The anomalous short relaxation length of the cathode beam and the existence of a Maxwellian electron energy distribution function (EEDF), $F(\varepsilon)$, in the positive column of a dc arc discharge at low gas pressure $p$ were found by Langmuir [1, 2] and have been known in the literature as the Langmuir paradox. Under the condition of the Langmuir paradox, when the electron free path $\lambda$ exceeds the tube radius, $R (pR \leq 20 \text{ mTorr cm})$, the relaxation length of the electron cathode beam (of a few mm) appeared to be about 3–4 orders of magnitude less than the estimated collisional relaxation length. This part of the paradox was resolved by Merrill and Webb [3] by discovering the plasma-beam instability. They have found strong microwave oscillations with frequencies close to the local plasma frequency in the beam relaxation zone. Those oscillations transformed the cathode electron beam to a wide spectrum electron swarm.

Langmuir’s observation of a Maxwellian EEDF in a low pressure positive column was based on the fact that the measured electron part of the probe $I/V$ characteristic, $I_e(V)$ on a semi-log scale $\ln[I_e(V)]$ could fit a straight line for elastic ($\varepsilon < \varepsilon^*$), non-elastic ($\varepsilon > \varepsilon^*$) and wall escape ($\varepsilon > \varepsilon f$) electron energy ranges. Here, $\varepsilon^*$ is the excitation energy, and $\varepsilon f$ is the wall floating potential. Langmuir’s observation becomes surprising after taking into account fast losses of high energy electrons during excitation, ionization and escape to the wall of the tube. However, numerous experiments performed in the following decades after the paradox was formulated have confirmed Langmuir’s finding. The later developed techniques for EEDF measurements based on the Druyvesteyn formula [4], have confirmed a Maxwellian EEDF in the positive column at low gas pressures in mercury and noble gases [5], although others authors [6] have found an essentially Maxwellian EEDF with a small bump which they attributed to small residues of the cathode beam. Many hypotheses have been put forward to explain the paradox, but neither of them has been proven so far [7–9]. In spite of considerable advancements toward understanding of many plasma kinetic and electrodynamic phenomena in gas discharge plasmas and their successful modeling, the existence of Maxwellian EEDF in the positive column of dc linear discharges at low gas pressure has remained a mystery.

In [9], ‘Qualitative arguments are presented to the effect that a combination of already known mechanisms operating in low-pressure discharges can create electron energy distribution functions that are close to Maxwellian without relying
on any additional mechanisms for Maxwellization. However, EEPF calculations accounting for all these mechanisms showed a Druyvesteyn-like distribution for electrons in elastic energy range (\(\epsilon < \epsilon^*\)) \cite{10}.

The data base of EEDFs in low pressure positive columns at the Langmuir paradox condition has been obtained decades ago, when EEDF measurement techniques have not yet been well developed. The EEDFs in those measurements were lacking information on the lowest energy (\(\epsilon < T_e\)) electrons which account for the majority of the electron population. They also missed information about high energy electrons due to a limited dynamic range of the measurements. A prevalent view among specialists is a lack of reliable experimental data over a wide range of electron energies. The new EEDF measurement equipment with high energy resolution and high dynamic range makes it possible to resolve low energy electrons and electrons in the inelastic energy range. Therefore the EEDF data base has to be revisited.

Rigorous requirements for accurate EEDF measurement, problems causing the errors and remedies for their mitigation have been recently analyzed in review \cite{11}. Advances in modern instrumentation such as high resolution and wide dynamic range signal processing, smart filtering, low-frequency noise suppression, compensation of the stray impedance of the probe circuit and \textit{in situ} automated probe cleaning made possible accurate EEDF measurements over wide energy range.

In this paper, we present EEDF measurements under the Langmuir paradox conditions using the Multifunctional Plasma Probe Analyzer \cite{12} developed by the authors following requirements \cite{11}. The measurements were performed in the positive column of a dc discharge at low argon pressures corresponding to near collisionless plasma typical for the Langmuir paradox condition. A discharge Pyrex tube used in the experiment had its inner radius \(R = 2.5\) cm and length \(L = 90\) cm, with KF glass flanges on its ends. To minimize the discharge instability, a plasma cathode \cite{13} and a hollow anode with its electron collecting area greater than the discharge cross section, were set at the tube ends. The dc discharge was driven through an electronic ballast working as a dc current source at the fixed discharge currents 0.3, 1.0 and 3.0 A.

