Ion–ion plasmas and double layer formation in weakly collisional electronegative discharges

V. I. Kolobov[a] and D. J. Economou
Department of Chemical Engineering, Plasma Processing Laboratory, University of Houston, Houston, Texas 77204-4792

(Received 24 September 1997; accepted for publication 8 December 1997)

Plasmas of electronegative gases often separate into two distinct regions: an ion–ion core and an electron–ion periphery. Under certain conditions, a double layer may form at the boundary between the two regions. In weakly collisional three-component electronegative plasmas, formation of a double layer depends on the ratio of the electron to negative ion temperatures, and the ratio of the electron to positive ion densities. © *1998 American Institute of Physics.* [S0003-6951(98)00606-8]

Plasmas containing two negatively charged species with different temperatures frequently separate into two distinct regions. The cold species occupy the core of the plasma, the hot ones predominate at the periphery, forming two plasmas with different properties. The density of cold species drops abruptly at the boundary of the two plasmas. Such a scenario takes place in a conventional electron–ion plasma with two groups of electrons having different temperatures (e.g., a bi-Maxwellian electron distribution function[1,2]) and in a plasma of electronegative gases containing a considerable fraction of negative ions.[3,4] In a weakly collisional two-electron-temperature plasma, a double layer can form within the plasma.[1] In a collisional electronegative plasma a smooth potential profile in the plasma was reported.[3,4] Weakly collisional discharges in electronegative gases have not been explored yet.

Recent interest in weakly collisional discharges in electronegative gases has been generated by their use in advanced semiconductor manufacturing. Novel plasma sources used for etching of submicron features operate in the weakly collisional regime, and often contain a considerable fraction of negative ions. The temperature of negative ions is near room temperature, whereas the electron temperature is a few eV. In a continuous-power regime, negative ions are confined in the plasma and give no contribution to etching. In a pulsed-power regime they can be extracted from the decaying afterglow. The extraction of negative ions was claimed to be responsible for amelioration of charge-induced etch damage and other benefits observed in pulsed-power discharges.[5,6] However, the formation and dynamics of ion-ion plasmas at low gas pressures, and the mechanism of negative ion extraction from the plasma remain poorly understood. In this letter we try to shed some light on the spatiotemporal dynamics of ion–ion plasmas in low-pressure discharges and, in particular, to identify the conditions that favor the formation of a double layer in the plasma.

Steady-state discharge: Consider a simple model of a steady-state electronegative discharge. Figure 1 shows schematically the spatial distribution of a dimensionless electrostatic potential for the most interesting case when a double layer is formed within the plasma. The double layer constitutes a structure created by two equal but opposite space charge layers. It is characterized by an abrupt potential drop which separates an ion–ion plasma at the core of the discharge from an electron–ion plasma at the periphery. Point x_0 within the double layer corresponds to the first inflection point of the potential $\Psi(x)$. Another inflection point of $\Psi(x)$ occurs in the electron–ion plasma. The thickness of the double layer (and of the space-charge sheath near the wall) is usually much smaller than those shown in Fig. 1, provided that the Debye length is small compared to L. Thus, the double layer actually appears as a vertical line (potential ''jump'') at $x=x_0$. In Fig. 1, the potentials at the interface between the double layer and the two plasmas are denoted as Ψ_l or Ψ_r. The potential at the sheath edge is Ψ_s and that at the wall is Ψ_w.

Assuming one kind of negative ion and Maxwellian energy distribution for electrons and negative ions, the total density of negative carriers is given by

$$n(x)=n_{e0}\exp(-\Psi/\delta)+n_{i0}\exp(-\Psi), \quad (1)$$

where $\Psi=e\phi/T_i$ is a dimensionless potential (ϕ is the electrostatic potential), T_e and T_i are the electron and negative ion temperatures, $\delta=T_e/T_i$, and n_{e0} and n_{i0} are the electron and negative ion densities at the discharge center. The den-

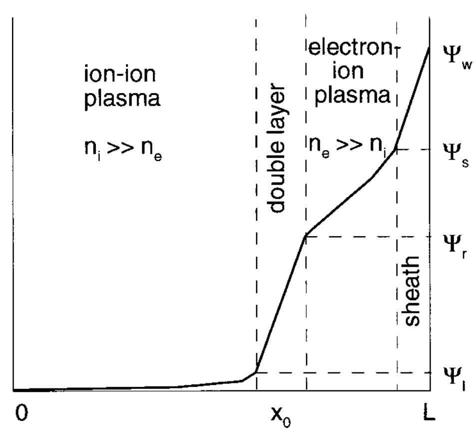

FIG. 1. Ion–ion and electron–ion plasmas separated by a double layer. The thickness of the double layer and the sheath is exaggerated for clarity.

