with a pulse laser or continuous wave (CW) laser [2].

Laser light has also been used to ignite pulverized coal and fuel particles [3–5]. In an experiment involving laser ignition of coal dust clouds, a pulse laser with a wavelength of approximately $1 \mu\text{m}$ and duration of $150 \mu\text{s}$ was used to ignite particles in the cloud. When the concentration of particles in the cloud was high enough, the authors found that flame propagation occurred throughout the cloud, rather than local deflagration at the location of the laser beam.

Rather than a dense cloud of coal, we can envision a system where dark (electromagnetically absorptive), possibly combustible particles are suspended in a droplet of liquid (or vaporized) fuel. If these particles are heated under laser light, we might suspect that that fuel ignition and flame propagation would occur.

Recent experiments [6] have shown that JP-10 can be ignited under a 25 W CW laser beam at $10.6 \mu\text{m}$ if and only if small aluminum particles with diameters of around 100 nm are added to the mixture. It is worth questioning whether laser induced heating and possibly ignition of the aluminum particles could be responsible for this change in behavior.

A CW laser provides a continuous source of power, under which, barring any chemical reactions that change the nature of the system, the system will eventually reach thermodynamic equilibrium. Combustible nanoparticles heated by laser light in an oxygen rich environment will only reach their final equilibrium, however, if the equilibrium temperature is below their ignition temperature. Therefore, we can determine whether or not nanoparticles will ignite under a given set of conditions by computing their equilibrium temperature.

This calculation involves setting the rate of energy absorption by the nanoparticles equal to their rate of energy emission due to thermal radiation. While the basic principle is fairly straightforward, the actual calculation is deceptively complex for three reasons. First, the intensity of the incoming radiation is not uniform but dependent on location within the laser beam. Second, the optical properties of small particles are dependent on their size, composition, and the wavelength of the incident radiation. Finally, the liquid fuel in which particles are suspended is absorptive, can heat locally, and may bubble or vaporize.

To address the first problem, we compared three different models for the laser light with different degrees of complexity. Our simplest model used a cylindrical beam with uniform intensity inside and zero intensity outside. Because this beam profile does not closely match that of an actual laser, we also used two more sophisticated beam models to test whether the beam shape has a strong effect on temperature. The intensity distribution of laser light is often modeled with a Gaussian profile, while light passing through a small aperture or lens actually produces an Airy diffraction pattern, and we calculated temperatures using both distributions.

We approached the problem of finding optical properties of the metal nanoparticles with Mie theory. Mie theory can be used to compute scattering cross sections of small particles with a given radius and wavelength-dependent complex refractive index. Because a wealth of free tools and published data exists relating to Mie theory, we drew information from two existing sources: a publication containing Mie theory scattering cross sections for aluminum oxide particles [7] and the nanoComposix Mie theory calculator [8].

Finally, rather than deal with the full complexity of local heating and boiling, we chose to ignore the difficulties associated with dynamic bubbling, which include lensing effects at liquid-vapor interfaces fluid flow. Instead, we treat the two regimes of liquid fuel and fully vaporized fuel separately and determine the degree to which the fuel is heated and the degree to which the nanoparticles are shielded in both cases.

2. TEMPERATURE CALCULATION

2.1 Formulae for the temperature of nanoparticles in a transparent droplet

Although the assumption that liquid fuel is completely transparent to the incident radiation is not, in general, accurate, we will use this as a starting point for a more sophisticated picture. We begin with a model of metal nanoparticles as spheres of radius r_0 , which at temperature T emit black body radiation with a power per unit area given by the Planck formula as

$$\frac{\pi k_B^4}{60\hbar c^2} T^4, \quad (1)$$

where k_B is Boltzmann's constant, \hbar is Planck's constant, and c is the speed of light. To compactify our equations, we will make the definition

$$\beta \equiv \frac{\pi k_B^4}{60\hbar c^2}. \quad (2)$$

Assuming the distribution of nanoparticles is sparse enough that they do not shield each other from the laser beam, at thermal equilibrium, the power radiated by each nanoparticle must be equal to the power absorbed from the laser. If we assume the nanoparticles are small enough that the beam intensity is constant over a single particle, we can express the condition for thermal equilibrium as

$$\pi r_0^2 A I = 4\pi r_0^2 \beta T^4, \quad (3)$$

where I is the local intensity of the beam, A is the (wavelength and size dependent) absorption efficiency. The factor of $4\pi r_0^2$ comes from the assumption that the temperature is constant across the nanoparticle so that thermal radiation is emitted equally from everywhere on the surface.