The measurements were performed at argon pressures \(p = 1.0\) and 3.0 mTorr monitored with two Baratrons set at the tube ends. At this range of gas pressure, the basic requirement for validity of Langmuir and Druyvestein diagnostics, \(\lambda_e(\epsilon) \gg (a_p + \lambda_D)\) \cite{11}, is well satisfied. In our experiment, at the largest argon pressure of 3 mTorr, \(\lambda_e(\epsilon) = 680; 25\) and \(17\) cm, correspondingly, for \(\epsilon = 0.3\) (Ramsauer minimum), 3 and 30 eV, while the probe radius, \(a_p = 5 \times 10^{-3}\) cm. Here, \(\lambda_e(\epsilon)\) is the electron free path, \(a_p\) is the probe radius, and \(\lambda_D\) is the electron Debye length. Due to the gas flow and cataphoresis, the difference in pressures at the tube ends could rich up to 15\%, so, the reported gas pressure is the average of the two Baratron’s readings.

Five rotatable Langmuir probes were set along the discharge tube with a 20 cm distance between them. The first one

![Figure 1. EEPFs measured with differently oriented probes (||—axial and \(\perp\) —radial) at the distance from the plasma cathode \(x = 65\) cm.](image-url)
was at 5 cm from the cathode and the fifth was at 5 cm from the anode. Probe rotation allowed for the probe orientation in the axial and radial directions, thus, allowing observation of EEDF anisotropy. In full range of argon pressure 1–3 mTorr (with background vacuum pressure less than $6 \times 10^{-7}$ Torr) and discharge current (0.3–3 A), the dc discharge was free of temporal instability, which facilitated EEDF measurements over large dynamic range allowing detection of high energy electrons.

The results of EEDF measurements at the positive column axis, 65 cm from the plasma cathode, discharge currents 0.3, 1.0 and 3 A, and argon pressure 1 and 3 mTorr are shown in figure 1. The measured EEDFs are presented in terms of the electron energy probability function, EEPF, $f(e) \sim e^{-1/2} F(e)$. Recall that in a semi-log scale, the $\ln[f(eV)]$ looks as a straight line for a Maxwellian EEDF.

As seen in figure 1, the found EEPFs strongly deviate from Maxwellian distributions. At the lowest gas pressure of 1 mTorr ($pR = 2.5 \times 10^{-3}$ Torr cm), best suited to the Langmuir paradox condition, the measured EEPF has a low energy peak (not observed in earlier EEPF measurements at such condition). At electron energy exceeding the argon excitation energy $\epsilon^* = 11.8$ eV, the EEPFs start to drop, and at some higher electron energy, $\epsilon > (20–25)$ eV at 1 mTorr, which corresponds to electron energies higher than the wall floating potential, a significant anisotropy in $f(e)$ is observed. Having in mind that Druyvesteyn formula is only valid for isotropic distributions, anisotropic tails of measured EEDFs serves just as qualitative illustrations. The EEPF anisotropy is due to the combined effect of the strong axial electric field to gas density ratio, $E/N$, and the escape to the wall of electrons whose kinetic energy in the radial direction exceeds the potential barrier of the wall sheath. The observed features of the enhanced population of low energy electrons and the anisotropy of the high energy electrons are also seen at 3 mTorr, but considerably less than at 1 mTorr. At 10 mTorr when the discharge transits to a collisional regime, the low energy peak and anisotropy in the measured EEPF practically disappear.

The obtained non-Maxwellian distributions for both, elastic ($\epsilon < \epsilon^*$) and inelastic ($\epsilon > \epsilon^*$) electron energies, contradict to the Langmuir paradox concept, as well as the calculations in [9, 10]. In those works, the EEPFs at $\epsilon < \epsilon^*$ are convex (Druyvesteyn-like), and at $\epsilon > \epsilon^*$ are Maxwellian. In contrast, our measurements show that the EEPFs at $\epsilon < \epsilon^*$ are concave, and at $\epsilon > \epsilon^*$ are non-Maxwellian.

We suggest that the Langmuir paradox statement of Maxwellian EEDF (in both, elastic and inelastic energy range) was based on inaccurate probe measurement technique of those days. Applying a modern measurement technique in our experiments, we found EEDFs which are non-Maxwellian in inelastic and, surprisingly, in elastic energy range. In traditional understanding of the Langmuir paradox, a Maxwellian distribution of bulk electrons in the elastic energy range was quite expected. Paradoxical phenomenon was the existence of fast electrons with energies exceeding the wall potential, and having their distribution temperature equal to that of bulk electrons.

