On revisiting our recent article (Liu et al [1]) after publication, we realised that a key sentence had been omitted from the beginning of section 3.2:

The following section closely follows Canal et al [2], but with extensions to accommodate multiple ionic charge states and so that the Druyvesteyn average energy will correspond numerically to the Maxwellian one, i.e. be a temperature in the conventional sense.

Since the absence of this text does not affect the scientific content of the paper, we had failed to notice that it had not been included in our submitted manuscript. We would like to apologize both to readers and to the authors of [2] for this inadvertent omission, which could give a false impression of the basis for our derivations.

References

[1] Liu H, Truscott B S and Ashfold M N R 2016 Position- and time-resolved Stark broadening diagnostics of a non-thermal laser-induced plasma Plasma Sources Sci. Technol. 25 015006

[2] Canal G P, Luna H, Galvão R M O and Castell R 2009 An approach to a non-LTE Saha equation based on the Druyvesteyn energy distribution function: a comparison between the electron temperature obtained from OES and the Langmuir probe analysis J. Phys. D: Appl. Phys. 42 135202
Position- and time-resolved Stark broadening diagnostics of a non-thermal laser-induced plasma

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Abstract
We present an analysis of the Stark-broadened line shapes of silicon ions in a laser-induced plasma using a model constructed, without assuming local thermodynamic equilibrium (LTE), using a Druyvesteyn electron energy distribution function (EEDF). The method is applied to temporally and spatially resolved measurements of Si$^{2+}$ and Si$^{3+}$ emissions from a transient plasma expanding into vacuum, produced by 1064 nm, nanosecond pulsed laser ablation of a Si (1 0 0) target. The best-fitting simulated line shapes and the corresponding electron number densities and temperatures (or equivalently, Druyvesteyn average energies) are compared with those returned assuming LTE (i.e. for a Maxwellian EEDF). Non-thermal behavior is found to dominate at all but the very earliest stages of expansion close to the target surface, consistent with McWhirter’s criterion for the establishment of LTE. The Druyvesteyn EEDF always yields an equivalent or better model of the experimental measurements, and the observed increasingly strong departure from the Maxwellian case with time and distance from the ablation event highlights the essential invalidity of the LTE assumption for moderate-power, nanosecond laser-induced plasma expanding in vacuo.

Keywords: Stark broadening, electron temperatures, laser-induced plasmas, silicon, optical emission spectroscopy, non-LTE

(Some figures may appear in colour only in the online journal)

1. Introduction

Pulsed laser ablation (PLA) methods are finding ever-growing use in fields as diverse as medicine [1], environmental analysis [2, 3], and many areas of manufacturing ranging from thin film deposition and surface coating to the fabrication of patterned nanomaterials [4]. Despite manifold applications, however, several aspects of the underlying physics remain incompletely understood [5, 6], and the early-time dynamics of the energetic electrons and ions in a pulsed laser induced plasma (LIP) remain a particular focus of fundamental study.

The present work demonstrates a new approach to imaging the optical emission accompanying nanosecond PLA of a silicon target, in vacuum, with simultaneous spectral, spatial and temporal resolution, and shows how data from such experiments can inform directly on the electron densities and temperatures prevailing in LIPs. The following summary description of the PLA process focuses on such conditions. Prior to laser excitation, no plasma exists. The arrival of an intense laser pulse leads to rapid (sub-picosecond) heating of the target surface, thermionic and photo-emission of electrons and the formation of a space-charge layer close to the target surface. These electrons couple strongly to the laser field, and thereby gain sufficient energy for further collisional ionization of the sparse vapor, leading to embryonic plasma formation. This nascent plasma can play an important role in further target heating, by absorbing incident laser radiation via inverse
bremssstrahlung (IB). At high irradiances, surface temperatures of several thousand kelvin are achieved relatively early in the laser pulse. The target material approaches its critical temperature and can undergo an explosive phase transition. Desorption of the surface layer(s), which possess a net positive charge due to the prior electron emission, is assisted by the electric field gradient. The plasma density thus increases rapidly, as does its rate of heating by IB absorption, particularly at the expansion front. The early stages of LIP formation unarguably involve the incident laser radiation interacting directly with the target, but the eventual properties of the LIP will also be sensitive to subsequent laser–plume interactions. Even for the present study involving just one combination of target (Si) and background medium (vacuum, at least prior to the arrival of the laser pulse), it is still necessary to consider several laser-related variables like wavelength, pulse energy, irradiance, etc.

Much of this complexity is captured in the 1D hydrodynamic model developed by Vertes, Bogaerts and coworkers for the nanosecond laser ablation of selected metal targets in vacuum [7, 8] and in ambient helium [9, 10]. The model assumes local thermodynamic equilibrium (LTE), but succeeds in replicating much of the foregoing detail. For example, it shows ejection of electrons, ions and neutral species from the target surface at very early times, and the formation of plasma which attenuates the subsequent laser radiation incident on the target surface, and it predicts that the efficiency of this attenuation and the nature of the dominant laser–plasma interaction will be both wavelength- and irradiance-dependent. This 1D model identifies electron–ion IB as the dominant absorption mechanism following 5 ns, 1064 nm PLA of a Cu target at the ≥10 GW cm⁻² irradiances used in the present study [10]. However, we also note a more recent report [11, 12] that identifies self-consistency issues in the earlier 1D model.

Other studies have sought to explore the mechanism of LIP formation by probing the expanding plume of ablated material. For example, Torrisi et al [13] reported temporally and spatially resolved measurements of the electrons and ions formed following 1064 nm PLA of a Ta target in vacuum that are broadly consistent with a proposed space charge acceleration model [14]. Such models assume a higher-energy tail to the kinetic energy distribution of the electrons formed in the PLA process. The fastest electrons emerge at the leading edge of the plume. Some escape, but some remain and thereby establish an electric field gradient with respect to the bulk of the plume (which has a net positive charge). This electric field accelerates positively charged particles in the plume, to extents that scale with their charge. The most highly charged particles partition towards the front of the expanding plume, are least influenced by the adiabatic cooling that accompanies plume expansion and appear with the greatest terminal velocities [13, 14].

