Serbian Academy of Sciences and Arts
Institute of Physics Belgrade

Proceedings of the

2nd International Workshop on Non-equilibrium processes

In plasmas and environmental science

Editors: D. Marić and Z. Lj. Petrović

Belgrade, Novi Sad
August 2008

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The workshop was prepared under sponsorship of:

Ministry of Science and Technological Development, Serbia
Serbian Academy of Sciences and Arts
INCO project IPN-CNP 026328
Institute of Physics Belgrade, project MNTRS 141025

Program and Contents

Saturday 23.08, Serbian Academy of Sciences and Arts, Belgrade

Sunday 24.08, Institute of Physics, Belgrade

Tuesday 26.08, Hotel Park, Novi Sad

Contributed Papers

Low Pressure Nonequilibrium Plasma for Topdown Nanoprocess: its structure and function

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The collisional plasma sustained in each of feed gas molecules has distinct characteristics induced by the quantum structure of the molecule activated through collisions with electrons or heavy particles. That is, there exists the proper characteristics to produce dissociated radicals, short- and long-lived excited molecules, and radiations based on the molecular quantum structure through a short-ranged interaction mainly with electrons. It differs from collisionless plasmas controlled by the long-range Coulomb interaction. Generally, the degree of ionization will be less than 10^{-3} in the collisional plasma. The quantum structure in the form of the collision cross section between the electron and the feed gas molecule is first essential quantity to investigate the collisional plasma structure and to predict the function. In a plasma interacting with surface, the energy and the angle of incident particles, especially ions are basic quantities as well as the flux in order to estimate the surface plasma process. Then, the flux velocity distribution of ions in the sheath in front of the wafer is estimated by using the set of cross section as a function of relative energy between the ion and the feed gas molecule.

In this talk we will discuss the nonequilibrum characteristics of electrons in the bulk plasma and ions in the passive sheath in the two-frequency capacitively coupled plasma for dielectric etching. The structure of the velocity distributions of the electron and ion in the nonequilibrium collisional plasma will be demonstrated by using VicAddress[1][2].

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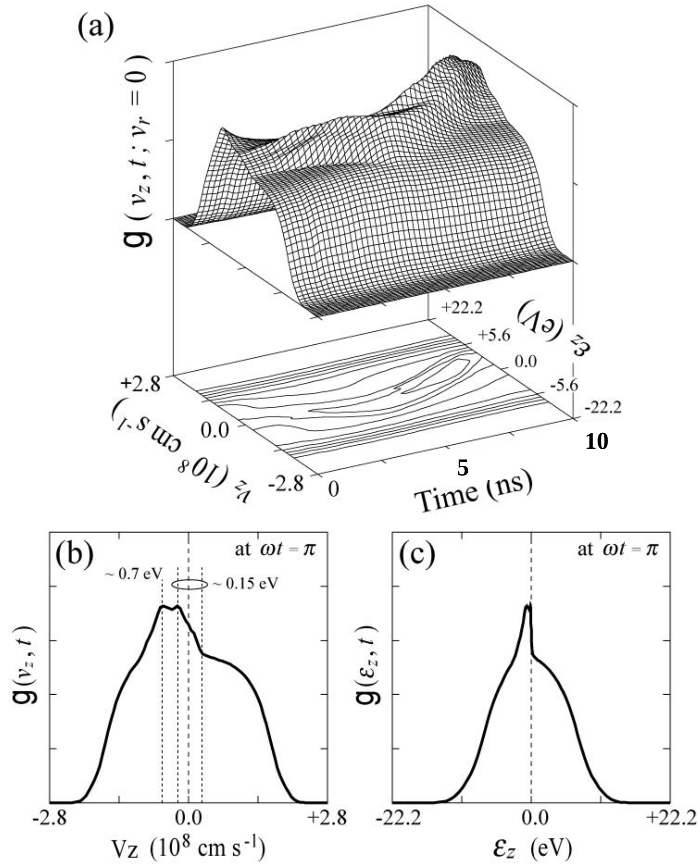

Figure: Time varying velocity distribution of electrons in the bulk plasma in collision dominated 2f-CCP, maintained at VHF(100MHz, 300V) and biased at LF (1MHz, 700V) at 50 mTorr in CF_4(5%)/Ar. $g(v_z, t)$ (a), $g(v_z, \omega t=\pi)$ (b), and $f(\varepsilon_z, \omega t=\pi)$ (c).

Formation of Non-equilibrium EEDF in Non-uniform RF Plasmas

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Ionization and electron energy balances in uniform along the heating electric field plasmas with Maxwellian electron energy distribution function, EEDF have some fundamental consequences. In such plasmas, the electron temperature does not depend on discharge power and on electron heating mechanism, being solely function of the product of gas pressure p and characteristic plasma size Λ, while the total number of plasma electron N is proportional to the power absorbed by the electrons P_d; $T_e = T_e(p\Lambda)$ and $N \sim P_d$. In real RF discharges at low gas pressure, the EEDF is not Maxwellian and has different behavior in elastic ($\varepsilon < \varepsilon^*$) an inelastic ($\varepsilon > \varepsilon^*$) energy range. In low pressure RF discharges, electron heating process occurs in non-uniform plasma with non-uniform electromagnetic field. At such condition the EEDF and its scalar integrals, like plasma density, mean electron energy and rates of plasma-chemical processes, are not local functions of electromagnetic field, (domain of nonlocal electron kinetics). Moreover, at the lowest gas pressure (mT range) RF current is not a local function of electric field, (domain of nonlocal plasma electrodynamics, anomalous skin effect). Variety of nonlocal kinetics and electrodynamics phenomena affects formation of EEDF in RF discharges. Mechanism of EEDF formation together with experimental data in RF capacitive and inductive discharges, dominated by nonlocal kinetics and nonlocal electrodynamics are considered in this presentation.

Positron Cooling, Trapping and Transport in Gases

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Ronald White, Kevin Ness, Sasha Djuko[2]
Ana Bankovic, Zoran Lj. Petrovic, Milovan Suvakov, Gordana Malovic[3]
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Positrons are now widely used in materials and bioscience. Their annihilation with their matter counterpart, the electron, provides the gamma ray signature that is used for a variety of applications, from polymer design to cancer imaging and therapy. We have commenced a program of studies aimed at a better understanding of positron interactions and transport in gases and, ultimately, soft condensed matter.

Positron interactions with gases are characterized by a number of significant differences from those of electrons, which are now well studied and understood. Positrons do not undergo the exchange interaction which, in the case of electrons, is responsible for many spin-flip excitations. They do however readily form positronium – an electron-positron pair – which is one of the major pathways to annihilation, and is clearly a non-conservative process.

We have an experimental program underway on positron interactions with atoms, molecules and materials. At the heart of this program is a 'Surko trap' where positrons are accumulated, trapped and cooled through controlled interactions with molecular gases such as N_2 and CF_4. The principle interactions in the trap are initially, electronic excitation of the N_2 molecules in which the positrons lose ~ 8 eV of energy and become trapped in a potential well and, finally, vibrational and rotational excitations of both the N_2 and the CF_4, which cool the positrons to room temperature.

This paper will briefly investigate what we understand about the cooling and trapping processes, the way in which these compete with annihilation via positronium formation, and the unique role that positronium formation plays in the transport of low energy positrons in atomic and molecular gases.

How is the Bohm criterion satisfied in the presence of several positive ions?

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Under most conditions, ions entering the sheath at the edge of a plasma satisfy the Bohm criterion. The place where the Bohm criterion is satisfied may be understood as the boundary between the quasineutral plasma and the spacecharge sheath. When there are several ions present, the Bohm criterion fails to uniquely determine the speeds with which the ions enter the sheath. Instead it prescribes a locus of possible solutions, and in general, we do not know which solution will be realized in any particular case. In a generalization of the Tonks-Langmuir model, and in other cases where essentially all ions have the same mean free path, it has been shown that the realized solution is that each ion leaves the plasma with its own Bohm speed, which is to say, with the same kinetic energy. This seems intuitively reasonable, because in such cases one may assert that all the ions reaching the sheath edge have traversed the same potential drop.

