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Modification of a nonlocal electron energy distribution in a bounded plasma

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It is demonstrated experimentally, in a pulsed discharge, that it is possible to modify the "tail" of a nonlocal electron energy distribution (EED) without significantly changing the electron density and temperature (mean energy). The EED tail is modified by changing the potential of a small portion of the plasma boundary and/or by changing the volume creation rate of electrons with energies in the range of the tail of the EED. The discussed effects are a direct result of the nonlocal nature of the EED and have applications to a number of basic research issues associated with discharges under nonequilibrium conditions. As an example, we discuss the possibility of utilizing these methods to measure electron impact excitation cross sections from the metastable states of atoms, which are difficult to measure by other means. The experiments have been conducted in an argon and argon-nitrogen pulsed rf inductively coupled plasma discharge.

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Modifying and controlling the parameters of a plasma is a fundamental problem of basic plasma research [1]. The advancement in methods for controlling these parameters is also a critical issue for the development of new plasma technologies [2,3]. It is particularly important to have the ability to adjust one of the main components of the plasma, namely, the electron energy distribution (EED), which is responsible for many plasma processes. Possibilities and techniques for altering the EED depend strongly on plasma type. In the simplest case, it is possible to modify the integral parameters of the EED, which are electron density N_e and temperature (mean energy) T_e. Ideally, it would be valuable to have the ability to change the form of the EED, as electrons of different energies may be responsible for different plasma processes.

In this paper we discuss methods for modifying the "tail" of the EED at a distance L from the plasma boundary, which is less than the electron energy relaxation length λ_ε. From this point on, we will refer to this region as the near-wall plasma, although if L is greater than the characteristic plasma size, then it is the entire plasma volume. Note, that in weakly ionized atomic gases $\lambda_\varepsilon \approx 100\lambda_e$, where λ_e is electron collision mean-free path. This implies that $L \sim 10/p$ Torr × cm [4], which allows us to estimate the size of this near-wall plasma region. Here, p is the gas pressure.

From our definition, the EED is nonlocal in the near-wall plasma and is a function of total (kinetic plus potential) energy of the electrons [4]. The notion of nonlocality was originated by Bernstein and Holstein [5] in 1950, and was rediscovered by Tsendin [6] more than 20 years later. Plasmas with nonlocal EED have been extensively investigated over the last 20 years [7–16] and have become an important aspect of basic plasma science. It is known that the nonlocality of the EED can lead to paradoxical behavior of the plasma [17] and, due to nonlocality, the EED can be, for the most part, non-Maxwellian (for instance, in stratified discharges [18]). The nonlocal EED generally depends on processes at any point in the plasma and on the plasma boundaries. This, in turn, creates the possibility of altering the EED by changing the potentials on the boundary of the plasma or, in some cases, the rate of production of electrons in the plasma volume. The experiments described below demonstrate this effect and the discussion that follows allows us to underline some specific details of the modification.

The experiments were conducted in the afterglow of a pulsed argon rf inductively coupled plasma (ICP) discharge. The ICP discharge has recieved significant attention in recent years due to its widespread use in plasma processing applications. When the rf power is modulated (100% in this case) the discharge can switch between capacitive mode (E mode) and inductive mode (H mode), and a precise, time-dependent description of the discharge characteristics becomes difficult for a specific configuration. In this experiment, we have restricted our investigation to the time period following shutoff of the rf power. Therefore, we avoid the necessity to present a detailed description of the discharge as it develops, following application of the rf voltage [19,20]. In general, the afterglow plasma is a convenient regime for these types of experiments because the number of electron-driven processes are greatly reduced due to low electron temperature (within ~100 μs after termination of rf power, the electron temperature becomes of order of 0.1 eV). The afterglow can also contain significant numbers of metastable atoms. Measurements of metastable densities during the active phase of an Ar ICP have been reported by Hebner [21] and Tadokoro *et al.* [22] and their effect on optical emission in pulsed ICP discharges has been discussed by Hioki *et al.* [23] and Miyoshi *et al.* [24]. Therefore, another key feature of the afterglow plasma is the importance of reactions which involve metastable (in our case, argon) atoms

