Direct evidence of departure from local thermodynamic equilibrium in a free-burning arc-discharge plasma

S. C. Snyder, G. D. Lassahn, and L. D. Reynolds
Idaho National Engineering Laboratory, EG&G Idaho, Inc., P.O. Box 1625, Idaho Falls, Idaho 83415
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Radial profiles of gas temperature, electron temperature, and electron density were measured in a free-burning atmospheric-pressure argon arc-discharge plasma using line-shape analysis of scattered laser light. This method yields gas temperature, electron temperature, and electron density directly, with no reliance on the assumption of local thermodynamic equilibrium (LTE). Our results show a significant departure from LTE in the center of the discharge, contrary to expectations.

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INTRODUCTION

Because the kinetic processes of thermal plasmas are dominated by electron collisions, it has been generally assumed for many years that local thermodynamic equilibrium (LTE) exists in the core or arc column of atmospheric-pressure free-burning arc plasmas [1–3]. This assumption is believed to be correct because of the agreement of temperatures calculated from the measured emission coefficients of several excited-state transitions of neutral and ion species in the plasma [2,3], although there is spectroscopic evidence of non-LTE in the thin cathode fall region (less than 0.2 mm thick) of the arc [2,3]. The temperature measured by emission spectroscopy is the gas temperature only if LTE exists [4]. Additionally, experiments have recently been performed on atmospheric-pressure argon-plasma jets and free-burning arcs relating the frequency-integrated intensity of laser light that has been Thomson and/or Rayleigh scattered by the plasma to the plasma gas temperature [5,6]. When the results of these experiments are compared with temperature values obtained from emission spectroscopy, there is good agreement in the center of the plasma. One concludes from this agreement that LTE exists in the arc column, although it must be noted that the integrated laser light scattering technique relies on the assumption of LTE to interpret the data. There is, however, significant disagreement in the outer regions of the plasma, indicating a departure from LTE probably due to resonance radiation trapping [6]. Here, integrated laser scattering is unaffected by departures from LTE since it is dominated by Rayleigh scattering from ground-state neutral argon, and the resulting gas temperatures are considered to be accurate. On the other hand, emission spectroscopy probably gives reliable electron-temperature values in accordance with the partial-local-thermodynamic-equilibrium (PLTE) model [4], which says the electrons are in thermal equilibrium with the upper-level excited atomic states.

Neither emission spectroscopy nor integrated laser light scattering provides a direct measurement of the true gas or kinetic temperature of the plasma. Accordingly, it is not possible to properly assess the degree of departure from LTE in a plasma. To our knowledge, the only method available to directly determine the kinetic temperature of a plasma is line-shape analysis of laser light scattered by the plasma [7]. The only assumption necessary is that the rest-frame velocity distribution functions of the electrons and heavy particles (ions and neutral atoms) are Maxwellian characterized by unique electron and gas temperatures, respectively. This technique is therefore independent of any assumptions about LTE. If the electron density is greater than 10^{22} m^{-3}, Thomson scattering dominates, while at lower electron densities and temperatures, Rayleigh scattering dominates. In general, however, the line shapes are a superposition of Thomson and Rayleigh line shapes. Under conditions where there is significant Thomson scattering, it is also possible to directly determine electron temperature and density. We report in this paper electron-temperature, gas-temperature, and electron-density profiles of an atmospheric-pressure free-burning argon arc plasma determined directly from line-shape analysis of laser light scattered by the plasma.

THEORY

The line shape of Thomson scattered light has two components. One component, called the electron feature, is due to the density fluctuations of the free electrons themselves. The other component is known as the ion feature and is due to the electrostatic influence of the density fluctuations of the ions on the free electrons.