In this paper, we consider a model in which the ion elastic collision frequency is large compared with the ionization frequency. With this assumption, there is a region adjacent to the sheath where the ion fluxes approaching the sheath may be assumed to be constant, and in this region an analytical solution to the transport equations can be found in which the ion motion is mobility limited. For two ion species, this analytical solution is characterized by two dimensionless physical parameters, which are essentially the ratio of the ion fluxes and the ratio of the mean free paths. In this model, the sheath solution must match this bulk transport solution, and this requirement uniquely determines the manner in which the Bohm criterion is satisfied. In fact, one can realize any and every solution of the Bohm criterion by an appropriate choice of the dimensionless parameters.

However, the range of solutions that can actually be realised is severely restricted, essentially by ion-neutral collision physics. We will show that in practice, this means that in most cases the assumption that each ion species enters the sheath at own Bohm speed is a reasonable one.

A Novel and Simple Method for Independent Control of Ion Energy and Flux

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One of the major demands in plasma processing has always been the independent control of ion energy and ion flux. Dual-frequency discharges with one low frequency in the MHz range and a second high frequency of typically several 10 MHz partially fulfill this requirement. However, recent investigations have shown that electron heating is dependent on both frequencies and a fully independent control is usually not achieved. Here we propose an alternative concept based on a simple, but previously overlooked asymmetry effect that should allow fulfilling the above demand in an almost ideal way [1, 2].

The idea is that when a temporally symmetric, multi-frequency voltage wave form containing one or more even harmonics is applied to a discharge, even a geometrically symmetric one, the two sheaths are necessarily asymmetric and a DC self bias develops. Optimally this is achieved with a dual frequency discharge that uses the phase locked fundamental frequency and its second harmonic, e.g. 13.56 MHz and 27 MHz, with both voltages having the same amplitudes. The resulting DC self bias and hence the ion energy is a nearly linear function of the phase angle between the two applied RF voltages (Fig. 1). This works especially well in geometrically symmetric discharges, and the roles of the two electrodes can be reversed using the phase. Therefore, the ion energy can be precisely controlled over a wide dynamic range of typically a factor three to four between the minimum and maximum energy (Fig. 2). While the energy at one electrode is increasing it is decreasing accordingly at the other electrode. The effect is self-amplifying since the different sheath voltages resulting from the temporal asymmetry lead to different sheath densities and thereby increase the asymmetry effect. While the ion energy changes with phase, the total power put into the discharge, the plasma density, and the ion flux to the substrate and electrode remain constant within a few percent.

The concept is developed and analyzed in three ways: An analytical proof and model, a hybrid hydrodynamic and Monte-Carlo kinetic model [1], and a self consistent particle-in-cell simulation (PIC) [2]. All three models yield identical results with the PIC simulation revealing further insight into kinetic details. The presentation will explain the theoretical basis of the novel concept and will present results from the model and simulations on the voltage waveform, the ion energy and flux, the electron heating and energy distribution function, the bias control, and parameter dependences.

Support by the DFG in frame of SFB591 and GK1051 and Hungarian Scientific Research Fund grants OTKA-T-48389, OTKA-IN-69892 is gratefully acknowledged. The method is patent pending (US provisional application No. 61/038,263).

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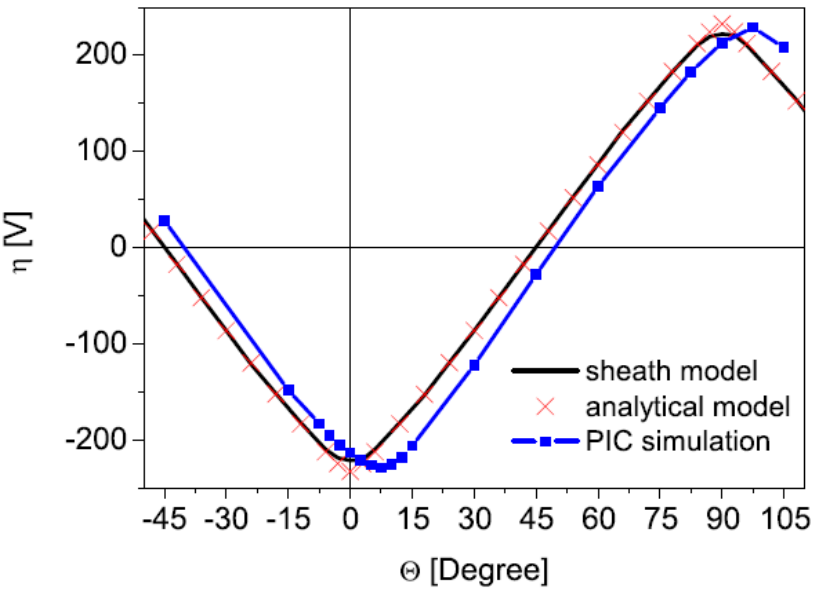

Fig. 1: Self-bias voltage η versus phase angle θ for a symmetric CCP discharge with the following discharge conditions: p = 2.7 Pa (Ar), electrode gap = 6.7 cm. The applied RF voltage is composed of a fundamental component at f = 13.56 MHz and its second harmonic with equal voltage amplitudes V_0 = 315 V: $V_{AC}(t)=V_0\left(\cos\left(2\pi f t+\theta\right)+\cos\left(4\pi f t\right)\right)$

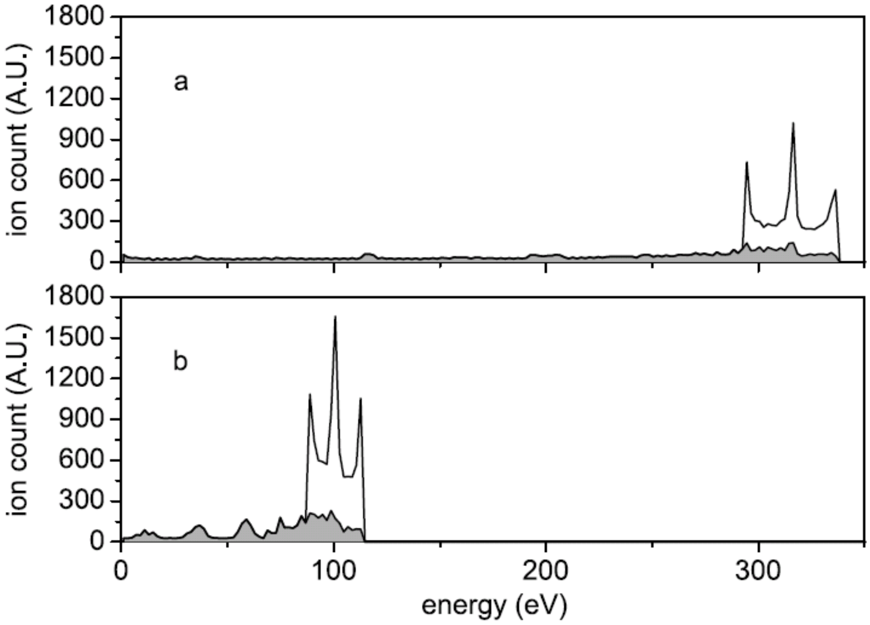

Fig. 2: Ar-ion energy distribution functions (IEDs) shown for phase-angles θ = 0 and θ = π/2. When θ = 0, (a) is the IED for the powered electrode and (b) is the IED for the grounded electrode. When θ = π/2, (b) is the IED for the powered electrode and (a) is the IED for the grounded electrode. The IED for all ions reaching the electrode is plotted. The shaded region only marks the fraction of the IED that is due to ions that underwent an ion exchange collision before reaching the electrode.