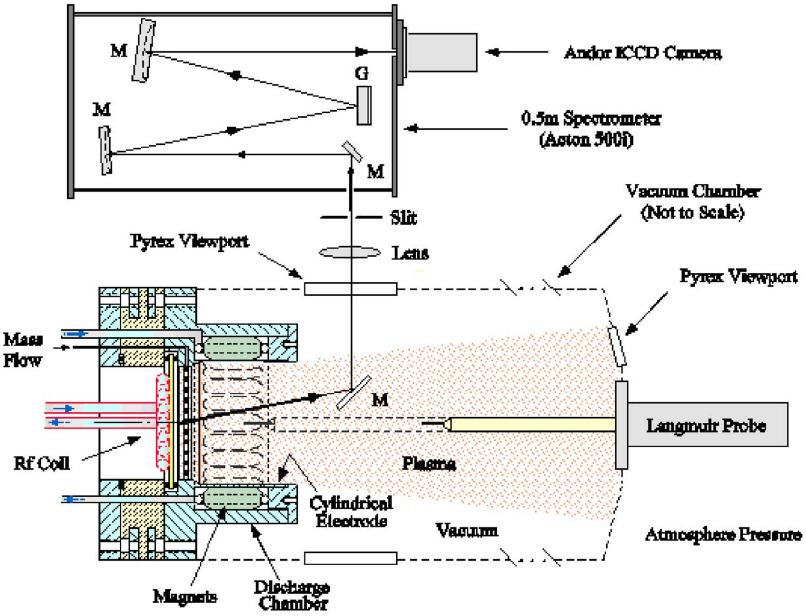

FIG. 1. (Color online) Schematic diagram of the experimental setup.

$$A^* + A^* \rightarrow \begin{cases} A^+ + A + e' \\ A_2^+ + e' \end{cases} \qquad (1)$$

and

$$A^* + e \rightarrow A + e', \qquad (2)$$

which create fast electrons with energies much greater than the average energy of electrons (for example, 7.3 and 11.5 eV for argon). Therefore, under conditions of nonlocality, the tail of the EED can be modified simply by altering the density of metastable atoms.

The plasma excitation experiment has been described in some detail in previous papers [25,26] and will be only briefly described here. A schematic of the experiment is shown in Fig. 1. The ICP system is a modified commercial ion-beam system built by Nordiko. Modifications include new rf power supply and matching network, new coil, and new coupling section which mates the matching network to the coil and incorporates both current and voltage probes. Finally, the extraction grids were removed from the original Nordiko system; hence, the plasma diffuses freely from the source. A Dressler rf generator (CESAR 1350) with matching network (VM 5000) was used to supply power (0–5 kW variable) to a four-turn planar coil at a fixed rf frequency of 13.56 MHz. Power could be 100% modulated using either an internal square-wave modulation or driven by an external pulse (SRS model DG535). Pressure in the system is controlled by a throttling valve and mass flow into the system is controlled by mks mass flow meters. For these experiments, either argon (99.999%) or mixtures of argon and nitrogen (99.999%) were used. Typical operating pressures range from 5 to 25 mTorr. The Langmuir probe (Scientific Systems Smart Probe), with boxcar averaging capability, is triggered by a delayed pulse from the rf pulse so that by sweeping the time delay, time-dependent probe data can be acquired. The probe has a tungsten tip, 7 mm in length and 0.38 mm in diameter, parallel to the direction of the plasma flow. The optical system includes an Acton 0.5 m spectrometer fitted with an Andor intensified charge-coupled device (ICCD) camera. A mirror M allows measurements of optical emission nearly parallel to the chamber's axis.

In Fig. 1, the discharge is formed in the "discharge chamber" near the rf coil and plasma can diffuse freely into the larger "vacuum chamber." The length of the vacuum chamber is 1.22 m and radius is 40 cm. The length of discharge chamber is $L=8$ cm and radius is $R=5.5$ cm. A cylindrical electrode (we refer to this below as a "ring") with a width of 4 cm is located inside the discharge chamber, near its walls and close to the rf window. This electrode allows the plasma boundary potential to be changed over part of the discharge chamber. By adding small concentrations of nitrogen to the argon plasma, the argon metastable density could be reduced by the well-known quenching reaction [27] to reduce the sources of fast electrons [see Eqs. (1) and (2)].

