

Article

Two-Temperature Electron Energy Distribution Function and Its Device Dependence in Atmospheric-Pressure Nonequilibrium Argon Plasma

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Abstract

Atmospheric-pressure nonequilibrium argon plasmas are used in many applications, and their electron properties may depend on the device configuration. Here, the electron temperature and density of two devices of contrasting geometry, a closed flow-channel type dielectric barrier discharge (DBD) and an open-air tube-type plasma jet, were determined from continuum optical emission spectra. The electron energy distribution function was represented by a two-temperature model combining a Druyvesteynian bulk component, which contains the great majority of the electrons, and a Maxwellian tail component, which is a small high-energy minority, with all parameters obtained by an exhaustive grid search. Introducing the tail component reduced the fitting residual by more than two orders of magnitude, supporting a two-component parameterization of the time-averaged distribution. The bulk temperature remained within 0.35–0.42 eV for every condition in which the two-component model was applicable, whereas the electron density spanned six orders of magnitude, from $6.6 \times 10^{16} \text{ cm}^{-3}$ in the DBD to $5.5 \times 10^{10} \text{ cm}^{-3}$ in the jet plume; at the same monitored power of 12 W, the DBD was about ten times denser. The continuum constrains only about 1% of the electrons, those above the photon-energy threshold, so the total density is a model-dependent extrapolation. Two checks that do not use the continuum, a Stark-broadening estimate and a collisional-radiative analysis of the line spectra, are both incompatible with the extrapolated total: inserting it into the collisional-radiative model overestimates the measured line emission by five to seven orders of magnitude, while the line spectra themselves require a density of order 10^{14} cm^{-3} . The two methods do not, however, reproduce each other's dependence on the operating condition. Within the continuum analysis, the device configuration therefore governs the density, whereas the bulk temperature is comparatively insensitive to geometry.



Academic Editors: Andrey Starikovskiy and Sylwia Ptasinska

Received: 8 September 2026

Revised: 13 October 2026

Accepted: 14 October 2026

Published: 15 October 2026

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Keywords: atmospheric-pressure plasma; optical emission spectroscopy; electron energy distribution function; continuum spectrum; electron density; dielectric barrier discharge; plasma jet

1. Introduction

Atmospheric-pressure nonequilibrium plasma operates without vacuum systems, maintaining low gas temperatures while exhibiting high electron temperatures. Owing to its low gas temperature, it can be applied to heat-sensitive materials in medical and dental

applications [1]. Furthermore, the absence of vacuum equipment allows the irradiation of biological and liquid samples that cannot be placed in a reduced-pressure environment. Consequently, the range of applications of atmospheric-pressure nonequilibrium plasma is more diverse than that of arc or low-pressure plasmas [2]. However, the accurate analysis of the electron temperature and density in atmospheric-pressure plasma has rarely been attempted, resulting in a lack of reliable data for numerical simulations that require these values as input parameters [3,4]. Furthermore, the diverse range of applications demands experimental setups tailored for specific purposes, suggesting that the plasma characteristics may vary depending on the device configuration. Therefore, establishing a unified apparatus-independent analytical method is crucial. Although various methods exist for plasma diagnostics [5], optical emission spectroscopy (OES) was employed in this study. Applying electrical probe measurements, which are commonly used in low-pressure plasmas, under atmospheric pressure is challenging because of the extremely short mean free path of electrons in the sheath [6,7]. Similarly, laser Thomson scattering requires a large-scale experimental setup and skilled engineers to operate it, and is thus unsuitable for practical applications [8]. At atmospheric pressure the difficulty is compounded, because the weak Thomson signal has to be separated from the far stronger Rayleigh scattering by the neutral gas, which makes the measurement experimentally demanding. Notably, although the interpretation of OES spectra can be challenging, establishing an analytical technique converts this method into a highly versatile diagnostic tool for diverse atmospheric-pressure plasma applications. Therefore, in the present study, the OES analysis was performed using the plasma continuum spectrum.

Although diagnostic methods using line spectra have been widely applied [9], continuum spectrum analysis offers two distinct advantages. The first advantage of the proposed method is its simplicity. Analyses based on the line spectrum typically require collisional-radiative (CR) models, which account for numerous elementary processes and incur high computational costs [10]. By contrast, under sufficiently low-ionization conditions, the continuum is often dominated by electron–neutral Bremsstrahlung, so it can be described by a single expression [11,12]. Another advantage is its adaptability to complex gaseous species. Establishing CR models becomes increasingly difficult as gas compositions become more complex. For a specified gas composition and EEDF, the electron–neutral continuum can be calculated by summing the contributions of the neutral species using their momentum-transfer cross-sections. This simplifies the emission calculation, but it does not imply that the same analytical EEDF is appropriate for every gas mixture: molecular collision processes can change the electron energy distribution itself, as discussed in Section 2.2.7.

Several previous studies have reported continuum spectrum analyses. Onishi et al. analyzed the continuum spectrum of atmospheric-pressure argon plasma and concluded that the Druyvesteynian distribution provided better fitting results than the Maxwellian distribution [13]. Van der Gaag et al. predicted that the electron energy distribution function (EEDF) did not possess a simple form, and they estimated it using machine learning [14]. They concluded that the EEDF exhibited a shape resembling a bi-Maxwellian distribution. Kikuchi et al. analyzed continuum and line spectra together, determining the shape parameter of a two-temperature generalized EEDF by a grid search of the continuum and then the electron temperature and density from the line spectra with a collisional-radiative model [15]. Building upon these preceding studies, a two-temperature EEDF combining the Maxwellian and Druyvesteynian EEDFs was employed for the analysis in the present study. This approach achieves better fitting accuracy than a single-temperature EEDF while maintaining lower computational costs than machine learning methods.

Three methodological points distinguish the present analysis from these earlier works. First, all fitting parameters, namely, the two electron temperatures, the mixing ratio, and the electron density, are determined by an exhaustive search over a prescribed parameter grid, so the solution no longer depends on manual adjustment or on the choice of an initial guess. Second, the shape parameter of the generalized EEDF is deliberately fixed at the two canonical values corresponding to the Maxwellian and Druyvesteynian forms rather than being treated as a free fitting parameter, and this choice is justified quantitatively by the model comparison presented in Section 2.2.6. Third, the energy range of the EEDF that the continuum actually constrains is evaluated explicitly, which turns out to be essential for the interpretation of the deduced electron density, as discussed in Section 2.2.9.

In this study, the electron temperature and density were determined from the continuum spectrum using a two-temperature EEDF analysis, which is also one of the objectives of the present study. The validity of this method is then to be confirmed for two different geometric configurations of the discharge apparatus, a closed flow-channel type DBD and an open-air tube-type plasma jet, which is the second objective of this study. These two configurations are referred to below as the closed-channel DBD and the open-air jet, respectively. The first is a typical example of a dielectric barrier discharge (DBD) apparatus, where a dielectric material is placed between two electrodes, and plasma is generated in the gas gap between them (a parallel-plate capacitor configuration is a typical example [16]). In the present apparatus the discharge gap forms part of a closed gas-flow channel that is isolated from the ambient atmosphere. Although this setup allows scalability, an electric field is inevitably applied to the irradiation target. Its applications include semiconductor cleaning and decomposition of pollutants in air and water [17–19]. The second is a plasma jet apparatus, in which the plasma generated inside a quartz tube is transported by gas flow and ejected from the tube [20]. Unlike a DBD apparatus, the target can be placed in an ambient atmosphere, enabling direct irradiation, which is required for agricultural, medical, and dental applications. Furthermore, as the target was not located between the electrodes, the electrical influence was minimal. Therefore, plasma jets have applications in fields such as cancer treatment and the promotion of plant growth [1,21,22]. For both apparatuses, OES measurements were performed to investigate the variation in the plasma spectrum, and the continuum was analyzed as described below.

2. Materials and Methods

2.1. Experimental Setup

2.1.1. Closed Flow-Channel Type DBD Apparatus

Figure 1 shows a schematic of the DBD apparatus used in this study [13]. The device consisted of one outer and two inner quartz tubes, of 24.5 and 8.1 mm diameter, respectively, and 120 mm in length [15]. Each inner tube contained a metal needle electrode and water for heat dissipation. The two inner tubes were arranged coaxially with a 1 mm gap between them. The space between the outer and inner tubes served as the gas-flow channel, which was sufficiently isolated from ambient air.

Argon gas was introduced into the channel at a flow rate of 4 L/min. The discharge voltage was applied using a high-voltage AC power supply (100-C-9HEP, LECIP SLP Corporation, Motosu, Japan), which delivers a sinusoidal waveform at 20 kHz with a maximum output of 11.7 kV peak-to-peak. Unless stated otherwise, the voltages quoted in this paper are the peak-to-peak voltages applied between the electrodes; the setting of the variable autotransformer on the primary side is distinguished explicitly where it is given. The plasma emission light was collected through an optical fiber guide tube positioned adjacent to the discharge region. The spectral characteristics were measured at applied voltages of 3.6, 4.5, 5.4, 6.3, and 7.2 kV.

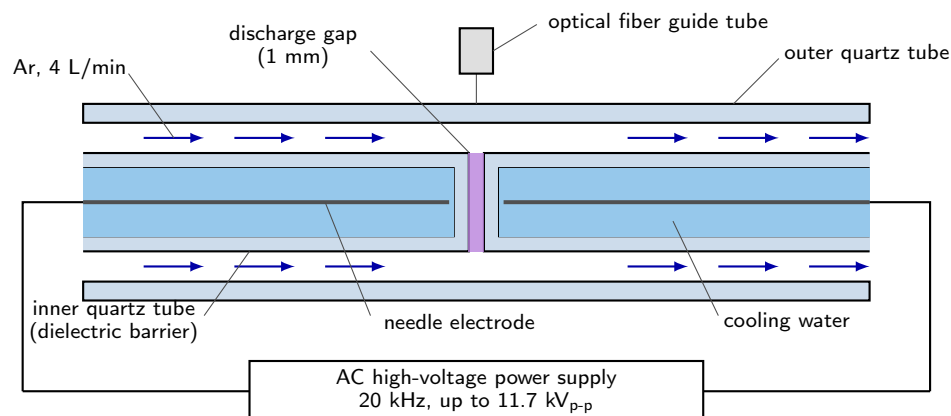


Figure 1. Schematic of the closed flow-channel type DBD apparatus. Two inner quartz tubes, each containing a metal needle electrode and cooling water, are arranged coaxially inside an outer quartz tube with a 1 mm discharge gap between their facing ends. Argon flows through the annular channel between the outer and inner tubes, which is isolated from the ambient atmosphere. The inner quartz walls act as the dielectric barriers. The apparatus is the same as that used in [13].

2.1.2. Open-Air Tube-Type Plasma Jet Apparatus

The open-air plasma jet apparatus consisted of a quartz tube of 4 mm inner diameter with two ring electrodes wrapped around its exterior and an inter-electrode distance of 12 mm. Insulating tape was wrapped just below the upper electrode to suppress the creeping discharge on the outer tube surface. The power supply was identical to that used in the DBD apparatus. The working gas was supplied to the quartz tube at a flow rate of 4 L/min, and this gas flow transported the generated plasma downstream.

The spatially resolved plasma emission spectra were measured at six positions along the tube axis, denoted A–F and indicated by the red dots in Figure 2: immediately above and below the upper ring electrode (A and B), immediately above and below the lower ring electrode (C and D), at the nozzle exit (E), and in the plume ejected into ambient air (F).

