Diagnostics of the Electronegative Plasma Sheath at Low Pressures Using Microparticles

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Levitated particles are a new powerful diagnostic of the midplasma sheath region. They can reveal features undetectable either to plasma or to surface measurements. The equilibrium position of microparticles suspended in an oxygen plasma sheath, together with a model of the levitation force and Langmuir probe measurements, gives evidence of secondary electropositive plasmas in the already established plasma sheath, in the range of parameters where the modified Bohm criterion breaks down into multiple solutions.

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Electronegative discharges are often used in plasma processing of materials because they are highly chemically reactive and because they show peculiar plasma characteristics, as the transport and the plasma boundaries, useful for etching and deposition. At present several physical effects of the electronegative sheath are still unexplored. Physically a discontinuity in the electrostatic potential may arise because the colder, usually heavier, negative species is confined in the plasma while the electrons extend further in the sheath. This problem was originally pointed out by [1] and discussed further in a number of theoretical contributions, which included ionization, collisions and different techniques of analytical or numerical analysis, see Refs. [2,3] and Section 15 of Ref. [4], and references therein. So far there has been no experimental validation of the theories. The reason lies in the difficulty of midsheath diagnostics under the conditions of significant negative ion density and high temperature ratio. In this work we have traced microparticles injected into the plasma. They levitate in the sheath region, gravity being compensated mainly by the upward electrostatic force. The plasma is perturbed only in the immediate vicinity of the microparticles, therefore microparticles provide a new experimental approach for sheath diagnostics. The equilibrium position depends on the presence of negative ions in two ways: the electric field of the sheath can be a nonmonotonic function of the electronegativity, and the particle charge is strongly affected by the modified Bohm flux of positive ions.

We present a collisionless model of the levitation force as a function of α, the ratio of the negative ions to the electron density. We measured this ratio in the collisionless range by Langmuir probe and extrapolated it to the collisional regime using the trend obtained by photo detachment techniques [5]. A correspondence between the temperature of the negative ions and the observed double equilibrium position (due to the stratified plasma) was also found as predicted [3].

Experimental evidence. The plasma was generated in oxygen by radio frequency excitation at 13.56 MHz and 300 V (peak-peak). The power was applied to the upper of two parallel plane electrodes, which have diameters of 30 mm, and are 30 mm apart. The lower electrode was grounded and surrounded by a positively biased ring to confine the levitated particles electrostatically. These were illuminated by a thin vertical laser-light sheet and filmed by a video camera at 90°, see also [6]. Melamine-formaldehyde particles of diameters 6.81, 3.42, and 1.29 μm were injected into the plasma through a fine mesh from a dispenser at the side edge of the plasma, just above the confining external ring.

As mentioned before, the main aim of this Letter is to study the sheath of an electronegative plasma, unperturbed by the presence of many particles; a typical picture of noninteracting particles is shown in Fig. 1. The 3.42 μm particles had one stable position for pressure in the range $4.7 < P < 17$ Pa and for $P > 70$ Pa. In the intermediate range the particles had two metastable equilibrium positions, the lower being more stable (a few minutes residence time) than the upper (residence time of the order of tens of seconds). From 1.4 to 4.7 Pa the particles acquired a large kinetic energy and no particles could levitate below 1.7 Pa. The 6.81 μm particles show the same behavior as the previous ones, and, within the experimental error, the same positions. The 1.29 μm particles always had two equilibrium positions with the

FIG. 1. Particles 3.42 μm shortly after the injection in the plasma. $P = 46$ Pa and electrode excitation $V_{RFpp} = 300$ V. The picture shows 17×8.8 mm.

same trend with respect to pressure, as the upper layer of the heavier ones. For the analysis it is important to "accept" particles in the lower layer only if they are not interacting with particles in the upper layer (i.e., if the particle was not directly below another one, or in the midpoint between particles in the upper layer, or showing any other correlation). The position of the particles is shown in Fig. 2.

The levitation model.—When a particle has reached its equilibrium position, the sum of all the forces is zero. If ion drag and thermophoresis can be neglected [7] we simply have the electrostatic force equal to mg. This means that we need a model for the electrode sheath in electronegative discharges and a model for the charging of the particle in that sheath. In the planar sheath of an electronegative plasma the positive ions enter with an energy given by the modified Bohm criterion [1] derived from the quasineutrality condition at infinity: $\eta_s = 1/2(1+\alpha_s)/(1+\gamma\alpha_s)$ where $\eta = -eV/kT_e$, $\alpha = n_-/n_e$, $\gamma = T_e/T_-$ and the subscript s refers to the sheath edge. This condition is multivalued for $\gamma \geq 5+\sqrt{24}$. In our analysis we have chosen the smaller solution which corresponds to the first plasma edge encountered by the ions arriving from the plasma [8]. By using conservation of ion flux we can now write the Poisson equation as follows:

$$\epsilon_0 \frac{d^2\eta}{d\xi^2} = -n_{es}\left[(1+\alpha_s)\left(1-\frac{\eta}{\eta_s}\right)^{-1/2} - e^{\eta} - \alpha_s e^{\gamma\eta}\right] \quad (1)$$

with ξ the space with respect to the plasma edge normalized to the Debye length. Equation (1) is integrated analytically to obtain the electric field as a function of the potential and integrated a second time numerically to obtain the dependence of the potential with respect to the space. When the particle is much smaller than the electron Debye length the space charge just near its surface is small compared to the charge at the surface. In this case the vacuum approximation for the potential is valid and the charge acquired by a particle of fixed radius is directly proportional to the floating potential η_{DC} measured with respect to the local space potential η_0. η_{DC} has been calculated from

$$(1+\alpha_s)|\eta_s|^{1/2}\left(1+\frac{\eta_{DC}}{\eta_s+\eta_0}\right) = 2\left(\frac{m_i}{\pi m_e}\right)^{1/2} e^{\eta_0} e^{\eta_{DC}} + 2\alpha\left(\frac{m_i}{\pi\gamma m_-}\right)^{1/2} e^{\eta_0\gamma} e^{\eta_{DC}\gamma} \quad (2)$$

where the left hand side term comes from orbital theory, modified to take into account the directed motion of the flux of ions out of the electronegative plasma. For the given gas, particle radius, and electron temperature we then obtain the levitation force. By choosing the other plasma parameters we can specify the absolute length scale unit keeping in mind that for a constant ion density $\lambda_{De}(\alpha) = \lambda_{De}(0)\sqrt{1+\alpha}$. The levitation force is plotted as a function of position z, with the abscissa going from the floating electrode $z(v_f) = 0$ upwards, see Fig. 3. The intercept with the gravitational force mg gives the equilibrium positions plotted in Fig. 4. In this way it is possible to make a direct link to the experiments when α is known.

The measurements of α.—The relative value of the negative ion density to the electron density, α, has been deduced from Langmuir probe characteristics using the following equation

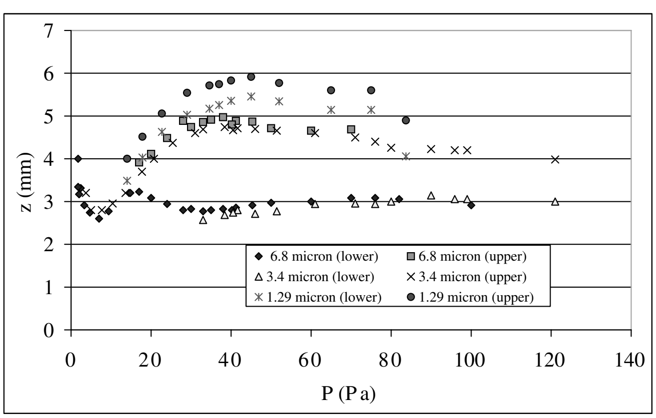

FIG. 2. The position of the particles above the electrode versus pressure.

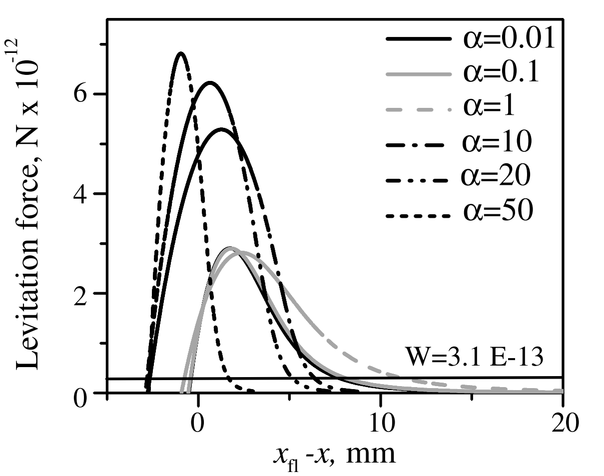

FIG. 3. Theoretically calculated levitation force of the 3.44 μm radius with $kT_e/e = 3$ eV, $n_0 = 10^{15}(\mathrm{m}^{-3})$ and $\gamma = 10$ versus the height above the electrode. The zero of the abscissa corresponds to the floating condition. The weight is also shown.