The most noteworthy aspects of the current study are the insights it provides into the evolving electron densities ($N_e$) and temperatures ($T_e$) within a LIP. The existing literature details several alternative routes to such information. For example, Saha–Boltzmann analysis of optical emission spectroscopy (OES) data from a Fe LIP in 1 atm air [15] returned $N_e = 10^{22}–10^{23}$ m⁻³. Two-wavelength laser interferometry studies of an air plasma gave $N_e$ values of similar magnitude ($10^{22}–10^{24}$ m⁻³) [16] and Thomson scattering measurements of Mg [17] and Al [18] LIPs both yielded $N_e \sim 10^{23}$ m⁻³. Thomson scattering and laser interferometry both require relatively complex instrumentation and can be compromised by unintended probe-laser-induced heating effects [18, 19]. OES offers potential benefits with regard to convenience, cost and efficiency, and is now a popular method for estimating temporally and spatially resolved $N_e$ and $T_e$ values in LIPs. However, most analyses of OES data assume LTE, i.e. a Maxwellian electron energy distribution function (EEDF) and the validity of the Saha equation when deriving the various level populations needed in order to determine the emission and self-absorption coefficients. The validity, or otherwise, of such assumptions when considering laser ablation in ambient air (e.g. in laser induced breakdown spectroscopy, LIBS) remains a matter of some debate [16]; the assumption of LTE is unlikely to be appropriate in the case of a LIP expanding in vacuum [20, 21].

The present study offers a new route to determining temporally and spatially evolving $N_e$ and $T_e$ values from the Stark widths and shifts of atomic emission lines from LIPs in vacuum. The method is demonstrated by analysis of individual line shapes in the time-gated, spatially resolved optical emission accompanying the 1064 nm nanosecond PLA of a Si (100) target. Key to the improved analysis is the use of a model based on a Druyvesteyn (rather than a Maxwellian) EEDF, which should be applicable to most LIPs even under non-LTE conditions. The $N_e$ and $T_e$ values so derived, their temporal and spatial variation and the progressive deviation from LTE conditions when such a LIP evolves into vacuum are all reassuringly similar to those determined in recent Thomson scattering studies of Mg LIPs in vacuum [17, 18].

2. Experimental

A detailed description of the apparatus and experimental procedure can be found elsewhere [22]. PLA was achieved using a Nd:YAG laser that provided output pulses with energies of 20–72 mJ and durations in the range 9–20 ns (full width at half maximum, FWHM, with a Gaussian temporal profile). All data shown in this paper were obtained using the laser fundamental wavelength (1064 nm). The laser output was focused, using an adjustable (∼350 mm focal length) Galilean telescope, at 45° angle of incidence onto the surface of a slowly rotating Si (100) target mounted in a vacuum chamber, which was maintained at a pressure of 10⁻⁷ mbar. The spot size at the target was adjusted to be ∼4.8 × 10⁻⁴ cm², and the absolute timings, total energies, and durations of the laser pulses were continuously measured using a calibrated 350 MHz photodiode connected to an oscilloscope. We are thus able to specify either fluence (J cm⁻²) or pulse-averaged irradiance (GW cm⁻²), calculated as fluence divided by pulse duration. However, because the pulse energy was adjusted by varying the laser Q-switch delay, we prefer to acknowledge the resulting variation in pulse duration by quoting irradiance in the narrative that follows.
Spatially resolved plume emission spectra were recorded at different time delays ($\Delta t$) after the ablation event using a time-gated intensified charge coupled device (iCCD) camera attached to a 0.3 m Czerny–Turner spectrograph and imaging optics. The iCCD comprised $626 \times 255$ active pixels, each with dimensions of $26 \times 26 \mu m$, and the optical system had an overall magnification of unity. The ablation event was defined as occurring at the earliest time $t = t_0$ for which plasma emission could be observed, and $t_0$ and $\Delta t$ were both determined to $\pm 1$ ns. Spatiospectral images were recorded over the time period defined by $t = t_0 + \Delta t - 5$ ns and $t = t_0 + \Delta t + 5$ ns (i.e. a 10 ns total gate width), chosen to be sufficiently short to permit only minimal plume evolution during the course of a measurement.

3. Results and discussion

3.1. OES measurements

Figure 1 shows spatially resolved optical emission $I(z, \lambda; \Delta t)$ images measured in the wavelength range $450 < \lambda < 490$ nm following 1064 nm PLA of a Si target in vacuum at an approximate irradiance of 25 GW cm$^{-2}$ measured at two different time delays $\Delta t = (a) 40$ ns and (b) 70 ns. The vertical axis in these images is the distance, $z$, from the target surface (placed at $z = 0$ by definition). The emission features in this wavelength range are all attributable to Si$^{2+}$ and Si$^{3+}$ ions, henceforth referenced using spectroscopic notation as Si$^{\text{III}}$ and Si$^{\text{IV}}$. The specific Si$^{\text{IV}}$ lines are listed but not assigned in the NIST Atomic Spectra Database [23], but from the listed level energies can be assigned to the $2p^66h \rightarrow 2p^65g$ and/or $2p^66g \rightarrow 2p^65f$ transitions. Each emission feature spans a range of $z$, illustrating that both emitting species are formed with a spread of velocities. However, the more striking observations are the spatial fractionation between the different emitters and the uniformity of the spatial distribution displayed by all emission lines associated with a given charge state. In practice, the second (spatial) dimension allows assignment of the various carriers contributing to such wavelength-dispersed spectra simply by inspection. The logarithmic false-color intensity scale ranges from red (high) to blue (low) as shown to the right of panels (a) and (b), and the displayed spectra represent the accumulation of (a) 150 and (b) 300 laser pulses.