Surface Functionalization of Organic Materials by Weakly Ionized Highly Dissociated Plasma

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A review on surface modification of different polymers by treatment in oxygen plasma is presented. Plasma is created in a high frequency inductively coupled gaseous discharge at the power of several 100W. In such discharge created in pure oxygen or a mixture of oxygen with argon, plasma with the following parameters is obtained: the electron temperature of several 10.000 K, the charged particle density around $1x10^{16}$ m^{-3}, and the neutral oxygen atom density of the order of 10^{21} m^{-3}. A huge flux of neutral oxygen atoms on the surface of samples exposed to plasma assures for rapid interaction with polymer materials. The modification of surface properties of the following polymers was studied: polyethyleneterephthalate (PET), polyethersulphone (PES), polyphenylenesulfide (PPS), Nylon 6 polyamide (PA6), polytetrafluoroethylene (PTFE), polystyrene (PS), polypropylene (PP) and cellulose (ink-jet paper and textile). The polymer samples were treated for 3 s in oxygen plasma (glow region as well as early afterglow) at a pressure of 75 Pa. The appearance of the functional groups on the surface of the samples was monitored by high resolution X-ray photoelectron spectroscopy (XPS). The results show that oxygen plasma treatment is an effective tool for surface modification. On all polymer surfaces increased concentration of oxygen is detected. The high resolution C1s peaks indicate formation of several new oxygen-containing functional groups. On all polymers groups like C-O, C=O and O=C-O are observed. The concentration of these groups depends on the type of polymer. The highest uptake of oxygen by the polymer was found for cellulose and the lowest for polypropylene. The only exception was polymer PTFE where practically no chemical changes were observed after plasma treatment.

Plasma propulsion with electronegative gases

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A new concept of plasma propulsion is proposed, where the thrust is provided by both positive and negative ions resulting in a globally neutral beam downstream in space. The basic idea is to create an ion-ion plasma (electron free region) at the periphery of a highly ionized plasma core such that positive and negative ions can be extracted either simultaneously or alternately by dc biased extractor grids. As the extracted beam is globally neutral there is no need for a neutralizer downstream. The recombination of positive and negative ions is very efficient and will result in a fast recombination downstream of the thruster and hence the common problems of downstream plasma behind the thrusters are suppressed.

Study of Higher Excited States of Some Polyatomic Molecules Relevant for Plasma Physics and Environment

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Since the extensive studies of polyatomic molecular spectra by Herzberg [1] and Robin [2] there have not been attempts for systematic research of higher excited states and elucidation of electronic structure that would lead to comprehensive understanding of the behaviour of bound electrons in molecules. However, a tremendous advancement in both experimental methods and theoretical analysis of particular cases became evident trough a number of published papers covering all aspects of complex molecular spectra and their manifolds. On the other hand, the role of electronically excited states of polyatomic molecules had been profoundly investigated when the specific questions had been raised off like the influence of chlorofluorocarbons (CFC) on ozone layer depletion and global warming [3-5], the replacement for plasma etching molecules [6] or radiation damage of DNA deoxyribose analogue molecules [7-10].

Even for triatomic molecules such as H_2O, H_2S, CS_2 and N_2O there are many discussions about the assignment of electronically excited states in terms of valence, Rydberg of mixed character. Electron excitation of the higher states of H_2S molecule will be presented and the tentative assignment will be discussed. A particular interest in this molecule comes from its participation in a great number of processes. It has been recently found in interstellar molecular clouds; it is known as one of the major pollutants of the Earth’s atmosphere which gives the origin of corrosive processes in metals; it is used in the synthesis of a semiconductor, tungsten sulphide (WS2); in mixtures with other gases it is used in plasma nitrocarburizing processes. The H_2S molecule has a very strong dipole moment, and its presence in a gas can have significant effects on the physical properties of the gas, first of all on electrical conductivity.

Acknowledgments

The work has been supported by the Ministry of Science project 141011 of Republic of Serbia.

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Production of molecule on a pyrex surface under plasma exposure: example of NO

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Extensive experimental and theoretical study of NO_x production in low pressure N2/O2 containing plasmas in continuous [1,2,3] and pulsed mode [4], as well as computational fluid dynamics simulation of space vehicles re-entry reveal an important role of O and N atom surface-catalyzed recombination into NO molecule. However, in all above cases analysis of the relative yield of this reaction is not straightforward and it requires sophisticated numerical modeling. We propose to study NO production on the surface pretreated in different low pressure plasmas. In ref [5], Authors claim, that O and N atoms are chemically adsorbed on the glass surface with bonding energy of about 5 eV. It allows us to expect, that atoms remain sticked on the discharge tube wall for a long time after plasma exposure.

Experimental procedure consists of several steps – pretreatment with N2, O2, Air and Ar plasmas, pumping and cooling of the tube and then O2 (or N2) plasma in which we detect NO production. The discharge tube is 2 cm inner diameter and 50 cm long, and the gas pressure is around 1 Torr. In order to eliminate plasma contamination by metallic electrodes inside the reactor, we use CCP discharge symmetrically driven by 13.56 MHz pulsed power supply, the coupling electrodes being located outside the plasma tube. During the plasma phase, the monitoring of the formation/loss of NO is made by in situ time resolved TDLAS. Depending upon the experimental condition, a time resolution as high as 5 ms may be achieved. Experiments may be carried out with a closed reactor (no gas flow) or under flowing conditions.

In N2 plasma with small admixture of NO, NO molecules are efficiently destroyed in collisions with N-atoms [6], what makes it difficult to detect nitric oxide produced on the surface. On the contrary, after a nitrogen pre-treatment of the pyrex surface, and under O2 plasma, NO production is evidenced. Figure 1 shows such an example.

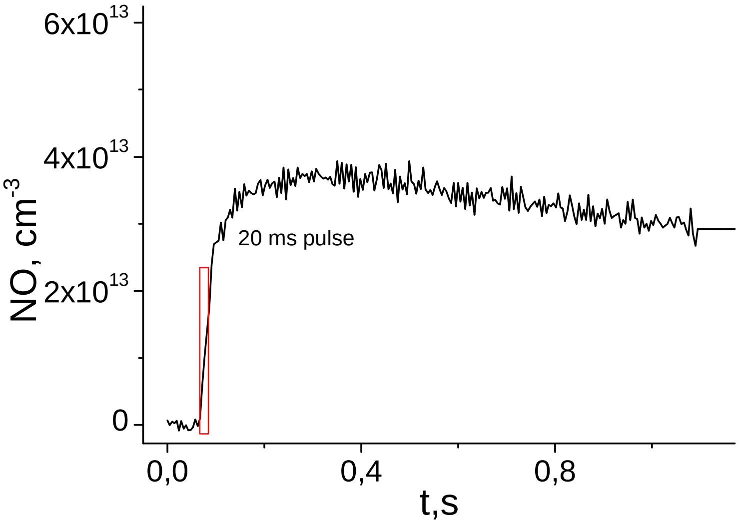

Figure 1. Production of NO molecules in a pure O2 plasma, after the pyrex surface of the reactor has been treated by 30 mn pure N2 plasma. The O2 plasma pulse is 20 ms (single shot), in a closed reactor. The monitoring of NO is made by in situ TDLAS with a time resolution of 5 ms.

It is shown that under O2 plasma pulses after N2 plasma pretreatment NO concentration reaches 1-10 10^{13} cm^{-3} depending upon the plasma pulse duration. Such a surface production corresponds to about 5-50 10^{12} cm^{-2} N atoms grafted on the pyrex surface during the N2 pretreatment. No NO formation is detected after an argon or oxygen plasma pre-treatment or a neutral nitrogen gas glow. By varying the length of N2 plasma column, proportionality between pretreated surface and amount of NO produced was verified.

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High resolution, low energy positron scattering from neon

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While positron scattering from the noble gases has been investigated both experimentally and theoretically for many years, there is large disagreement between different theories and experiments for even the grand total and total elastic cross sections. A new positron scattering apparatus has been constructed at the Australian National University, with an energy resolution of 60 meV, which promises to make highly accurate measurements of these cross sections, as well as for a host of other scattering processes.