[a]Current address: CFD Research Corp., 215 Wynn Dr., Huntsville, AL 35805. Electronic mail: kolobov@uh.edu

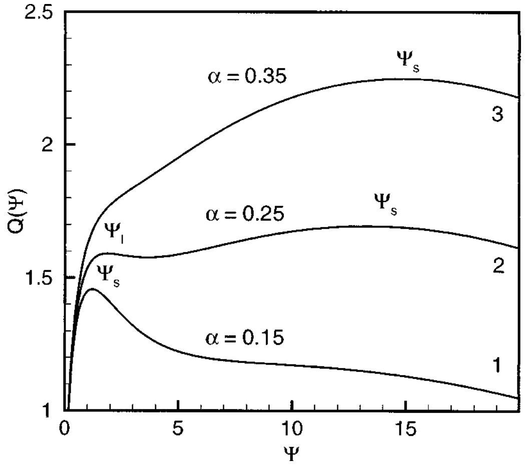

FIG. 2. Function $Q(\Psi)$ for $\delta=20$ and different α. A single maximum of $Q(\Psi)$ (curves 1 and 3) corresponds to no double layer formation, and the potential at the maximum, Ψ_s, corresponds to the sheath edge. Two maxima of $Q(\Psi)$ (curve 2) correspond to double layer formation. The potential at the boundary between the ion–ion plasma and the double layer is then Ψ_l, and that between the plasma and the sheath is Ψ_s (see also Fig. 1).

sity of positive ions in the free-flight regime (no collisions) is determined by the spatial distributions of ionization rate $I(x)$ and potential $\Psi(x)$[1]

$$p(x)=\frac{1}{v_{th}}\int_0^x \frac{dx' I(x')}{\sqrt{\Psi(x)-\Psi(x')}}, \tag{2}$$

where $v_{th}=(2T_i/M)^{1/2}$ is the ion thermal velocity. The potential distribution in the plasma is found from the quasineutrality condition

$$\int_0^x \frac{I(x')dx'}{\sqrt{\Psi(x)-\Psi(x')}}=\Gamma[(1-\alpha)\exp(-\Psi) + \alpha\exp(-\Psi/\delta)]. \tag{3}$$

Here $\alpha=n_{e0}/n_0$, $n_0=n_{i0}+n_{e0}$ is the plasma density at the center, and $\Gamma=n_0 v_{th}$ is an ion flux. Assuming that $I=n_e\nu$, where ν is the ionization frequency (assumed spatially constant), the solution of (3) can be found in the form

$$\frac{\pi\alpha\nu x}{v_{th}}=Q(\Psi). \tag{4}$$

The function $Q(\Psi)$, shown in Fig. 2, is given by

$$Q(\Psi)=\int_0^{\Psi} F(\Psi')\exp(\Psi'/\delta)d\Psi', \tag{5}$$

where

$$F(\Psi)=\Psi^{-1/2}-2(1-\alpha)D(\sqrt{\Psi})-2\alpha\delta^{-1/2}D(\sqrt{\Psi/\delta}), \tag{6}$$

and $D(z)$ is the Dawson integral.[7] The spatial distribution of $\Psi(x)$ found from (4) has a singularity $d\Psi/dx=\infty$ (an infinitely high field) where $Q(\Psi)$ has a maximum. The quasineutrality condition is violated at these points. The maxima of $Q(\Psi)$ correspond to roots of $F(\Psi)$. These roots are independent of the shape of the ionization rate and are determined solely by α and δ.[1] Setting $F(\Psi)=0$ gives

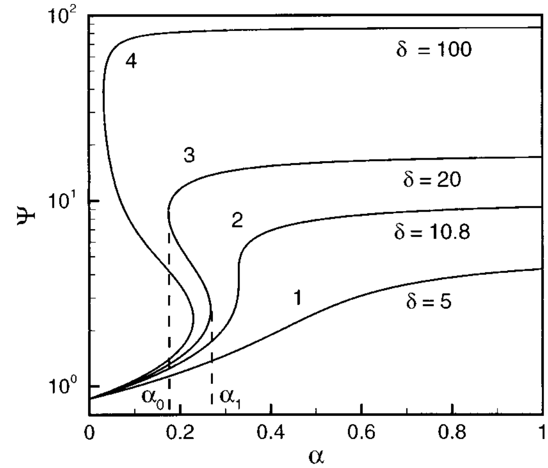

FIG. 3. The normalized potential Ψ at the point(s) where quasineutrality is violated shown as a function of electron density fraction α for various ratios of electron to ion temperatures, δ.