Multidimensional datasets, such as those shown in figures 1(a) and (b), can be analyzed in several ways. Figure 2(a) shows the time-evolving spatial profile of the Si$^{\text{III}}$ emission intensity, obtained by integrating over the 455.262 nm line shape measured at different times $t$. The displayed envelopes are all from $I(z, \lambda; \Delta t)$ images recorded for the same number of laser shots and progressively later time delays, so the relative peak intensities can be meaningfully compared. Equivalent data for a Si$^{\text{IV}}$ emission (obtained by integrating over the 465.432 nm line shape) is shown in figure 2(b). Clearly, the Si$^{\text{IV}}$ $I(z)$ profile recorded for any given $\Delta t$ is broader and peaks at larger $z$ than the corresponding Si$^{\text{III}}$ emission profile—as inferred from the spatiospectral images shown in figure 1. Plotting $z_{\text{max}}$ (the peak of the emission intensity distribution) versus $\Delta t$, as in figure 2(c), confirms the different propagation velocities of the Si$^{\text{III}}$ and Si$^{\text{IV}}$ emitters, and reveals the early time acceleration of these multiply charged emitters, consistent with the space charge acceleration model summarized previously [14].

The $I(z, \lambda; \Delta t)$ images also allow detailed study of the $z$-dependence of each line shape for any given $\Delta t$, which is illustrated for the case of the Si$^{\text{III}}$ 455.262 nm transition in the inset in figure 1(a). Figure 1(c) shows the reduction of the Si$^{\text{IV}}$ emission intensities and the narrowing of all features in the later-time spectrum measured at $z = 1$ mm. In vacuum, instrumental, Doppler and Stark broadening are the principal contributors to the measured widths of emission lines. The
The instrumental FWHM line width was 0.074(3) nm, as determined by measuring the 435.834 nm line from a low-pressure Hg lamp and fitting to a Gaussian line shape. Relative to this instrumental contribution, Doppler broadening is insignificant, given that the optical set-up is optimized to sample emission from the center of the plume, and that the plume propagates perpendicularly to the viewing axis. Figure 3 shows the way the measured FWHMs of the various Si iii emission lines vary with (a) $\Delta t$, at a constant irradiance (25 GW cm$^{-2}$) and a range of different $z$, and (b) irradiance, at $z = 0.6$ mm and various $\Delta t$. As these figures show, the measured FWHM is greatest at the temporal and spatial origin of the ablation plume (i.e. at small $z$ and $t$), increases with incident irradiance, and maximizes at later $t$ when monitored at larger $z$ (reflecting the time taken for the expanding plume to reach the viewing region). All line widths measured at $\Delta t \geq 100$ ns exceed the instrumental line width. We attribute this additional broadening to the Stark effect, which is the dominant source of line broadening observed at the earliest times. The next section describes an approach that allows analysis of such Stark-broadened line shapes measured under non-LTE conditions.

### 3.2. Theoretical approach to Stark broadening under non-LTE conditions

Allowing for possible self-absorption of emission from the centre to the edge of a LIP, the 1D radiative emission equation is
\[
\frac{dI_e(\nu, N_e, T_e)}{d\nu} = \varepsilon(\nu, N_e, T_e) - \mu(\nu, N_e, T_e)I_e, \tag{1}
\]

where \(I_e\) is the emission intensity at frequency \(\nu\), \(T_e\) is the electron temperature, and \(\varepsilon(\nu, N_e, T_e)\) and \(\mu(\nu, N_e, T_e)\) are the emission and self-absorption coefficients, respectively. These latter quantities are given by [24]

\[
\varepsilon(\nu, N_e, T_e) = \frac{1}{4\pi} h\nu A_{12}N_2 Y(\nu, N_e, T_e) \tag{2}
\]

\[
\mu(\nu, N_e, T_e) = \frac{1}{4\pi} h\nu (B_{12}N_1 - B_{21}N_2) Y(\nu, N_e, T_e), \tag{3}
\]

where \(A_{12}, B_{12}\) and \(B_{21}\) are the Einstein coefficients, and \(N_1\) and \(N_2\) are the number densities in the first (lower) and second (upper) levels. \(Y(\nu, N_e, T_e)\) is the spectral distribution, which, for a purely Stark-broadened line shape, can be expressed as [24]

\[
Y(\nu, N_e, T_e) = \frac{1}{\pi} \frac{\Delta\nu_{\text{width}}^2}{(\Delta\nu_{\text{width}}^2/2 + (\nu - \nu_0 + \Delta\nu_{\text{shift}})^2)} \tag{4}
\]

Here, \(\nu_0\) is the field-free spectral line centre frequency, and \(\Delta\nu_{\text{width}}(N_e, T_e)\) and \(\Delta\nu_{\text{shift}}(N_e, T_e)\) are the Stark-broadened FWHM line width and the Stark shift, i.e.

\[
\Delta\nu_{\text{width}} = \frac{2wc}{\lambda_0} \frac{N_e}{10^{22}} \left[ 1 + \frac{7a}{4} \left( \frac{N_e}{10^{22}} \right)^{\frac{3}{2}} \left( 1 - \frac{3N_D}{4} \right) \right] \tag{5}
\]

and

\[
\Delta\nu_{\text{shift}} = \frac{dc}{\lambda_0^2} \frac{N_e}{10^{22}} \left[ 1 + \frac{2aw}{d} \left( \frac{N_e}{10^{22}} \right)^{\frac{3}{2}} \left( 1 - \frac{3N_D}{4} \right) \right], \tag{6}
\]

where \(w\) and \(d\) are the electron impact parameters (with units of length) for the Stark width and shift, respectively. \(\lambda_0\) is the field-free centre wavelength of the transition, \(\alpha\) is a dimensionless ion impact parameter (which, for any given species, is nearly constant [24–26]), \(N_e\) is the electron density (\(m^{-3}\)) and \(N_D\) is the number of particles in the Debye sphere, given as

\[
N_D = \frac{(\epsilon_0 T_e)^{3/2}}{\epsilon^3 N_e^{2/3}} \tag{7}
\]

with \(T_e\) in units of energy.