The apparatus is based on a Surko trap [1], combined with a rare gas moderator, and provides a pulsed beam of positrons which is magnetically confined in a 500 gauss magnetic field. This beam is directed through a gas cell containing the target gas (neon in the case of this paper) and then energy analysed and detected using a retarding potential analyser and microchannel plate combination. The resultant energy spread contains information about the scattering cross sections for the positron-target interaction [2].

The goal of the work presented in this paper is to make some progress towards benchmark standards for positron scattering from rare gas targets. In addition to elastic and grand total scattering measurements, the total positron formation cross section has been measured and future plans to measure other processes, such as ionisation and electronic excitation will be presented.

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Progress on the construction of software tools designed to help solve the plasma chemistry data problem.

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Here we present progress on the construction of a sophisticated global model for plasma processing. Quantemol-P [1] (Q-P) builds upon GlobalKin [2], a non-equilibrium zero-d plasma source model that includes a Boltzmann solver for the electron energy distribution and a stiff ODE solver for the chemical kinetics. Q-P uses cross-section data and a model of plasma chemistries to help automate the process of chemistry generation and simulation. Both existing cross-section data and new cross-section data from Q-P's sister software tool Quantemol-N [3] are used to populate the database.

Quantemol-N calculations for electron-impact excitation and dissociation and are shown for CF2 giving effective cross-sections for the following reactions,

$$\begin{aligned} e + CF_2 &\rightarrow e + CF_2^*(^3B_1) \\ e + CF_2 &\rightarrow e + CF + F \\ e + CF_2^*(^3B_1) &\rightarrow e + CF_2 \\ e + CF_2^*(^3B_1) &\rightarrow e + CF + F. \end{aligned}$$

Q-P calculations are demonstrated for a chemical SF6/O2 plasma-enhanced silicon etch using an inductively coupled plasma source.

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Mode transitions in radio-frequency plasmas

Deborah O'Connell

Nonequilibrium calculations of the role of electron impact in the production of NO and its emissions

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Electron impact (photoelectron and auroral) in the Earth's upper atmosphere plays a major part in the production of nitric oxide and in infrared emissions from this species. The main production mechanism is electron impact ionisation and dissociation of atmospheric species, which produces $N(^2D)$ (excited N) that then reacts with O_2 to produce NO. A minor source is electron impact excitation of $N_2[A^3\Sigma_u^+]$, which reacts with O atoms to produce NO and $N(^2D)$. This $N(^2D)$ reacts with further O_2 to produce even more NO, enhancing the effect of this excitation source. The NO produced by $N(^2D) + O_2$ is vibrationally excited, leading to chemiluminescent infrared emissions. Recently direct electron impact excitation has also been shown to contribute to infrared emission by NO.

In order to investigate the importance of the $N_2[A^3\Sigma_u^+]$ source of NO, a model which predicts NO density in the atmosphere was developed. Above 130 km the NO density reaches a chemical equilibrium value that varies with solar insolation and auroral input. NO is transported downwards by molecular diffusion at altitudes above about 110 km and by eddy diffusion below this height. Vertical winds produced by auroral heating may also redistribute NO vertically. As a result of these transport processes the NO density does not reach a chemical equilibrium value at altitudes below 130 km, so a nonequilibrium calculation is required to predict the NO density in the region of its peak at around 110 km.

The model has been applied to predict the NO density profile in the upper atmosphere at the equator, and at 65° N with moderate auroral input. It was run with and without the $N_2[A^3\Sigma_u^+] + O$ reaction and in both the equatorial and high-latitude cases it was found that the contribution of this reaction is significant, and that the predicted densities are closer to the observed values when the $N_2[A^3\Sigma_u^+]$ contribution is included.

The model was then used to calculate the background NO density as part of an investigation of infrared emissions from NO. Auroral electron impact produces such emissions principally by chemiluminescent emission from NO* (vibrationally excited NO) that is produced by the $N + O_2$ reaction. However, measurements [1,2] of electron impact excitation of the first three vibrational levels of NO made possible calculations of the contribution of electron impact to the infrared emissions. It was found that the contribution is significant relative to chemiluminescence for the $v'=1$ level, while the smaller contribution for the other levels may nevertheless alter the spectrum from that of chemiluminescence in a way that could be exploited in remote sensing [3].

The nonequilibrium model to calculate NO density allowed a detailed calculation of these electron-driven infrared emissions for the particular conditions of a rocket measurement. It allowed both a calculation of the background NO density for the time and place, and of the increase in the density due to the auroral input. While there was a discrepancy between the absolute value of the predicted emissions and the experiment, it was found that the shape of the predicted spectrum of NO fundamental emissions matched the measurements better when direct electron excitation was included.

This simulation of the rocket measurements was recently repeated with new measurements [4] and theoretical calculations [5] of electron impact vibrational excitation of NO. In both cases the agreement with the measurements is improved for the $v'=1$ level [6], particularly using the new theoretical cross sections. However, the new values lead to an overestimation for $v'=2$.

In the three cases above, the reactions involved have a very wide range of reaction rates. Some of them (such as the excitation rates and radiative transition probabilities involved in calculating the production of $N_2[A^3\Sigma_u^+]$) have high rates so that equilibrium is reached in a small time. Others, such as those that produce and destroy NO, are sufficiently slow that the NO density does not reach chemical equilibrium in the time scale set by solar insolation and auroral variations. We use statistical equilibrium calculations for the fast reactions and time-step simulation for the slow reactions, so these two approaches need to be combined. For $N_2[A^3\Sigma_u^+]$ this is straight forward. The population densities of the excited states are calculated using statistical equilibrium and then imported into the time-step calculation. However, there are sets of related reactions, such as those involving $O^+(^4S)$, $O^+(^2D)$ and $O^+(^2P)$, where some of the reactions are too fast to be included in the time-step calculation. Our approach so far to these has been to identify the fast reactions and put an equilibrium calculation for each into the time-step code. We are currently looking at both conceptual and coding improvements to the methods of merging the equilibrium and nonequilibrium calculations.

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Rate coefficients for vibrational and electronic excitation of the CO molecule

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Low energy electron impact vibrational and electronic excitation cross sections of the CO molecule are measured by use of a high resolution crossed-beams double trochoidal electron spectrometer [1,2]. Rate coefficients for vibrational excitation of the carbon-monoxide molecule, via the $^2\Pi$ shape resonance in the energy region from 0 eV to 5 eV have been calculated. Calculations are performed for a Maxwellian electron energy distribution. By using extended Monte Carlo simulations the electron energy distribution functions and rate coefficients are determined in non-equilibrium conditions, in the presence of homogeneous electric and magnetic fields. Integral cross sections and rate coefficients for vibrational excitation of the excited carbon-monoxide molecule, via the $^2\Pi$ shape resonance in the energy region from 0 to 5 eV have been calculated. Cross sections are calculated by using measured cross sections for the ground level CO excitation and the most recent cross sections for elastic electron scattering, applying the principle of detailed balance. Calculations are performed [3,4] for typical, moderate values of the electric field over gas number density ratios, E/N.

The energy dependences of the near threshold resonant excitation of the valence and Rydberg states of the CO molecules have been measured. The cross sections of the near threshold resonant excitation of the a $^3\Pi$ valence state, and the b $^3\Sigma^+$ and B $^1\Sigma^+$ Rydberg states have been determined [5,6]. Rate coefficients for electronic excitation of the a $^3\Pi$ valence state, and the b $^3\Sigma^+$ and B $^1\Sigma^+$ Rydberg states of the carbon-monoxide molecule are performed for both Maxwellian and non-equilibrium electron energy distributions in the presence of homogeneous electric and magnetic fields in the energy region from 0 to 10 eV.