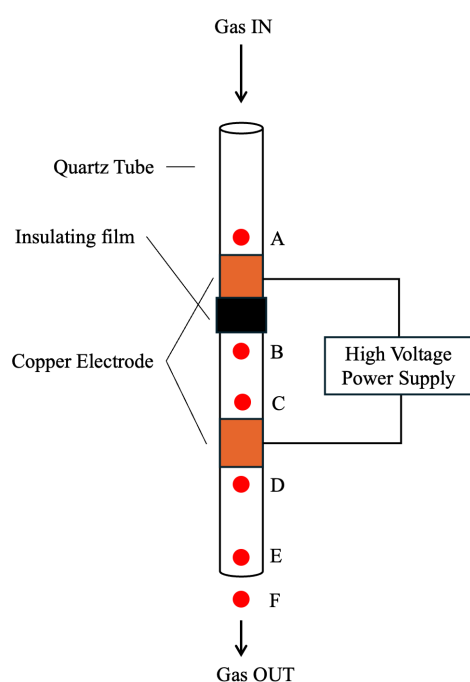


Figure 2. Schematic of the plasma jet apparatus. The red dots A–F indicate the positions where the spectra are measured. The inter-electrode distance is 12 mm. Insulating film is wrapped to prevent creeping discharge along the outer surface of the quartz tube.

2.1.3. Plasma Spectroscopy

Argon plasma was generated in the two discharge devices described above, both driven by the same power supply at 20 kHz. The two devices require different ignition procedures because of their different geometries. In the DBD apparatus, with the gas flowing into the glass tube, the autotransformer on the primary side of the supply was set to 80 V, giving a secondary voltage of 7.2 kV peak-to-peak between the electrodes and initiating the discharge; once the discharge had been allowed to stabilize, the voltage was adjusted to the desired value with a variable autotransformer (Volt Slider, Yamabishi Electric Co., Ltd., Tokushima, Japan). Spectra were then recorded at 3.6, 4.5, 5.4, 6.3, and 7.2 kV. In the plasma jet apparatus the plasma was generated by applying 9.9 kV directly, and this voltage was held constant at 9.9 kV while the observation position was varied. The power supply was equipped with a monitoring function for the applied voltage and power consumption, and these monitored values were used as the measurement data. The monitored power consumption was 12 W for all plasma jet measurements and 9 W and 12 W for the DBD at 6.3 and 7.2 kV, respectively. It should be noted that this is the power drawn by the supply and not the power deposited in the plasma, so a comparison at equal monitored power is not strictly a comparison at equal deposited power; this limitation is revisited in Section 3.5.

The plasma emission was guided through an optical fiber into a spectrometer (MS3504, SOL instruments Ltd., Minsk, Belarus) for spectroscopic measurements. The collecting lens, of 67 mm diameter, was placed 145 mm from the discharge axis, which subtends a solid angle of 0.17 sr. Because the source is optically thin and smaller than the field of view, the power reaching the spectrometer is proportional to the product of the emission coefficient, the observed volume, and the solid angle, so only the volume, and not the way it is divided between a projected area and a depth, enters the conversion from the measured signal to the emission coefficient of Equation (2). For the DBD apparatus, the observed region was taken to be the discharge gap itself, of projected area equal to the 1 mm gap multiplied by the 8.1 mm inner-tube diameter and of the same 8.1 mm depth along the line of sight, giving $6.6 \times 10^{-2} \text{ cm}^3$. For the plasma jet, whose quartz tube has an inner diameter of 4 mm, the observed region was taken to be a cylinder of that diameter and 5 mm axial extent, giving $6.3 \times 10^{-2} \text{ cm}^3$. The two observed volumes therefore agree to within 5%, so the conversion from the measured signal to the emission coefficient is essentially the same for both devices and the uncertainty in it largely cancels in the comparison between them. The 5 mm axial extent also sets the spatial resolution of the position scan along the jet. The obtained spectra were calibrated for absolute sensitivity using a standard light source (JPD100V500WCS, Ushio Inc., Tokyo, Japan) together with a standard diffuse reflectance plate (Zenith Polymer, SphereOptics GmbH, Herrsching, Germany), viewed with the same optics at 45° and at a distance of 0.73 m; the calibration constant depends on the plate measurement only through the product of the illuminated spot area and the solid angle subtended by the lens, which is independent of that distance. The exposure time was 0.5 s and 10 accumulations were recorded, the same values being used for the calibration and for the plasma measurements.

The density is obtained by fitting a homogeneous emission model to the signal integrated over the observed volume and the exposure time. If the neutral density and EEDF shape are uniform and constant during the exposure, the continuum emissivity is $\varepsilon(\lambda, \mathbf{r}, t) = C(\lambda)n_e(\mathbf{r}, t)$ with a common coefficient $C(\lambda)$. In this limiting case, dividing the integrated emission by the observed volume and exposure time and applying the same coefficient yields

$$n_{e,\text{fit}} = \frac{1}{V_{\text{obs}}t_{\text{exp}}} \int_0^{t_{\text{exp}}} \int_{V_{\text{obs}}} n_e(\mathbf{r}, t) dV dt, \quad (1)$$

where V_{obs} is the observed volume and t_{exp} the exposure time. Thus, under these assumptions the inferred density is a volume- and time-averaged density, not an emission-weighted average of the local density. When the neutral density or EEDF varies in space or time, $C(\lambda)$ also varies and the fitted density is an effective parameter of the assumed homogeneous model; it cannot in general be assigned a unique, wavelength-independent spatial weighting or identified with the local maximum density. The assumed observed volume and the unresolved discharge structure therefore contribute to the uncertainty of the absolute density, as discussed in Section 3. Because the exposure time greatly exceeds the period of the 20 kHz excitation (50 μ s), every spectrum reported here is a time-averaged spectrum accumulated over a large number of discharge cycles.

2.2. Analysis Method

2.2.1. Continuum Spectrum

The continuum spectrum of the plasma consists of three components: electron–neutral Bremsstrahlung, electron–ion Bremsstrahlung, and recombination radiation [23]. However, in atmospheric-pressure plasmas, electron–neutral Bremsstrahlung dominates because of the sufficiently low degree of ionization [11,13–15,24,25]. Therefore, only electron–neutral Bremsstrahlung was considered in this study, and its spectral emission coefficient was defined by the following equation [11,23]:

$$\varepsilon_{\text{ea}} = \sqrt{\frac{2}{m_e}} \frac{n_e n_a}{\lambda^2} \frac{hc}{4\pi} \int_{h\nu}^{\infty} Q_{\text{ea}}^{\text{B}}(\lambda, E) \sqrt{E} f(E) dE \quad (2)$$

Here, m_e , n_e , n_a , λ , h , c , Q_{ea}^{B} , E and $f(E)$ represent the electron mass, electron density, atom density, wavelength, the Planck constant, speed of light in vacuum, cross-section of bremsstrahlung due to electron–atom impact, electron energy, and EEDF, respectively, and $h\nu = hc/\lambda$ is the photon energy. The factor $\sqrt{2E/m_e}$, written here as $\sqrt{2/m_e}$ outside the integral and $\sqrt{E}$ inside it, is the electron speed; $f(E)$ is the EEDF normalized by Equation (5), so $\sqrt{2E/m_e} n_e f(E) dE$ is the flux-weighted number of electrons in dE . In the numerical evaluation the energy is expressed in eV and converted to SI units within the integrand.

Q_{ea}^{B} depends on the type of gas species and is given by its electron–neutral momentum transfer cross-section, $Q_{\text{ea}}^{\text{mom}}(E)$ [12].

$$Q_{\text{ea}}^{\text{B}} = \frac{8\alpha}{3\pi} \frac{E}{m_e c^2} \left(1 - \frac{hc}{2\lambda E}\right) \sqrt{1 - \frac{hc}{\lambda E}} Q_{\text{ea}}^{\text{mom}}(E) \quad (3)$$

where α is the fine structure constant.

$$\alpha = \frac{e^2}{2\varepsilon_0 hc} = 7.297 \times 10^{-3} [-] \quad (4)$$

where ε_0 is the vacuum permittivity, and e is the elementary charge. Momentum-transfer cross-sectional data for the relevant gases are available in databases such as those distributed through the LXCat project [26]. The argon cross-section used in this study was taken from the Biagi database [27], in which the cross-sections are transcribed from the MAGBOLTZ code of S. F. Biagi; the data used here correspond to MAGBOLTZ version 8.97. The momentum-transfer cross-section of argon was used at every measurement position, including position F, at which the plume is ejected into ambient air. Because position F is located immediately below the nozzle, argon is expected to remain the dominant gas species there, although some entrainment of ambient air is unavoidable. Furthermore, although the momentum-transfer cross-sections of Ar, N₂, and O₂ differ appreciably in shape as functions of electron energy, Equation (2) involves them only through an integral over the EEDF, which is expected to reduce the sensitivity of the resulting continuum

shape to the assumed composition. The local composition at position F was not measured, and the parameters reported for that position are therefore subject to an additional systematic uncertainty. The magnitude of this uncertainty was assessed by repeating the analysis of the plume spectrum with effective momentum-transfer cross-sections obtained by weighting the Ar, N₂, and O₂ cross-sections by their mole fractions, since Equation (2) is a sum over the neutral species. Two mixtures were examined, Ar/N₂ = 90 : 10 and Ar/N₂/O₂ = 90 : 8 : 2, and the analysis used the single-temperature Maxwellian model ($\gamma = 1$) adopted for position F for the reasons given in Section 3.4. Relative to the pure-argon case, the deduced temperature changed by less than 6% and the electron density by about 40%. Within the adopted single-temperature EEDF family and the compositions tested, the retrieved temperature is therefore only weakly sensitive to the assumed emission cross-sections, whereas the density is affected more strongly. This calculation assesses the sensitivity of the continuum inversion to the emission kernel; it does not solve the electron kinetic equation or account self-consistently for changes in the EEDF caused by molecular inelastic collisions. Consequently, the changes of less than 6% in temperature and about 40% in density do not establish that air entrainment has only a small effect on electron kinetics. The residuals obtained for the three compositions differed by less than 10%, and the pure-argon case did not give the smallest residual, so the continuum alone does not determine the gas composition; this is consistent with the discussion of correlated systematic errors in Section 2.2.6.

2.2.2. Definition of the Bulk and Tail Components

In this study, the “bulk component” denotes the low-temperature majority of the electrons, which dominates the long-wavelength region of the spectrum, and the “tail component” denotes the high-temperature minority, which governs the short-wavelength region. Each component is characterized by its own temperature, and “bulk temperature” and “tail temperature” refer throughout this paper to the temperatures kT_e of these two components as defined by Equation (7). These labels are defined operationally, by the part of the spectrum that each component controls, and they do not by themselves imply any particular physical origin; the kinetic status of the two functional forms is examined in Section 2.2.7, and possible physical interpretations are discussed in Section 3.1.

The lower limit of integration in Equation (2) is the photon energy $h\nu = hc/\lambda$, so only electrons with $E \geq hc/\lambda$ contribute to the emission at wavelength λ . Over the analyzed range of 310–850 nm, this threshold varies from 4.0 to 1.46 eV. Evaluating Equation (2) for the best-fit distribution obtained at 7.2 kV in the DBD apparatus shows that the emission at the short-wavelength edge (310 nm) originates essentially entirely from the Maxwellian tail component, whereas, at the long-wavelength edge (850 nm), 99.9% of the contribution comes from the Druyvesteynian bulk component. The changeover between the two is rapid and is centered at about 520 nm: the tail component supplies more than 97% of the emission below 450 nm and less than 7% of it above 600 nm. Because the two components therefore dominate different parts of the measured range, their parameters can be determined largely independently, which limits the ambiguity of the fitting solution.

