Additional Information:

Problems arising when attempting to apply classical theory to the data

Although early texts state that[2] "the mechanism of the positive column is fairly well understood", Chapman warns us[4] that, "We should heed the warning of Cobine (1958) ...., that no sources are infallible, that all proofs should be questioned, and that no discharge phenomena are so well understood that data can be applied precisely." On the face of it, the I_p-V_C curve in our experiments is unremarkable in that it is similar to any other probe characteristic curve measured for a GD plasma. However there are a significant number of indicators which demonstrate that both the downstream FAG and FD plasmas cannot be the free ion-electron medium usually assumed. Because this goes very much against the received wisdom, it is incumbent upon us to consider, in some detail, why classical 'free ion-electron plasma' theory does not appear to work in this case.

1. The classical model; electron temperature, and architecture of the discharge

The GD is sustained in its steady state by acceleration, to high energy, of electrons emitted from the Cathode surface (due to ion and fast atom bombardment) across the steep CF voltage region causing EI of the discharge gas. The cations are accelerated back towards the Cathode whilst the electrons are carried by their forward momentum into the gas, where they are rapidly cooled by collision. This part of the discharge, next to the CF, does contain a high density of cations and free electrons and is the region of the NG. On a potential diagram it is usually represented with a flat potential surface between the CF and the anode, but it is not a uniform isotropic plasma. As Loeb states[2]: "At the NG the potential reaches a maximum or a plateau. It is possible that on the anode side of the NG, electrons predominate giving a drop in potential, which may become negative. It rises again to take on a practically linear slope in the PC." The cation density is therefore at its maximum in the NG, but must fall off at the anode side of the boundary, as it spreads towards the PC. If the picture painted by Loeb (supported by Langmuir's experiments, and adopted in many other texts) is correct, then the energy of electrons is also bound to decay due to collision and deceleration, until it reaches a minimum; it will then pick up again as the electrons are accelerated into the PC plasma, and reach a steady state in the uniform positive axial field. The plasma density also increases to a steady state value due to ionisation in the PC, where $n_+ \approx n_e$.

At the NG_PC boundary, the potential must therefore go through a minimum, and this is usually shown in schematic potential energy diagrams (e.g. p 79 of ref. 4, p 83 of ref. 3, p 566 of ref. 2). This can occur only if n_e becomes > n_+, achieved by the rapid collisional slowdown of high energy primary electrons accelerated from the Cathode. The negative decelerating field created will of course enhance the cooling of high energy electrons moving in the direction of the current. The net current in this portion of the discharge is then carried only by the forward momentum of high energy primary electrons, until the upturn in voltage at the entrance to the PC plasma. The boundary would then, in effect be the same as the negative sheath which develops at the plasma boundary due to the separation of charge. It is unlikely therefore to stretch over a long timescale (distance), especially at 'high' pressures. It, in effect, constitutes a 'virtual' cathode (source of electrons) which separates the PC plasma from the NG.

If the classical plasma decays, then so must T_e. Left to its own devices, T_e, in the absence of an applied field, decays rapidly, for example dropping from 0.32 to 0.17 eV in only 0.06 ms at 0.6 Torr of Ar[i]. See also Smith and Plumb's experiment[7]. Since the electron collision cross-section increases rapidly for energy values >1 eV, up to ~15 eV (after which it decreases) the loss of energy of these electrons will be much faster, and over twice as fast at a pressure of $\geq$2 Torr of Ar. Theoretically, the T_e required to sustain the PC plasma in a tube of 1 cm radius, at 1 Torr of Ar, is ~ 1 eV (p590 of ref. 2). The T_e in the NG-PC boundary region of our experiments would therefore need to be <1 eV.