$$\alpha=\frac{1/2x-D(z)}{D(z/\sqrt{\delta})/\sqrt{\delta}-D(z)}, \tag{7}$$

where $z\equiv\sqrt{\Psi}$. For a given δ, Eq. (7) defines the potential $\Psi(\alpha)$ at the points where quasineutrality is violated. For $\delta<10.8$, $\Psi(\alpha)$ has a single value for each α which corresponds to the plasma-sheath boundary, Ψ_s. In this case, the potential drop in the plasma changes continuously from 0.855 to 0.855δ with an increase of α (curve 1 in Fig. 3). For $\delta=10.8$, there is an inflection point of $\Psi(\alpha)$ at $\alpha=0.33$ (curve 2). For $\delta>10.8$, there are three different values of $\Psi(\alpha)$ in a range $\alpha_0<\alpha<\alpha_1$ and a single value for $\alpha<\alpha_0$ or $\alpha>\alpha_1$ (curves 3 and 4). In the range $\alpha_0<\alpha<\alpha_1$ the potential in the plasma changes discontinuously with changing α.

The case of three different roots of $F(\Psi)$ corresponds to the formation of a double layer in the plasma.[1] In the quasineutral model, the double layer is formed where $d\Psi/dx\rightarrow\infty$. The spatial location of the double layer (x_0 in Fig. 1) depends on the specific ionization mechanism whereas the values of Ψ_l or Ψ_r do not. Equation (3) is not valid in the double layer and the potential profile is to be found from Poisson's equation. The potential drop in the layer, $\Psi_r-\Psi_l$, can be derived from

$$\int_{\Psi_l}^{\Psi_r} d\Psi'(p-n)=0. \tag{8}$$

At $\Psi>\Psi_r$, in the electron–ion plasma, the quasineutrality condition is valid again, and the potential profile is given by Eq. (3). To estimate the maximum potential drop in the double layer, we equalize the density of positive ions created at $x<x_0$ and accelerated in the layer to the electron density at the boundary of the electron–ion plasma where $\Psi=\Psi_r$. For $\alpha\ll 1$, when $\Psi_l=0.855$, this gives for Ψ_r

$$0.344/\sqrt{\Psi_r}=\alpha\ \exp(-\Psi_r/\delta). \tag{9}$$

According to (9), the maximum value of $\Psi_r=\delta/2$ is reached at $\alpha=0.94(\delta/2)^{-1/2}$. The potential drop in the double layer can therefore be of the order of the electron temperature.

Figure 4 shows the normalized electron and negative ion densities, and the potential profiles in the plasma for the three different cases shown in Fig. 2. At low α the potential

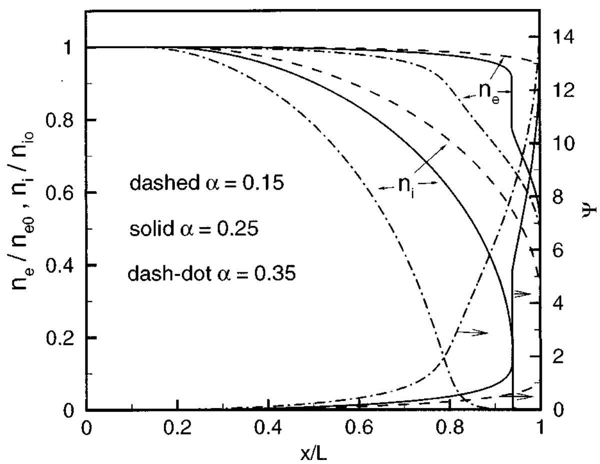

FIG. 4. Spatial distributions of negative ion and electron densities, and the potential profile in a plasma for the conditions of Fig. 2.

drop in the plasma is fairly small and the ion–ion plasma extends up to the sheath edge. This is the case when $Q(\Psi)$ has only one maximum and there is no double layer formed (curve 1 in Fig. 2). With an increase of α, a double layer forms as an abrupt potential jump separating the ion-ion plasma from the electron–ion plasma. The potential at the plasma-sheath boundary, Ψ_s, corresponds to the second maximum of $Q(\Psi)$ whereas the first maximum corresponds to Ψ_l (see Figs. 1 and 2). The potential profile in the ion–ion plasma is rather flat (defined by ion temperature), so that the electron density and the ionization rate in this plasma must be almost uniform. At larger α the double layer disappears and the potential drop in the plasma becomes of the order of electron temperature. This case corresponds to curve 3 in Fig. 2.