2.2.3. EEDF/EEPF

The EEDF is normalized as

$$\int_0^\infty f(E) dE = 1 \quad (5)$$

To describe the nonequilibrium electron energy distribution, the general expression for the EEDF given in [28,29] is adopted.

$$f(E) = \gamma \left[\Gamma\left(\frac{5}{2\gamma}\right) \right]^{\frac{3}{2}} \left[\Gamma\left(\frac{3}{2\gamma}\right) \right]^{-\frac{5}{2}} \left(\frac{3}{2} kT_e \right)^{-\frac{3}{2}} \sqrt{E} \exp \left[- \left(\frac{\Gamma\left(\frac{5}{2\gamma}\right) E}{\Gamma\left(\frac{3}{2\gamma}\right) \frac{3}{2} kT_e} \right)^\gamma \right] \quad (6)$$

where k is the Boltzmann constant, and Γ is the gamma function. The EEDF corresponds to a Maxwellian EEDF when $\gamma = 1$ and a Druyvesteynian EEDF when $\gamma = 2$.

Throughout this paper the electron temperature is expressed in energy units, that is, as kT_e in eV. For every member of the family of Equation (6), including both the Maxwellian and the Druyvesteynian forms, the temperature defined in this way is related to the mean electron energy by

$$\langle \varepsilon \rangle = \int_0^\infty E f(E) dE = \frac{3}{2} kT_e, \quad (7)$$

so $kT_e = (2/3)\langle \varepsilon \rangle$ irrespective of γ . This convention allows the temperatures of the two components to be compared directly, even though their distribution shapes differ.

$$f_{\text{mix}}(E) = \alpha_1 f_1(E) + \alpha_2 f_2(E) \quad (8)$$

A two-temperature EEDF is constructed as a linear combination of two EEDFs at different temperatures, as expressed in Equation (8). Here, f_1 and f_2 represent the single-temperature EEDFs, and f_{mix} denotes the two-temperature EEDF. The coefficients α_1 and α_2 are the mixing ratios of f_1 and f_2 , respectively, which satisfy the condition $\alpha_1 + \alpha_2 = 1$. Throughout this paper f_1 denotes the Maxwellian tail component and f_2 the Druyvesteynian bulk component, so $\alpha_1 \equiv \alpha_{\text{tail}}$. The coefficients describe electron population fractions within the fitted distribution, not gas mole fractions; the two components are not assigned separately to argon and entrained air. Because each component is normalized and $\alpha_1 + \alpha_2 = 1$, f_{mix} also satisfies Equation (5). The use of a two-temperature EEDF enables analysis of a continuum spectrum with complex shapes that cannot be described by a single-temperature EEDF.

To visualize the electron energy distribution, the electron energy probability function (EPPF) is introduced [30]. The EPPF is defined as the EEDF divided by $\sqrt{E}$. In a semi-logarithmic plot of the EPPF versus energy, the Maxwellian distribution appears as a straight line, whereas the Druyvesteynian distribution exhibits a downward-curving profile. This representation facilitates comparison with a Maxwellian distribution and allows for a visual understanding of the energy distribution characteristics.

2.2.4. Separation of the Line and Continuum Spectra

The measured spectrum contains atomic line emission superimposed on the continuum, and the two must be separated before the analysis described above can be applied. The separation was carried out following the procedure established by Kikuchi et al. [15], in which the wavelength intervals occupied by atomic lines are identified and excluded, and the continuum underneath them is reconstructed by interpolation of the logarithm of the intensity using the adjacent line-free regions. Interpolation in logarithmic intensity is appropriate because the continuum varies by more than an order of magnitude over the analyzed range, so a linear interpolation would systematically underestimate the continuum beneath the strongest lines. The procedure was applied automatically to every measured spectrum, which ensures that the same criterion is used for all devices, applied voltages, and measurement positions compared in this study.

All of the fitting and all of the residuals reported in this paper were evaluated on the reconstructed continuum, that is, on a spectrum from which the atomic line emission has been removed; the residual is evaluated at every point of this continuum, including the intervals in which it was reconstructed by interpolation. It should be noted that the reconstructed intervals inevitably retain a small, smooth systematic error. This contribution is correlated between neighboring wavelength points and is one of the reasons why the fit residuals cannot be treated as independent random noise, as discussed in Section 2.2.6.

2.2.5. Exhaustive-Search Fitting Procedure

Because the emissivity of Equation (2) is linear in the EEDF, the emissivity of the two-temperature model can be decomposed as

$$\varepsilon_{\text{mix}}(\lambda; T_1, T_2, \alpha_1) = \alpha_1 \varepsilon_1(\lambda; T_1) + (1 - \alpha_1) \varepsilon_2(\lambda; T_2), \quad (9)$$

where ε_i is the emissivity produced by a single-temperature EEDF at temperature T_i , with $kT_1 = kT_{\text{e,tail}}$ and $kT_2 = kT_{\text{e,bulk}}$ in the notation of the tables. The single-temperature spectra can therefore be pre-computed once for each temperature on the search grid, and every mixed spectrum is obtained by a linear combination, which makes an exhaustive search computationally inexpensive.

The parameters of the search are collected in Table 1. The temperature of the Maxwellian tail component was searched from 0.01 to 10 eV and that of the Druyvesteynian bulk component from 0.01 to 2.5 eV, each in 400 linearly spaced steps, while the mixing ratio α_1 of the tail component was searched from 10^{-7} to 10^{-2} in 40 logarithmically spaced steps. The wider range adopted for the tail component reflects the fact that it is constrained by the short-wavelength part of the spectrum, where the photon-energy threshold is highest. A logarithmic grid was used for α_1 because the mixing ratio is expected to span several orders of magnitude. The resulting grid contains 6.4×10^6 parameter combinations, which is tractable only because the decomposition of Equation (9) reduces each combination to a linear superposition of pre-computed spectra.

Table 1. Parameters of the exhaustive search. The objective function is the logarithmic residual of Equation (10).

Parameter	Range	Sampling
kT_{e} , Maxwellian tail component	0.01–10 eV	400 linear steps
kT_{e} , Druyvesteynian bulk component	0.01–2.5 eV	400 linear steps
Mixing ratio $\alpha_1 = \alpha_{\text{tail}}$	10^{-7} – 10^{-2}	40 logarithmic steps
Shape parameters γ	fixed at 1 (tail), 2 (bulk)	–
Electron density n_{e}	–	closed form, after the shape fit
Normalization wavelength	500 nm	–
Fitting range	310–850 nm	271 points at 2 nm

Both the calculated and the measured spectra were normalized at 500 nm, which removes the electron density from the shape fitting, and the goodness of fit was evaluated by the sum of squared residuals in logarithmic space,

$$S = \sum_j [\log_{10} \hat{\varepsilon}_{\text{calc}}(\lambda_j) - \log_{10} \hat{\varepsilon}_{\text{exp}}(\lambda_j)]^2, \quad (10)$$

where the caret denotes the normalized emissivity and the summation runs over the 271 wavelength points sampled at 2 nm intervals within 310–850 nm. A logarithmic metric was adopted because the emissivity varies by more than an order of magnitude

over the analyzed range, so a linear metric would be dominated by the long-wavelength region alone.

After the shape parameters were fixed, the electron density was obtained from the absolute intensity. Since $\varepsilon_{\text{ea}} \propto n_e$, the scaling factor that minimizes the logarithmic residual is given in closed form by the mean logarithmic offset between the measured and the calculated absolute spectra, and n_e follows directly. This procedure removes the manual adjustment used in earlier work and guarantees that the reported solution is the optimum on the prescribed grid for this two-stage objective, in which the normalized shape is fitted first and the density is then obtained from the absolute intensity. It is not in general identical to the optimum of a single objective in which shape and density are fitted simultaneously to the absolute spectrum.

The scripts implementing this search, together with the measured spectra, are openly available in Zenodo at <https://doi.org/10.5281/zenodo.22670842>, so the results reported here can be reproduced directly.

2.2.6. Choice of the Shape Parameter and Model Selection

The generalized EEDF of Equation (6) contains the shape parameter γ , which some previous studies treat as an additional fitting parameter. In the present work γ was fixed at the two canonical values, $\gamma = 1$ for the tail component and $\gamma = 2$ for the bulk component. It should be emphasized that this is a choice of functional basis for representing the measured continuum, and it is logically separate from the question of which physical process produces each component, which is deferred to Sections 2.2.7 and 3.1. The choice was examined quantitatively, and the results are summarized in Table 2 for the DBD apparatus operated at 7.2 kV.

Table 2. Comparison of EEDF models for the DBD apparatus at 7.2 kV. S is the logarithmic residual defined in Equation (10) evaluated over 271 wavelength points, S_{2T} its value for the two-temperature model, and k is the number of free shape parameters. The free- γ model is listed for reference only and is not adopted; see Section 2.2.6.

Model	Shape Parameters	k	S	S/S_{2T}
Single Maxwellian ($kT_e = 0.27$ eV)	$\gamma = 1$	1	73	110
Single Druyvesteynian ($kT_e = 0.68$ eV)	$\gamma = 2$	1	110	160
Two-temperature (this work)	$\gamma = (1, 2)$ fixed	3	0.69	1
Two-temperature, γ released	γ searched	5	0.39	0.57

Because the fit residuals contain smooth, correlated systematic contributions and cannot be treated as independent random noise, the following criterion was adopted and is applied consistently to every model-selection decision reported in this paper. An additional component or an additional free parameter is accepted only when it reduces the residual by at least one order of magnitude, that is, by far more than the correlated systematic errors described in Sections 2.2.4 and 2.2.8 can plausibly produce. A reduction by a factor of a few is regarded as being within the range of those systematic errors and is not, by itself, taken as evidence for a better physical description. This single criterion governs the adoption of the tail component in the discharge region, the decision to fix γ , and the use of a single-temperature model in the plume, which are discussed below and in Section 3.4.

Introducing the tail component has a decisive effect on the quality of the fit. The best single-temperature model, a 0.27 eV Maxwellian, gives $S = 73$, and the best single Druyvesteynian, at 0.68 eV, gives $S = 110$, whereas the two-temperature model gives $S = 0.69$. The residual is therefore reduced by a factor of 110–160, that is, by more than two orders of magnitude. A reduction of this magnitude cannot be attributed to noise or to

parameter degeneracy, and it establishes that a two-component functional form is required to reproduce the measured continuum.

By contrast, releasing γ as a free parameter produces only a marginal improvement. Searching both shape parameters over $\gamma \in \{1, 2, 3, 4, 5, 6\}$ reduces the residual from 0.69 to 0.39, a factor of only 1.8, and this is achieved only by driving the tail shape parameter to the upper boundary of the search range while the deduced electron density changes by a factor of about eight. An optimum that lies on the boundary of the search domain, together with a strongly unstable density, is characteristic of an ill-conditioned inversion rather than of a physically meaningful refinement: the continuum is a smooth, featureless function of wavelength, and the number of independent shape parameters that it can constrain is correspondingly small. By the criterion stated above, a factor of 1.8 lies well below the threshold of one order of magnitude and is within the range that the correlated systematic errors can produce, so the free- γ model is not adopted. The decisive comparison is one of magnitude. Introducing the tail component reduces the residual by more than two orders of magnitude, which can be produced neither by such systematic errors nor by parameter degeneracy, whereas releasing γ reduces it by less than a factor of two, which can.