Although we will develop more sophisticated models, the simplest model of laser light is a cylindrical beam of uniform intensity inside and zero intensity outside. If the total power emitted by the laser is W , the local intensity inside is simply $\frac{W}{\pi r_l^2}$, where r_l is the radius of the beam. Solving Eq. (3) for temperature, we then have that the temperature of a nanoparticle inside the beam at thermal equilibrium is

$$T = \left(\frac{AW}{4\pi r_l^2 \beta} \right)^{1/4}. \quad (4)$$

Although we might intuitively expect the temperature derived from this model to be a reasonable back of the envelope calculation, we might also question how strongly our result depends on the assumed shape of the beam. The actual distribution of laser intensity is determined by the diffraction pattern of light passing through an aperture. A beam of light that passes through a circular aperture exhibits an Airy diffraction pattern with an intensity given by

$$I = I_0 \left(\frac{2J_1(x)}{x} \right)^2 \quad (5)$$

$$x = ka \sin \theta \approx ka \frac{r}{L}, \quad (6)$$

where r is the distance from the center of the beam, k is 2π over the laser wavelength, a is the size of the aperture, L is the distance from the source, and θ is the angle from the source. If the aperture contains a lens, its radius must be divided by an appropriate geometric factor. For a spherical lens, this factor is 1.22, meaning that $a \rightarrow a/1.22$. J_1 is the first Bessel function, which is given by

$$J_1(x) = \frac{\sin x}{x^2} - \frac{\cos x}{x}. \quad (7)$$

The distance from the beam center to the first diffraction minimum provides a useful definition of the beam radius, r_l , and is given by $2a \sin \theta = 2\pi/k$. This distance is related to the aperture size and wavenumber by

$$\sin \theta = \frac{\pi}{ka} = \frac{r_l}{\sqrt{r_l^2 + L^2}} \approx \frac{r_l}{L}. \quad (8)$$

From this, we find

$$r_l = \frac{\pi L}{ka}. \quad (9)$$

Making the substitution $u = \pi r/r_l$, we can write the intensity as

$$I = I_0 \frac{4}{u^2} \left[\frac{\sin u}{u^2} - \frac{\cos u}{u} \right]^2 \quad (10)$$

The value of I_0 is related to the total power emitted by the laser, W . We can find the exact relationship by noting that W is the integral of the laser's flux through a planar surface perpendicular to the beam, given by

$$W = 2\pi \int I r dr = \frac{2r_l^2}{\pi} \int I u du = 8I_0 \frac{r_l^2}{\pi} \int_0^\infty \frac{1}{u} \left[\frac{\sin u}{u^2} - \frac{\cos u}{u} \right]^2 du = \frac{2r_l^2}{\pi} I_0, \quad (11)$$

and from there, we have

$$I_0 = \frac{\pi}{2r_l^2} W, \quad (12)$$

$$I = \frac{\pi W}{r_l^2} \frac{2}{u^2} \left[\frac{\sin u}{u^2} - \frac{\cos u}{u} \right]^2.$$

At thermal equilibrium, the temperature of a nanoparticle at a given point on the plane, by Eq. (3) is, then

$$T = \left[\frac{\pi}{2r_l^2} \frac{AW}{\beta u^2} \left(\frac{\sin u}{u^2} - \frac{\cos u}{u} \right)^2 \right]^{1/4}. \quad (13)$$

Although the maximum value of T is less meaningful than the average temperature over some volume, T is maximized at $u = 0$ and its maximum value is

$$T_{max} = \left[\frac{\pi}{2r_l^2} \frac{AW}{\beta} \lim_{u \rightarrow 0} \frac{1}{u^2} \left(\frac{\sin u}{u^2} - \frac{\cos u}{u} \right)^2 \right]^{1/4} = \left(\frac{\pi}{18r_l^2} \frac{AW}{\beta} \right)^{1/4}. \quad (14)$$

The average temperature of nanoparticles over a droplet with radius R is

$$T_{avg} = \frac{3}{4\pi R^3} \int T dV, \quad (15)$$

where the integral is performed over the volume of the droplet.