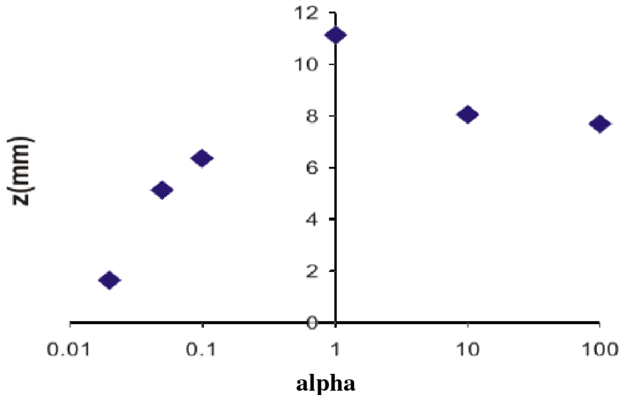

FIG. 4 (color online). The theoretical calculated height of the equilibrium position for the 3.42 μm particles and $\gamma = 10$ in an oxygen plasma.

$$\alpha = \sqrt{\frac{M_-}{m_e}\frac{\int_{-\infty}^{V_p}\sqrt{|V - V_p|}I_-''(V - V_p)dV}{\int_{-\infty}^{V_p}\sqrt{|V - V_p|}I_e''(V - V_p)dV}} \quad (3)$$

where I'' is the second derivative of the $I - V$ characteristics. This method is sensitive to instrumental broadening of the second derivative of the curves if this broadening does not conserve the area. However, it has been chosen instead of the positive ion analysis [9] because it is independent of the estimated values of γ and the hypothesis of Maxwellian distribution for the electrons. In fact the electron energy distribution function (EEDF) has been found strongly depleted in the low energy range. The above equation can only be used for pressures up to 20 Pa. At higher pressures the second derivative of the current was dominated by electrons/positive ions at low energies so that the negative ion

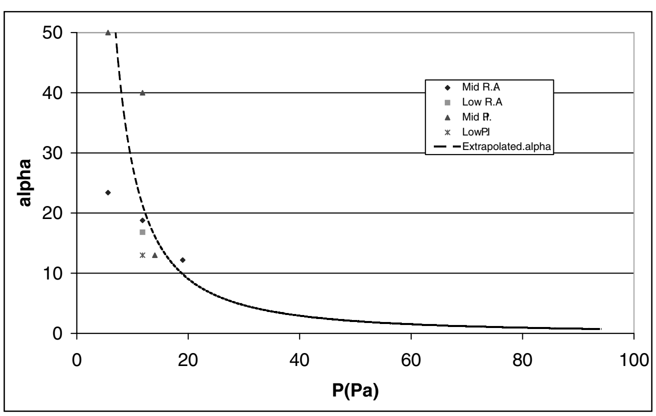

FIG. 5. The experimentally measured value of α versus pressure. Up to 20 Pa the data are obtained by Eq. (3) (Ratio areas: R.A.) or by conventional probe techniques (Positive Ions analysis: P.I.) in the middle of the discharge (Mid) or just above the lower plasma sheath (Low). The line shows the ratio between the theoretically calculated trend of n_- and the experimentally measured value of n_e.

distribution could not be clearly identified. Figure 5 shows the measured values of α. The curve has been extended above 20 Pa using the theoretical trend of n_- outlined in Section IV C of Ref. [5] and our experimental values for n_e. In Fig. 2 we see that the position of the upper layer of particles has a maximum at $P \approx 45$ Pa for all the diameters. At this pressure Fig. 5 shows $\alpha = 2$ in the center of the discharge, which agrees well with the maximum position shown in Fig. 4. In this maximum position the suspended particles experience an ion flow that comes directly from the main plasma, and is not much affected by collisions or by the multiple solution "instability", which develops for values around $\alpha = 1.17$ at $\gamma = 10$.

The temperature of the negative ions.—We refer here to the chemistry of the plasma processes. In the plasma bulk the dominant negative ions are O^-, but O_2^- and O_3^- also make a significant fraction (about 10%) [5]. The O^- ions can be created by the dissociative attachment of an electron to molecules O_2 and $O_2(a)$. The latter is a metastable state. The energy of the negative ion produced by dissociative attachment of an electron to a molecule can be written following [10] as $\varepsilon_0 = \frac{1}{2}(\varepsilon - D + \varepsilon_A)$, where the factor $\frac{1}{2}$ arises because the products of the dissociative attachment have the same mass. ε is the electron energy (about 3 eV in our case), ε_A is the electron affinity energy of atomic O^-, which is 1.46 eV [10]. D is the dissociation energy of the molecule. For O_2 it is 4.6 eV and for $O_2(a)$ D is 3.6 eV [11] ($O_2(a)$ is 0.99 eV above the ground state). This means that in dissociative attachment to O_2 negative ions do not get energy, but in the attachment to $O_2(a)$ the energy acquired is 0.4 eV. The negative ions do not acquire or lose much energy by collisions and remain distinct until they are destroyed by a detaching mechanism. The density of the negative ions is estimated by multiplying the production rate of negative ions by the lifetime. The ratio of reactions $O_2 + e \rightarrow O^- + O$ and $O_2(a) + e \rightarrow O^- + O$ has been calculated for two pressures with the coefficient given in [5] and the data are listed in Table I. This ratio is ≈ 4 at both pressures. The lifetime is related to the detachment mechanism and is dependent on the energy of the ions. The cold negative ions are destroyed mainly by reactions $O^- + O_2(a) = O_3 + e$ and $O^- + O_2(a) = O + O_2^-$ [5], while the ions with the energy 0.4 eV are destroyed only by the latter reaction because

TABLE I. The values of the densities at different pressures in (m^{-3}).