The Thomson line shape can be written as [8]

$$S(\mathbf{k},\omega)=\frac{2\pi}{k}\left|1-\frac{G_e}{\epsilon}\right|^2 f_{0e}\left[\frac{\omega}{k}\right]+\frac{2\pi Z}{k}\left|\frac{G_e}{\epsilon}\right|^2 f_{0i}\left[\frac{\omega}{k}\right], \tag{1}$$

where k is the magnitude of the difference between the scattered wave vector and the incident wave vector ($\mathbf{k}=\mathbf{k}_s-\mathbf{k}_0$), ω is the difference between the angular frequency of the scattered light and the incident laser ($\omega=\omega_s-\omega_0$), and $\epsilon=1+G_e+G_i$ is the longitudinal dielectric constant of the plasma. The functions G_e and G_i are screening integrals defined by

$$G_e(\mathbf{k},\omega)=\lim_{\gamma\to 0}\int_{-\infty}^{\infty}\frac{4\pi e^2 n_e}{m_e k^2}\frac{\mathbf{k}\cdot\dfrac{\partial f_{0e}}{\partial \mathbf{v}}}{\omega-\mathbf{k}\cdot\mathbf{v}-i\gamma}d\mathbf{v} \tag{2}$$

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and

$$G_i(\mathbf{k},\omega)=\lim_{\gamma\to 0}\int_{-\infty}^{\infty}\frac{4\pi Ze^2n_i}{m_ik^2}\frac{\mathbf{k}\cdot\frac{\partial f_{0i}}{\partial \mathbf{v}}}{\omega-\mathbf{k}\cdot\mathbf{v}-i\gamma}d\mathbf{v}\ , \quad (3)$$

where the f's are the generalized one-dimensional velocity distribution functions for electrons and ions, denoted by the subscripts e and i, respectively, the m's are the electron and ion masses, the n's are the electron and ion number densities, e is the electron charge, and Z is the ion charge, equal to 1 for this experiment. If electrons and ions have Maxwellian velocity distributions characterized by electron and ion temperatures T_e and T_i, we have in one dimension for electrons,

$$f_{0e}(v)=\left[\frac{m_e}{2\pi k_BT_e}\right]^{1/2}\exp\left[-\frac{m_ev^2}{2k_BT_e}\right]\ , \quad (4)$$

and for ions,

$$f_{0i}(v)=\left[\frac{m_i}{2\pi k_BT_i}\right]^{1/2}\exp\left[-\frac{m_iv^2}{2k_BT_i}\right]\ , \quad (5)$$

where k_B is Boltzmann's constant. The first term in Eq. (1) is the electron feature, and the second term is the ion feature. The electron feature is considerably broader than the ion feature, scaling roughly as $(m_i/m_e)^{1/2}$. Ion-ion and ion-neutral collisions can affect the spectrum of scattered light. However, for our experimental conditions the effect of collisions on the line shapes is negligible, as discussed elsewhere [7].

The line shape of Rayleigh scattered light in thermal plasmas is a simple Doppler-broadened Gaussian with a full width at half maximum (FWHM) given by [9]

$$\Delta\omega_{\text{FWHM}}=4\left[\frac{2k_BT_g\ln2}{mc^2}\right]^{1/2}\omega_0\sin\theta/2\ , \quad (6)$$

where m is the atomic mass of the scatterer, θ is the scattering angle, c is the speed of light, and T_g is the gas temperature. Because the difference in the masses of neutral and ionized argon is negligible, it is assumed that $T_i=T_g$ [10].

EXPERIMENT

Radial profiles of electron temperature, gas temperature, and electron density profiles were measured in a 100-A dc atmospheric-pressure vertical free-burning argon arc discharge 2 mm below the 2.4-mm-diam conical thoriated-tungsten cathode. The arc was generated by a standard gas-tungsten arc (GTA) welding torch, which is described in more detail elsewhere [2]. The anode was water-cooled copper. There is no evidence of copper or tungsten atoms or ions contaminating the arc of GTA torches operating under these conditions [11]. The cathode-to-anode gap was 9 mm. An injection-seeded pulsed Nd:YAG (neodymium-doped yttrium aluminum garnet) laser operating at 532 nm and a scanning tandem Fabry-Pérot interferometer (FPI) were used for high-resolution measurements of the ion-feature Rayleigh line shapes of scattered light. Satisfactory Thomson scattered light line-shape measurements to determine gas and electron temperatures of low- and high-pressure transferred arcs and inductively coupled plasma (ICP's) have been previously made [12–14]. However, the fairly recent availability of narrow-band injection-seeded Nd:YAG pulsed lasers has made possible the collection of very high quality line shapes. The details of this aspect of the experiment can be found elsewhere [7]. The electron feature was recorded using an unseeded Nd:YAG laser operating at 532 nm and a scanning 1.3-m monochromator. In both cases, the laser beam was normally incident to the flow axis of the arc discharge, and the scattering angle was 90° to the flow axis and incident laser beam.