Typical plasma density in the discharge chamber is between 10^{10} and 10^{12} cm^{-3}. Under these conditions, the fast electron energy relaxation length in the afterglow is determined by the electron-atom elastic collisions, since the region of high electron density is limited to the dimensions of the discharge chamber and, therefore, electron-electron collisions have little effect on λ_ε. In this case, at a pressure of 20 mTorr and an electron energy 7.3 eV $\lambda_\varepsilon \approx 3.8$ m, which is much greater than the vacuum chamber diffusion length. At the same time, $\lambda_e \approx 1.7$ cm. Additionally, at a pressure of 20 mTorr, fast electrons loose less than 0.5 eV in collisions with atoms over a time of 200 μs. This means that for times of this order, fast electrons produced in reactions (1) and (2) will have energy distributions with half widths of not more than a few tenths of an eV.

The Langmuir probe allows us to conduct measurements of electron density N_e and temperature T_e. Unfortunately, this system does not have the sensitivity to measure the density of fast electrons arising in reactions (1) and (2) due to their small density [28]. It should be pointed out, however, that under higher pressure conditions in helium, Overzet and Kle-

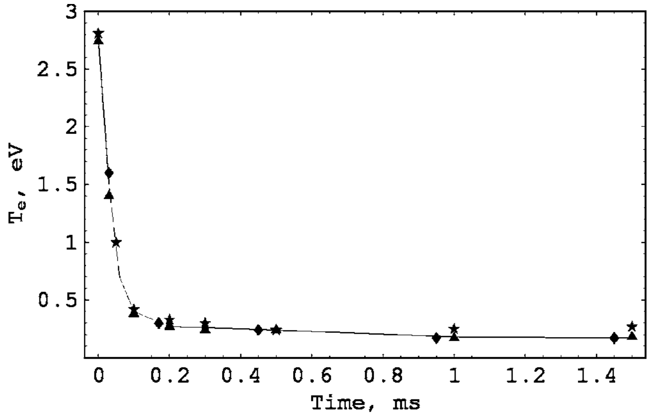

FIG. 2. Electron temperature after termination of rf pulse. Average power is 250 W and rf pulse duration is 300 μs. Gas pressure is 20 mTorr. Ring potential is −9 V: pure Ar (solid line), Ar with 0.6% of N_2 (triangles), Ar with 1.6% of N_2 (stars). Ring potential is 0 V: pure argon (diamonds).

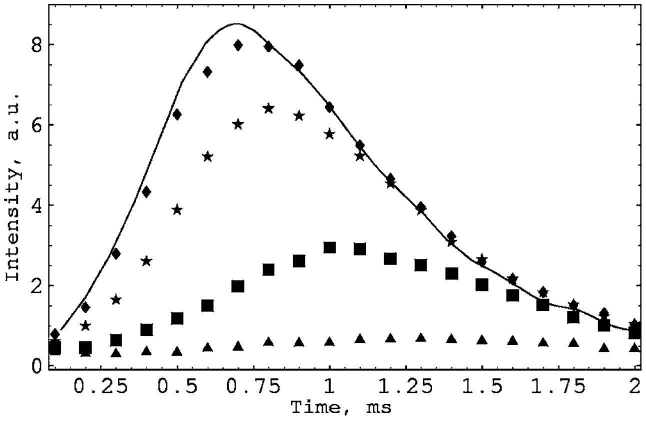

FIG. 4. Intensity of the Ar spectral line 420.1 nm after termination of rf pulse. Average power is 250 W and rf pulse duration is 300 μs. Argon pressure is 20 mTorr. Ring potential is −12 V (solid curve), −9 V (diamonds), −6 V (stars), −3 V (boxes), and 0 V (triangles).

ber [29] successfully used a similar probe system to measure the density of the fast group. In our experiment, we determined the presence of fast electrons from optical emission measurements. The data presented here is for the argon 420.1 nm emission line; however, all of the lines in the 400–900 nm range showed the same qualitative behavior. In the afterglow, emission from this line can only originate from collisions of electrons, with energy greater than 4 eV, with argon metastables. The intensity, therefore, is proportional to the product of the density of these species.

