Second derivative Langmuir probe diagnostics of gas discharge plasma at intermediate pressures (review article)

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Abstract. The second-derivative Langmuir probe method for precise determination of the plasma potential, the electron energy distribution function (respectively the electron temperature,) and the electron density of gas discharge plasma at intermediate pressures (100-1000 Pa) is reviewed. Results of applying the procedure proposed to different kinds of gas discharges are presented. Factors affecting the accuracy of the plasma characteristics evaluated are discussed.

1. Introduction
The literature on Langmuir probe measurements contains thousands of references. Among the contact methods of plasma diagnostics, the electric probes are the least expensive and are still the fastest and most reliable diagnostic tools allowing one to obtain the values of very important plasma parameters - Langmuir probes are known for their ability to provide local measurements of the plasma potential, the density and the energy distribution functions (EDF) of charged particles.

The probe technique is relatively simple when all the requirements of the “classical” theory are satisfied, namely [1]:
\begin{itemize}
  \item[a)] The plasma is isotropic within a scale much larger then the mean free path of the charged particles;
  \item[b)] the probe holder does not disturb the plasma in the vicinity of the probe tip;
  \item[c)] there is neither generation nor recombination of charged particles, nor are there chemical reactions in the probe sheath and at the probe surface as well;
  \item[d)] the mean free paths of the electrons, $\lambda_e$, and ions, $\lambda_i$, are much larger than the probe radius, $r_p$, and than the thickness of probe sheath, $d$;
  \item[e)] the surface area of the reference probe is large enough to sustain all the current collected from the measuring probe without a noticeable potential drop;
  \item[f)] there are no fluctuations of the plasma characteristics;
  \item[g)] the probe surface is free of contamination, like dielectric films, etc;
\end{itemize}

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Probes usually operate at gas pressures in the range of 0.1 Pa to 100 Pa. In many different contemporary technologies, such as plasma chemistry, etching, plasma polymerisation, thin layer dielectric deposition, etc., a relatively high gas pressure of 100 – 1000 Pa is required. In this case the theoretical interpretation of the experimental data acquired becomes more complicated.

This paper is a review of the contributions advancing the use of probes at extended gas pressures. We present an overview of the deviations from the "ideal" conditions for probe measurements mentioned above and the latest solutions that we have been using to overcome such problems. The main task of our considerations is how to determine the actual plasma characteristics from the data measured by a Langmuir probe, especially in what concerns the plasma potential, the density and the electron energy distribution function (EEDF) at intermediate gas pressures (The term ‘intermediate gas pressure’ will be clarified below). In this respect, we describe a refinement of the second derivative technique that takes into account the charged particles depletion caused by their sinking on the probe surface, and we discuss how the results can be processed in order to retrieve the correct values of the plasma parameters under these extended pressure conditions.

2. Basis of the Langmuir probe experimental method

The experimental method of Langmuir probe measurement is well known and discussed in many publications [1,2,3,4]. When the requirements of the “classical” probe theory are satisfied, the ampere-volt (IV) probe characteristics (Figure 1b) may be acquired by use of a simple probe circuit (Figure 1a). The electron probe current at negative probe potentials is [4]:

$$I_e(U) = \frac{2\pi e S}{m} \int_{-\infty}^{\infty} (W + eU)f(W)dW$$

where $m$, $e$ and $c$ are the electron mass, charge and velocity, $S$ is the probe area; and the total electron energy in the probe sheath is $W = \frac{1}{2} mc^2 + eU$, where $U$ is the probe potential with respect to the plasma potential $U_{pl}$.

![Figure 1a](image1.png)

**Figure 1a.** 1 probe, 2 reference probe, 3 potentiometer, 4 battery

![Figure 1b](image2.png)

**Figure 1b.** $U_{pl}$ – plasma potential, $U_f$ – floating potential; $I_{es}$ – electron and ion saturation current

The electron energy distribution function (EEDF) $f(\varepsilon)$ is connected with distribution function $f(c)$ in plasma undisturbed by the probe by:
\[ f(e) = \frac{4\pi \sqrt{2}}{m^{3/2}} \int_{0}^{\infty} f(e) e^2 \, de = n \]

The EEDF, \( f(e) \), can be determined by using the Druyvesteyn formula [5]:

\[ f(e) = \frac{2\sqrt{2m} d^2 I}{e^3 S \, dU^2} \]

The second derivative of the probe characteristic, \( I''(U) = d^2 I/dU^2 \), can be obtained in practice by superimposing a low frequency voltage \( \Delta U \) (differentiating signal) over the DC probe potential \( U \) or by numerically differentiating the IV probe characteristic. Whatever the method is, it does not give a direct measure of value of \( I''(U) \) but, instead, a convolution of \( I''(U) \) with the instrumental function (IF), \( \varphi(U-U') \) of the method of differentiating:

\[ J''(U) = \int I''(U') \varphi(U-U') \, dU' \]

So, to correctly obtain \( f(e) \), a deconvolution procedure must be applied and the knowledge of the instrumental function \( \varphi(U-U') \) is required.