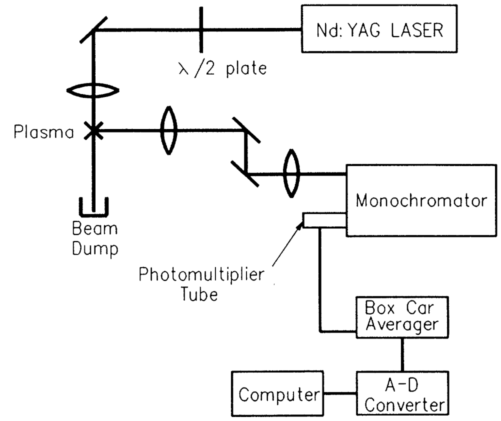

FIG. 1. Schematic of the experiment performed to resolve the electron feature of Thomson scattered light.

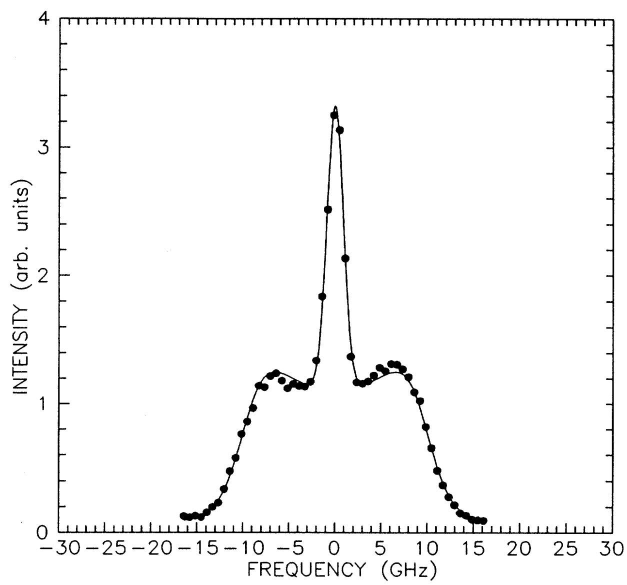

FIG. 2. Ion-feature Rayleigh line shape of light scattered by the plasma taken at the $r=0$ mm position, 2 mm below the cathode tip. The gas temperature was determined from this line shape, after deconvolution of the FPI instrument function, to be 14 200 K±5%. In this case, the contribution of Rayleigh scattering to the total line shape is less than 1%. The solid line is the fit of the data by the theory. The estimated uncertainty of the temperature is a combination of fitting errors, uncertainty in the scattering angle, and uncertainty in deconvolution of the FPI instrument function.

The GTA torch was mounted on a translation stage, and radial positions were determined by translating the torch relative to the incident laser beam. The spatial resolution of the measurements was $\sim 3\times10^{-3}$ mm^3. Up to 2 h were required to collect a complete set of line-shape data at five radial positions. The arc remained stable for the duration of the experiment. The schematic of the electron-feature experiment is given in Fig. 1.

A typical ion-feature Rayleigh line shape is shown in Fig. 2. The solid curve represents a fit with a function including the Thomson term of Eq. (1), the Rayleigh term of Eq. (6), and a Gaussian term to represent the spike at 0 GHz. This central spike is unscattered laser light, used to provide a frequency reference and to determine the FPI instrument response function for deconvolution purposes. The ion or gas temperature was determined from this fit. The line shape shows a slight asymmetry, which was determined to be due to minor misalignment of the FPI. The effect of this asymmetry on the gas temperature determined from the line shape was a small increase in the fitting error.

RESULTS AND DISCUSSION

A typical electron-feature line shape is shown in Fig. 3. Fitting these data gives the electron temperature and electron density. Ion-temperature values cannot be obtained from these data because the ion feature is not resolved. The ion feature is included with the unscattered laser light in the central peak, which has no significance in determining n_e or T_e. The good agreement of the experimental ion and electron features with the line-shape theory, as evident in Figs. 2 and 3, supports the assumption that the velocity distribution functions of the electrons and ions can be described as Maxwellian.