The boundary region is thought to correspond to the Faraday Dark Space, FDS, in which n_+ must reach a minimum, and therefore the axial rates of n_+ diffusion into the FDS from the two axial directions, plus ionisation, must be exactly balanced by their rates of loss by radial diffusion and recombination. In the PC, the rate of ionisation must be just enough to balance the rate of loss by radial diffusion, but it must be higher at the anode in order to supply the net axial current of cations (however small) towards the NG_PC boundary. This requires that the field increases close to the anode, and this is presumed to be the upturn which is observed experimentally. The occurrence of such an upturn is, on the other hand, contradictory (see section *3.* below).

When the anode is immersed in the NG, ionisation is mainly by energetic primary electrons; the only sinks for ions and electrons are diffusion to the walls and recombination. The net current to the anode is then supplied from the electron distribution, by the portion of the high energy tail which can overcome the negative barrier at the anode. According to Chapman, these electrons are mainly survivor high energy primary electrons. At pressures $\approx$ 0.1 Torr the NG is a region which apparently stretches over several cm, although the actual distance depends on the geometry of the container (p. 562 of ref. 2). It is reasonable to suppose that at 2 Torr, it would therefore be only a few mm. In GD mass spectrometer ion sources (low power DC), using pin cathodes, without a flow tube, and of otherwise similar dimensions to ours, cations are detected at the anode surface and it is assumed that this is due to migration from the bulk plasma by ambipolar diffusion across the negative sheath field which must form. However, the cations disappear when the anode to cathode distance exceeds <10 mm (at pressures of Ar <1 Torr). This is presumed by experimenters to be the point where the NG crosses over to the PC.

We would expect the electron temperature in the NG to be the highest of any part of the plasma and therefore certainly >1 eV (at low pressures very much greater). It is interesting therefore that Langmuir probe measurements give energies which are fractions of an eV; e.g., as mentioned above, when the pressure is 0.7 Torr, V_d = 1000 volts and I_d = 4 mA, the T_e measured at only 4 mm from the end of the Cathode pin is already <0.3 eV[20]. Although there are criticisms over the use of probes in sputtering discharges, this value is similar to that made by others. Since the Cathode Dark Space (effectively the region between the Cathode and the NG) in such conditions is in the region of 1-2 mm, it suggests that the NG is itself only 1-2 mm wide under these conditions.

2. The effect of fast flow

In the conditions of our experiments, in FAG mode when $I_p \approx 0.02\ I_d$, the plasma decays (as measured from the change in cation density, see above) from a value of ~ 3.5×10^{11} down to ~10^{10} cm^{-3}, approximately exponentially, with $k_{decay} \approx 1\times10^3\ s^{-1}$.

This is very much greater than the rate of recombination; the only other loss mechanism is diffusion to the wall. When the full discharge current passes down the flow tube ($I_p = I_d$), for otherwise the same conditions, it still decays significantly, although it does so more slowly, and $k_{decay} \approx 0.5 \times 10^3$ s^{-1}. If the flow speed is decreased, the profile flattens out as you would expect.

The value of T_e as derived from the value of V_f at probe B is 0.12 eV. With fast flow imposed in the axial direction, the different regions will be stretched away from the Cathode. It appears therefore, at face value, as if the plasma within the flow tube could be part of the FDS section described above, rather than a PC plasma. If so the axial field would be negative.

The axial field was monitored using the value of V_{ab}, and negative values have been measured on different apparatus[ii], when flow speeds are much faster than was possible with the present apparatus (for example giving $\tau_R < 1$ ms at $p < 1$ Torr); but in the experiments described here V_{ab} was positive in both FAG and FD modes when carrying electrons downstream. According to theory, the axial field required to sustain T_e at 1 eV would require just a few mV cm^{-1}. The resolution of our V_{ab} measurements was too poor to measure such small values and it is possible that they are misleading because if T_e is falling as a function of distance down the flow tube, then so must V_f {= $-5.2\times T_e$ (units of eV)}. ΔV_f across AB would therefore be a positive quantity, and since $V_{ab} = \Delta V_{p} + \Delta V_f$, this change could mask the true direction of the axial field if $|\Delta V_p|$ is $< |\Delta V_f|$.