The shape parameter was therefore fixed for three reasons. First, $\gamma = 1$ and $\gamma = 2$ are the two members of the family of Equation (6) for which a derivation from first principles exists: the Maxwellian form is the equilibrium distribution approached when electron–electron collisions dominate the relaxation, and the Druyvesteynian form is the classical solution for electrons that gain energy from an electric field and lose it in elastic collisions with neutrals, which depletes the high-energy tail relative to a Maxwellian. Intermediate or larger values of γ are purely phenomenological. Second, fixing γ regularizes an inversion that is otherwise degenerate, as demonstrated by the instability described above. Third, a common functional form is required if the parameters obtained for different devices, applied voltages, and measurement positions are to be compared with one another, which is the principal aim of this study. The sensitivity of the deduced density to this choice, a factor of about eight, is carried through the following sections as a systematic uncertainty. An independent test of the same choice, carried out on the line spectra rather than on the continuum, is presented in Section 3.3.2; it favors the Druyvesteynian form for the bulk component at every operating condition examined.

2.2.7. Kinetic Context of the Adopted Functional Forms

Since the two components are labeled Maxwellian and Druyvesteynian, it is necessary to state what these labels do and do not imply about the electron kinetics.

Gas composition provides an important physical context for these functional forms. Argon has no rotational or vibrational excitation channels; below its electronic excitation thresholds, electron energy loss to ground-state atoms occurs predominantly through elastic collisions. Under the classical assumptions of field-driven heating, elastic energy loss, an approximately constant electron mean free path, and negligible electron–electron collisions, this balance yields a Druyvesteynian distribution [31]. This motivates considering a Druyvesteynian component in an argon-dominated discharge, but gas identity alone does not determine the EEDF. The energy dependence of the actual cross-sections, collisions involving excited species, electron–electron interactions, and spatial and temporal variations can all produce departures from that idealized solution.

Molecular admixtures introduce additional collision processes. For N_2 and O_2 these include rotational and vibrational excitation, electronic excitation, and dissociation; oxygen also introduces electron attachment. The different thresholds and energy-dependent cross-sections of these processes can selectively redistribute or remove electrons in particular energy ranges, producing EEDFs more complex than either of the canonical analytical forms.

Boltzmann calculations for molecular gases show that the distribution can depart substantially from a Maxwellian as a consequence of electron–molecule energy exchange [32]. The EEDF of a mixture is therefore not generally a gas-composition-weighted sum of the EEDFs in its constituent gases.

Such distortions compete with electron–electron collisions, which redistribute energy within the electron population and drive the distribution towards a Maxwellian form; this tendency has been demonstrated in calculations of atomic afterglow plasmas [33]. If this redistribution is sufficiently rapid relative to molecular energy-loss and gain processes and changes in the heating conditions, an approximately Maxwellian distribution may remain useful despite molecular admixture. Thus, molecular admixture does not by itself require a large departure from a Maxwellian, although neither a small molecular fraction nor a high total collision frequency guarantees proximity to that form. The outcome depends on the electron density, gas composition and excited-state populations, including those responsible for superelastic collisions in which internal excitation energy is transferred to electrons. These competing rates were not established independently at position F, so this argument provides a physical motivation for considering a Maxwellian approximation rather than evidence that the plume has that distribution. The single-component treatment of position F is instead justified by the model-selection and identifiability results of Section 3.4, within the observable energy range.

For the conditions of this study, the electron–neutral collision frequency evaluated at the bulk temperature is $\nu_{\text{en}} \approx 1.5 \times 10^{10} \text{ s}^{-1}$, and with $\delta = 2m_e/M_{\text{Ar}} = 2.7 \times 10^{-5}$, where M_{Ar} is the mass of an argon atom and δ the mean fractional energy transferred in an elastic electron–atom collision, the energy relaxation frequency is $\nu_u = \delta\nu_{\text{en}} \approx 4 \times 10^5 \text{ s}^{-1}$. The electron–electron collision frequency, evaluated for the densities deduced here, lies between 5×10^{10} and $5 \times 10^{12} \text{ s}^{-1}$, so ν_{ee}/ν_u is of order 10^5 to 10^7 . By the usual criterion this suggests that the instantaneous distribution is Maxwellized by electron–electron collisions. The estimate is, however, only indicative: ν_{ee} scales with n_e , and the densities used here are the time-averaged values deduced in this work, the larger of which is argued in Section 2.2.9 to be an overestimate; using instead the supra-threshold densities lowers ν_{ee}/ν_u by about two orders of magnitude, which does not change the conclusion but does weaken it. A separate consideration is that the energy relaxation length $\ell_u = \ell_{\text{en}}/\sqrt{\delta} \approx 5 \text{ mm}$, with ℓ_{en} the electron–neutral mean free path, exceeds the 1 mm discharge gap; this indicates that the electron energy distribution is non-local, so the local field approximation underlying the steady-state Druyvesteynian solution is not satisfied, without by itself implying a Maxwellian form.

The Druyvesteynian form adopted for the bulk component is therefore a functional basis for representing the measured, time- and line-of-sight-averaged distribution, and it is not a claim that the instantaneous EEDF obeys steady-state Druyvesteynian kinetics. What the measurement establishes is narrower but firm: within the observable window of 1.46–4 eV the distribution falls off faster than a single exponential. This cannot be reproduced by a mixture of two Maxwellians; such a fit is worse by a factor of about two and, more decisively, requires an electron density two orders of magnitude higher, corresponding to an ionization degree of about 0.3, which is impossible for an atmospheric-pressure barrier discharge. It may further be noted that a superposition of Maxwellians with positive weights cannot decay asymptotically faster than its slowest exponential component, so the faster-than-exponential fall-off observed here cannot be produced by time-averaging over a distribution of Maxwellian temperatures alone. The same preference is found independently in the line spectra, where a collisional-radiative analysis that shares no atomic data or observable with the continuum returns a lower residual for the Druyvesteynian form at every one of the ten operating conditions examined (Section 3.3.2).

Below 1.46 eV the measurement provides no constraint at all, and the extension of the Druyvesteynian form into that region is an assumption, as discussed in Section 2.2.9.

2.2.8. Sensitivity and Uncertainty

Figure 3 illustrates the theoretical curves of the normalized emissivity for kT_e ranging from 0.3 to 0.7 eV, assuming a Druyvesteynian distribution. Curves are normalized at a wavelength of 600 nm. As shown in the figure, the spectral slope exhibits an extremely high sensitivity to variations in kT_e , particularly in the short-wavelength region (300–500 nm). At 400 nm the normalized emissivity varies by five orders of magnitude over the range 0.3–0.7 eV, that is, by rather more than one order of magnitude for each 0.1 eV change in kT_e . The temperature is therefore tightly constrained by the shape of the spectrum, and a deviation of order 10% already produces a discrepancy that is clearly visible against the measured curve.

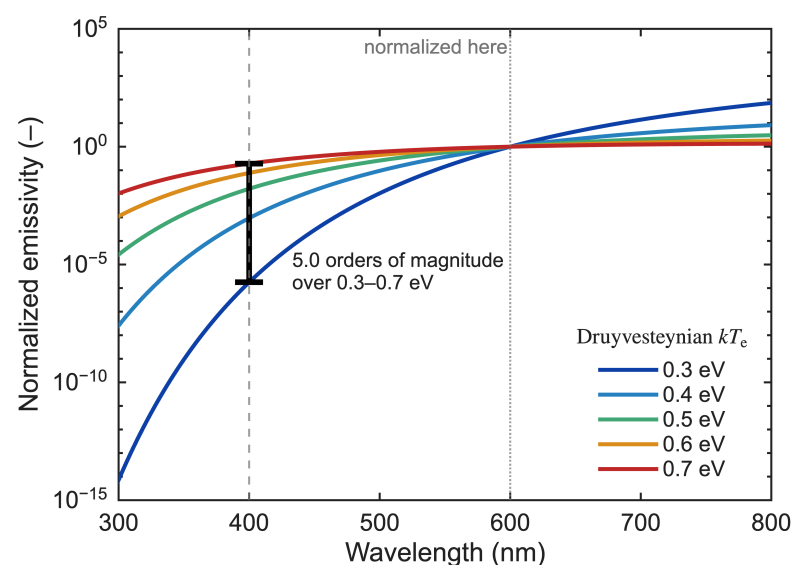


Figure 3. Sensitivity of the normalized emissivity to the electron temperature, assuming a Druyvesteynian distribution. The spectra are normalized at 600 nm. The vertical bar at 400 nm marks the spread between the 0.3 and 0.7 eV curves, which amounts to five orders of magnitude. The strong divergence of the curves at short wavelengths demonstrates the high sensitivity of the fit to the electron temperature.

This argument constrains the statistical precision of the temperature only, and the total uncertainty is dominated by systematic contributions of three kinds: the momentum-transfer cross-section adopted in Equation (3), the residual error of the line–continuum separation of Section 2.2.4, and the absolute intensity calibration. The first of these was quantified in Section 2.2.1 by varying the assumed gas composition for the plume spectrum, which changed the deduced temperature by less than 6% and the density by about 40%. The first two affect the spectral shape and hence the temperature, whereas the third enters the density directly, since $\varepsilon_{ea} \propto n_e$; the calibration uncertainty alone is of the order of 20%. For the density, however, the dominant uncertainty is neither statistical nor calibrational but arises from the extrapolation discussed in Section 2.2.9, which is an order-of-magnitude effect. A formal uncertainty analysis, based on the profile of S in the neighborhood of the optimum together with a propagation of these systematic contributions, was not carried out here and remains a task for future work.

2.2.9. Observable Energy Window and the Interpretation of n_e

Because the integral in Equation (2) is truncated at $E = hc/\lambda$, the continuum carries information only about electrons whose energy exceeds the photon energy. For the analyzed range this means $E \gtrsim 1.46$ eV, which is far above the bulk temperature of approximately 0.35 eV. The fraction of electrons able to contribute to the continuum is obtained by integrating the best-fit distribution above the photon-energy threshold,

$$P(E \geq E_{\text{th}}) = \int_{E_{\text{th}}}^{\infty} f_{\text{mix}}(E) dE, \quad (11)$$

with f_{mix} given by Equation (8) and normalized by Equation (5). Evaluating Equation (11) for the best fit obtained at 7.2 kV gives $P = 7.9 \times 10^{-3}$ at $E_{\text{th}} = 1.46$ eV, so only 0.79% of the electrons lie above the long-wavelength threshold, and $P = 7.1 \times 10^{-7}$ at the 4.0 eV threshold that corresponds to the short-wavelength edge of the measurement. The density of electrons that actually contribute to the observed continuum is therefore about $5.2 \times 10^{14} \text{ cm}^{-3}$, whereas the reported total density of $6.6 \times 10^{16} \text{ cm}^{-3}$ is obtained by extrapolating the fitted distribution down to energies at which no emission is produced, an extrapolation factor of about 127.

This has two consequences for the interpretation of the results. First, the quantity that the continuum constrains robustly is the supra-threshold electron density, whereas the total density inherits the full model dependence of the assumed low-energy distribution. The eightfold change of n_e that accompanies the release of γ , described in Section 2.2.6, is a direct manifestation of the same effect, since altering the shape parameter changes the ratio of unobservable bulk electrons to observable tail electrons. Second, the sign of the error is not determined a priori: the extrapolation overestimates the total density if the true low-energy distribution is more strongly depleted than the assumed analytical form and underestimates it in the opposite case. The large nominal densities reported below should therefore be read as model-dependent values rather than as directly measured quantities; the independent checks of Section 3.3 indicate that in the present case they are overestimates.