The intense incident laser beam causes heating of the electrons by inverse bremsstrahlung. It was therefore necessary to measure the electron temperature at a fixed spatial location for several laser energies and extrapolate to the unperturbed electron temperature at 0 mJ pulse^{-1} laser energy. This is possible because the relationship between the increase in electron temperature and laser energy has been shown to be linear [15]. Electron density and ion temperature were not observed to vary significantly with laser energy. A typical plot of measured electron temperature as a function of laser energy is presented in Fig. 4.

A plot of our experimental values of electron and gas temperature as a function of radial position is given in Fig. 5. There is a striking discrepancy in the two temperature profiles. In particular, the peak electron temperature measured is 20 900 K±8%, while the peak gas temperature measured is 14 200 K±5%. These results clearly show *a significant departure from LTE in the core of the arc,* contradicting the premise of LTE inherent in previous interpretations of spectroscopic- and frequency-integrated laser light scattering data [1–3,6].

At these electron temperatures, doubly ionized argon is formed. One can estimate from the LTE Saha equation [16] and the ideal-gas law that the amount of Ar III formed when $T_e = 21\,000$ K is about 4% of the total ionized species. One can examine the effect of Ar III on the line shape by using a generalized form of Eq. (1) for multicomponent plasmas [17]. It was found that the influence of this amount of Ar III on the line shapes is insignificant, and we treated all ion features as if they were due to singly ionized argon. When Ar III concentrations become greater than about 10%, the line-shape theory shows that the ion-acoustic resonance structure becomes quite pronounced, and it is not possible to fit these line shapes with the single-component model of Eq. (1). This was never observed experimentally.

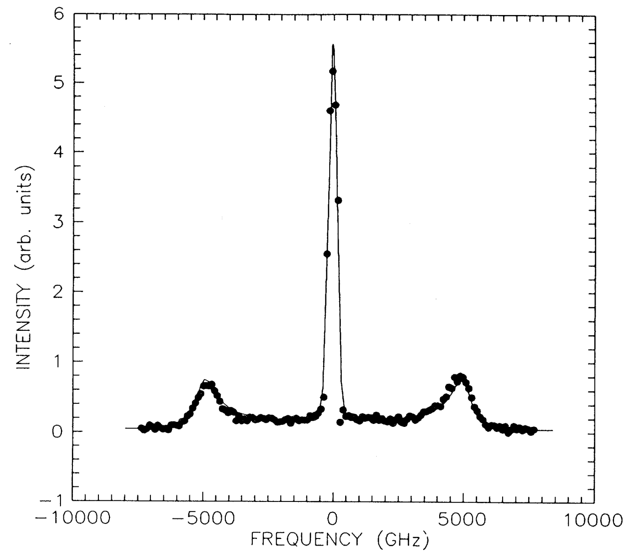

FIG. 3. Electron feature of light scattered by the plasma taken at the $r = 0$ mm position, 2 mm below the cathode tip. The electron temperature and density determined from this line shape are 28 240 K±3% and 1.62×10^{23} m^{-3}±3%, respectively. The value of the electron temperature was strongly influenced by laser heating. The solid is the fit of the data by the theory. The estimated uncertainties of the temperature and electron density are a combination of fitting errors, uncertainty in the scattering angle, and uncertainty in deconvolution of the FPI instrument function.

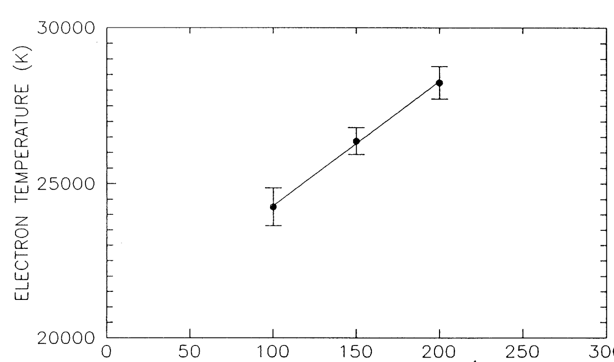

FIG. 4. Experimental values of electron temperature plotted as a function of laser energy. The data were taken at the $r = 0$ mm position, 2 mm below the cathode tip. The y intercept of the linear fit of this data is the electron temperature unaffected by laser heating.