If the true field is indeed negative, the drift current would be net positive. A net negative current, as measured, could then be sustained only by the persistence of momentum of high energy primary electrons forcing their way against the field as they decelerate, as across the sheath field of the anode immersed in the NG. This seems improbable stretched over a timescale of > 4 ms between the end of the Cathode pin and the tip of the Cone, given the evidence quoted above of such rapid electron cooling in high pressure Ar (notwithstanding the added decelerating effect a negative field gradient). Also, given the geometry of the main discharge, the momentum of >90% of primary electrons is in a direction which is perpendicular to the direction of flow, and therefore would be lost to the walls.

The V_{ab} value recorded, when positive, therefore represents the maximum possible positive axial gradient down the flow tube; from this it is possible to estimate the maximum possible drift current, as in part *4.*, below.

3. Random current density

The most obvious and overriding indicator that the downstream FAG and FD plasmas are not the free ion-electron gas usually assumed, is demonstrated by the fact that when $V_C = V_A$, V_{bc} = +0.32 and +1.3 volts for the FAG and FD experiments respectively. V_p is therefore below Anode potential. This has been pointed out by us before[8]. Whilst this is a necessary condition for the PC plasma as outlined above, it is contradictory as shown below.

In a free ion-electron plasma the random current density is given by $j_{rc} = \frac{1}{4} e\, n_e\, \hat{c}_e$. If we assume $T_e = 0.1$ eV (as measured from V_f at B), and $n_e = 10^{10}$ cm^{-3} (assumed = n, the plasma density, as measured by the rate of flow of cations onto the Cone surface in FAG mode; it is less in FD mode; it is even more if it is the negative part of the plasma as discussed above), then $\hat{c}_e = 7.5\times10^6$ cm s^{-1} and j_{rc} = 3 mA cm^{-2}. This is much greater than either I_p/A_{Cone} or I_d/A_{Cone} (8×10^{-3} and 0.6 mA cm^{-2} respectively). As pointed out by Chapman (p 80 of ref. 4), there must always be a net decelerating field at the anode, to suppress the random current and bring the net electron current down to experimental values. It is a necessary condition therefore that $V_p > V_A$, unless the surface area of the collecting electrode is very much less than the conducting plasma cross-section. In our case the plasma cross-section is less than the Cone surface area. To get a random current density as low as 8×10^{-6} A cm^{-2} as in the FAG plasma, would therefore require a value of T_e <1^{o}K at the Cone!

4. Comparison of theoretical (classical) current maximum and experiment

The current through the downstream FAG plasma, I_p, is 50 μA when $V_C = 0$. Assuming that the current is carried across the whole cross-section of the tube, the plasma current density $j_{expt} = 0.16 \times10^{-4}$ A cm^{-2}. Theoretically it is given by the rates of migration of cations and electrons (velocity v_+ and v_e respectively) along the axial field, given by

$$j/e = n_e v_e - n_+ v_+ \approx n_e v_e$$

where j is the current density and *e* is the electronic charge; and since v_+ is << v_e, the cationic contribution can be ignored.

The plasma density at probe B (upstream from the Cone) is ca. 2×10^{10} cm^{-3}. The axial field gradient (from V_{ab} taken at face value) is ≤ 0.017 volts cm^{-1}; hence E/p is ≤ 8.3×10^{-3} volts cm^{-1} Torr^{-1}. The drift velocity (v_e) of electrons, free of ions, in this field is ~1.2×10^5 cm s^{-1} (p 541 of ref. [iii]); therefore j_p is theoretically < 3.8×10^{-4} A cm^{-2} (note[iv]). The conditions therefore appear more than adequate to carry the current in this fashion; but this is not true when the full discharge current passes down the tube. In that case, $I_p = I_d$ = 2.6 mA ($j_p \approx$ 0.9 mA cm^{-2}), V_{ab} was 0.2 volts, and therefore E/p is ≤ 0.1 volts cm^{-1} Torr^{-1}, when v_e is < 2.1×10^5 cm s^{-1}. The plasma density was a factor of 0.66 lower in density (from Fig. 2). Therefore j_{theory} is < 0.23 mA cm^{-2}, which by this mechanism is not enough.