Finally, the wall potential Ψ_w is set up to equalize the electron production and loss rates. In low pressure discharges, Ψ_w must exceed the ionization potential of the atoms. Since the potential at the plasma sheath boundary Ψ_s is reduced by the presence of negative ions (see Fig. 4), the potential drop in the sheath becomes larger. The presence of a double layer modifies the energy distribution of positive ions escaping the plasma which then becomes double peaked.[1] The lower energy peak corresponds to ions formed in the electron–ion plasma and accelerated by the sheath field. The higher energy peak corresponds to ions formed in the ion–ion plasma and accelerated by both the double layer and the sheath fields.

Pulsed-power discharges: In pulsed-power discharges, the power sustaining the plasma is modulated (e.g., square-wave modulation) with a certain frequency and duty cycle. Some predictions on the temporal dynamics of ion–ion plasmas in pulsed-power discharges can be made based upon the steady-state solutions obtained above. In particular, two key quantities, α and δ define the spatial distribution of plasma parameters. Under favorable conditions, a double layer may form during the power-on fraction of the cycle. During the power-off fraction of the cycle, high energy electrons continue to escape to the wall, but the ionization is effectively switched off. While the decaying plasma is continually depleted of high energy electrons, both δ and α keep decreasing due to electron losses to the wall and attachment to molecules. At some point in the afterglow, the double layer must disappear as $\delta < 10.8$ or $\alpha < \alpha_0$ (see Fig. 3). Sufficiently late in the afterglow, the negative ion density begins to exceed the electron density in the entire discharge volume, and a virtually electron-free plasma is formed.[8] At this time it becomes possible to extract negative ions out of the plasma.

An important difference exists between the properties of ion-ion plasmas in the collisional and near-collisionless regimes. Although collisional electronegative plasmas also tend to separate into ion–ion and electron–ion regions, quasineutrality remains throughout the plasma and the potential profile remains smooth. In our case, the quasineutrality is violated in the double layer which is formed within the plasma under certain conditions. This double layer has much in common with the double layer observed in a two-electron-temperature plasma.[1] Such direct consequences of the double layer as an abrupt potential drop within the plasma and the appearance of two peaks in the energy distribution of positive ions extracted out of the plasma should be detectable experimentally.

In summary, an ion–ion plasma can coexist with an electron–ion plasma in the same vessel. The boundary between the two plasmas may be smooth or abrupt. In the latter case, a double layer separates the two plasmas. Conditions favoring the formation of such a double layer have been presented in this letter. Depending on conditions, potential oscillations corresponding to multiple double layers[9] may also form. Relevant theories that have been developed for electropositive plasmas with bi-Maxwellian electron energy distributions can be applied directly to electronegative plasmas.

The work was supported by NSF Grant No. CTS-9713262.

[1] K. Sato and F. Miyawaki, Phys. Fluids B **4**, 1247 (1992).
[2] V. A. Godyak, V. P. Meytlis, and H. R. Strauss, IEEE Trans. Plasma Sci. **23**, 728 (1995).
[3] L. D. Tsendin, Sov. Phys. Tech. Phys. **34**, 11 (1989).
[4] M. Lieberman and A. J. Lichtenberg, *Principles of Plasma Discharges and Materials Processing* (Wiley, New York, 1994).
[5] S. Samukawa and T. Mieno, Plasma Sources Sci. Technol. **5**, 132 (1996).
[6] T. H. Ahn, K. Nakamura, and H. Sugai, Plasma Sources Sci. Technol. **5**, 139 (1996).
[7] W. H. Press, S. A. Teukolsky, W. T. Vettering, and B. P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, 1992).
[8] S. A. Gutsev, A. A. Kudryavtsev, and V. A. Romanenko, Tech. Phys. **40**, 1131 (1995).
[9] L. Schott, Phys. Fluids **30**, 1795 (1987).