3. EEDF measurements at intermediate gas pressures
We assume that points a), b) and c) of the requirements of the probe theory are satisfied. When the gas pressure is raised, the inequality \( \lambda e \gg r_p+d \) (point d) becomes no longer valid and distortions of the second derivative of the probe characteristic occur due to the depletion of electron which sink on the probe surface at a finite \( r_p/\lambda e \) ratio, as emphasised by Swift [6]. Thus, Druyvesteyn formula can no longer be used as a means to measure the EEDF and must be extended. Similar results were also obtained in ref. [1,7] through a more detailed analysis of the applicability of the second derivative probe method.

To simplify our subsequent analysis, let us assume that the width of the instrumental function \( \varphi(U-U') \) can be neglected, i.e. \( J''(U) = I''(U) \). Then following [1] we can write:

\[ I''(U) = C f(eU) - C \int_{eU}^{\infty} K''(e,U) f(e) \, de \]

where

\[ K''(e,U) = \frac{2\psi(e) e^2}{(1+\psi)-\psi e U} \]

\[ C = \frac{e^3 S}{2\gamma \sqrt{2m}} \quad \text{and} \quad \psi(e) = \frac{\gamma \lambda(e)}{r_p \ln \left( \frac{\pi l_p}{4 r_p} \right)} \]

The first term in equation (5) is the well-known Druyvesteyn formula. The second term describes the effect of plasma depletion caused by charged particles sinking on the probe surface. The geometric factor \( \gamma = \lambda(r_p/\lambda) \) assumes values in the range \( 4/3 \geq \gamma \geq 0.71 \) ( \( \gamma = 4/3 \) at \( r_p/\lambda >>1 \), and \( \gamma = 0.71 \) at \( r_p/\lambda <<1 \)). When \( r_p/\lambda \geq 1 \) the approximation for a cylindrical probe \( \gamma = 0.71+0.25\lambda/\lambda' \) can be used.

Regarding the value of the diffusion parameter, \( \psi(e) \), we can consider different limiting cases:

- When \( \psi(e) << 1 \), (low gas pressure), neglecting the second term in equation (5) yields Druyvesteyn formula (3). Although, as was shown by Swift, drain of electrons to the probe is present at a finite \( r_p/\lambda e \) ratio, the true value of \( f(e) \) at low probe potentials differs by less than 25% from that determined by the “classical” theory and the EEDF is well characterised by \( I''(U) \).

- At \( \psi(e) >> 1 \), (high gas pressure) it is shown in [1] that the EEDF is represented by the first derivative instead of the second derivative:
We will concentrate our attention on the case when $\psi(\varepsilon) \sim 1$, which corresponds to a plasma at intermediate gas pressures.

Figure 2 presents model calculations [1] at constant $\psi_0 = 1$ for Maxwellian EEDF. It is seen that neither the second derivative nor the first derivative are a good representation of the EEDF at low energy.

For the second derivative, $K''(\varepsilon, U)$ decreases with the increase of $eU$ and $\varepsilon$ and only the high energy part of EEDF at small $r_p$ is well characterised by $I''(U)$. At small values of $eU$, $K''(\varepsilon, U) = \frac{2\psi}{\varepsilon(1 + \psi)}$, and at $\varepsilon \to 0$, $K''(\varepsilon, U)$ increases indefinitely and $I''(U)$ decreases. In addition, as $f(0)$ has a finite value at $\varepsilon \to 0$, the plasma potential $U_{pl}$ does not coincide with the potential at which the second derivative is zero, $I''(U(0)) = 0$ [1]. Consequently, an additional error will result if the concentration of the charged particles is obtained by integration over the second derivative.

\[
f(\varepsilon) = -\text{const} \frac{\psi(\varepsilon)}{eU} I(U)
\]
It should be noted that the departure from the ideal ($\psi(\varepsilon) \ll 1$) case is more noticeable in measurements in molecular gases as their rotational and vibrational excitation cross-section values [8] are one order of magnitude higher than the value of the elastic scattering cross-section for inert gases in the energy range under interest (Figure 3).

Figures 4, 5 and 6 show the results of model calculations with real elastic cross sections ($\psi(\varepsilon)$), for Ar, O$_2$ and N$_2$ at different gas pressures.

It is clearly seen that as a result of the distortion to the second derivative caused by the effects mentioned above, a straightforward application of the Druyvesteyn formula for the determination of the plasma parameters will yield incorrect values.