In plasma probe diagnostics, according to Langmuir’s procedure, almost always, the electron current, $\ln[I(V)] = \ln[f(eV) - I(V)]$ can be fitted to a straight line in some range of electron energies (that is expected for a Maxwellian EEDF). Here, $I_e$ and $I_I$ are the electron and ion components of the probe current. Recall that decades ago, when the last experimental data related to the Langmuir paradox were obtained and discussed [5, 6, 8], digital electronics for data acquisition and processing was not available. The measurement and processing of the probe $I/V$ characteristics were performed slowly (thus, affected by the discharge drift), point by point, and in many instances EEDFs were obtained through graphic differentiation. The error in inferring of EEDFs was additionally exacerbated by the uncertainty in the plasma potential evaluation and by the arbitrariness in the ion current approximation, which affected the accuracy of the EEDFs measurements in their low ($\epsilon < T_e$) and high ($\epsilon > \epsilon^*$) energy parts [11].

The probe $J/V$ characteristic $J(V)$, its electron part $J_e(V)$, and $f(e)$ that is proportional to $dJ_e(V)/dV^2$ are shown in the semi-log scale in figure 2. Here, $J$ is the probe current density. For the $J_e(V)$ evaluation (as is common in practice) a linear approximation of the ion current was used.

A practically Maxwellian distribution in the wide range of energies (up, to 36 eV) which corresponds to the dynamic range of $dJ_e(V)/dV^2$ measurements of three orders of magnitude, is illustrated by $\ln[J_e(V)]$ shown in figure 2. Meanwhile, the corresponding EEPF is essentially non-Maxwellian. This example demonstrates the sensitivity of the inferred EEPF to a practically invisible deviation of $J_e(V)$ from the exponential function seen in figure 2 as a straight line.
The EEPF inferring process from the measured probe characteristics is prone to error augmentation which is inherent to differentiation, especially, multiple differentiations. Therefore, a negligible error in the probe characteristic measurement may lead to an enormous error in the inferred EEPF [11].

The EEPFs measured with different probes placed along the discharge tube, at the distance \( x = 5; 25; 45; 65 \) and \( 85 \) cm from the cathode, for discharge current \( I_d = 1.0 \) A, and \( p = 1.0 \) and \( 3.0 \) mTorr are given in figure 3. These data demonstrate a significant non-uniformity with a sign of periodicity and an increasing anisotropy along discharge path to the anode. In figure 3, the values of the plasma density \( n \) and effective electron temperature \( T_e = \frac{2}{3} \epsilon \), found as appropriate integrals of the measured EEDF, also demonstrate the non-uniformity of the plasma parameter along the positive column.

The axial non-uniformity of the plasma parameters we attribute to standing striations, which has not been considered in previous EEPF measurements or calculations found in the literature. Having fixed probe positions we were not able to measure the axial discharge structure. But at 10 mTorr we were able to make the EEPF measurements in a quiescent discharge with standing striations and time resolved (with 2.5 \( \mu s \) time resolution) EEPF measurement in different phase for running striations. We found an essential similarity in EEPFs measured in the fixed axial positions of the quiescent discharge and at the fixed probe position for different phases of the running striations.

We suggest that the discharge axial non-uniformity is the key factor leading to non-Maxwellian EEPFs. The EEPFs with low energy peaks were found before in rf capacitive [14] and inductive [15] discharges. They were explained within the framework of non-local electron kinetics [16, 17] as the result of spatially localized, non-uniform electron heating combined with a trapping of low energy electrons by the ambipolar potential outside of the heating zone. Similar structures of electron heating non-uniformity and dc potential distribution occur in the standing (or moving) striations of a dc discharge [18, 19], which point to predictable similarity for rf and striated dc plasmas at low gas pressure.

The possibility of EEDF enrichment in its low energy (\( \epsilon < T_e \)) and high energy (\( \epsilon > \epsilon^* \)) parts has been considered for plasma in dc spatially periodic electric fields as a possible explanation of the Langmuir paradox [20]. However, a self-consistent 2D calculation of EEDFs in a stratified positive column at low pressures (\( \lambda > R \)) still is missing, while the existing the most rigorous calculations in 1D argon positive column at condition of our experiment [10], shows a Druyvesteyn-like distribution in the elastic energy range, which contradicts both the Langmuir paradox and our experimental results.

Figure 3. EEPF axial evolution along the positive column.
The non-Maxwellian EEDFs in argon gas found in our experiment cast doubts on the Langmuir paradox existence (in any case, on its universality), and calls for farther experiments.

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