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Recent developments on PLASMAKIN – a software package to model the kinetics in gas discharges

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PLASMAKIN is a software package for handling physical and chemical data used in plasma physics modeling and for computing gas-phase and gas-surface kinetics data: particle production and loss rates, photon emission spectra and energy exchange rates. It can handle an unlimited number of chemical species and reactions, is independent of problem dimensions, and can be used in both steady-state and transient problems. The package supports a large number of species properties and reaction types, namely: gas or electron temperature dependent collision rate coefficients, vibrational and cascade levels, evaluation of branching ratios, superelastic and other reverse processes, three-body collisions, radiation imprisonment and photoelectric emission. Support of non-standard rate coefficient functions can be handled by a user-supplied shared library.

The library has been expanded to (a) include a module to compute the electron kinetics; (b) allow the simulation of emission spectra in the chemical kinetics module; (c) simplify data input and (d) develop a Python interface [1].

Presently, the electron kinetics is limited to the case of zero magnetic field. The electron velocity distribution function (evdf) can be obtained under two different sets of assumptions:

a) Spatially homogeneous electron density with the angular dependency on velocity represented by a two-term spherical harmonic expansion; and

b) Non-constant electron density with the electrons moving in the hydrodynamic regime. The evdf is represented by a density gradients expansion.

The first case can be used to study DC and HF discharges at relatively low reduced field (E/N) and solves the Boltzmann equation following the treatment in [2]. The second case is useful for moderate to high constant E/N, when non-conservative processes are important or high precision values of transport coefficients are needed. In this case the Boltzmann equation is solved following the treatment in [3].

The chemical kinetics module now includes the simulation of emission spectra in two idealized situations: infinite slab and infinite cylinder. In mixtures with atomic vapours, radiation trapping is taken into account assuming complete frequency redistribution in the laboratory rest frame [4].

The data input file, characterizing the species and reactions considered on a given discharge model, has been simplified with the use of a database of species properties.

The interface of procedures in the package has been engineered to allow the use from either Fortran or C programs. To allow prototyping or rapid development of programs using an interpreted language, a Python module providing function interfaces and classes has been developed [1] allowing access to the package when it has been compiled as a shared library.

Several examples of applications centered on the new capabilities will be presented.

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The dynamics of radio-frequency atmospheric pressure plasma jets

Timo Gans

Hollow Cathode Discharges: Volt-Ampere Characteristics and Space-Time Resolved Structure of the Discharge

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Hollow cathode discharges were studied almost as long as gas discharges. In addition to applications in spectrometry and ion gas lasers [1,2], plasma processing applications such as ion etching, thin film deposition, surface treatment [3] and analysis of nanostructured surfaces [4] have been recently introduced.

Compared to parallel plate glow discharges with similar dimensions and gas pressure, hollow cathode discharges have lower breakdown voltages and operate at lower voltages for the same current density [5,6]. Enhanced discharge efficiency is due to the fast electrons and ions, which are confined inside the cathode hole [7]. When a negative glow regions facing the opposite cathode surfaces overlap, “hollow cathode effect” appears. Hollow cathode effect is the most specific feature of these devices. It is manifested as a large increase in the current density and discharge light intensity followed by a drop of a sustaining voltage. Appearance of this effect depends on both geometry and properties of the discharge.

Our aim was to establish a relationship of the discharge structure to the electrical properties in a wide range of discharge currents for steady state conditions, but also in transient stages during formation of the discharge. We were particularly interested in formation of the hollow cathode effect. Analysis of formation and maintenance of the hollow cathode discharges is based on comparisons with more simple parallel-plate discharges (e.g. [8]).

We use a commercial hollow cathode lamp which is normally applied as a spectral source. The lamp is a sealed glass tube filled with Ne (p=3.5 Torr) containing a Mn cylindrical hollow cathode open at one end and a ring shaped anode. Cathode hole is 3 mm in diameter and 15 mm long. Our measurements include ICCD imaging of the discharge emission, supported by voltage and current measurements. It was possible to identify and explain several critical points in the Volt-Ampere characteristics where the shape of the discharge changes.

We believe that such measurements may be of interest for micro discharges where hollow cathode geometry is often applied albeit the conditions for the hollow cathode effect are not always met. Thus, one may perhaps check the regime of operation from the Volt-Ampere characteristics.

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An overview of post-discharge systems used for plasma sterilization

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In the last decade the use of polymer based heat sensitive tools in the medical praxis or pharmaceutical industry have brought the need of new low temperature sterilization and decontamination methods, which ensure complete inactivation or removal of all possible infectious microorganism: e.g. bacterial spores, viruses, or other potentially harmful biological residuals: e.g. endotoxins, proteins, present on the used instruments. For the heat sensitive medical devices the most common sterilization methods in use are based on chemical treatment, which imply toxic active agents, or exposure to ionizing radiation, which may alter the bulk properties of polymers being sterilized.

A new method, which overcomes these drawbacks, implies the use of low-temperature plasmas. Low-temperature plasmas can be created either at atmospheric or low ($p \leq 10$ Torr) pressures. Numerous experimental studies have been carried out in different discharge configurations in a wide pressure range: i.e. atmospheric e.g. [1,2], mTorr [3,4] and Torr regions [5,6] in various gas mixtures: e.g. N_2 [3], O_2 [3], N_2-O_2 [2,7], Ar [8], Ar-O_2 [9], Ar-H_2 [4], O_2-CF_4 [10], in order to test the sterilizing ability of these plasmas. Either the active discharge regions have been used [3,4,10], or the afterglow region of discharges [2,9]. The afterglow is believed [5] to have advantage over the discharge region since it provides at relatively low temperatures high concentration of chemically active radicals, such as excited species and UV photons, capable to inactivate microorganisms, while is free of charged species, which may be damage the material to be sterilized. The post-discharges of N_2-O_2 and Ar-O_2 microwave discharges, shown to be efficient sterilizers, have been extensively investigated [5,6,9]. Although the reaction kinetics in the afterglow is more simple than in the active discharge region, it is difficult to isolate the action of different species as has been done in [11], when the role of H atoms, Ar^+ ions and O atoms in the etching of bacteria spores has been investigated. The numerical model of such a post-discharge system provides the spatial distribution of absolute densities of active species in the sterilization reactor as a function of discharge parameters, and thus contributes to the identification of the species relevant for sterilization under given conditions and to the understanding of the processes occurring in the system. Further, the numerical results can help in the optimization of the experimental systems.

A post-discharge system can be described with two different models valid for the discharge and early afterglow region, and for the late afterglow present in the large reactor, respectively. The species densities in the discharge region are calculated with a 1-D kinetic model, which solves the homogeneous electron Boltzmann equation coupled together with the rate balance equations describing the creation and destruction of different species. The concentrations obtained for the steady-state discharge are used as initial values to the early afterglow taking place in the tube connecting the discharge to the main reactor, where the same system of rate balance equations for species is solved in time under zero electric field. The evolution of the species densities in the post-discharge reactor are followed with a 3-D hydrodynamic model composed of: (*i*) the total mass conservation equation (*ii*) the momentum conservation equation, (*iii*) the energy conservation equation and (*iv*) the species continuity equations [12]. In the post-discharge model only the neutral active species are taken into account, since due to recombination the density of ions and electrons become negligible at the end of the early afterglow region.

With the aim to understand the processes occurring in the sterilization system and to contribute to their optimization, an N_2-O_2 microwave discharge and its afterglow have been studied by investigating the effect on the species densities distribution in the reactor of several parameters: (*i*) distance between the discharge and post-discharge reactor,(*ii*) discharge characteristics: tube radius, microwave field frequency, input power, (*iii*) gas pressure, (*iv*) initial gas mixture composition and (*v*) gas flow rate. The model is validated by comparing the measured emission intensities with the calculated densities of emitting species.

In the presentation a full characterization of this system will be given, both the advantages and disadvantages of the system will be discussed, as well as the contribution of the modeling results to the understanding of sterilization processes.