To determine correctly the electron temperature, $T$, the electron density, $n$, and the plasma potential $U_{pl}$, we chose a different approach:

In the case of a Maxwellian EEDF at non-negligible pressure and probe size, a refined procedure has been proposed and proved [9-19] as follows:

- calculations of the second derivative using equation (5); convolution of the result with the instrumental function $\varphi(U - U')$;
- obtaining the best fit with the experimental curve. The fitting parameters are the electron temperature, $T$, the electron density, $n$, and the plasma potential $U_{pl}$.

The best fit with the experimental results was sought using the second derivative probe characteristics at a relatively high probe potential to evaluate the temperature of the electrons. The results of the model calculations with this temperature were fitted to the experimental curve using its maximum at low probe potentials. The plasma potential was evaluated by shifting the model curve along the $U$-axis, while the electron density was estimated by multiplying the model data by a coefficient to achieve the best fit.

When the EEDF differs from Maxwellian, a deconvolution procedure has been proposed in [20].

4. Experimental results and discussion.
The procedure proposed could be successfully applied in second derivative probe measurements for different gas discharges.
4.1. Application of the procedure proposed – examples.

Figure 7 presents an example [14-18] of second derivative probe measurements during high-pressure on-axis sputter deposition of Y124 thin films at 70%Ar+30%O₂ gas mixture at 260 Pa corresponding to diffusion parameter values $\psi \sim 1$.

Figure 7a is a photograph of the discharge, while Figure 3b presents experimental second derivatives $J''(U)$ of the probe current (circles). It can be clearly seen that the EEDF is bi-Maxwellian (low-energy ultimate electrons and high-energy secondary electrons), typical for the negative glow and Faraday dark space of gas discharges. The dashed line and the solid line are the fitted results of the calculations for ultimate and secondary electrons using equation (5), convoluted with the instrumental function. The dots are the sum of the solid line and dashed line data.

Similar results were obtained [19] in Ar volume afterglow plasma using a specially constructed d.c. discharge tube with coaxial sectional cathodes and cylindrical grid anode (Figure 8a). The normalized electrical field $E/N$ should be close to zero inside the anode region. The electrons that move from the negative glow into the cavity inside the anode volume form the afterglow plasma. The measurements were conducted at gas pressure in the range 60-130 Pa and discharge current 80 mA. The measuring probe, made of platinum ($r_p = 5.10^{-5}$ m, $l_p = 0.005$ m) is situated in the central part of the anode volume.
The experimental second derivative of the probe current (circles) at discharge current 80 mA and gas pressure \( p = 130 \text{ Pa} \), and the calculated curves (solid lines) are shown in Figure 8b. The bi-Maxwellian electron energy distribution function is clearly seen, similarly to the situation for the negative glow and Faraday dark space of the gas discharges.

Seeking the best fit a 5% change of the electron temperature value leads to a visible discrepancy between the calculated and experimental curves. We may thus accept 5% as an upper limit of the electron temperature uncertainty and (taking into account the uncertainty in the calibration of the second derivative curves) 10%, for the electron densities.

In the next Figure 9, an example of the second derivative corresponding to a non-Maxwellian EEDF in nitrogen flowing afterglow [11,12] is presented. The EEDF were deduced from the second derivative of the digitised probe characteristics measured using a triple probe technique.

The experimental arrangement is shown in Figure 9a. The experiments were carried out for a discharge operating at frequency 433 MHz, pressure \( p = 270 \text{ Pa} \), in a Pyrex tube of inner radius \( R = 1.9 \text{ cm} \). The discharge tube was adapted in order to position the different components of the probe measurement set-up. A tungsten wire of \( 3 \times 10^{-3} \text{ m} \) length and \( 5 \times 10^{-5} \text{ m} \) radius forms the probe tip. The probe is supported by a glass capillary tube covered by a partially insulated stainless steel tube whose exposed region plays the role of auxiliary electrode. In order to minimize plasma and flow perturbations, the reference electrode was chosen to be an emissive one and was inserted downstream into the discharge tube while the probe enters radially through a PTFE sleeve, which enables its radial motion under vacuum.

Mathematically speaking, to deduce the EEDF from probe measurements under collisional conditions requires that two coupled inverse problems be solved, since the distortion of the second derivative includes an integral over the unknown EEDF and the data is convoluted by the instrumental function. The situation is simpler when the EEDF can be assumed Maxwellian. Then, the problem solution requires only two unknown parameters, the electron density and temperature, which can be used as fitting parameters through a comparison between measured and theoretical probe characteristics. However, under the present experimental conditions, the probe current is clearly distorted by collisions (the mean free path is about twice the probe radius) and the assumption of a Maxwellian EEDF constitutes a rough approximation. So, we felt the need to devise a method to correct for the collisional effects on the second derivative of the probe characteristics. Basically, the theoretical probe characteristic corresponding to a seeded EEDF is obtained using equation (5) and it is compared against the measured one. The corrections are iteratively introduced into the EEDF until acceptable matching is achieved. The scaling factor between the theoretical and measured probe characteristics provides the value of the electron density. Details of this method can be found in [20].
The evaluated data for the electron concentration agree very well with those obtained by microwave interferometry [11].