A consistency argument supports this view. For a neutral density of $2.5 \times 10^{19} \text{ cm}^{-3}$ at atmospheric pressure and room temperature, the nominal total density of $6.6 \times 10^{16} \text{ cm}^{-3}$ implies an ionization degree of about 2.6×10^{-3} , at which the electron-ion contribution to the continuum would no longer be entirely negligible. A model containing only electron-neutral Bremsstrahlung nevertheless reproduces the measured continuum well. This is suggestive rather than conclusive, since an unmodeled electron-ion contribution could in principle be absorbed by a change of the fitted EEDF parameters, and a quantitative estimate of the ratio of the two emission components would be needed to settle the point. Two independent determinations of n_e , from the Stark broadening of the hydrogen Balmer H_α line and from a collisional-radiative analysis of the line spectra, are presented in Section 3.3 and support this expectation; the latter returns an ionization degree of about 10^{-5} , at which the neglect of electron-ion Bremsstrahlung is unambiguously justified. For the same reason, the comparison between devices presented in Section 3.5 is discussed primarily in terms of relative changes, which are unaffected by a common extrapolation factor.

3. Results and Discussion

Figure 4 shows the fitting results of the Ar plasma spectrum obtained from the DBD apparatus at 7.2 kV using both single- and two-temperature EEDFs. The spectrum plotted is the line-subtracted continuum obtained as described in Section 2.2.4, which is the quantity to which all of the models were fitted. The two-temperature result combines a 0.35 eV

Druyvesteynian bulk component and a 0.81 eV Maxwellian tail component with a mixing ratio of 3.6×10^{-5} for the tail. For comparison, the best single-temperature models found by the same exhaustive search are a 0.27 eV Maxwellian and a 0.68 eV Druyvesteynian. Although the single-temperature models reproduce only a limited part of the spectrum, the two-temperature model follows the measured continuum over the entire wavelength range, and the residual is smaller by more than two orders of magnitude as listed in Table 2.

The total electron density obtained at this condition is $6.6 \times 10^{16} \text{ cm}^{-3}$, of which the tail component accounts for $2.4 \times 10^{12} \text{ cm}^{-3}$. As emphasized in Section 2.2.9, the directly constrained supra-threshold density is $5.2 \times 10^{14} \text{ cm}^{-3}$ and the total value is an extrapolation. Even the supra-threshold density is high compared with typical volume-averaged values, which is physically consistent with the filamentary nature of atmospheric-pressure DBDs. Previous studies, such as Kogelschatz [16], have established that the local electron density inside microdischarge channels reaches $10^{14} \sim 10^{15} \text{ cm}^{-3}$. Dense microdischarges can contribute strongly to the integrated spectrum, particularly when their EEDF differs from that in the surrounding plasma. However, the density inferred from the homogeneous fit is not generally the emission-weighted average of the local density. As explained in Section 2.1.3, it reduces to a volume- and time-averaged density only when the EEDF shape and neutral density are uniform; otherwise it is an effective parameter dependent on the assumed EEDF, observed volume and unresolved spatial and temporal structure. The comparison with reported local microdischarge densities is therefore qualitative, and the inferred value should not be identified with the local maximum density.

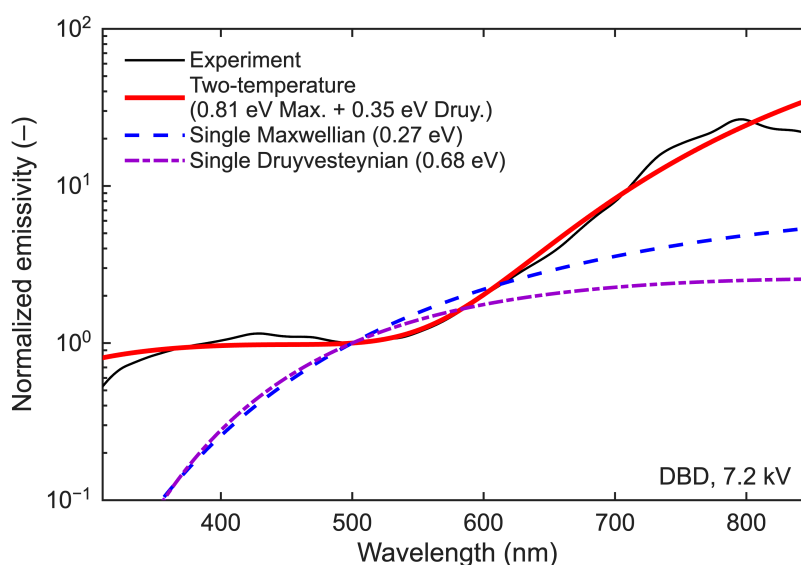


Figure 4. Fitting results for the continuum spectrum of atmospheric-pressure plasma in the 310–850 nm spectral range, for the DBD apparatus at 7.2 kV. All spectra are normalized at 500 nm. The black solid line is the line-subtracted continuum obtained as described in Section 2.2.4, which is the spectrum to which the models were fitted. The red solid line indicates the theoretical spectrum calculated using the two-temperature EEDF (a 0.35 eV Druyvesteynian bulk component and a 0.81 eV Maxwellian tail component with a tail mixing ratio of 3.6×10^{-5}), showing the best agreement with the experimental data. For reference, the best fits obtainable with a single temperature are also plotted: the blue dashed line is the Maxwellian distribution with a kT_e of 0.27 eV, and the purple dash-dot line the Druyvesteynian distribution with a kT_e of 0.68 eV. Neither single-temperature model reproduces the curvature of the measured continuum; both fall far below it at short wavelengths and saturate at long wavelengths, and their residuals are larger than that of the two-temperature model by factors of 110 and 160, respectively (Table 2).

The EEPF corresponding to the best fit is presented in Figure 5 together with its two constituent components, and it makes the role of the mixing ratio explicit. Although the Maxwellian component accounts for only 3.6×10^{-5} of the electrons, its exponential decay is far slower than the $\exp[-(E/E_0)^2]$ decay of the Druyvesteynian bulk, E_0 being the energy scale of Equation (6), so the two contributions cross at 2.64 eV; below this energy the distribution is essentially the Druyvesteynian bulk, whereas above 3 eV it is more than 97% Maxwellian. A minority population of this size therefore controls the entire high-energy part of the distribution, and it is this crossing that produces the separation between the short- and long-wavelength parts of the continuum described in Section 2.2.2. The shaded region marks the energies above 1.46 eV, which are the only ones that contribute to the measured continuum, and it shows directly how small a fraction of the distribution the measurement constrains. Compared with a pure 0.35 eV Druyvesteynian distribution, the fitted distribution contains a large excess of high-energy electrons.

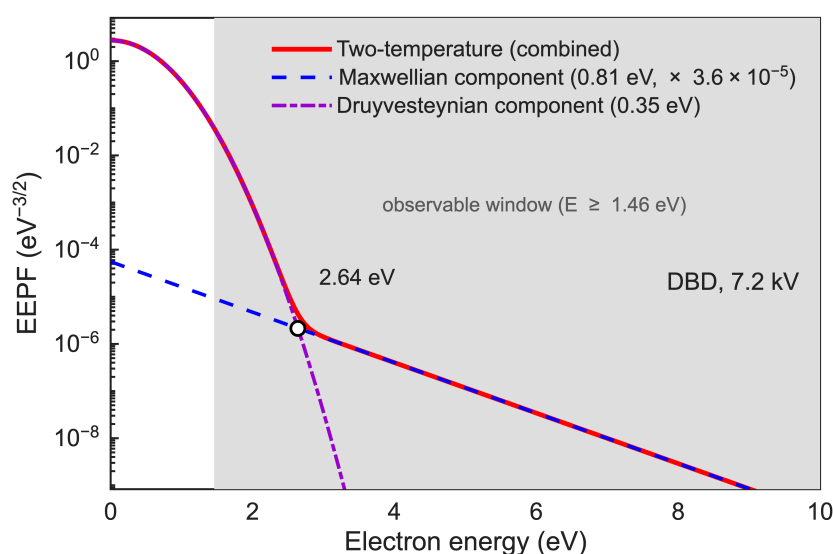


Figure 5. Best-fitted two-temperature EEPF and its constituent components for the DBD apparatus at 7.2 kV. The red solid line represents the combined two-temperature EEPF. The blue dashed and purple dash-dot lines are the Maxwellian ($kT_e = 0.81$ eV, $\times 3.6 \times 10^{-5}$) and Druyvesteynian ($kT_e = 0.35$ eV) components, each weighted by its mixing ratio so that their relative contributions can be compared directly; the two cross at 2.64 eV, indicated by the open circle. The shaded region marks the energy range above 1.46 eV, which is the only part of the distribution that contributes to the measured continuum.

3.1. Interpretation of the Two-Component Form

The preceding results establish that a two-component functional form is required to reproduce the time-averaged continuum, but they do not by themselves identify the physical origin of the two components. As shown in Section 2.2.7, the labels Maxwellian and Druyvesteynian describe the functional forms used to represent the time-averaged distribution and do not identify the underlying kinetics; the interpretation offered below is correspondingly tentative. The limits of what can be concluded from the present data are stated first.

A time-integrated measurement cannot distinguish two electron populations that coexist at every instant from two discharge phases that are separated in time and are averaged by the detector. Since the exposure time exceeds the excitation period by more than four orders of magnitude, both descriptions reproduce the same measured spectrum, and OES alone cannot discriminate between them. The two-temperature EEDF reported here is

therefore to be understood as a time-averaged distribution, and any assignment of the components to particular discharge phases is an interpretation rather than a measurement.

Within this limitation, a plausible interpretation is provided by the temporal structure of the discharge. Atmospheric-pressure DBDs are not continuous but consist of transient microdischarges: the discharge comprises a streamer phase, in which a strong electric field accelerates the electrons, and a much longer afterglow phase, in which the field has collapsed and the electrons relax and diffuse. Because the streamer phase lasts only a few nanoseconds, the accelerated electrons do not have time to reach equilibrium before the field collapses. The superposition of a brief, energetic phase and a prolonged, relaxing phase would produce a time-averaged distribution with an enhanced high-energy part relative to a single relaxed distribution, which is qualitatively what is observed. On this interpretation the tail component is associated with the streamer phase and the bulk component with the afterglow phase.

The order of magnitude of the mixing ratio is consistent with this picture. The duration of a typical microdischarge in an atmospheric-pressure Ar DBD is of the order of nanoseconds [16,34], which for the 20 kHz excitation used here (a period of 50 μ s) corresponds to an active fraction of the cycle of the order of 10^{-4} , comparable to the fitted mixing ratios of 3.6×10^{-5} to 2.9×10^{-4} . This agreement should not be over-interpreted. The mixing ratio is a ratio of electron populations in the time-averaged EEDF, whereas the duty cycle is a ratio of durations, and the two coincide only if the emission is weighted equally in the two phases. Since the electron density is expected to differ substantially between the streamer and afterglow phases, and the continuum emissivity is proportional to n_e , the time-averaged spectrum is not weighted by duration alone. The agreement is therefore reported as an order-of-magnitude coincidence that is consistent with the proposed interpretation, and not as a quantitative confirmation of it.

Independent support for or against this interpretation would require phase-resolved measurements, in which the spectrum is recorded at successive instants within the excitation cycle. Such measurements were not performed in this study and constitute the natural next step.

3.2. Voltage Dependence in the Closed-Channel DBD

Table 3 shows the voltage dependence of the electron temperatures and the density measured using the closed-channel DBD. As the applied voltage increases from 3.6 to 7.2 kV, the temperature of the bulk component remains essentially constant, changing only from 0.37 to 0.35 eV, and that of the tail component decreases from 0.91 to 0.81 eV, whereas the electron density increases monotonically from 3.5×10^{15} to 6.6×10^{16} cm^{-3} , that is, by a factor of about 19. The two-temperature EEDF provides good fitting results at all the applied voltages.

Table 3. Voltage dependence of the electron temperatures, the tail mixing ratio, and the electron density obtained for the DBD apparatus. The monitored power consumption is also listed where available. Values are quoted to two significant figures.