In FAG plasma mode, the current of electrons to the Cone increases when a positive bias is applied, rapidly rising to its transport limited threshold, at $V_C \approx 1$ volt. It then stays constant (increasing by < 10%) until $V_C \approx 15$ volts (the point which coincides with the switch of path for I_p to pass between the Mesh and the Cone). I_p then jumped from 0.1 mA to a new plateau value of 0.39 mA (G-H of Fig. 6). The E/p value (from V_{ab}) was < 0.15 volt cm^{-1} Torr^{-1}, when v_e has a value < 4×10^5 cm s^{-1}, which, assuming that n_e remains at 2×10^{10} cm^{-3} (at probe B) gives j_p < 1.3 mA cm^{-2} for the theoretical value. This might be enough, but the current beyond J in Fig. 6, continued to increase up to 16 mA, apparently without a significant increase in plasma density, and with < 2.1 mA (of the downstream current) passing via the Cathode. The same effect occurs without the Mesh (see Fig. 12), although the proportion passing through the Cathode is greater. This increase in I_p by a factor >160 (as V_C increases from 5 to 78 volts) was accompanied by an increase in V_{ab} to a value < 1 volt. In this range: 10^{-3} < E/p < 1 volts cm^{-1} Torr^{-1}, v_e values change by a factor < 5. The steepest changes to v_e occur at E/p values <10^{-3} volts cm^{-1} Torr^{-1}, when the migration current would be much too small to give the experimental value. Once again, it appears as if the conventional mechanism is theoretically inadequate to supply the measured current changes.

5. Plasma decay and steady state current paradox

The plasma decays as it flows downstream. This is true, whether it carries the full discharge current (the FD plasma) or just a small portion of it (the FAG plasma). If this was a true PC plasma, the density should remain uniform. When carried by the electron migration current, I_p requires a positive axial field, as discussed above. In order to maintain a constant value of n_e v_e under steady state conditions, in which n_e is decreasing requires that v_e must increase to compensate.

As discussed in *2.*, if n decays in a conventional plasma, then so must T_e; but, then it cannot, as a matter of principle, sustain a steady state migration current, for the following reason. In a region of falling plasma density, the axial field would have to continually increase towards the anode in order to increase v_e, to compensate for the decrease in n_e. To do that would require an increase in n_+, hence an increase in ionisation, requiring an increase in T_e and hence n_e. Obviously this is inconsistent. In a steady state system, in which the current is not carried by the forward momentum of primary electrons, the T_e, and the plasma density would have to be uniform (as is always assumed), except across the boundaries where the separation of charge occurs. V_{ab} is greater in the FD mode, when I_p (=I_d) is much greater, and, although k_{decay} and n_+ are both lower, the same arguments must apply.

6. Plasma density and plasma potential variations

As the anodic bias voltage is applied to the Cone we would expect, because of its large size compared to the plasma cross-section, two effects if the downstream plasma was composed of free ions and electrons: (i) the drain of electrons from the plasma (leaving cations behind) would cause the plasma potential to rise significantly, and (ii) the current would become very large and cause an increase in the Cathode current, I_d. The rise in V_p does not occur until EI at the Cone sets in, but even then I_d stays constant until $V_C > 32$ volts, rising by < 13% of the downstream current at high (+)V_C.

At the anodic plateau, the total current carried by the downstream plasma is 95 μA. At the cathodic plateau it carries only 2.5 μA. Yet there is no change in plasma density in either case, and its conductivity remains identical (as measured in the double probe experiment) even though the axial field is reversed. The same appears to be true (although not measured specifically), even at high anodic bias voltages, when auxiliary electron currents of up to 16 mA flowed.

Steady state GD plasmas, when studied by probe methods usually also carry the full discharge current, which is responsible for sustaining the plasma. However when the full discharge current of 2.6 mA is diverted through the downstream plasma, its density is not more, as we might have expected; it is obviously less, as shown by Fig. 2 (note[v]). The plasma density therefore appears to be largely independent of size of the current flowing through it and this is contrary to theory. The conduction therefore appears to be more like that of a current down a wire.