The line widths in the present study are measured in terms of wavelength, with FWHM \(\Delta\lambda_{\text{meas}}\) (or, equivalently, \(\Delta\nu_{\text{meas}}\) in frequency space). These measured FWHMs include both Stark \((\Delta\lambda_{\text{width}}; \Delta\nu_{\text{width}})\) and instrumental \((\Delta\lambda_{\text{instr}}; \Delta\nu_{\text{instr}})\) contributions, which we deconvolute assuming \(\Delta\lambda_{\text{meas}} = \sqrt{(\Delta\lambda_{\text{width}})^2 + (\Delta\lambda_{\text{instr}})^2}\). The FWHM values given in figure 3 are the measured quantities, \(\Delta\lambda_{\text{meas}}\), while those reported in all later figures are the \(\Delta\lambda_{\text{width}}\) values, post-deconvolution, that we attribute to Stark broadening.

Detailed prediction of a Stark-broadened line shape depends not just on \(N_e\) and \(T_e\), but also on the population ratio between the two states connected by the transition. Under LTE conditions, this ratio is given by the Saha–Boltzmann equation,

\[
\frac{N_e}{N_i} = \frac{g_2}{g_1} \left( \frac{2\pi m_e T_e}{h^2} \right)^{3/2} \exp \left[ -\frac{\varepsilon_2 - \varepsilon_1}{T_e} \right]. \tag{8}
\]

LTE requires a sufficient collision frequency for exchange of energy between the ions and electrons; more precisely, the Saha equation requires that the collisional transition rate between the levels of interest is significantly larger than the competing radiative rate. Using semi-classical arguments, McWhirter [27] and Griem [28] have proposed the following necessary, but not sufficient, criterion for LTE:

\[
N_e > 10^{18}Z^2T_e^{1/2}(\Delta c)^3 \text{ (m}^{-3}\text{)}, \tag{9}
\]

where \(\Delta c\) is the energy gap \(\varepsilon_2 - \varepsilon_1\) (in eV), \(T\) is the electron temperature (in K), and \(Z\) varies according to the charge state of the emitting species (i.e. \(Z = 1\) for the neutral, \(Z = 2\) for the single ionized cation, etc), which reduces, for neutral emitting species, to the oft-quoted [20, 21] version of the McWhirter criterion:

\[
N_e > 1.6 \times 10^{16}T_e^{1/2}(\Delta c)^3 \text{ (m}^{-3}\text{)}, \tag{10}
\]

As noted above, this condition will often be satisfied in the case of PLA at atmospheric pressure. It may well also be achieved in the near-target volume at the very earliest stages of LIP expansion into vacuum, but cannot be expected to prevail as the plasma continues to expand in time and space, and the local density (and collision frequency) falls off.

The assumption of a Maxwellian EEDF is invalid under non-LTE conditions, and consequently the Saha–Boltzmann ionization balance does not apply. Various alternative EEDFs have been proposed, mostly based on the form [29]

\[
f_E(\varepsilon) = C_\nu \sqrt{\frac{\varepsilon}{T_e}} \exp \left[ -a_\nu \left( \frac{\varepsilon}{T_e} \right)^{b} \right], \tag{11}
\]

where \(C_\nu\) and \(a_\nu\) are dimensionless coefficients. This reduces to the Maxwell–Boltzmann distribution in the case that \(b = 1\) but, more importantly in the present context, produces the Druyvesteyn distribution for \(b = 2\). The latter EEDF has been used previously to model non-LTE plasmas [30, 31] and, as we now show, provides a much better fit to the Stark-broadened line shapes observed in the present work. The Druyvesteyn EEDF can be written as

\[
f_D(\varepsilon) = K_d \sqrt{\frac{\varepsilon}{T_e}} \exp \left[ -K_d \left( \frac{\varepsilon}{T_e} \right)^2 \right], \tag{12}
\]

with

\[
K_d = \frac{\Gamma(1/4)^4}{6\sqrt{3} \ 2^{1/4} \ \pi^{3/2}} \approx 0.565 \tag{13}
\]

and

\[
K_b = \frac{\Gamma(1/4)^4}{72 \ \pi^{3/2}} \approx 0.243 \tag{14}
\]

while \(T_e\) is the electron temperature (i.e. a physical quantity proportional to the mean electron energy) in the context of both the Maxwellian and Druyvesteyn distributions. It is important to note that these temperatures are introduced differently as...
parameters of the respective EEDFs, and hence their values are not mathematically comparable. It should thus be borne in mind that in much of the following the electron temperature $T_e$ specifies a Druyvesteyn, rather than a Maxwellian, average energy.

For neutral atoms, the population of any given excited state $i$, with energy $\varepsilon_i$ (defined relative to the neutral ground state energy $\varepsilon_{i=0}$), is given by

$$\frac{dN_i^\text{II}}{N_\text{total}} = \int f(\varepsilon_i)d\varepsilon,$$  

(15)

where, following spectroscopic convention, the Roman superscript I indicates a neutral state of the atom (II would represent an atom in its $1^+\text{charge state}$, etc.). The population ratio between excited states 2 and 1 of the neutral atom is thus given by

$$\frac{N_2^\text{II}}{N_1^\text{II}} = \frac{g_2^\text{I}}{g_1^\text{I}} \exp \left[ -K_0 \frac{(\varepsilon_2^\text{I})^2 - (\varepsilon_1^\text{I})^2}{T_e^2} \right],$$  

(16)

rather than the expression

$$\frac{N_2^\text{I}}{N_1^\text{I}} = \frac{g_2^\text{I}}{g_1^\text{I}} \exp \left[ -\frac{\varepsilon_2^\text{I} - \varepsilon_1^\text{I}}{T_e} \right],$$  

(17)

that would apply in case of LTE.