V (kV)	$kT_{e,\text{tail}}$ (eV)	$kT_{e,\text{bulk}}$ (eV)	α_{tail}	n_e (cm^{-3})	P (W)
3.6	0.91	0.37	2.9×10^{-4}	3.5×10^{15}	—
4.5	0.89	0.37	1.6×10^{-4}	8.3×10^{15}	—
5.4	0.76	0.38	2.1×10^{-4}	1.2×10^{16}	—
6.3	0.84	0.36	3.6×10^{-5}	4.2×10^{16}	9
7.2	0.81	0.35	3.6×10^{-5}	6.6×10^{16}	12

The increase in the electron density is attributed to the increased energy input to the plasma at the higher voltage. The most notable feature of Table 3 is that a nearly twentyfold change of the electron density is accompanied by a change of about 5% in the bulk temperature and of about 11% in the tail temperature. The additional power supplied to the discharge is therefore accompanied by a large increase in the electron density and almost no change in the mean electron energy. This is the behavior expected of a strongly collisional atmospheric-pressure plasma, in which the mean energy is set by the balance between field heating and elastic losses; it does not, however, determine how the input power is partitioned, since excitation, ionization, gas heating, and wall losses are not measured here.

The modest decrease of the tail temperature with an increase in density deserves comment, because a natural explanation in terms of enhanced collisional relaxation is not straightforward. The energy relaxation of an electron on neutrals is governed by the electron–neutral collision frequency $\nu_{en} = n_n \langle \sigma v \rangle$, in which n_n is the neutral density, σ the momentum-transfer cross-section, v the electron speed and the angle brackets denote an average over the EEDF. This depends on the neutral density and not on n_e , so an increase of n_e alone does not increase the rate at which a given electron loses energy to the gas. A dependence on n_e would require electron–electron collisions, whose frequency does scale with n_e and which drive the distribution towards a Maxwellian; alternatively, the reduced tail temperature may reflect a change of the discharge structure, such as a larger number of weaker microdischarges, rather than a change of the relaxation rate of an individual electron. The present time-averaged data cannot distinguish these possibilities, and the observed anticorrelation between density and tail temperature is therefore reported as an empirical trend rather than as evidence for a specific relaxation mechanism.

3.3. Independent Checks of the Electron Density

The interpretation of the electron density developed in Section 2.2.9 can be tested against diagnostics that do not rely on the continuum. Two were carried out, one from the Stark broadening of a line profile and one from a collisional-radiative analysis of the line intensities. The two are not equivalent: the Stark width responds to the perturbation by charged particles and is not restricted to electrons above the photon-energy threshold, so it provides a bound on the total density rather than a measurement of the supra-threshold population; the line intensities, by contrast, are produced by excitation processes with their own energy thresholds.

3.3.1. Stark Broadening of the H_α Line

The Stark broadening of the hydrogen Balmer H_α line at 656.3 nm was analyzed. Hydrogen is present as a trace impurity, and the line was not detectable at every condition: at most of the operating points the H_α signal was too weak to be separated from the underlying continuum at the available spectral resolution. A usable line profile was obtained only for the DBD apparatus at 6.3 kV, and the analysis is therefore restricted to that condition.

All widths quoted in this subsection are full widths at half maximum. The measured profile was fitted with a Voigt function, the Gaussian part representing the convolution of the instrumental function with Doppler broadening and the Lorentzian part representing the sum of the Stark, van der Waals, and resonance contributions. The instrumental width was 0.240 nm. The Doppler width was evaluated from

$$\Delta\lambda_D = 7.16 \times 10^{-7} \lambda_0 \sqrt{T_g/M_a}, \quad (12)$$

with $\lambda_0 = 656.3$ nm, the emitter mass $M_a = 1.008$ in atomic mass units, and an assumed gas temperature $T_g = 300$ K, which gives 0.0081 nm; the expected Gaussian width is therefore 0.240 nm. The van der Waals contribution was estimated from the standard expression [35]

$$\Delta\lambda_W = 8.18 \times 10^{-19} \lambda_0^2 (\bar{\alpha} \bar{R}^2)^{0.4} (T_g/\mu)^{0.3} N, \quad (13)$$

in which $\bar{\alpha} = 1.64 \times 10^{-24}$ cm³ is the polarizability of argon, $\bar{R}^2 = 165 a_0^2$ the difference of the squared radii of the upper and lower levels of H_α in units of the Bohr radius a_0 , $\mu = 0.98$ the reduced mass of the emitter–perturber pair in atomic mass units, and $N = 2.4 \times 10^{19}$ cm^{−3} the neutral density at $T_g = 300$ K; this yields 0.11 nm. Resonance broadening was neglected because hydrogen is present only as a trace impurity. The Stark width is related to the electron density through the tabulated H_α result of Gigos et al. [36], which includes the effect of ion dynamics,

$$n_e = 10^{17} \left(\frac{\Delta\lambda_S}{1.098} \right)^{1/0.680} \text{ cm}^{-3}, \quad (14)$$

with $\Delta\lambda_S$ expressed in nm.

The fitted Gaussian width was 0.23 nm, in good agreement with the expected value of 0.240 nm, which confirms that the profile decomposition is self-consistent. The fitted Lorentzian width, however, was only 0.058 nm, which is smaller than the van der Waals contribution of 0.11 nm estimated from Equation (13). The Stark width is thus smaller than the uncertainty of the van der Waals subtraction and could not be extracted; an indicative upper estimate can nevertheless be obtained, under the adopted line-profile model, by attributing the entire Lorentzian width to the Stark effect in Equation (14), which yields

$$n_e \leq 1.3 \times 10^{15} \text{ cm}^{-3} \quad (\text{DBD, 6.3 kV}). \quad (15)$$

This estimate is informative despite its weakness, although it is conditional on the line-profile model adopted: the instrumental width was held fixed, and the uncertainty of the Lorentzian width, which is obtained close to the resolution limit, was not propagated. The total electron density obtained from the continuum at the same condition is 4.2×10^{16} cm^{−3}, which exceeds the conditional Stark estimate by a factor of about 32. The supra-threshold density deduced from the continuum is 4.2×10^{14} cm^{−3} and lies below that estimate. Under the adopted line-profile assumptions, this comparison is inconsistent with the extrapolated total density, but lying below a conditional upper estimate does not validate the supra-threshold value.

Two reservations must be stated. First, subtracting the estimated van der Waals contribution gives a formally negative Stark width, which means either that the van der Waals contribution is overestimated by the approximate broadening constants used or that the Lorentzian width is underestimated by a fit performed close to the resolution limit. Assigning the full fitted Lorentzian width to the Stark effect gives an upper estimate only conditional on the adopted line-profile model and fitted width. Because uncertainty in that width was not propagated, Equation (15) is not a statistically established or guaranteed conservative upper bound. Second, the check could be performed at a single operating point only, so it constrains the magnitude of the extrapolation but does not establish its dependence on the discharge condition. A measurement at higher spectral resolution, or with a deliberately added trace of hydrogen to strengthen the Balmer lines, would allow this comparison to be extended to all of the conditions reported here.

3.3.2. Collisional-Radiative Analysis of the Line Spectra

The second check uses the atomic line emission, which was discarded in the continuum analysis of Section 2.2.4 and therefore carries information that is entirely independent of it. The densities n_i of the excited levels i , divided by their statistical weights g_i , were obtained from the calibrated line emission coefficients through $\varepsilon_{i,j} = (hc/4\pi\lambda_{i,j})A_{i,j}\Lambda_{i,j}n_i$, where $A_{i,j}$ is the Einstein coefficient and $\Lambda_{i,j}$ the optical escape factor; where several lines share an upper level, the mean of the resulting densities was taken [15]. These were fitted with the 65-level argon collisional-radiative model of Vlček [37] as implemented by Kikuchi et al. [15], with no continuum constraint imposed. The model includes electron- and atom-impact excitation, de-excitation and ionization, three-body and radiative recombination, spontaneous emission with radiation trapping, excimer formation and the diffusion of metastable atoms to the wall; following [15,37] the escape factor was set to unity for all transitions except those terminating on the ground state, so only the resonance lines are treated as optically thick. The discharge column radius was taken as 4.05 mm and the gas temperature fixed at 300 K. The levels available in the measured spectra were numbers 6–11, 15, 20, and 21 of [37], which lie between 12.91 and 14.98 eV above the ground state, that is, between 1.08 and 3.43 eV above the 4s levels at 11.55–11.83 eV. The distribution was taken to have the same two-component form as in Equation (8), and the objective function was the mean squared logarithmic error of the level densities,

$$\text{MSLE} = \frac{1}{N_{\text{lev}}} \sum_i \left[\ln \frac{(n_i/g_i)_{\text{model}}}{(n_i/g_i)_{\text{exp}}} \right]^2, \quad (16)$$

where N_{lev} is the number of levels included, which is 7 to 9 depending on the condition. The objective was minimized by differential evolution with a Sobol initialization, followed by a local refinement, over the ranges 0.1–10 eV and 0.3–20 eV for the two temperatures and 10^8 – 3.2×10^{15} and 3.2×10^6 – $3.2 \times 10^{13} \text{ cm}^{-3}$ for the two densities. It should be emphasized that this analysis shares no observable, no atomic data and no objective function with the continuum analysis; the only element in common is the assumed family of distribution functions.

The results are listed in Table 4, and three conclusions follow.

First, among the four combinations examined, the line spectra prefer a Druyvesteynian form for their dominant component. Repeating the fit with γ fixed at each of the four combinations of 1 and 2 gave a lower MSLE for $\gamma_{\text{bulk}} = 2$ at every one of the ten conditions, by factors of 1.8 to 3.7. The Maxwellian solutions are moreover not merely worse but unphysical: in four of them, the density of the dominant component collapses to the lower bound of the search range, 10^8 cm^{-3} , with the second component pinned at its upper bound, which is the same signature of an ill-conditioned inversion described in Section 2.2.6. The criterion of Section 2.2.6, which requires an improvement of at least one order of magnitude, governs the admission of additional parameters; the comparison between $\gamma = 1$ and $\gamma = 2$ is a choice between two models of equal complexity, to which that criterion does not apply, and the argument here rests on the unanimity of the preference across ten independent conditions rather than on the size of any single margin. This preference is obtained without using the continuum at all. It should not, however, be read as a confirmation of the bulk component of the continuum analysis: the dominant component of the collisional-radiative fit has a temperature of 1.3–1.5 eV, close to the tail temperature rather than to the bulk temperature of 0.35 eV, so what is supported is the functional form and not the parameters assigned to it.

Second, the extrapolated total density is excluded by the line spectra. The comparison is most direct in the forward direction: the distribution deduced from the continuum is

inserted into the collisional-radiative model and used to predict the excited-level densities, with no fitting at all. Used in this way, with the total density of Tables 3 and 5 unchanged, the model overestimates the measured level densities by five to seven orders of magnitude per level for the DBD and by one to five orders for the jet, where the extrapolated totals are smaller. The resulting error exceeds that of the free fit by factors of between 5.6 and 524.

The sensitivity of this result to the assumed density can be examined by holding the shape of the two-temperature distribution fixed at its best-fit values and varying only the total density, which gives the curves of Figure 6. Each curve has a well-defined minimum, and the extrapolated total lies a factor of between 7 and 932 above it, without exception. Writing R for the ratio between the assumed density and the density at that minimum, the aggregate error is found to depend on R in a simple way,

$$\sqrt{\text{MSLE}} = (2.42 \pm 0.06) \ln R + 0.22, \quad (17)$$

over the eight conditions with $R > 15$. The predicted line emission is therefore a steeply, in fact super-quadratically, amplified measure of the assumed density, which is qualitatively consistent with excitation proceeding in part through the metastable levels, whose population itself grows with n_e . Since $d \ln n_i / d \ln n_e$ was not evaluated level by level, Equation (17) should be read as an empirical description of the aggregate error over the range examined rather than as a demonstration that every level scales with the same power.