7. The anodic I_p-V_C curve varies in a staccato fashion

The shift of path occurs and I_p increases only when EI occurs at the anode (Cone). This provides an increase in the rate of formation of electrons within the anode sheath, but not through the plasma or at the cathode. Whatever the current transport mechanism, it is obviously true that the current must be equal at all points between the electrodes. At this stage (G in Figs. 6 and 7), the electron current to the Cone is limited by the rate of transport of ions onto the Mesh surface, which in this region of the scan is acting as the cathode of the downstream circuit.

The extra ions produced by EI at the Cone, even if they migrated back towards the Mesh could never do so at a rate fast enough to provide the requisite increase in cathode current (the drift velocity of Ar^+ in Ar, when E/p = 0.5 volt cm^{-1} $Torr^{-1}$ for example, is << 1×10^4 cm s^{-1} (p464 of ref. iii). There was no change in the main Cathode current, and no change in plasma density, therefore there has to be a new cathodic reaction at the Mesh to provide the extra cathode current.

This reaction is obviously one that is induced by the increase in $\Delta V_{c(Mesh)}$ from < 0 to +5 volts. The extra cathode (Mesh) current is obviously not secondary electron emission due to ion bombardment of the Mesh because the secondary electron coefficients (γ) for ion energies of 5 eV are << 1. The only other possibility in a conventional plasma is EI across the holes of the Mesh.

Normally the cathode fall (ΔV_c) would occur across the sheath gap, a distance which, in the absence of EI, is normally thought to be of the order of the Debye length[vi], which under our conditions would, for example be ~0.01 mm if T_e = 1eV.We do not know the T_e value at the Mesh, but even if it were as high as 5 eV, the sheath gap would still be < the collision mean free path ($\approx$ 0.035 mm for Ar at 2 Torr and 310 ^oK). This compares with the 0.5 mm hole dimension of the Mesh, wire thickness 0.03 mm. If, nevertheless, the voltage drop occurred across the body of the plasma between the upstream and downstream side of the mesh hole, rather than at the Mesh surface, it could accelerate free electrons by the value of $\Delta V_{c(Mesh)}$ (= 5 volts at maximum), from the upstream side, through the hole to the downstream side of the mesh. Electrons already moving in that direction would need an initial energy of 11 eV, in order to gain enough energy to ionise Ar^0. The plasma density at the Mesh is ca. 3.5×10^{11} cm^{-3} and therefore electrons with a T_e > 0.8 eV would probably be enough to supply the required high energy tail current (assuming Maxwellian distribution; note[vii]) sufficient to cause enough ionisation to make up the extra current through the downstream plasma. Also, at 5 eV all the electrons would be available to ionise the Ar metastables, and many would be energetic enough to ionise the sputtered Cu vapour, and this too could provide a sufficient current.

There are three objections to this model however. The first is that the cations created, would follow the same potential surface path as the electrons (but in the opposite direction) and therefore would have to migrate through the hole into the upstream plasma and become part of the Cathode current (which experimentally does not change). The second is that there is no obvious reason why this should be a singular process. With a Maxwellian (or any continuous) distribution we would expect a continuous gradation, not the step function(s) observed for the increases in current. The kinetics is therefore more complex than appears provided for by EI in the plasma. The third is that we would expect EI at the Mesh to cause a significant increase in both downstream and upstream plasma densities. We do observe this to happen, but only when ΔV_c (and therefore V_C) values are very much larger than here (see section **III.**, section **F.**, part *2.*). It is our conclusion therefore that the extra electrons making up the downstream current at the lower applied voltages probably ultimately come from a specific cathode (Mesh) process.