In the first series of experiments, we investigated the argon afterglow plasma for different potentials on the ring. The first results from this series showed that changing the ring potential between −15 and +10 V with respect to ground (walls of the vacuum chamber are grounded) had no measurable effect on the temporal behavior of N_e and T_e, as shown in Figs. 2 and 3. These data were taken on the axis of the discharge chamber at a distance of 6.5 cm from the rf window. Recent results [30,31] have shown that due to the joint electric and magnetic fields present during the active phase of an ICP, there is a drift field which drives the electrons and can increase input power. One might be tempted to conclude that the ring electrode would add a drift field which could perturb the input energy into the afterglow. If this were the case, heating of the bulk electrons would be seen in temporal measurements of T_e (or perhaps N_e), which is clearly not seen in this experiment. In contrast, the temporal behavior of the argon emission line intensities depend strongly on ring potential. Typical results of the measurements are shown in Fig. 4 for the 420.1 nm line. Application of more negative potentials leads to a dramatic increase in emission intensity, which indicates a change in the density of the EED tail ($\varepsilon > 4$ eV) by more than a factor of 20 for the conditions shown in Fig. 4. This behavior can also be seen in Fig. 5, which shows the dependence of the line intensity on the ring potential (solid curve) at a fixed time of 0.75 ms after termination of the rf pulse (close to the intensity maximum). Changing of ring potential, as in Figs. 4 and 5, also changes the plasma potential. Therefore, in Fig. 5, the dashed line shows the dependence of the intensity on voltage between the ring and

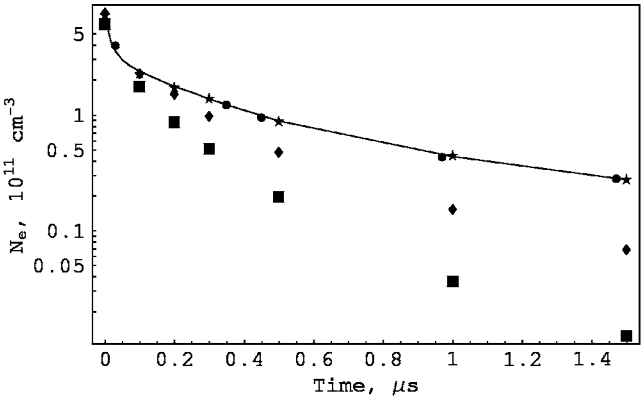

FIG. 3. Electron density after termination of rf pulse. Average power is 250 W and rf pulse duration is 300 μs. Gas pressure is 20 mTorr. Ring potential is −9 V: pure Ar (solid line), Ar with 0.6% of N_2 flow (stars), Ar with 1.6% of N_2 flow (diamonds), and Ar with 3.2% of N_2 flow (boxes). Ring is grounded: pure Ar (dots).

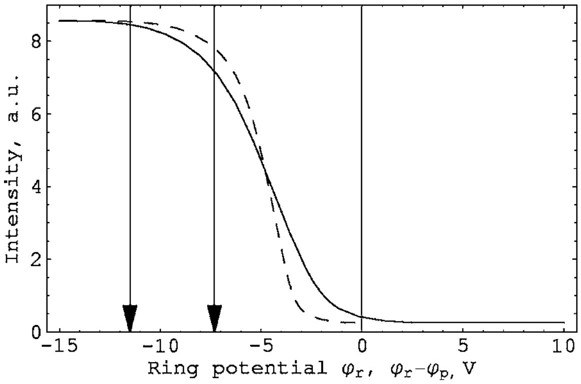

FIG. 5. Dependence of intensity of the Ar spectral line 420.1 nm for time 0.75 ms after termination of rf pulse on ring potential, φ_r (solid curve), and ring-plasma voltage, $\varphi_r-\varphi_p$ (dash curve). Voltage corresponding to energy of free electrons, arising in reactions (1), 7.3 eV, and to (2), 11.5 eV, are shown by arrows.