It must be emphasized what this test does and does not establish. Reducing the total density while holding the shape fixed reduces the supra-threshold population in the same proportion, so it does not isolate the extrapolation below 1.46 eV; a test that did so would have to preserve $n_e f(E)$ for $E \geq 1.46$ eV while altering the distribution only below that energy, which requires a different shape and not merely a different normalization. What Figure 6 shows is that the pair of values deduced from the continuum, the two-temperature shape together with the extrapolated total density, is not compatible with the measured line emission, and that the incompatibility is dominated by the density: no choice of density reproduces the level densities as well as the free fit, but the error at the best choice is smaller by two orders of magnitude than at the extrapolated total. The residual difference reflects the shape, and it is not negligible: with the density free to adjust, the distribution deduced from the continuum reproduces the level densities with an aggregate logarithmic error corresponding to about a factor of five, against about two for the freely fitted distribution.

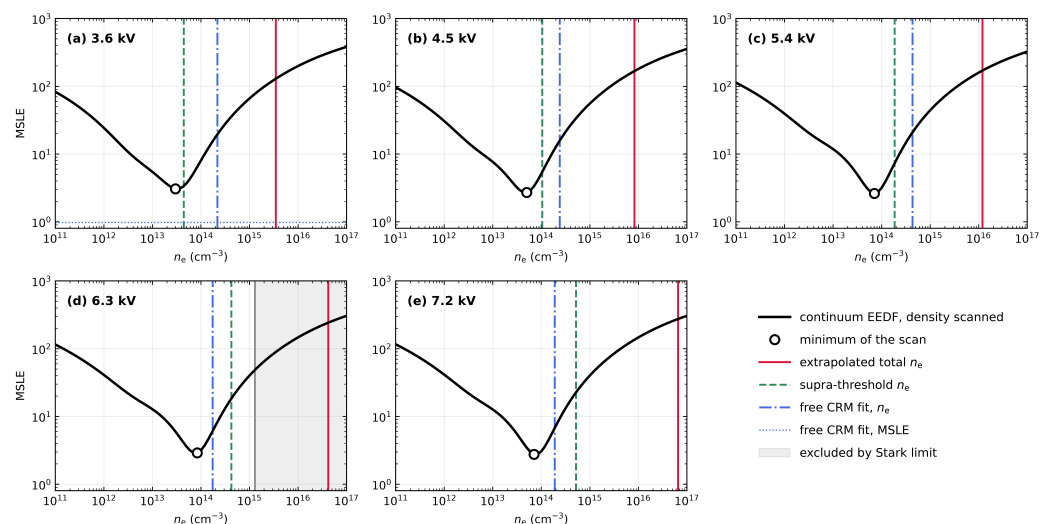


Figure 6. Line emission predicted from the distribution deduced from the continuum, for the DBD apparatus. The shape of the two-temperature distribution is held fixed at the best-fit values of Table 3 and only the total electron density is varied; the ordinate is the mean squared logarithmic error of the excited-level densities, Equation (16). The extrapolated total density (solid red) lies far above the minimum at every applied voltage, by factors of 117 to 932, whereas the supra-threshold density (dashed green) and the density returned by the free collisional-radiative fit (dash-dotted blue) lie close to it. The dotted horizontal line is the error attained by the free fit. At 6.3 kV the shaded region lies above the conditional Stark estimate of Equation (15).

The density returned by the free fit, of order 10^{14} cm^{-3} , is of the same order as the supra-threshold density deduced from the continuum, and for the DBD, the two lie within a factor of between 0.4 and 4.9 of one another at all five applied voltages. That the two should be comparable is not unreasonable, since the levels observed here lie 1.08 to 3.43 eV above the 4s levels, so stepwise excitation draws on an energy range overlapping the 1.46–4.0 eV window of the continuum. The overlap is nevertheless incomplete: electron-impact excitation from the ground state populates the 4s levels through electrons above approximately 11.5 eV. Electrons in this energy range also contribute to the continuum, because the upper integration limit in Equation (2) is infinite. However, the present continuum data do not independently resolve the population and shape of the EEDF in that range; the inferred values depend strongly on extending the assumed tail beyond the photon-energy thresholds of the measured spectrum. This correspondence should not be over-read. The two quantities are not equal, their ratio varies systematically with the applied voltage, and at 7.2 kV the total density returned by the collisional-radiative model is in fact smaller than the density that the continuum assigns to the supra-threshold population alone, which the two determinations cannot both be right about. For the jet the correspondence is weaker still, and the comparison between the devices is not reproduced at all: at the matched power of 12 W the continuum gives a density about ten times higher in the DBD than anywhere in the jet, whereas the collisional-radiative analysis gives $1.9 \times 10^{14} \text{ cm}^{-3}$ for the DBD at 7.2 kV against $2.9 \times 10^{14} \text{ cm}^{-3}$ at position B of the jet, reversing the ordering. The dependence on the operating condition is likewise not reproduced: the density required by the line spectra varies by a factor of 2.8 across the applied voltages of the DBD and by 16 along the axis of the jet, against factors of 12 and 88 for the supra-threshold density of the continuum. Which of the two diagnostics is at fault cannot be established from the present data; the small number of levels available, the different weighting of line and continuum emission along the line of sight, and the limited accuracy of the collisional-radiative fit itself are all candidates.

What the comparison supports robustly is accordingly the narrowest of these statements, and it is the one that matters for the argument of Section 2.2.9: the total electron density obtained by extrapolating the fitted distribution below the photon-energy threshold is not consistent with an independent measurement of the same plasma, and it should not be treated as a measured quantity. It should also be recorded that the two analyses are independent only in their spectral content and atomic data; they share the same measurement, the same intensity calibration, the same observation geometry, and the same line–continuum separation, so systematic errors of those origins are common to both.

Third, the second component is not constrained by the line spectra. Its density is six to seven orders of magnitude below that of the dominant component at every condition, so its temperature has almost no influence on the objective function. Two independent runs of the optimizer returned tail temperatures differing by a factor of 7.2 at one condition while the MSLE changed by 0.8%, and the fitted values repeatedly lie on the bounds of the search range. The tail parameters are therefore not reported in Table 4. The dominant component is by contrast robust: the same two runs reproduced its temperature and density to better than 1% at nine of the ten conditions. The line spectra thus corroborate the functional form and the magnitude of the density but, unlike the continuum, do not resolve the two-component structure itself.

The plume (position F) was excluded from this analysis. The collisional-radiative model describes pure argon and contains no interaction with the entrained ambient air, whereas the $4s[3/2]_2$ metastable at 11.55 eV, which in pure argon at atmospheric pressure is lost mainly by three-body conversion to Ar_2^* on a timescale of the order of 10^2 ns, is quenched by N_2 and O_2 with rate coefficients of the order of 10^{-11} to $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [38]; for a 10% admixture, this gives a quenching frequency of $(0.2\text{--}2) \times 10^8 \text{ s}^{-1}$ and shortens the lifetime by about an order of magnitude, which invalidates the stepwise excitation ladder on which the model relies; the vibrational excitation of N_2 , a dominant electron energy loss channel below 3 eV, is likewise absent. Consistently with this, the fit at position F gives $\text{MSLE} = 4.7$, against about 1.1 at every other position. Unlike the pure-argon collisional-radiative model used here, the electron–neutral continuum emission calculation can include additional neutral species through their momentum-transfer cross-sections. Within the assumed single-temperature EEDF family, varying the plume composition changes the deduced temperature by less than 6% and the density by about 40%, as shown in Section 2.2.1. This illustrates the simpler treatment of composition in the continuum emission kernel, but does not validate the assumed EEDF in the mixture. Molecular collisions can reshape the actual distribution, and the kinetic applicability of the fitted form remains a separate issue, as discussed in Section 2.2.7.

Table 4. Electron temperature and density obtained from the collisional-radiative analysis of the line spectra, with the shape parameters fixed at $\gamma = (2, 1)$ as in the continuum analysis. MSLE is defined in Equation (16); the corresponding discrepancy per level is $\exp(\sqrt{\text{MSLE}})$, between 1.9 and 2.9. Only the dominant component is listed, since the second component is not constrained by these data (Section 3.3.2). The last column reproduces, for comparison, the supra-threshold density deduced from the continuum, that is, the total density of Tables 3 and 5 multiplied by $P(E \geq 1.46 \text{ eV})$ from Equation (11). Position F was not analyzed because the argon model does not describe the entrained air.

	Condition	Collisional-Radiative			Continuum
		kT_e (eV)	n_e (cm ⁻³)	MSLE	n_e Supra (cm ⁻³)
DBD	3.6 kV	1.35	2.2×10^{14}	0.98	4.4×10^{13}
	4.5 kV	1.43	2.4×10^{14}	0.77	1.0×10^{14}
	5.4 kV	1.44	4.3×10^{14}	0.52	1.9×10^{14}
	6.3 kV	1.51	1.8×10^{14}	0.58	4.2×10^{14}
	7.2 kV	1.50	1.9×10^{14}	0.52	5.2×10^{14}
Jet	A	1.32	9.4×10^{13}	0.91	3.1×10^{12}
	B	1.44	2.9×10^{14}	0.39	6.1×10^{13}
	C	1.42	2.7×10^{14}	0.55	2.7×10^{13}
	D	1.35	1.7×10^{14}	0.69	8.5×10^{12}
	E	1.28	5.2×10^{13}	1.12	6.9×10^{11}
	F	not analyzed (see Section 3.3.2)			

Table 5. Spatial dependence of the electron temperatures, the tail mixing ratio and the electron density obtained for the plasma jet apparatus at an applied voltage of 9.9 kV and a monitored power consumption of 12 W. Positions A–F correspond to the locations indicated by the red dots in Figure 2. At position F (the plume region) the two-temperature model no longer provided a decisive improvement over a single-temperature one, and a single-temperature Maxwellian EEDF ($\gamma = 1$) was therefore adopted; see Section 3.4. Values are quoted to two significant figures.

	Position	$kT_{e,\text{tail}}$ (eV)	$kT_{e,\text{bulk}}$ (eV)	α_{tail}	n_e (cm ⁻³)
A	above upper electrode	1.5	0.42	3.7×10^{-5}	1.0×10^{14}
B	below upper electrode	0.63	0.36	1.6×10^{-4}	6.0×10^{15}
C	above lower electrode	1.2	0.40	4.9×10^{-5}	1.2×10^{15}
D	below lower electrode	1.6	0.41	3.6×10^{-5}	3.2×10^{14}
E	nozzle exit	1.0	0.41	1.1×10^{-4}	2.6×10^{13}
F	plume	0.45 (Maxwellian)		–	5.5×10^{10}

3.4. Spatial Dependence in the Open-Air Jet

Table 5 lists the spatial dependence of the parameters obtained using the open-air jet at a monitored power consumption of 12 W. In the inter-electrode region, a spectrum similar to that of the closed-channel DBD is observed and the two-temperature model again applies. The electron density reaches its maximum of $6.0 \times 10^{15} \text{ cm}^{-3}$ immediately below the upper electrode and then decreases monotonically downstream, falling to 1.2×10^{15} , 3.2×10^{14} and $2.6 \times 10^{13} \text{ cm}^{-3}$ at the successive positions, and finally to $5.5 \times 10^{10} \text{ cm}^{-3}$ in the plume. Over the same interval the tail temperature rises from 0.63 to 1.6 eV, so the anticorrelation between density and tail temperature already noted for the DBD is reproduced within the discharge region.