Extension of the above analysis to population ratios between different cationic states for a Druyvesteyn EEDF is straightforward. For example, the ratio of singly charged cations to neutral atoms is given by

$$\frac{dN_{1}^{\text{II}}}{N_{0}^{\text{I}}} = \frac{dg_{1}^{\text{II}}}{g_{0}^{\text{I}}} \exp \left[ -K_{0} \frac{(\varepsilon_{1}^{\text{II}})^{2} - (\varepsilon_{0}^{\text{I}})^{2}}{T_{e}^{2}} \right].$$  

(18)

$dN_{1}^{\text{II}}/N_{0}^{\text{I}}$ in equation (18) is the differential population of ground state $1^+$ cations associated with free electrons in the velocity range $\nu \rightarrow \nu + d\nu$, and $E^{\text{II}}$ is the first ionization potential. The degeneracy term is $dg_{1}^{\text{II}} = g_{0}^{\text{I}}dg_{e}$, where $g_{0}^{\text{I}}$ is the degeneracy of the ground state cation, $dg_{e} = \frac{\Delta V \sqrt{2m_{e}}}{\hbar^2}$ is the degeneracy of a free electron [32], $\Delta V = 1/N_e$ and

$$\Delta p_{e} = 4\pi p_{e}^{2}d_{p_{e}} = 4\pi m_{e}^{3}\nu^{2}d\nu.$$

Substituting (19) into (18) yields

$$\frac{dN_{1}^{\text{II}}}{N_{0}^{\text{I}}} = \frac{8\pi m_{e}^{3}g_{0}^{\text{I}}}{g_{0}^{\text{I}}} \nu^{2} \exp \left[ -K_{0} \frac{(E^{\text{II}} + \frac{1}{2}m_{e}\nu^{2})^{2}}{T_{e}^{2}} \right] d\nu.$$

(20)

and, as shown in the appendix,

$$\frac{N_{1}^{\text{II}}}{N_{1}^{\text{I}}} = \frac{g_{1}^{\text{II}}}{g_{1}^{\text{I}}} \exp \left[ -K_{0} \frac{(E_{1}^{\text{II}} + E_{2}^{\text{II}})^{2}}{T_{e}^{2}} \right].$$

(22)

and, in the particular case that state 1 is the ground state,

$$\frac{N_{2}^{\text{II}}}{N_{0}^{\text{II}}} = \frac{g_{2}^{\text{II}}}{g_{0}^{\text{II}}} \exp \left[ -K_{0} \frac{(E_{1}^{\text{II}} + E_{2}^{\text{II}})^{2}}{T_{e}^{2}} \right].$$

(23)

Equivalent expressions for the population ratios in the case of more highly charged states (e.g. $N_{2}^{\text{III}}/N_{1}^{\text{II}}$ and $N_{2}^{\text{IV}}/N_{1}^{\text{IV}}$) are presented in the Appendix.

3.3. Extracting the temporal and spatial variations of $N_e$ and $T_e$

Three parameters—the Stark width $\omega$, shift $\delta$ and the ion impact parameter $a$—are required in order to calculate the line shapes under non-LTE conditions. The values for the Si iii transitions appearing in figure 1, determined via absolute twowavelength interferometry experiments [33, 34] without any assumptions regarding LTE, are listed as $\nu_{0}^{\text{III}}$ and $d\nu_{0}^{\text{III}}$ in table 1. The ion impact parameter has minimal effect on the line shape when $0.05 < a < 0.5$ [25, 26, 35], so the present analysis assumes a constant value, $a = 0.08$ [35]. Given these parameters, and the theory described in section 3.2, we can

| Si iv transition | Multiplet | $\lambda$ (nm) | $\nu_{0}^{\text{IV}}$ (pm) | $d\nu_{0}^{\text{IV}}$ (pm) |
|------------------|-----------|----------------|--------------------------|--------------------------|
| 3s4p–3s4s       | $3p^{0}–3s$ | 455.262 | 53 ± 8% | −10 ± 11% |
|                  |           | 456.784 | 50 ± 9% | −8 ± 19% |
|                  |           | 457.476 | 50 ± 10% | −9 ± 22% |
| 3s5g–3s4f       | $3G^{−}2p^{0}$ | 481.333 | 398 ± 38% | −98 ± 55% |
|                  |           | 481.971 | 425 ± 30% | −98 ± 55% |
|                  |           | 482.896 | 405 ± 15% | −98 ± 55% |

Table 1. Stark parameters for Si iii transitions of interest (from refs. 33 and 34) along with those determined for the Si iv transitions monitored in the present study.
using the Stark parameters in table 1 and varying local electron density and temperature. Convolving the simulated spectrum with the instrumental line differences (SSD) when compared with experiment, after $T_e (b)$ multiplet emissions of the Si iii cation at a laser irradiance of 25 GW cm$^{-2}$.

The present time-gated spatiotemporal imaging measurements thus offer a route to mapping the temporal variation of $N_e$ and $T_e$ at any given $z$, with the obvious constraints that the location of interest must fall within the available viewing zone and that Stark broadening must be a major contributor to the measured line width. The latter consideration limits detailed analysis of the Stark broadening of Si iii lines in the present work for $z \geq$ 3 mm, although this could be alleviated by use of a higher-resolution spectrometer. But the data contained within figure 1 suggest another way of extending the useful analysis space. The Si iv features are more strongly broadened, and extend to larger $z$ at early times, but extracting meaningful $N_e$ and $T_e$ values from Si iv is hampered by the lack of $w^{IV}$ and $d^{IV}$ parameters determined without the assumption of LTE. However, the observation of Si iii and Si iv features at the same $z$ and $t$ in the present 2D OES images allows us to obtain $w^{IV}$ and $d^{IV}$ parameters for the Si iv transitions by transferring the $N_e$ and $T_e$ values obtained from fitting the Si iii features. (Lacking alternative data, the present analysis assumes the same ion impact parameter $a = 0.08$, but we note that the returned $N_e$ and $T_e$ values differ by less than 15% even if we use $a = 0.15$.)