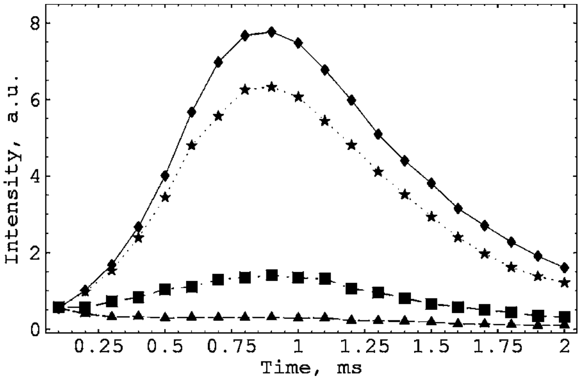

FIG. 6. Intensity of the Ar spectral line 420.1 nm after termination of rf pulse. Average power is 250 W and rf pulse duration is 300 μs. Gas pressure is 20 mTorr. Ring potential is −9 V. Pure Ar (diamonds), Ar with 0.3% of N_2 (stars), Ar with 0.6% of N_2 (boxes), and Ar with 1% of N_2 (triangles).

the central part of the plasma. As can be clearly seen, the intensity increases sharply for potentials from −4 to −7 V with a much smaller change for more negative potentials. Again, this indicates a change in density of electrons with energies greater than 4 eV and demonstrates that we can remove a part of those electrons smoothly. An interesting point is that after 20–25 hours of operation, the ring becomes coated with a thin film of ceramic (presumably from the rf window) and the intensity no longer changes with the ring potential. Polishing the ring returns the system to the state characterized by Figs. 4 and 5. These experiments demonstrate that the tail of EED can be modified without measurably altering N_e and T_e.

A second series of experiments was undertaken to demonstrate how modifying the source terms for fast electrons changes the EED. Adding nitrogen to the gas mixture can affect the overall characteristics of the active phase of the discharge as well as the afterglow. Some of the possible changes to the system include alteration of the EED, additional quenching of excited states, and possible electron heating, specifically in the afterglow. We used measurements of the temporal decay of N_e and T_e as an indicator of the sensitivity of the bulk EED, in the afterglow, to nitrogen addition. We also monitored the light emission during the rf pulse as another indicator of the significance of nitrogen perturbation to the system. It was first determined that adding a small amount of nitrogen (up to 0.6% of flow) does not change the temporal behavior of N_e and T_e (see Figs. 2 and 3). A further increase in flow leads to a slight increase in T_e and a decrease in N_e (increased decay rate of N_e and decreased ion production in the afterglow). The light emission *during the rf pulse*, while not shown, did not measurably change with up to 3.2% nitrogen flow. In contrast, Fig. 6 shows the behavior of the 420.1 line as a function of nitrogen in the flow and shows a dramatic change as the nitrogen concentration approaches 1%. Nitrogen is known to be an effective quencher of Ar^* [27] [leading to N_2 (C-B) emission, which we observe in the afterglow] and, thus, reduces the production of fast electrons. If the fast electron density goes as $(\mathrm{Ar}^*)^2$ [as in reaction (1)] and the emission goes as $\mathrm{Ar}^* * e'$, then one expects the emission to go as $(\mathrm{Ar}^*)^3$ and, therefore, depend strongly on the metastable density in the afterglow.

The above experiments allow us to discuss the general principles of modifying the nonlocal EED. The nonlocal EED can be conventionally divided into two clearly distinguished groups. In the first group of electrons, $\varepsilon \leqslant eV_w$, where V_w is the wall potential and e is the electron charge. As a result, this group cannot reach the walls and, therefore, are trapped in the plasma volume (we will refer to these as "trapped" electrons). For the second group, electrons have total energies $\varepsilon > eV_w$ and this group constitutes the tail of the EED, which we have discussed modifying in this paper. These electrons can be referred to as "free" electrons as they have free diffusion in the plasma volume (their kinetic energies are much greater than the potential energy of electrons in the ambipolar electric field of the plasma) and can reach walls. The density of the free electrons (second group) N_{ef} is much less than the density of the trapped electrons (first group) N_{et}, and to maintain quasineutrality, the flux of ions to the walls should be equal to the flux of electrons from the second group. Then from $D_a \nabla N_i = D_{ef} \nabla N_{ef}$, we find that N_{ef} is on the order of $N_i D_a / D_{ef}$, where D_{ef} and D_a are the free diffusion coefficient of the first group and the ambipolar diffusion coefficient for ions, respectively. From this we find that $N_{ef} < 10^{-3} N_{et}$, so that $N_{et} \approx N_e$.