The decrease in the electron density downstream is ascribed to the weakening of the electric field; new ionization events become rare and loss mechanisms such as collisions with atoms and diffusion to and loss at the walls become dominant. As discussed for the DBD, the accompanying rise of the tail temperature is reported as an empirical trend; a

quantitative attribution to a change of the relaxation rate would require electron–electron collisions or a change of the discharge structure to be established independently. Beyond the electrodes this trend does not continue: at the nozzle exit the tail temperature falls to 1.0 eV and in the plume the two-component structure is no longer resolved.

In the plume region, where the plasma jet is ejected into ambient air, a significantly different spectrum is detected. Here, the advantage of the two-temperature model largely disappears. Whereas in the discharge region the introduction of the tail component reduces the residual by a factor of 110–160, as shown in Table 2, the same comparison at position F gives $S = 9.9$ for the single-temperature model and $S = 2.2$ for the two-temperature model, an improvement of only about a factor of four. This is more than an order of magnitude smaller than in the discharge region, and it falls below the threshold of one order of magnitude set by the model-selection criterion of Section 2.2.6; it is of the same order as the factor of 1.8 obtained by releasing γ , which was argued there to lie within the range that the correlated systematic errors can produce. Moreover, when the second component is admitted at this position it is very poorly determined. Its temperature is returned as 6–9 eV and varies by more than 30% depending on the assumed gas composition, while the corresponding residual changes by less than 1%. The concern is therefore its poor identifiability rather than the temperature magnitude alone: location beyond the powered electrodes does not establish the absence of a local electric field. A parameter that can be varied over such a range without affecting the quality of the fit is not constrained by the data, which is the same signature of an ill-conditioned inversion that led to the rejection of the free- γ model in Section 2.2.6. By the model-selection criterion adopted in this work, the tail component is therefore not warranted at this position. The plume spectrum was accordingly analyzed with a single-temperature Maxwellian EEDF ($\gamma = 1$ in Equation (6)), which gives $kT_e = 0.45$ eV, while the electron density drops sharply to $5.5 \times 10^{10} \text{ cm}^{-3}$. It should be emphasized that this is a modeling decision taken on grounds of parsimony in a case that the data do not sharply resolve, and not a demonstration that only a single electron population is present. This result nevertheless suggests that the plume represents a distinct plasma regime. One possible interpretation is that changes in the balance between electron heating and relaxation weaken the resolved high-energy contribution relative to that in the discharge region. Air entrainment also changes the available energy-loss and gain processes, so this difference cannot be attributed uniquely to either gas composition or discharge dynamics. The single-component fit is an effective representation of the measured continuum, not evidence that the actual molecular-mixture EEDF has a simple analytical form. It should be emphasized, however, that this does not establish the absence of a streamer phase in the plume. Guided ionization waves are known to propagate well beyond the powered electrodes in atmospheric-pressure plasma jets, and the present time-integrated measurement cannot exclude their presence; the robust statement is that the two-component signature is no longer resolved. Two further reservations apply to this position: the continuum signal is weak at such a low electron density, so the ability of the fit to discriminate between $\gamma = 1$ and $\gamma = 2$ is limited, and the local gas composition is affected by air entrainment, which is treated as described in Section 2.2.1. Repeating the single-temperature analysis with cross-sections for the mixtures of Section 2.2.1 changes the deduced temperature by less than 6% and the density by about 40%. These results indicate limited composition sensitivity of the fitted temperature within the assumed EEDF family, but do not exclude molecular-collision-induced structures outside that family. In particular, the fitted temperature is an effective parameter of the selected analytical distribution; its relation to the mean energy of the actual EEDF depends on the validity of that distribution. The molecular-mixture emission calculation is simpler to extend than the

pure-argon collisional-radiative model used here, but this computational advantage should not be confused with a kinetic validation of the single-component approximation.

3.5. Comparison Between the Two Apparatuses

Finally, the characteristics of the closed-channel DBD and of the open-air jet are compared. The discharge region of the open-air jet exhibits a spectrum comparable to that of the closed-channel DBD, and both systems show an anticorrelation between the electron density and the tail electron temperature.

Before the two devices are compared, it is useful to state which operating parameters were matched and which could not be. Both devices used the same working gas (argon) at the same flow rate (4 L/min), the same power supply and the same excitation frequency (20 kHz), and the comparison below is made at the same monitored power consumption of 12 W. The applied voltages necessarily differ, 7.2 kV for the closed-channel DBD and 9.9 kV for the open-air jet, because each geometry requires its own voltage to sustain a stable discharge. The remaining parameters cannot be matched at all, since they are properties of the geometry itself: the discharge gap is 1 mm in the DBD, whereas the inter-electrode distance is 12 mm in the jet, and the discharge volumes differ accordingly. The comparison is therefore between two devices operated at the same input power and gas conditions, and not between two realizations of the same discharge.

The most striking result of this comparison is the contrast between the behavior of the temperature and that of the density. For every condition in which the two-component model was applicable, the bulk electron temperature lies between 0.35 and 0.42 eV: across the closed-channel and open-air configurations, across a factor of two in applied voltage, and across five measurement positions spanning the discharge region and the nozzle exit. Even at position F, where the two-component model no longer applies, the single-Maxwellian effective temperature of 0.45 eV is of the same order. The electron density, in contrast, varies from $6.6 \times 10^{16} \text{ cm}^{-3}$ in the closed-channel DBD to $5.5 \times 10^{10} \text{ cm}^{-3}$ in the plume of the open-air jet, a range of six orders of magnitude. These observations suggest that, within the continuum analysis, the device configuration is a major factor governing the magnitude and the spatial distribution of the electron density, whereas the bulk electron temperature is comparatively insensitive to the device geometry under the conditions examined. This is consistent with the voltage dependence discussed above, in which a twentyfold change of density was accompanied by an almost constant temperature. It should be noted that the collisional-radiative analysis of Section 3.3.2 does not reproduce this ordering, returning a slightly higher density in the jet than in the DBD at the matched power; the comparison made here therefore rests on the continuum model.

A comparison at nominally equal operating power is possible because the monitored power consumption was 12 W both for the open-air jet measurements and for the closed-channel DBD operated at 7.2 kV. Under this condition the closed-channel DBD reaches $6.6 \times 10^{16} \text{ cm}^{-3}$, whereas the highest density anywhere in the open-air jet is $6.0 \times 10^{15} \text{ cm}^{-3}$, about one order of magnitude lower. The observed volumes of the two devices agree to within 5%, so this ratio is not an artifact of the conversion from the measured signal; it should nevertheless be read alongside the fact that the collisional-radiative analysis of Section 3.3.2 does not reproduce it. A plausible explanation follows directly from the contrast between the two geometries: the closed flow-channel confines the discharge to a 1 mm gap isolated from the ambient atmosphere, concentrating the deposited power into a much smaller volume, whereas in the open-air tube-type jet the plasma extends along the tube and expands into the surrounding air. Two qualifications are necessary before this is regarded as established. The monitored 12 W is the power drawn by the supply, and supply losses, capacitive current, and the discharge volume differ between

the two devices, so equal monitored power does not guarantee equal power deposited in the plasma. Furthermore, only a single matched point is available, since the jet was operated at a fixed condition. A measurement of the deposited power, for example, from the charge–voltage Lissajous figure, together with a scan of both devices over a common range of deposited power, would be required to establish the comparison firmly. Because both densities are subject to the same extrapolation discussed in Section 2.2.9, however, the ratio between them is considerably more reliable than either absolute value.

The plume of the open-air jet displays spectral characteristics that have no counterpart in the closed-channel DBD, since the closed configuration has no region equivalent to an effluent discharged into the ambient atmosphere. Because the plume is spatially separated from the powered electrodes, the electron temperature and density differ markedly from those in the discharge region. Given that the irradiation target in the open-air jet is placed in this plume, the properties of the plume plasma are arguably more relevant for applications than those of the discharge plasma.

4. Conclusions

The continuum spectrum of atmospheric-pressure nonequilibrium argon plasma was reproduced using a two-temperature EEDF, combining a Druyvesteynian bulk component and a Maxwellian tail component, with all parameters determined by an exhaustive grid search. Introducing the tail component reduced the fitting residual by more than two orders of magnitude relative to the best single-temperature model, whereas releasing the shape parameter improved it by less than a factor of two while producing an unphysical, boundary-limited solution. The two canonical shape parameters were therefore retained as a functional basis for the time-averaged distribution, which, as the collision-frequency estimates show, is not a claim about the instantaneous kinetics; an independent collisional-radiative analysis of the line spectra favored the same form at every one of the ten operating conditions examined.

Comparing a closed flow-channel DBD with an open-air plasma jet revealed a clear separation of roles between temperature and density. The bulk electron temperature remained within 0.35–0.42 eV for every device, applied voltage and measurement position at which the two-component model was applicable, whereas the electron density spanned six orders of magnitude; at the same monitored power of 12 W the DBD attained a density about ten times higher than the maximum in the jet. Within the continuum analysis the device configuration is therefore a major factor governing the magnitude and the spatial distribution of the electron density, while the bulk temperature is comparatively insensitive to the geometry. The collisional-radiative analysis does not reproduce this ordering (Section 3.3.2), and the conclusion is accordingly stated as one drawn from the continuum model.

The principal methodological conclusion is that continuum OES tightly constrains only the part of the EEDF above the photon-energy threshold, about 1% of the electrons here, so the total electron density customarily reported from such measurements is a model-dependent extrapolation. Two independent checks support this. Under the adopted line-profile assumptions, the Stark broadening of H_{α} gives a conditional upper estimate of $1.3 \times 10^{15} \text{ cm}^{-3}$, above the supra-threshold density of $4.2 \times 10^{14} \text{ cm}^{-3}$ but a factor of 32 below the extrapolated total. Inserting the extrapolated density into a collisional-radiative model overestimates the measured excited-level densities by five to seven orders of magnitude, and the density that the line spectra themselves require is of order 10^{14} cm^{-3} , comparable to the supra-threshold value. Neither check validates that value, since the Stark result is a bound and the two methods do not reproduce each other's dependence on the operating condition; what they establish is that the extrapolated total is not supported.

Reporting the supra-threshold density alongside the extrapolated total is accordingly recommended. At the plume position, the single-temperature Maxwellian fit should likewise be interpreted as an effective parameterization; the unknown local gas composition and competing molecular collision processes limit its kinetic interpretation. Phase-resolved measurements, measurements of the local gas composition, and an extension of the Stark comparison to all operating conditions remain for future work.

Author Contributions: Conceptualization, J.E. and H.A.; methodology, J.E., W.K., A.N., and H.A.; software, J.E. and W.K.; validation, J.E. and W.K.; formal analysis, J.E.; investigation, J.E.; resources, J.E. and A.N.; data curation, J.E.; writing—original draft preparation, J.E.; writing—review and editing, J.E., W.K., and H.A.; visualization, J.E.; supervision, H.A.; project administration, H.A.; funding acquisition, H.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was partially supported by JSPS KAKENHI, grant number 25K00991.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The original data presented in this study, together with the scripts used for the continuum analysis, are openly available in Zenodo at <https://doi.org/10.5281/zenodo.22670842>. The collisional-radiative model used in Section 3.3.2 is that of Vlček [37] as implemented by Kikuchi et al. [15], and it is not redistributed here.

Conflicts of Interest: The authors declare no conflicts of interest.

Abbreviations

The following abbreviations are used in this manuscript:

CR	Collisional-radiative
DBD	Dielectric barrier discharge
EEDF	Electron energy distribution function
EEPF	Electron energy probability function
MSLE	Mean squared logarithmic error
OES	Optical emission spectroscopy

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