4.2. Discussion

The considerations in section 3. make clear the importance of the position of the maximum of the calculated second derivative when the best fit with the experimental results is sought. Here we will discuss the reasons, which may cause uncertainties in the position of the experimental second derivative probe characteristic maximum. In general, they coincide with the case when the requirements of the Langmuir probe theory are not satisfied.

4.2.1. The reference probe surface area must be large enough to sustain all the current collected from the measuring probe without a noticeable potential drop. The Langmuir probe technique usually requires that the inequality [4] be satisfied:

\[
\frac{S_r}{S_p} > \frac{M_i}{m_e} \quad (7)
\]

The indices \( r \) and \( p \) are related to the reference and measuring probe; \( M_i \) and \( m_e \) are the ion and electron mass.

At intermediate gas pressures and non-negligible probe size, a more severe criterion for sufficient reference probe area is to be used [21]:

\[
\sum_{\alpha} \frac{S_r n_e (kT_e)^{1/2}}{S_p n_p (kT_p)^{1/2}} G_\alpha \geq 10^4 \quad (8)
\]

Since the plasma parameters may vary with the probe and reference position, the electron densities \( n_{e,p} \) and temperatures \( T_{e,p} \) are related to them.

The factor \( G_\alpha \) is tabulated in [16] for different probe and reference probe geometry. It is remarkable that \( G_\alpha^{-1} \) practically coincides with the ion diffusion parameter \( \psi_i \) from [1].

To enlarge the effective reference probe area, a heated emissive electron probe may be used [12].

4.2.2. Influence of the plasma parameters fluctuations. Oscillations of the plasma potential cause enlargement of the instrumental function [22]. When the amplitude of the oscillations is comparable with the amplitude of the differential signal, a double hump structure of the IF may appear. In Figure 10, an example of model calculations of the IF distortions is presented. The differential signal is:

\[
\Delta U = V_0(1 + \sin \omega_1 t) \sin \omega_2 t \quad \omega_2 \gg \omega_1
\]

and the oscillations of the plasma potential are considered as sinusoidal: \( A \sin \omega_1 t \).

4.2.3. Influence of the probe circuit and plasma resistance. The probe circuit resistance must be much smaller then the differential resistance of the IV characteristics near the plasma potential. The plasma resistance \( R \) between the probe sheath and the reference probe may also influence the second derivative results near the plasma potential. The connection between the measured values of \( J''(U_{\text{plasma}}) \) and the real values \( J''(U) \) is [2]:

\[
J''(U) = \left(1 + \frac{R}{R_{sh}}\right)^3 J''(U_{\text{plasma}}), \quad \text{where} \quad U_{\text{plasma}} = I R + U \quad \text{and} \quad R_{sh} = (dI/dU)^{-1} \quad (9)
\]
It is clear that the measured values are smaller than the real ones, with the difference increasing with the decrease of $R_{sh}$ as it approaches $U_{plasma}$.

Obviously the reference probe must be positioned as close as possible to the measuring probe.

4.2.4. Influence of probe surface contamination. In studies of chemically reactive plasma one of the most serious causes of uncertainties in the derived results are interactions of the plasma components with the probe surface and, therefore, the cleanliness of this surface. Dielectric films upon the probe surface cause distortions of the second derivative probe signal and shift the plasma potential [23] (Figure 11.)

Cleaning the probe by pulse ion current (by applying a high negative potential) before the measurements or before each step of the potential change is not always sufficient due to the high rate of some chemical reactions taking place on the probe surface.

It was shown [2, 24] that the electrically heated probe (constant d.c.) can be successfully applied to ensure the destruction and evaporation of probe contamination and to eliminate the deformations of the second derivative probe current.

5. Summary
The second derivative Langmuir probe method for diagnostics of gas discharge plasma at intermediate pressures is reviewed.

- It is shown that in the case of a Maxwellian EEDF at non-negligible pressure and probe size, a refined procedure must be applied to determine correctly the plasma parameters:
  - calculations of the second derivative of the probe current taking into account the depletion of electrons sinking on the probe surface; convolution of the result with the instrumental function of the method of differentiating;
  - obtaining the best fit with the experimental second derivative curve. The fitting parameters are the electron temperature, $T$, the electron density, $n$, and the plasma potential $U_{pl}$.
- When the EEDF differs from Maxwellian, a deconvolution procedure has been proposed.
- Factors affecting the accuracy of the experimental data acquired are discussed.

The results presented in this work show that the procedure proposed allows one to extend the applicability of the EEDF probe measurements to the range of intermediate (100-1000 Pa) gas pressures.

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