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Cross section Data for Modeling Non-equilibrium Plasmas in N_2O

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In this paper we present a swarm analysis of electron scattering cross sections in nitrous oxide (N_2O). Experimental results for drift velocities and effective ionization coefficients, obtained by using a Pulsed-Townsend technique [1] over a broad range of the density-normalized electric field strength (E/N), were compared with numerical solution of Boltzmann equation in two term approximation [2] and with the results of Monte Carlo simulations [3]. Measurements and calculations were performed for pure gas and for a number of N_2O/N_2 mixtures up to 80% of N_2O. The cross section set for nitrogen that we have used is well established and well tested and it was taken from the *Sigmalib* database of cross sections [2].

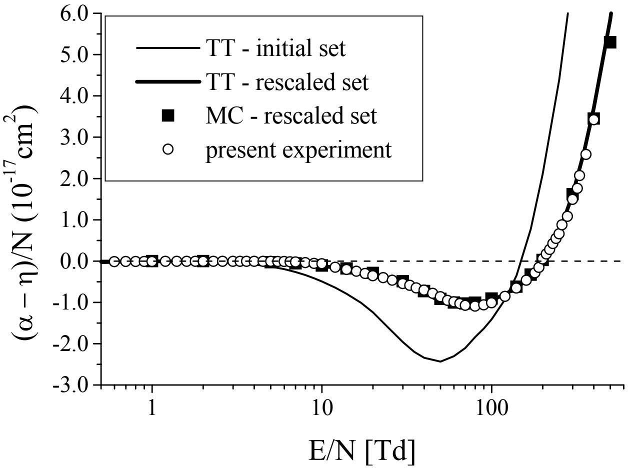

Fig1. A fit of the effective ionization coefficient

Our analysis shows that commonly used sets of cross sections [4, 5] for N_2O have to be modified in order to fit experimental data, in particular the dissociative attachment and electronic excitation cross sections (with the threshold energy of 4.0 eV). In Figure 1 we show the fit of effective ionization coefficient obtained with the initial and rescaled set of cross sections for pure N_2O.

In order to complete the data base for modeling non equilibrium plasmas and plasma devices containing N_2O, a number of transport and rate coefficients for the case of both DC and RF electric and magnetic fields were calculated. A behavior of transport coefficients under the influence of the magnitude and the frequency of the fields was studied separately revealing some complex features in the time dependence, such as anomalous anisotropic diffusion and time-resolved negative differential conductivity.

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SiO2 deposition by microplasma jets

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Organic and inorganic silicon dioxide films have been deposited by means of an atmospheric pressure microplasma jet. Tetramethylsilane (TMS), oxygen, and hexamethyldisiloxane (HMDSO) are injected into argon as the plasma forming gas. In case of TMS injection, inorganic films are deposited if an admixture of oxygen is used or if the substrate temperature exceeds 200°C. In case of HMDSO injection, inorganic films can be deposited at room temperature even without any oxygen admixture: at low HMDSO flow rates (< 0.1 sccm), SiOxHz films contain no carbon and exhibit an oxygen to silicon ratio close to 2 according to X-ray photoelectron spectroscopy (XPS). At high HMDSO flow rates (> 0.1 sccm), SiOxCyHz with up to 21 % of carbon are obtained. The transition between organic to inorganic film is confirmed by Fourier transformed infrared spectroscopy (FTIR). The deposition of inorganic SiO2 films from HMDSO without any oxygen admixture is explained by an ion-induced polymerization scheme of HMDSO.

Progress report: Direct injection of liquids into low-pressure plasmas

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While laboratory based plasmas are always in contact with solid surfaces (often vacuum chambers) they have historically been formed in gas environments. In more recent times, the use of plasmas has grown to include plasma contact with liquids including biological items. Inevitably the plasmas in contact with liquids had been at or near atmospheric pressures. This need not be the case.

We have developed a novel method for injecting liquids directly into low-pressure discharges. As such, this technique opens new areas of possible industrial use for plasmas. For example, we have injected inorganic nano-particles into argon plasma by suspending them in hexane (or ethanol) as a high vapor pressure liquid carrier. As a result, we believe that metals, dielectrics, superconductors, aromatics, proteins, viruses, etc. could all potentially be injected into low-pressure plasma environments using this technique. The resulting films indicate the ability to synthesize nano-structured composites.

The technique also opens new areas of plasma science research. For example we find that the plasma reacts in fascinating ways to the pressure wave induced by the injection process. This is seen in the emission from the discharge as shown Figure 1. Models of the inject liquid have also been developed. The model indicates that the time required for the droplet to fully evaporate is a function of the background pressure, initial (wall) temperature, the number of droplets inserted simultaneously and initial size. A typical evaporation time for a 50 micron diameter droplet is ~3 seconds for hexane and up to 10 seconds for ethanol without plasma. The presence of plasma can reduce these times greatly. In the first few milliseconds after insertion into the low-pressure environment, the droplet temperature plummets as the first few microns evaporate. The temperature falls to a minimum value where the heat flow in and out of the droplet balances. After the solvent has fully vaporized, the remaining solute can be heated by the plasma to as high as 700K. All this can take place within 0.5 sec. Typical droplet parameter curves are shown in Figure 2.

This work was funded in part by a grant from AFOSR through the SPRING consortium, contract FA 9550-05-1-0393

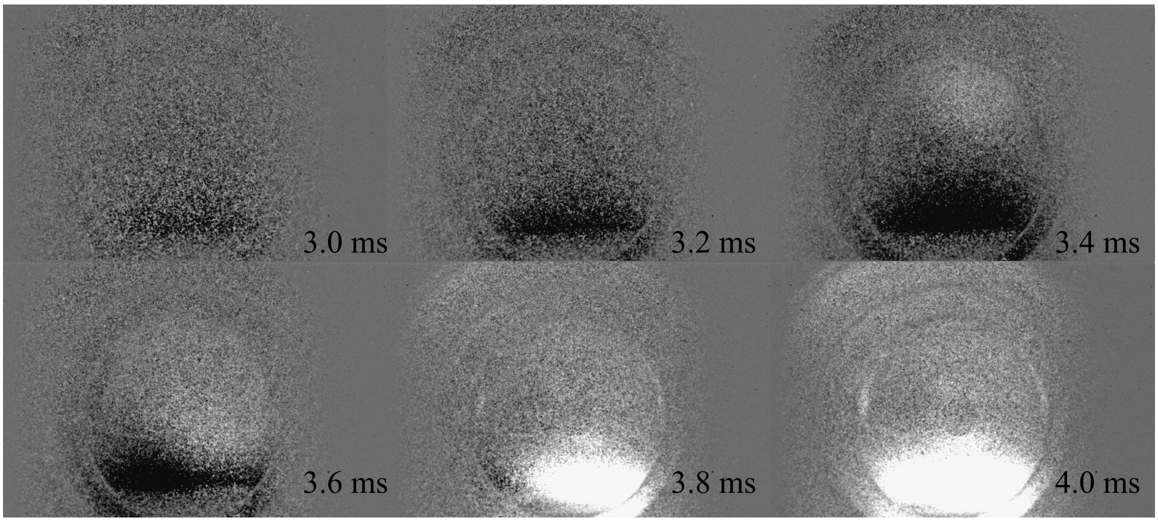

Figure 1: Time sequence of change in emission during N_2 injection into Ar plasma. Change in emission is determined via background subtraction. Here black represents a decrease in emission, white represents an increase and gray is no change. Time is given relative to initiation of injection.