We illustrate this strategy by reference to figure 1(a), measured for $\Delta t = 40$ ns following PLA with an incident irradiance of 25 GW cm$^{-2}$. For orientation, figure 5(a) shows the $z$-dependence of $\Delta \lambda_{\text{width}}$ for the 456.784 nm Si iii line, determined for each pixel (i.e. at 25 $\mu$m intervals). The equivalent measurement at lower incident irradiance returns smaller $\Delta \lambda_{\text{width}}$ values, consistent with reduced Stark broadening. Both show an empirical $z^{-n}$ dependence (with $n \approx 0.23$) over the range investigated.

Figure 5(b) compares the $z$-dependence of $\Delta \lambda_{\text{width}}$ for the Si iii transition with that for the 463.124 and 465.432 nm lines of Si iv. Clearly, the Si iv species are expanding faster (extending to greater $z$ at any given $t$) and display much broader emission lines. Figures 5(c) and (d) show (as blue lines) $N_e(z)$ and $T_e(z)$ determined out to $z = 3.1$ mm from the Si iii data. Since both carriers show measurably broadened emissions for $1.4 \leq z \leq 3.1$ mm, we can use $N_e(z)$ and $T_e(z)$ derived from Si iii to obtain $w^{IV}$ and $d^{IV}$, and then use these parameters to estimate the electron characteristics at larger $z$. In practice, we use the Si iii line shapes to determine $N_e(z)$ and $T_e(z)$ for $1.4 \leq z \leq 1.9$ mm (the calibration region), with the resulting best-fit estimates of $w^{IV}$ and $d^{IV}$ given in table 1. We then test how well Si iv reproduces $N_e(z)$ and $T_e(z)$, as derived from Si iii, in the validation range $1.9 \leq z \leq 3.1$ mm. Figures 5(c) and (d) illustrate the success of this strategy when applied to either Si iv emission (black and red lines). We are thus able to follow $N_e$ over more than two orders of magnitude, with a simultaneous more than 20-fold variation in $T_e$.

The method presented here for investigating the electron characteristics in LIPs expanding under non-LTE conditions is potentially rather general, and complementary to techniques like Thomson scattering. The spatial extent of the present OES measurements is limited to $z \approx 5.6$ mm by the

Figure 4. Independent best fits to the (a) $^3P^o-^3S$ and (b) $^3G^o-^3F^o$ multiplet emissions of the Si iii cation at $z = 1.0$ mm, $\Delta t = 40$ ns and a laser irradiance of 25 GW cm$^{-2}$ shown in figure 1(a). These were obtained assuming a Druyvesteyn EEDF function and varying $N_e$ and $T_e$ along with the spectroscopic parameters listed in table 1. The best-fit $N_e$ and $T_e$ values are (a) $N_e = 3.11 (25) \times 10^{22}$ m$^{-3}$, $T_e = 1.98 (17)$ eV; (b) $N_e = 2.94 (91) \times 10^{22}$ m$^{-3}$, $T_e = 1.88 (67)$ eV.

Predict the detailed profile of every line within each of the Si iii multiplets for any chosen combination of $N_e$ and $T_e$. Performing many such simulations allows determination of the values of $N_e$ and $T_e$ that give the smallest sum of squared differences (SSD) when compared with experiment, after convolving the simulated spectrum with the instrumental line shape: these we take as the experimental determinations of local electron density and temperature.

Figure 4 shows independent best fits to the $^3P^o-^3S$ and $^3G^o-^3F^o$ multiplets of Si iii at $z = 1$ mm measured at $\Delta t = 40$ ns, using the Stark parameters in table 1 and varying $N_e$ and $T_e$ so as to minimize the SSD. The latter multiplet is accompanied by an unassigned feature centered at 484 nm, which, from its $z$ versus $\Delta t$ dependence (figure 1), we can identify as another Si iii transition. The former ($\approx 456$ nm) multiplet is more widely separated and thus better resolved, but the values, i.e. (a) $N_e = 3.11 (25) \times 10^{22}$ m$^{-3}$; $T_e = 1.98 (17)$ eV and (b) $N_e = 2.94 (91) \times 10^{22}$ m$^{-3}$; $T_e = 1.88 (67)$ eV returned by these independent analyses agree to within one standard deviation.

The present time-gated spatiotemporal imaging measurements thus offer a route to mapping the temporal variation of $N_e$ and $T_e$ at any given $z$, with the obvious constraints that the location of interest must fall within the available viewing zone and that Stark broadening must be a major contributor to the measured line width. The latter consideration limits detailed analysis of the Stark broadening of Si iii lines in the present work for $z \geq 3$ mm, although this could be alleviated by use of a higher-resolution spectrometer. But the data contained within figure 1 suggest another way of extending the useful analysis space. The Si iv features are more strongly broadened, and extend to larger $z$ at early times, but extracting meaningful $N_e$ and $T_e$ values from Si iv is hampered by the lack of $w^{IV}$ and $d^{IV}$ parameters determined without the assumption of LTE. However, the observation of Si iii and Si iv features at the same $z$ and $t$ in the present 2D OES images allows us to obtain $w^{IV}$ and $d^{IV}$ parameters for the Si iv transitions by transferring the $N_e$ and $T_e$ values obtained from fitting the Si iii features. (Lacking alternative data, the present analysis assumes the same ion impact parameter $a = 0.08$, but we note that the returned $N_e$ and $T_e$ values differ by less than 15% even if we use $a = 0.15$.)

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The method presented here for investigating the electron characteristics in LIPs expanding under non-LTE conditions is potentially rather general, and complementary to techniques like Thomson scattering. The spatial extent of the present OES measurements is limited to $z \approx 5.6$ mm by the
collection optics and viewing window, while the minimum Stark broadening that can be traced is limited by the resolution of the available spectrometer. Neither of these constraints is fundamental. The method is dependent on the availability of appropriate Stark broadening parameters determined without assuming LTE but, as shown here, the presence of multiple emitters can be highly advantageous provided that at least one set of Stark parameters is well characterized.

Figure 6 shows (a) \(N_e(z)\) and (b) \(T_e(z)\) derived from the Si iii and Si iv line shapes in images measured at constant incident irradiance of 25 GW cm\(^{-2}\) using a 10 ns gate width and different time delays in the range 40 \(\leq \Delta t \leq\) 120 ns.