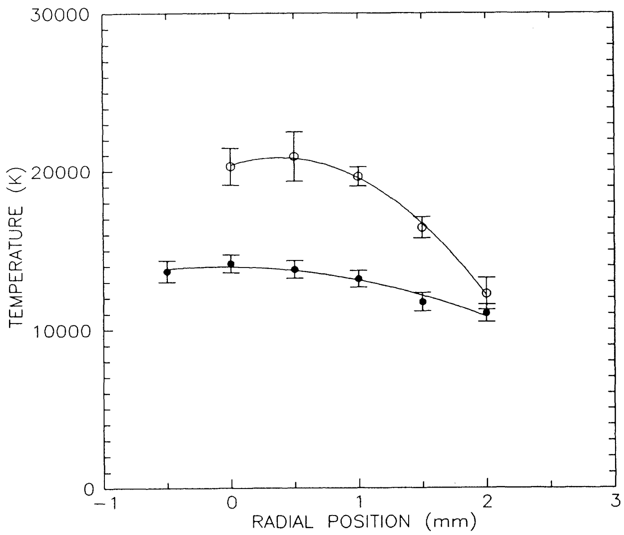

FIG. 5. Radial profiles of electron temperature and gas temperature taken 2 mm below the cathode tip. The open circles are the electron temperatures, and the solid circles are the gas temperatures. The uncertainties of the electron-temperature values now represent additional error introduced by extrapolating the value of T_e at 0 mJ pulse^{-1} laser energy from the T_e vs laser energy plot.

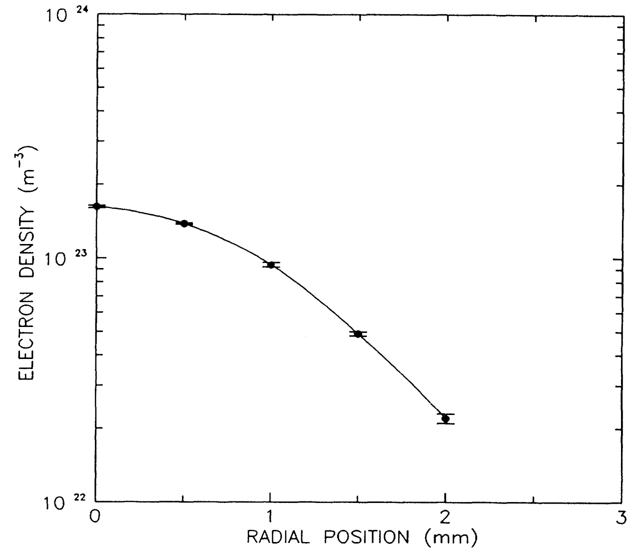

FIG. 6. Radial profile of electron density determined from line-shape analysis of scattered laser light. The experimental data were taken at 2 mm below the cathode tip.

A radial profile of the electron density determined from the line-shape analysis is given in Fig. 6. The electron density measured in the center of the arc is 1.62×10^{23} m$^{-3}\pm3\%$. Recent spectroscopic evidence of LTE in the arc column combined with spectroscopic measurements of the electron density [3] support the Griem criterion [18] that LTE occur in thermal plasmas when electron densities are $\sim10^{23}$ m^{-3}. Our measurements imply that this criterion is not correct in arc plasmas. Recent calculations [19] suggest that this critical electron density is $\sim10^{24}$ m^{-3}.

CONCLUSIONS

The direct measurements of electron temperature, gas temperature, and electron density profiles by line-shape analysis of scattered laser light presented in this paper reveal severe departures from LTE in the core region of a free-burning arc plasma, contradicting the widely held assumption that LTE exists there. In addition, the supposed critical electron density of $\sim10^{23}$ m^{-3} for LTE to occur is evidently too low for LTE to occur in arc plasmas.

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