8. The presence of a free ion-electron plasma at the anode is readily detected by the appearance of cations at its surface

Another feature of the I_p-V_C behaviour at the anodic Cone, is the sudden appearance and disappearance of cations at the aperture. These ions disappear quickly as the anodic bias is applied, but reappear just with the onset of EI in the anode (Cone) sheath. It is obvious in this case that a free ion-electron plasma will be created by EI so close to the surface and that the cations are observed because there is a drop in potential (ΔV_b) towards the surface which must occur, created by the separation of charge engendered. The corollary is that if cations are not observed there cannot be a free ion-electron plasma adjacent to the anode.

Cations first disappeared from the mass spectrum in this experiment, when V_C was > +1.7 volts, but suddenly reappeared when the cathode switches from the NG to the Mesh, at V_C = 14.9 and V_{bc} = 15.1 volts, which coincided with the EI of trace gases at the anode. However, they promptly disappeared again as soon as the plasma potential shifted and the extra downstream current started to flow. At the point where cations are observed due to EI at the anode, there must be a region between the plasma and the sheath where the voltage drops sharply (= ΔV_a) down to the much lower plasma potential. The value of V_{bc} at this point ≈ (ΔV_a - ΔV_b). When the free ion-electron plasma disappears ΔV_b goes to zero and the remaining 'plasma' experiences only the positive field between it and the surface.

The current does not increase again until V_C > 24.6 volts (J), caused when EI of Ar^0 sets in (and there is a very steep increase in I_p, see Fig. 5). Cations once again appear in the spectrum as a new free ion-electron plasma is created at the anode. They then curiously disappear and reappear at intervals, indicating the appearance and disappearance of a free ion-electron plasma on top of the non-free 'plasma' which must constitute the bulk of the medium, and which allows the existence of a positive field at the anode surface. The same effects occur without a Mesh, when the extra electrons involved must ultimately originate from part of the cylindrical Anode surface. If the flow tube is also maintained at Anode potential, this behaviour becomes greatly exaggerated as shown in Fig. 11, where the ionisation at the Cone aperture occurs as a series of peaks as V_C is scanned. Again this indicates to us that the kinetics is more complex than is provided for by simple EI in the plasma.

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[i] M. A. Gusinov, J. B. Gerards, and J. T. Verdeyen, *Phys. Rev.*, 1966, 149 **,** 91.

[ii] K. Newman, Ph.D. Thesis, Swansea University, 2005.

[iii] E.W. McDaniel, in *Collision phenomena in ionised gases*, Wiley, New York, 1964.

[iv] Of course, electrons moving against a field of free cations will move at a lower speed. It is also true that v_e is inversely dependent on the collision cross-section, so that the higher energy electrons (> 1 eV in Ar) also have a lower drift velocity; on the other hand the cross-section increases below 1 eV (by a factor of ~2.5 between 1 and 0.5 eV).

[v] possibly due to the fact that there is a significantly larger surface area for the loss of plasma by radial diffusion, because the Anode part of the flow tube is now floating.

[vi] $\lambda_D = (\bar{k}T_e\varepsilon_0 / n_e e^2)^{1/2}$, where ε_0 is the vacuum permittivity.

[vii] The plasma density at the mesh is 3.5×10^{11} cm^{-3}. The proportion of electrons, assuming Maxwellian distribution when T_e = 1 eV, for example, would be $e^{-11}/4 = 4.2\times10^{-6}$. If the rate of ionisation = R_i, the extra current generated would be given by $R_i\, e$ (A cm^{-2}). Hence $j_{(Mesh)}$would be given by:

$$j_{(Mesh)} = R_i\, e = n_e\, v_e\, \sigma\, [Ar]\, e$$
$$= 4.2\times10^{-6} \times 3.5\times10^{11} \times 2.37\times10^{8} \times 2.6\times10^{-16} \times 6.4\times10^{16} \times 1.6\times10^{-19} = 0.93 \text{ mA cm}^{-2}$$

where v_e here is the velocity of electrons with an energy of 16 eV (=2.37×10^{8} cm s^{-1}), and σ is the ionisation cross-section (2.6×10^{-16} cm^2, see ref 4).