Electrons from the second group reach the walls and recombine before their energy is significantly altered. This means that during their lifetime in the plasma their energy is characteristic of the source term (a possible exception are electrons with energies only slightly above eV_w). Therefore, by introducing or removing processes which are a source of electrons with energies which lie within the second group, it is possible to modify the EED in that particular range of energies and, therefore, exercise some control over the EED. It should be emphasized that due to the small number of the electrons in the second group (say, $10^{-5} N_e$), even a small perturbation in the density of this group may be very important and can, for instance, significantly change V_w [32]. The EED for trapped electrons can be found from a solution of the nonlocal kinetic equation and has a more complicated relationship to the form of electron source terms. For this group, a source of electrons of a particular energy may affect the entire EED or create a continuous electron energy spectrum [33]. It should be emphasized that the above situation cannot be described within the framework of a fluid approach and its description requires a nonlocal framework.

These results allow the study of a number of fundamental problems of physics of plasmas, spectroscopy, etc. As an example, we discuss the unique possibility of reliable measurements of relative cross sections for electron impact excitation from metastable states. In spite of the much lower density of metastable states as compared to ground states, the significantly lower thresholds for excitation from these levels makes these cross sections important under typical plasma conditions. As a result, the measurement of cross sections from metastable states has attracted a large amount of attention over the last 20 years (see, for example, Refs. [34–37]).

Measurements of this type can be made in the device shown in Fig. 1. As can be seen from above, in the afterglow of a low-pressure rf ICP discharge, a plasma exists with a bimodal electron energy distribution. This consists of a large group with low mean energy (~ 0.1 eV) and a much smaller group ($\sim 10^{-5}$) consisting of a narrow electron peak (~ 0.5 eV) at energies of a few eV, which can exist for a few hundred microseconds. Therefore, for electron impact excitation from metastable states to levels with thresholds large enough to avoid excitation by the bulk, slow electrons (of order of 1 eV), the intensity of a spectral line is proportional to the corresponding cross section *at the energy of the fast group*.

As an example, we measured the ratio of the intensities of the Ar emission lines at 420.1 and 419.8 nm in the afterglow. These lines originate from $3p_9$ and $3p_5$ (Paschen notation) levels in Ar. The ratio of $I_{420.1}/I_{419.8}$ should equal the ratio of the apparent cross sections for stepwise excitation from the Ar $1s_5$ metastable level by electrons at 7.3 eV (since the energy does not spread significantly). The measurements were made at a gas pressure of 20 mTorr. It was found that this ratio is equal to 3.8 ± 0.1 and is relatively constant in the afterglow. Note that these two lines are very convenient for spectroscopic measurements due to their close proximity to one another, which usually does not require correction for the sensitivity of the detection system. This large ratio is not seen in the early stages of the rf pulse (ratio <1) but is seen to increase as the discharge loads. This loading has previously been shown to correspond to the rapid buildup of metastables in the discharge [26]. This suggests that the 420.1 line is more sensitive to stepwise excitation than the 419.8 line. This leads us to speculate that this ratio may be a sensitive indicator of the metastable density in the discharge. We are currently investigating this proposition.

In summary, it has been shown that in a nonlocal plasma, it is possible to alter the EED by changing the source of fast electrons and potentials on the boundary. The fast electron density can be modified by introducing additional sources of fast electrons in the plasma volume or to remove an existing source. It is also possible to change the potential on a part of the walls by an additional voltage source. This can change the diffusion time (loss rate) of fast electrons and, therefore, their density. Varying the density of fast electrons by even a small amount can significantly alter the plasma properties. The discussed effects can be used, for example, for measurements of cross sections of electron excitation from metastable states of atoms.

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