P(Pa)	n_{O_2}	n_e	$n_{O_2(a)}$	n_{O^-}
10	2.6×10^{21}	1×10^{14}[a]	2×10^{20}[b]	1×10^{15}[a]
100	1.7×10^{22}	2×10^{14}[a]	9.8×10^{21}[c]	2×10^{14}[d]

[a]Experimentally measured in our apparatus.
[b]From [5].
[c]See text.
[d]Extrapolated as in [5].

the rate constant of reaction $O^- + O_2(a) = O_3 + e$ decreases rapidly with the energy [12]. The ratio of the lifetimes is ≈ 0.25 and is independent on the pressure in our range of interest.

We can now characterize our plasma as composed by three negative species. The electrons, the cold negative ions, and the hot (fast) negative ions, with α_c, α_f and γ_c, γ_f the normalized densities and temperatures. From the above considerations we know that $\alpha_c/\alpha_f = 1$ for both pressures. The ratios n_e:n_-^c:n_-^f is 1: $\approx$ 5: $\approx$ 5 at 10 Pa. This result is in agreement with the Langmuir probe measurement for α_{total}. The ratios 1: $\approx$ 0.5: $\approx$ 0.5 would match α_{total} at 100 Pa if the density of $O_2(a)$ is fitted as in Table I. This density is compatible with the estimated quadratic dependence on the pressure as in [5]. In this condition the modified Bohm criterion, Eq. (1), can be rewritten as

$$\eta_s = \frac{1}{2}\left(\frac{1 + \alpha_s^c + \alpha_s^f}{1 + \gamma^c \alpha_s^c + \gamma^f \alpha_s^f}\right). \tag{4}$$

This represents the energy of the positive ions at the sheath edge as well as a distribution of potential in the plasma bulk. The negative ions created at the periphery of the plasma are accelerated towards the center by a potential $\leq \eta_s kT_e/e$ and this may lead to a spread in the energy in the core of the discharge as seen by the simulation of [13]. This effect is small, if $\alpha_c/\alpha_f = 1$ and $\gamma_c = 100$ and $\gamma_f = 10$. Multiple solutions appear only for α_{total} between 0.3 and 0.4. For higher electronegativity η_s is lower than 0.03 so that we can assume the two distributions of negative ions are effectively monoenergetic.

The results reported in Fig. 2 can be interpreted in the light of the three negative species being retarded in different layers. At an intermediate pressure, e.g., 40 Pa, the small particles settle at the edge of an electronegative inner plasma, where the cold ions are retarded, as well as at the edge of a secondary electronegative plasma, where the hotter negative ions are retarded. We propose that a charge double layer develops between the two plasmas, in analogy to the work of [14] for cold and hot electrons, with a potential difference on the order of 0.4 V. Finer calculation would go along the lines outlined by [15], who obtained double layers in an electronegative plasma sheath when an electron beam was injected from the cathode (here from the secondary plasma). The thickness of the secondary plasma is independent of pressure as the temperature and density ratios of the two negative ions species. The medium and large particles settle on either side of another secondary plasma, electropositive, whose thickness develops with decreasing α_{total} and goes through a maximum in the region of instability. In fact for $\alpha_c/\alpha_f = 1$ we have calculated an equivalent γ to be 55 for which multiple solutions of Eq. (1) exist in the range $2 \leq \alpha_{\text{total}} \leq 4$. From probe measurement at 20 Pa $\alpha_{\text{total}} = 8$ in the center of the discharge but has a lower value in the plasma in front of the lower electrode [16].

Conclusion.—The results presented are, to our knowledge, the first experimental proof of a structured electronegative plasma sheath, a possibility so far only mathematically and numerically investigated. There are, however, some caveats that we need to include in that discussion: the range of instability is narrow and the equilibrium positions for the microparticles, used in the diagnostic, are subject to fluctuations. We also cannot exclude that the conditions reported could be (in part) dependent on the apparatus. In fact the purity of the gas is essential, as already pointed out by [5]. Another important effect is the rf voltage drop at the electrode sheath. Although this effect has not been taken in account in the calculation of the levitation force we know that both the charge of the particle and the sheath electric field are affected. The dependence on the energy of all the collision coefficients is not accurately known. Despite the above problems, using the most probable reactions we have identified the existence of three negative species in a rf Oxygen plasma. The experimental data confirm our deductions.

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