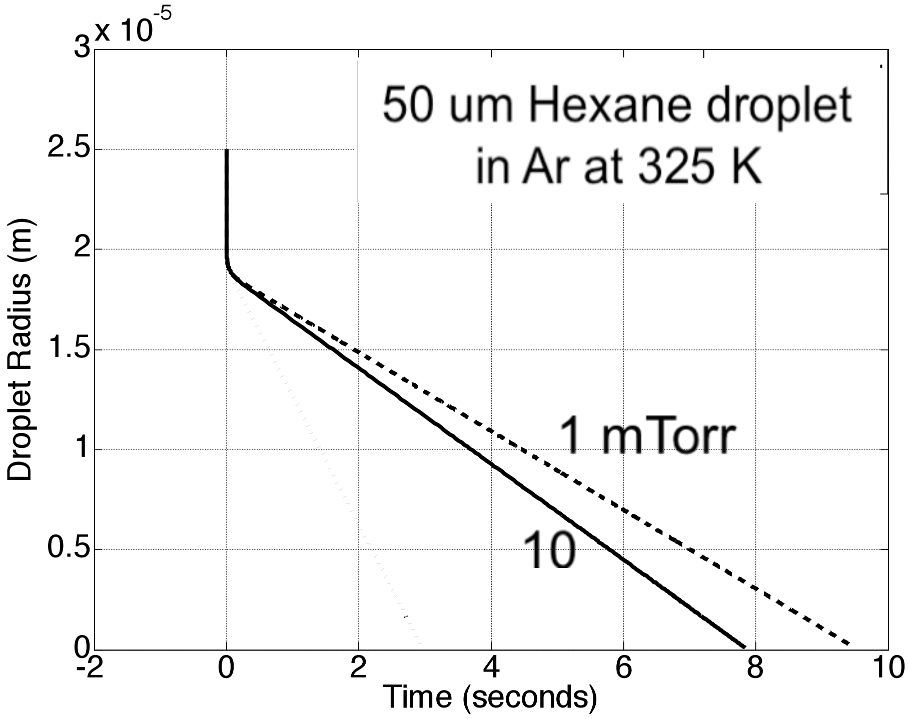

Figure 2: Time sequence of 50 μm n-hexane droplet injected into 1 a nd 10 mTorr Ar. Plasma greatly speeds this evaporation rate.

Effects of friction on modes in collisional multicomponent plasmas

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Plasmas both in the laboratory and in space are frequently in the state of partial thermodynamic equilibrium (i.e., with an initial temperature disparity of the plasma constituents). Collisions in such plasmas will after some time eventually result in equal temperatures of the species, implying an evolving plasma. There exists a long standing controversy in the literature, which deals with the effects of this temperature disparity on the perturbations in such an evolving plasma, more precisely on the ion acoustic (IA) waves. In Ref. 1 it is claimed that the corresponding energy transfer may result in the instability of the acoustic mode at large wavelengths (within the quasi-neutrality limit), and that this growth may be described within the fluid theory. The necessary condition for the instability obtained in Ref. 1 for an electron-ion plasma is, in fact, very easily satisfied because it requires only a very small temperature difference between the two species (electrons and ions), viz. Te>4 Ti/3. This instability condition is obtained by using the energy equations including the source/sink terms originating from the collisional transfer, together with the corresponding friction force terms in the momentum equations. The sufficient instability condition is stronger because of additional dissipative effects, like viscosity and thermal conductivity.

However, the current-less instability described in Ref. 1 is based on a model which disregards the same temperature disparity in the description of the spatially homogeneous background, which, due to the same reasons, must be time evolving. In other words, the effects of collisions in the background plasma have been explicitly neglected. Note that because of the time evolution, the term background is used instead of the equilibrium. These effects of collisions have been discussed in Ref. 2, published one year after Ref. 1, and for the same quasi-neutrality case. There, it is claimed that there is no instability for any temperature ratio of the two plasma components, and moreover, that this holds even in a current-carrying plasma, as long as the difference between the electron and ion equilibrium velocity remains below the sound speed. All that was needed to come to that conclusion was to let the background plasma evolve freely in the presence of the given temperature difference.

However, we observe that Ref. 2 has apparently remained almost unnoticed by researchers, in contrast to the widely cited Ref. 1.

In the present work, this controversy is revisited for any two-component plasma. Essential for the problem is the energy equation describing the temperature variation. In the simplified form that we shall use, it contains only the collisional energy transfer source/sink term on the right-hand side. This simplified form is used for clarity only because, according to Ref. 1, in the absence of currents, that term alone is supposed to yield an instability. The results obtained here can be summarized as follows. i) The friction does not affect the IA mode in the limit of quasi-neutral perturbations. ii) Even using the non-evolving model equivalent to Ref. 1, there is no instability of the IA mode, contrary to claims from Ref. 1. iii) When the background plasma is properly described as evolving in time, and as long as the quasi-neutrality is used, collisions do not produce a growth of the ion acoustic mode. iv) When the Poisson equation is used instead of quasi-neutrality, in principle there is a possibility for a positive growth-rate of the IA mode. It appears as a combined effect of the breakdown of the charge neutrality from one side (introduced by the Poisson equation), and the heat transfer (the compressibility and advection in energy equation) from the other side, all within the background of a time-evolving plasma. However, as the equilibrium plasma evolves in time, with the relaxation time τ, the obtained growth time must be (much) shorter than the relaxation time. Yet, this shows to be impossible and we conclude that there is no instability in the electron-ion plasma with an initial temperature disparity if the plasma evolves freely and if there is no a source acting in such a way as to maintain the temperature difference.

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Two-dimensional dusty plasma crystals and liquids

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Strongly coupled plasmas - in which the average potential energy per particle dominates over the average kinetic energy - appear in a wide variety of physical systems [1]. Among these systems, dust plasma crystals and liquids realized in low-pressure gas discharges by dispersing mesoscopic grains into the plasma have attracted a lot of attention during the past years. Quasi-two-dimensional (single layer) configurations of dust particles can be created using a horizontal planar electrode arrangement. Here the dust layer is levitated near the sheath edge of the lower electrode due to the balance between gravity and the electrostatic force acting on the grains (which acquire a high negative charge in the plasma). The grain-grain interaction in such systems can be well described through a Yukawa potential, which accounts for the Coulomb repulsion of charged dust particles and for the screening by the embedding plasma.

We describe the experimental realization of the quasi-two-dimensional dust system; summarize the basics of the computer simulation and theoretical approaches capable of their description in the liquid and solid phases. We discuss the properties of the dynamical density and current correlation spectra, generated by molecular dynamics simulations [2,3]. Three different collective excitations develop in the systems: in the liquid phase (i) the compressional (longitudinal) mode exhibits a quasi-acoustic dispersion, (ii) the in-plane shear (transversal) mode is acoustic with a cutoff at finite wave number, and (iii) the out-of-plane transversal mode is of optical nature [4]. Harmonic generation due to nonlinear wave-wave interaction is also observed.

We also address the issues associated with the existence of different structural phases [5] and transport coefficients (e.g. superdiffusive behavior) [6] in the low-dimensional system under study.

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Cross Sections and Transport Properties of Negative Ions in Rare Gases

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Negative ions determine kinetics of electronegative plasmas [1] and their presence may change critically the nature of plasmas (examples of obvious changes can be seen in [2]). Ion-Ion plasmas [3] have very distinct characteristics. Numerous applications relay on electronegative reactive gases including plasma etching [4], atmospheric plasmas for biomedical application [5], and many more. Furthermore, negative ions may be used directly, for example to reduce the charging [6] of high aspect ratio structures or to be converted to fast neutrals with the aim to achieve fast neutral etching [7]. Modeling of such processes requires either cross sections or transport data or both.

The purpose of this work is to provide plasma modelers with cross section data and transport coefficients that may be used in simulations of plasmas containing negative ions. It is important to represent properly the effect of detachment on the transport coefficients, as detachment is a nonconservative process.