An integral over a spherical volume is most easily performed in spherical coordinates. Our definition of r comes from cylindrical coordinates, because it is the distance from the center of a cylindrically symmetric beam. In spherical coordinates, this distance becomes $r = \rho \sin \phi$, and we can therefore make the substitution $u = v \sin \phi$. Eq. (15) then becomes

$$T_{avg} = \frac{3}{2R^3} \frac{r_l^3}{\pi^3} \left(\frac{\pi}{2r_l^2} \frac{AW}{\beta} \right)^{1/4} \int_0^{\frac{\pi R}{r_l}} \int_0^\pi v^2 \sin \phi \left[\frac{1}{v^2 \sin^2 \phi} \left(\frac{\sin(v \sin \phi)}{v^2 \sin^2 \phi} - \frac{\cos(v \sin \phi)}{v \sin \phi} \right)^2 \right]^{1/4} d\phi dv. \quad (16)$$

Instead of finding the average temperature over the entire droplet, we can instead find the average temperature over a sphere with a radius equal to the width of the beam by making the substitution $R \rightarrow r_l$ in the limits of the integral, so that the integral over v goes from 0 to π .

Often, rather than using a true Airy diffraction pattern, the laser light is modeled as a beam with a Gaussian distribution to its intensity. The beam width, $2r_l$, is usually taken to be the full-width half-max of the pulse, and the intensity can then be written as

$$I = 2^{-\frac{r^2}{r_l^2}} I_0. \quad (17)$$

By following the same steps we went through above, we can find the average temperature of a droplet under such a beam to be

$$T_{avg} = \frac{3}{2R^3} \left(\frac{\ln 2}{4\pi\beta r_l^2} AW \right)^{1/4} \int_0^R \int_0^\pi r^2 \sin \phi \left(2^{-\frac{r^2}{4r_l^2} \sin^2 \phi} \right) dr d\phi, \quad (18)$$

and the maximum value obtained at $r = 0$ is

$$T_{max} = \left(\frac{\ln 2}{4\pi c r_l^2} AW \right)^{1/4}. \quad (19)$$

Although the actual maximum values of T for the two different beam shapes are not strictly meaningful, it is somewhat instructive to take their ratio. The maximum T under an Airy diffraction pattern distributed beam divided by the maximum T under the Gaussian distributed beam is

$$\frac{T_{max}^{Airy}}{T_{max}^{Gauss}} = \left(\frac{4\pi^2}{18 \ln 2} \right)^{1/4} \approx 1.334. \quad (20)$$

Compared to our original model of a cylindrical beam of constant intensity, we find

$$\frac{T_{max}^{Airy}}{T_{const}} = \left(\frac{2\pi^2}{9} \right)^{1/4} \approx 1.22. \quad (21)$$

In the next section, we will compare the average temperature over a small droplet and over the width of the beam using all three beam distributions.

2.2 Calculated temperatures of perfectly absorbing nanoparticles in a transparent droplet

The assumption that the nanoparticles of interest will absorb close to one-hundred percent of incident radiation does not typically hold, but it is somewhat instructive as an upper bound on the possible temperatures, and in Section 2.4, we will improve upon our results here using Mie theory. If The nanoparticles are perfectly absorbing (*i.e.* $A = 1$), for a 25 Watt beam following an Airy diffraction patter with a radius of 0.25 mm, the average temperature over a 1 mm droplet is

$$T_{1mm}^{Airy} = 744.36 \frac{3}{2R^3} \frac{r_l^3}{\pi^3} \left(\frac{\pi}{2r_l^2} \frac{AW}{\beta} \right)^{1/4} = 960.8 \text{ K}. \quad (22)$$

Likewise, for a Gaussian beam, the average temperature over a 1 mm droplet is

$$T_{1mm}^{Gauss} = 1.0736 \times 10^{-11} \frac{3}{2R^3} \left(\frac{\ln 2}{4\pi\beta r_l^2} AW \right)^{1/4} = 761.8 \text{ K}. \quad (23)$$

These two values differ by a factor of 1.26.