Figure 5. (a) \(z\)-dependent \(\Delta \lambda_{\text{width}}\) values of the 455.262 nm Si iii line for \(\Delta t = 40\) ns and irradiances of 25 and 12 GW cm\(^{-2}\), together with best fits to these data assuming a \(z^{-n}\) dependence. (b) Comparison of the \(z\)-dependent \(\Delta \lambda_{\text{width}}\) values for the 455.262 nm Si iii, 463.124 nm Si iv and 465.432 nm Si iv lines. (c) and (d) show, respectively, the \(z\)-dependent \(N_e\) and \(T_e\) values determined from these Si iii and Si iv data as described in the text.

Figure 6. (a) \(N_e(z)\) and (b) \(T_e(z)\) profiles from analysis of the Si iii and Si iv line shapes in images measured at constant incident irradiance of 25 GW cm\(^{-2}\) using a 10 ns gate width and different time delays in the range 40 \(\leq \Delta t \leq\) 120 ns.

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electrons) are formed during the laser–target interaction, and by laser–plume interactions during the later stages of the laser pulse, and ions in different charge states expand in different velocity sub-groups. To maintain approximate local charge neutrality, each ion group will propagate with an attendant electron cloud. Those electrons that are coupled with the expanding Si iv ions will have the highest \( T_e \), due to the high charge on the proximal cations and their consequent position at the front of the expanding plume, where laser–plume interactions (especially electron–ion IBA \[9, 10\]) should be greatest.

Such a description agrees well with the maxima of \( N_e \) and \( T_e \) falling at \( z \approx 0 \) and early \( t \), and can account for the delayed maximum of \( N_e(z \approx 4 \text{ mm}) \) for \( \Delta t \approx 60 \text{ ns} \), as in figure 6(a), which also accords with the leading edge of the Si iv emission seen in figure 1. The more complex behavior of \( N_e(z \approx 3 \text{ mm}) \), and in particular its increase at later \( t \), can be understood in terms of the declining contribution from electrons expanding with the Si iv ions, superimposed with the increasing contribution from those associated with the slower Si iii ions. Figure 1 also suggests that the latter should maximize for \( \Delta t \approx 120 \text{ ns} \), before diminishing again at later \( t \). The preferential escape of hot electrons, along with electron–ion recombination and adiabatic and bremsstrahlung cooling, are all likely to contribute to the observed decline in \( T_e \) for larger \( \Delta t \).

### 3.4. LTE or non-LTE conditions?

LTE—an essential condition for a Maxwellian EEDF—can be attained only when collisions between the electrons and other particles constitute the dominant energy transfer process, and many prior studies \[16, 18, 21, 24, 30\] have sought to determine the validity (or otherwise) of assuming LTE in the case of expanding LIPs. The present experiments provide a particularly direct means of addressing this question. As shown above, comparing measured line shapes with those calculated for various EEDFs provides an independent assessment of the applicability of LTE, as well as identifying when, if at all, the McWhirter criterion is satisfied.

Figure 7 shows three spectra of the Si iii (\(^{3}P_0–^{3}S\)) multiplet centered at \( \approx 456 \text{ nm} \). The figure shows the spectra at \( z = 0.2, 1.4 \) and \( 2.6 \text{ mm} \), respectively, along with the best fits to each assuming both Maxwellian \((b = 1, \text{ red})\) and Druyvesteyn \((b = 2, \text{ blue})\) EEDFs. Each is derived from an \( I(z; \lambda; \Delta t = 40 \text{ ns}) \) image recorded following 1064 nm PLA of a Si target in vacuum at an incident irradiance of 25 GW cm\(^{-2}\) using a 10 ns time gate centered at \( \Delta t = 40 \text{ ns} \) assuming Druyvesteyn and Maxwellian EEDFs (red and dashed black lines, respectively). The \( z \)-dependences of the \( R^2 \) values associated with these fits are shown in (c).

Figure 8. Best-fit (a) \( N_e(z) \) and (b) \( T_e(z) \) values derived from analysis of Si iii and Si iv emission line shapes measured at every eighth pixel in images recorded following PLA of a Si target in vacuum at an incident irradiance of 25 GW cm\(^{-2}\) using a 10 ns time gate centered at \( \Delta t = 40 \text{ ns} \) assuming Druyvesteyn and Maxwellian EEDFs (red and dashed black lines, respectively). The \( z \)-dependences of the \( R^2 \) values associated with these fits are shown in (c).
simulated line shape assuming a Druyvesteyn EEDF provides a significantly better fit to the experimental data.

Figure 8 compares the best-fit (a) \( N_e \) and (b) \( T_e \) values derived from spectra over a wider range of \( z \), again using Maxwellian and Druyvesteyn EEDFs. Taking \( b = 1 \) (the Maxwellian case) results in a progressively poorer fit to the data at large \( z \), as illustrated by the \( z \)-dependence of the associated \( R^2 \) values, shown in figure 8(c). Several of the Si\textsc{iii} line shapes measured at larger \( z \) were also fitted with another variant of equation (11) having \( b = 3 \), and again, the best-fit line shapes replicated the experimental data less well than those calculated for the Druyvesteyn EEDF. For example, the \( R^2 \) values for \( z = 2.6 \text{ mm} \) were 0.816 (\( b = 1 \)), 0.979 (\( b = 2 \)) and 0.923 (\( b = 3 \)). In figure 9, the EEDFs assuming \( b = 1 \) and \( b = 2 \) are compared for \( N_e \) and \( T_e \) derived from the \( z = 1.0 \) and 2.6 mm data. Clearly, the best-fitting Druyvesteyn EEDF peaks at higher kinetic energy, but has a less pronounced high-energy tail for each \( z \) than its Maxwellian analog.