We have determined a set of cross sections for negative halogen ions in rare gases based on the available experimental transport data [8,9] in a wide range of reduced electric field E/N of 1 Td - 1000 Td by employing a standard swarm technique. The resulting momentum transfer cross section is supplemented by detachment cross section [10,11] that was

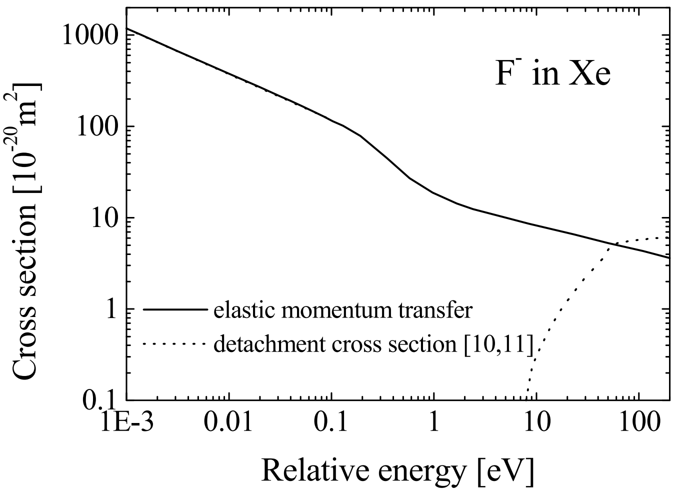

Figure 1. Cross sections for F^- in Xe.

used from the threshold around 6 eV up to 100 eV. As an example of obtained cross sections, in fig. 1 we show the derived momentum transfer cross section for F^- in Xe.

The procedure used here to determine the cross sections is to apply first the MTT which is fast albeit with limited accuracy to fit the cross sections until the transport data fit the experimental results. In the next step further, but always slight adjustments are made to have a good agreement between experimental data and MC calculations which provide exact results. Normally, the disagreement between MTT and MC (and thereby experimental) results was within 11% for all gases.

The cross sections provided here should be employed with the assumption of isotropic scattering and are very accurate in the region covered by the experiments. We have extrapolated data to somewhat higher energies based on behavior of similar ions in similar gases and by the addition of reactive processes so a relatively complete set was derived which can be used in modeling of plasmas by both hybrid, PIC (particle in cell) and fluid codes [1,12]. It is important to note that so far the data presented here and other similar results were interpreted by using interaction potentials [13] which while producing results of high accuracy is not directly applicable in plasma modeling. As both hybrid and PIC models involve MC simulations for collisions and as applications to plasma etching devices requires control of negative ions in the afterglow or for neutralization [7,14] the data for cross sections of negative ions found in argon-fluorocarbon mixtures are of great importance.

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MODELING OF NON-THERMAL PLASMA IN FLAMMABLE GAS MIXTURES

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An idea of using plasma-assisted methods of fuel ignition is based on non-equilibrium generation of chemically active species that speed up the combustion process. It is believed that gain in energy consumed for combustion acceleration by plasmas is due to the non-equilibrium nature of discharge plasma, which allows radicals to be produced in an above-equilibrium amount. Evidently, the size of the effect is strongly dependent on the initial temperature, pressure, and composition of the mixture. Of particular interest is comparison between thermal ignition of a fuel-air mixture and non-thermal plasma initiation of the combustion. Mechanisms of thermal ignition in various fuel-air mixtures have been studied for years, and a number of different mechanisms are known providing an agreement with experiments at various conditions. The problem is – how to conform thermal chemistry approach to essentially non-equilibrium plasma description. The electric discharge produces much above-equilibrium amounts of chemically active species: atoms, radicals and ions. The point is that despite excess concentrations of a number of species, total concentration of these species is far below concentrations of the initial gas mixture. Therefore, rate coefficients for reactions of these discharge produced species with other gas mixture components are well known quantities controlled by the translational temperature, which can be calculated from the energy balance equation taking into account numerous processes initiated by plasma.

A numerical model was developed combining traditional approach of thermal combustion chemistry with advanced description of the plasma kinetics based on solution of electron Boltzmann equation. This approach allows us to describe self-consistently strongly non-equilibrium electric discharge in chemically unstable (ignited) gas. Equations of pseudo-one-dimensional gas dynamics were solved in parallel with a system of thermal chemistry equations, kinetic equations for charged particles (electrons, positive and negative ions), and with the electric circuit equation. The electric circuit comprises power supply, ballast resistor connected in series with the discharge and capacity. Rate coefficients for electron-assisted reactions were calculated from solving the two-term spherical harmonic expansion of the Boltzmann equation. Such an approach allows us to describe influence of thermal chemistry reactions (burning) on the discharge characteristics.

Results of comparison between the discharge and thermal ignition effects for mixtures of hydrogen or ethylene with dry air will be reported. Effects of acceleration of ignition by discharge plasma will be analyzed. In particular, the role of singlet oxygen produced effectively in the discharge in ignition speeding up will be discussed.

Comparison of Decontamination Properties of the Impedance-Stabilized Negative and Positive Corona Discharge

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Various concepts of the corona discharge applications in decontamination or sterilization of material surfaces, liquids and gases were studied in many previous publications. The low power of the discharge represents the basic limitation of its applications in this field. The power ranges from hundreds of milliwatts up to units of watts. The discharge transits in to a spark when its voltage exceeds a particular limit.

To stabilize the discharge and consequently to increase its power, we used the parallel resistor-capacitor impedance connected serially to the discharge. Incorporating these stabilizing components into the electrical circuit, the maximal discharge current increases for about six times. Further increase was limited by the parameters of used high voltage power supply only.

Decontamination abilities of the stabilized positive and negative corona discharge were tested on the bacterium *Staphylococcus epidermidis*. The bacterial suspension was placed in wells of the dot plate. Its volume was 400 μl and its concentration was 2200 cfu (colony forming units) ml^{-1}. This suspension was used as a plane electrode and was grounded by immersed wire. Stabilized positive or negative corona discharge was generated at the tip of injection needle as the point electrode placed vertically 6 mm above the suspension. The samples of bacterial suspension were exposed for 2 minutes to the positive and negative corona discharge, respectively. The used discharge voltage was approximately $V = 7$ kV and average current $I = 150$ μA. Consecutively, 40 μl of each bacterial suspension was inoculated onto the surface of Mueller-Hinton agar as a cultivating medium and incubated overnight. The numbers of bacteria before the exposition and of survived bacteria after the exposition were evaluated by the visual counting of bacterial colonies grown on the agar after the incubation.

In case of the negative corona discharge, the concentration of living bacteria decreased to 35 % of their original number, whereas 99.5 % of bacteria were inhibited by the positive corona discharge.

This research has been supported by the MSM 6046137306 and MSM 0021620806.

2nd International Workshop on Nonequilibrium Processes in Plasma Physics and Studies of Environment

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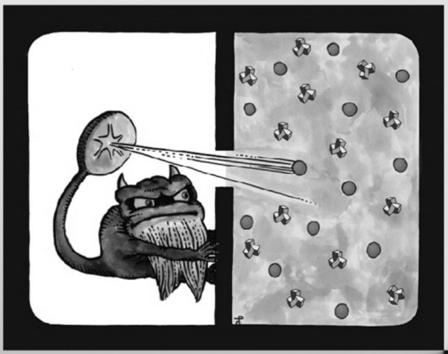

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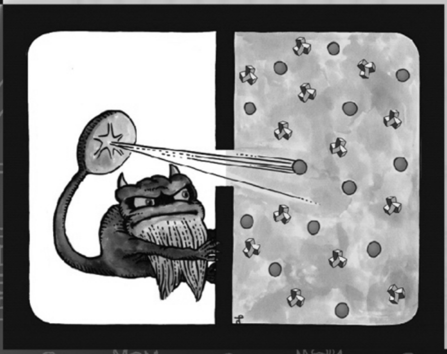

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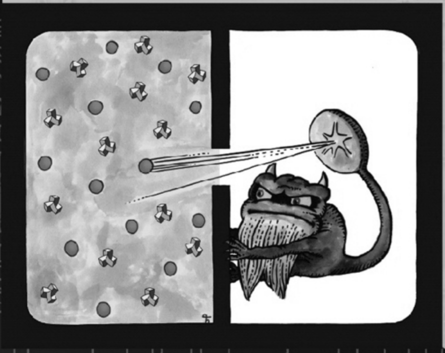

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