Rather than find the average temperature over the entire droplet, we could instead average over a spherical region with radius r_l , so that its diameter is equal to the beam width. Doing so, we get

$$T_{r_l}^{Airy} = 9.7084 \frac{3}{2R^3} \frac{r_l^3}{\pi^3} \left(\frac{\pi}{2r_l^2} \frac{AW}{\beta} \right)^{1/4} = 6415.9 \text{ K} \quad (24)$$

and

$$T_{r_l}^{Gauss} = 1.2161 \times 10^{-12} \frac{3}{2R^3} \left(\frac{\ln 2}{4\pi\beta r_l^2} AW \right)^{1/4} = 5523.1 \text{ K}, \quad (25)$$

which differ by a factor of 1.16. The temperature calculated using a cylindrical beam of uniform intensity works out to 6248.6 k over the beam and one eighth of that (781.1 K) over the entire droplet.

2.3 Calculation of fuel heating

The optical absorption properties of a liquid or gas are determined by its absorption cross section, usually given in units of m^2/mol . Multiplying by the molar density yields a number, α , with units of inverse length, which measures the fraction of incident intensity absorbed per unit distance. This relation describes a differential equation for the intensity of incident radiation as a function of distance,

$$\frac{dI}{dL} = -\alpha I \quad (26)$$

with solution

$$I = I_0 e^{-\alpha L}. \quad (27)$$

Therefore, the rate of energy absorbed by a cylindrical column of gas or liquid is

$$\pi r^2 (1 - e^{-\alpha L}) I_0, \quad (28)$$

where r is the radius of the cylinder and L is its length.

The rate of energy absorption for a cylindrical beam of radius r_l passing through a spherical droplet of radius R is more complicated, but by the same principle, we can calculate it from the integral

$$2\pi \int_0^{r_l} r \left(1 - e^{-2\alpha\sqrt{R^2-r^2}} \right) I dr. \quad (29)$$

If we assume that I is uniform over a given cross section, this integral can be solved analytically, and in the simplest case, where the beam diameter is greater than or equal to the radius of the droplet ($r_l \geq R$), we get

$$\pi I \left[R^2 - \frac{1}{2\alpha^2} (1 - e^{-2\alpha R} (2\alpha R + 1)) \right]. \quad (30)$$

This result is interesting because the rate of energy loss due to thermal radiation is proportional to the surface area of the droplet, which goes as R^2 , but the rate of energy absorption has a more complicated R dependence. Therefore, unlike in our previous calculations, the temperature of the droplet is size-dependent.

To illustrate this, it is useful to look at two different limits. In the limit that R is very small, if we carry out a Taylor series expansion of Eq. (30), the terms below third-order cancel, and we are left with an absorption cross section of $\frac{4}{3}\pi\alpha R^3$, which is proportional to the volume of the sphere. In this limit, the temperature is

$$T \approx \left(\frac{\alpha}{3\beta} IR \right)^{1/4}, \quad (31)$$

increasing with droplet radius.

In the limit that R is very large (in comparison to the length scale set by α), a series expansion around $R = \infty$ leaves us with $\pi(R^2 - \frac{1}{2\alpha^2})$. Because the leading term is proportional to R^2 , the temperature approaches a constant value of

$$T \approx \left(\frac{I}{4\beta} \right)^{1/4}, \quad (32)$$

which is equivalent to our result in Eq. (4) with $A = 1$.