A log–log plot of \( N_e(\lambda) \) versus \( T_e(\lambda) \) assuming a Druyvesteyn EEDF is given as figure 10, with a red line (with slope 0.5) also drawn, indicating the McWhirter criterion for the Si\textsc{iii} \(^{3}\text{P} \rightarrow ^{3}\text{S}\) transition. Such plots offer another assessment of the applicability of LTE under given conditions. All data measured at \( z > 1.0 \text{ mm} \) fall below the red line, reinforcing the view that, at least by this stage of plume expansion, the local conditions are far from LTE.

The method presented here should be quite widely applicable to non-LTE LIPs. We are currently applying it to PLA of multi-element targets in order to assess the reproducibility of \( N_e \) and \( T_e \), and hence the validity of cross-calibrating Stark broadening parameters, between elements, rather than only between different charge states of the same element. Another obvious application will be to explore emission spectra in ambient gas at different pressures, with the aim of identifying in more detail for which conditions it is reasonable to assume LTE.

4. Conclusions

This paper reports a versatile and general method for determining \( N_e \) and \( T_e \) in LIPs with good spatial (here sub-millimeter) and temporal (here 10 ns) resolution, and without requiring the assumption of LTE. We also show that, given Stark broadening parameters free of any LTE assumptions for at least one emitting species, the presence of other emissions (even for which no non-LTE Stark parameters are available) in the same spectra can be used to provide additional temporal and spatial dynamic range in the \( N_e \) and \( T_e \) measurements after cross-calibration between the emitters. The present study involved 1064 nm nanosecond PLA of a Si target in vacuum, and investigated the optical emission from the resulting LIP using time-gated, spatially and spectrally resolved imaging.
Both Si III and Si IV emission lines showed clear evidence of Stark broadening. These Stark-broadened line shapes were analyzed using an ionization balance equation derived for a Druyvesteyn (rather than a Maxwellian) EEDF, and without any preconceptions regarding the applicability (or not) of LTE. The analysis returned \( N_e \) and \( T_e \) values and their variation in space and time, and showed the progressive deviation from LTE with expansion of the LIP into vacuum. At early times and near to the target, \( N_e > 10^{23} \text{ m}^{-3} \) and \( T_e > 10 \text{ eV} \), and both values generally declined as the plume expanded in time and space. The time-gated emission images and the spatial and temporal variation of \( N_e \) and \( T_e \) both highlighted the inhomogeneity of the plasma plume, and support the view that ions in different charge states expand in different velocity subgroups, each propagating with attendant, quasi-independent, electron clouds.

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Data accessibility: the underlying data for this paper has been placed in the University of Bristol’s research data repository and can be accessed using the DOI 10.5523/bris.tavsvmgiyjjik1gctcdl0adm2c.

Appendix

A.1. The derivation of equation (21)

Starting from equation (20), we set \( K_e = \frac{g_n m^3}{7 \mu^2} \) and

\[
J = \int_0^\infty \nu^2 \exp \left[ -K_0 \left( \frac{E_{II}^i + \frac{4}{3} \mu m \nu^2}{T_e^2} \right)^2 \right] d\nu. \tag{A.1}
\]

This integral is solved by writing \( t = \nu^2 \) and

\[
J = \int_0^\infty \frac{\sqrt{t}}{2} \exp(-c_1 t^2 - c_2 t - c_3) dt,
\]

where \( c_1 = \frac{Km^2}{4T_e^2} \), \( c_2 = \frac{K\mu m^2 E_{II}^i}{T_e^2} \), and \( c_3 = \frac{K\mu m^2 E_{II}^i}{T_e^2} \).

Given the standard integral [36]

\[
\int_0^\infty t^{\epsilon-1} \exp(-at^2 - bt) dt = \left(2a\right)^{\epsilon/2} \Gamma(\epsilon) \exp\left(\frac{b^2}{8a}\right) D_\epsilon\left(\frac{b}{\sqrt{2a}}\right),
\]

we obtain

\[
J = \frac{1}{2} \exp(-c_1)(2c_1)^{\epsilon/2} \frac{3}{2} \exp\left(\frac{c_2^2}{8c_1}\right) D_\epsilon\left(\frac{c_3}{\sqrt{2c_1}}\right), \tag{A.2}
\]

where \( D_\epsilon(t) \) represents a parabolic cylinder function.

While \( \int_0^\infty \frac{t^{\epsilon-1}}{\Gamma(\epsilon)} \exp(-at^2 - bt) dt \) appears as an explicit formulation in mathematical handbooks, we did not find an explicit solution for \( \int_0^\infty \frac{t^{\epsilon-1}}{\Gamma(\epsilon)} \exp(-at^2 - bt - ct - d) dt \), required when using equation (11) with \( b = 3 \), and hence obtained it numerically.

A.2. Analogues of equations (21) and (23) for higher charge states

For Si III, Si IV etc, we use the sum of the ionization potentials (i.e. \( E_{II}^i + E_{III}^i, E_{II}^i + E_{IV}^i + E_{V}^i \), etc) in place of the first ionization potential \( E_{II}^i \) in the integral \( J \), yielding results \( J_{III} \), \( J_{IV} \), etc in place of (A.2).

By analogy with equation (23), the population ratio between any excited level \( i \) and the ground level \( (i = 0) \) of any particular charge state \( k \) is given by

\[
\frac{N_{i}^k}{N_{0}^k} = \frac{g_i^k}{g_0^k} \exp\left[-K_0 \left( \frac{E_k^i + E_k^i}{2} \right)^2 \right]. \tag{A.3}
\]

Similarly, the population ratio between the \( i = 0 \) level of any particular charge state \( j \) and the \( i = 0 \) level of the neutral species follows by analogy with equation (21), i.e.

\[
\frac{N_{0}^j}{N_{0}^j} = K_{0} \frac{g_i^j}{g_0^j} J_{0}^j, \tag{A.4}
\]

which enables calculation of the population of each excited level of each charge state species \( N_{0}^j \) relative to that of the ground state neutral. Finally, in the LIP plume, quasi-neutrality requires the relationship \( \sum_{j}(j - 1)N_{0}^j = N_e \).

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