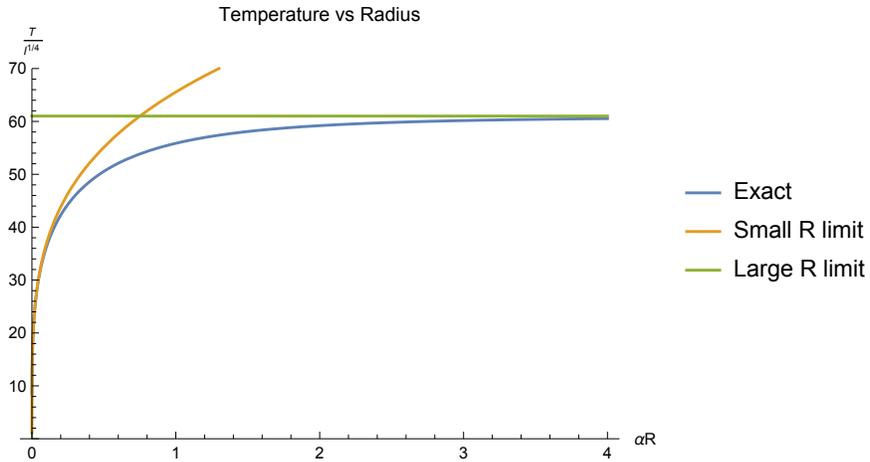


Fig. 1 — Temperature vs Radius at $I=1$ according to the exact formula (blue), small R limit (orange), and large R limit (green).

In Fig. 1, we have plotted temperature calculated using the exact formula for absorption in Eq. (30) along side the small R and large R limits from Eq.s (31) and (32). From this, we can see that deviation

from the small R limit begins to occur when R is approximately $0.2/\alpha$ and is close to the limiting value at approximately $3/\alpha$, which defines a rule of thumb for when a sphere becomes perfectly absorbing.

2.4 Effects of optical properties of Al and JP-10, boiling, and combustion

Aluminum nanoparticles smaller than 100 nm in diameter ignite at 933 K, while particles larger than 100 μm ignite at 2350 K because of the behavior of the oxide coating on larger particles [9]. Both of these numbers are significantly lower than the average temperatures we computed over the width of the laser beam for all three beam models. However, the optical properties of JP-10 and aluminum nanoparticles, as well as the effects of localized heating and phase transitions can significantly impact the actual temperatures that are achieved under laser heating. Additionally, aluminum has different optical properties from its oxide, and therefore, the two heat differently under an infrared laser.

Using Mie scattering theory, the absorption efficiency of an 80 nm aluminum nanoparticle at a wavelength of 10.6 μm comes out to 0.0044 [8]. Mie calculations for aluminum oxide, on the other hand, show that at a radius of 100 nm at a wavelength of 10 μm , the absorption efficiency is only 5.69×10^{-5} [7].

A thin oxide coating has little effect on the absorption properties of aluminum at such a long wavelength, and therefore, setting $A = 0.0044$, our calculated temperatures should be reduced by a factor of $0.0044^{1/4} = 0.258$. Even with this prefactor, the temperature of aluminum particles within the laser beam could theoretically reach up to 1654 K, which is hot enough to cause nanoparticles smaller than 100 microns to combust.

For nanoparticles composed of pure aluminum oxide, however, setting $A = 5.69 \times 10^{-5}$ results in a prefactor on the calculated temperature of 0.087. This reduces the average temperature within the laser beam to only 557 K.

In addition to the optical properties of the nanoparticles, infrared absorption by JP-10 also influences the computed temperature by reducing amount of radiation available for the nanoparticles to absorb. The absorption cross section for JP-10 at 10.6 μm , based on absorption spectra and measurements taken at nearby wavelengths [10, 11], is approximately 90 m^2/mol . The density of liquid JP-10 is 0.94 g/cm^3 [12], which at a molar mass of 136.2 g/mol , translates to 6901.6 mol/m^3 . The absorbance per unit length, α , for JP-10 is then calculated to be $6.21 \times 10^5 \text{m}^{-1}$, and the intensity of a laser beam passing through it is attenuated by a factor of $e^{-621000x}$, where the distance into the droplet, x , is measured in meters. The length scale set by this α is 1.6 μm , and by our rule of thumb from Section 2.3 a droplet with radius larger than 4.8 μm becomes perfectly absorbing. A 1 mm droplet of JP-10 would therefore absorb essentially all of the incoming radiation from a 10.6 μm CW laser.

However, the boiling point of JP-10 is 460 K [11], and once enough radiation is absorbed to heat liquid JP-10 beyond this point, it will vaporize, significantly reducing its density. Applying the ideal gas law, at a pressure of one atmosphere and temperature of 460 k, we find that the density of vaporized JP-10 is

$$\frac{n}{V} = \frac{PV}{rT} = 26.495 \text{ mol}/\text{m}^3. \quad (33)$$

At this density, the absorbance per unit length becomes 2384 m^{-1} , which sets a length scale of 0.42 mm. Again, by our rule of thumb, a droplet becomes perfectly absorbing when it has a radius greater than 1.26 mm,

or diameter of 2.52 mm. After penetrating one millimeter of vaporized JP-10, only approximately 90 percent of the power in the laser beam would be absorbed.

If only ten percent of the incident radiation is transmitted and available to aluminum particles for absorption, they will heat to approximately 930 K. This is close to the ignition temperature of 80 nm aluminum nanoparticles, and particles suspended at a depth of less than 1 mm into the droplet will reach higher temperatures. The autoignition point of JP-10 is 513 K, and therefore, if the aluminum nanoparticles get above this temperature, it is possible that they could cause JP-10 to ignite.

3. CONCLUSIONS

We have created a theoretical framework for calculating the temperature of nanoparticles suspended in a liquid droplet under a beam of CW laser light. The nanoparticles are treated as black bodies with absorption efficiencies determined by Mie theory and the liquid is treated similarly, with an absorbance per unit length, α determined from experimental data and its density.

We found that when the radius of the liquid droplet exceeds three times $1/\alpha$, it becomes essentially perfectly absorbing. For JP-10 in liquid form under laser light at $10.6 \mu\text{m}$, this length scale is approximately $4.8 \mu\text{m}$ and it increases to 2.5 mm for vaporized JP-10 at one atmosphere of pressure.

Because liquid JP-10 is highly absorbing in the infrared, it shields nearly all of the incoming laser light from any nanoparticles suspended in it, except for those that are a few microns from the surface of the droplet. However, if JP-10 heats above 460 K, it boils, and because the resulting vapor is much more transparent, nanoparticles suspended in it will get much hotter.

Aluminum nanoparticles are much more absorptive in the infrared than aluminum oxide, and without any shielding from JP-10, aluminum nanoparticles hit by a 25 W laser at $1.06 \mu\text{m}$ with a beam width of 0.5 mm can be expected to reach temperatures of up to 1654 K, while aluminum oxide particles would only get up to 557 K. Once shielding is taken into account, both temperatures drop quickly.

The dynamical problems introduced by JP-10 boiling and combustion are too complicated to be treated under the framework we have outlined here. Lensing due to local liquid-gas interfaces, fluid flow, and energy input from possible nanoparticle combustion are all factors that would influence the behavior of the real system. However, we can draw a few basic conclusions from this work.

First, if JP-10 vaporizes, a large volume of aluminum sub 100 micron nanoparticles within the vapor could be heated above their ignition temperature by laser light. An even larger volume of nanoparticles would be heated above JP-10's ignition temperature. Second, because of their lower absorption cross section, very few aluminum oxide nanoparticles could be expected to heat above JP-10's ignition temperature when suspended in JP-10 vapor. Third, because JP-10 itself is so absorptive, even as a gas, it would easily be heated above its ignition temperature if not for boiling and fluid flow.

We should expect, therefore, that fluid dynamics plays a crucial role in combustion in this system. While it is possible that aluminum nanoparticles under these conditions could get hot enough to combust, or at the very least, to ignite JP-10, it is difficult to say for certain whether this is a significant factor in experiments involving laser induced combustion of JP-10 with aluminum additives.

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