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Boltzmann-Equation Simulations of Radio-Frequency-Driven, Low-Temperature Plasmas

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Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550
for the United States Department of Energy
under Contract DE-AC04-94AL85000

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Boltzmann-Equation Simulations of Radio-Frequency-Driven, Low-Temperature Plasmas

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Abstract

We present a method for the numerical solution of the Boltzmann equation (BE) describing plasma electrons. We apply the method to a capacitively-coupled, radio-frequency-driven He discharge in parallel-plate (quasi-1D) geometry which contains time scales for physical processes spanning six orders of magnitude. Our BE solution procedure uses the method of characteristics for the Vlasov operator with interpolation in phase space at early time, allowing storage of the distribution function on a fixed phase-space grid. By alternating this BE method with a fluid description of the electrons, or with a novel time-cycle-average equation method, we compute the periodic steady state of a He plasma by time evolution from startup conditions. We find that the results compare favorably with measured current-voltage, plasma density, and excited state densities in the "GEC" Reference Cell. Our atomic He model includes five levels (some are summed composites), 15 electronic transitions, radiation trapping, and metastable-metastable collisions.

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Acknowledgment

The authors acknowledge informative discussions with J.B. Gerardo, W.N.G. Hitchon, M. Kushner, R.T. McGrath, and A.V. Phelps.

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Executive Summary

We have previously published a comparison of theoretical and experimental results on the radio-frequency driven He discharge (J. Appl. Phys., Vol. 75, p.2789, 1994). That publication represents the first successful prediction of the behavior of this type of discharge by an ab initio theory as verified by comparison with quantitative experimental measurements. In this report we elaborate on the numerical procedures used in the theory. We present a method for the numerical solution of the Boltzmann equation (BE) describing low temperature plasma electrons. We apply the method to a capacitively-coupled, radio-frequency-driven He discharge in parallel-plate geometry which contains time scales for physical processes spanning six orders of magnitude. By alternating this BE method with a fluid description of the electrons, or with a novel time-cycle-average equation method, we compute the periodic steady state of a He plasma by time evolution from startup conditions. We find that the predicted results compare favorably with the measured current-voltage, plasma density, and excited state densities obtained from experiment.

Boltzmann-Equation Simulations of Radio-Frequency-Driven, Low-Temperature Plasmas

1. Introduction

There has been a considerable interest in low temperature plasma discharges for over half a century. Practical applications of these plasmas include pulsed power, lighting, lasers, semi-conductor processing, and materials modification. In this paper, we will be concerned with the simulation of capacitively-coupled, radio-frequency (rf) driven plasmas which have a quasi-one-dimensional geometry in the active plasma region. We compare to measurements in the GEC Reference Cell[1], which is a laboratory device designed to facilitate comparisons of plasma diagnostics taken at different laboratories. The cell also simulates conditions in some designs of commercial semi-conductor-etching reactors. It is so named because of its conception at the 1989 Gaseous Electronics Conference. Typical gas pressures can range from tens to hundreds of mTorr, with the ionization fraction remaining quite small, on the order of 0.0001 or less. The plasmas are driven by applied 13.56 MHz rf potentials of tens to hundreds of volts across a one inch electrode separation. These discharges are not at thermal equilibrium and appear not to be well characterized by local field descriptions. The electron "temperatures" may reach several tens of thousands of degrees (several eV) and can drive electronic and chemical reactions which require very high temperatures.

In the operational region of interest to us there is an almost exponential dependence of the plasma density on the applied field. This suggests that accuracy in the theoretical simulation of these plasmas is essential because small errors in certain aspects of the simulation could lead to unpredictable results. An accurate simulation requires, among other things, that we compute electronic rates from the electron distribution function, and that we evaluate the electric field self-consistently within the plasma. The rates are not constant in space or time, nor simply related to the local field or mean electron energy. Thus, any model which hopes to do better than exhibiting, at best, *qualitative* behavior must be able to reliably and self-consistently determine rates for all contributing processes.

Fluid or so-called "continuum" methods are, by themselves, unable to provide rates for accurate simulation of non-Maxwellian plasmas. Instead, a Boltzmann equation (BE) type of solution, which incorporates an electron velocity distribution, is required. Approaches to combining the ab-initio character of the BE with the computational speed of the fluid description have been presented[2]. One still needs efficient numerical methods for the generation of solutions of Boltzmann's equation. These include direct solutions of Boltzmann's equation via finite-differences[3], polynomial expansions[4,5], methods of characteristics (also called convective schemes)[6,7], and separation of variables[8]. Other Boltzmann-like solutions have been obtained via PIC/Monte Carlo methods[9,10]. These Boltzmann methods provide much more information than a fluid model, but they are computationally intensive, requiring hundreds of times more computer time than a fluid calculation over the same time interval.

Some of these Boltzmann methods have been developed into very reliable and robust computer codes, capable of detailed simulations of the plasma. However, by themselves, they require far too much computer time to be of practical use for other than short simulations of plasma transients. This situation arises because of the tremendous range of time scales associated with different constituents of the plasma. For instance, collision and plasma periods can be as small as 0.1 ns. On the other hand, characteristic times for ions are on the order of microseconds, and metastables equilibrate on diffusion time scales which may be as long as milliseconds. The time steps in an explicit Boltzmann solution must be sufficiently small to resolve *all* of these processes. Thus, the plasma may take milliseconds to reach a steady state, and the BE might have to step through the calculation with picosecond time steps requiring 10^9 iterations.

To deal with this problem, we have developed 'mixed' hybrid procedures which treat the electrons *both* with the Boltzmann equation *and* with fluid-like equations, while maintaining fluid descriptions for the heavy species under all conditions. The *mixed* hybrid notion arises, in our context, when we alternate our treatment of the electrons between a Boltzmann and a fluid or averaged description. Since a fluid-like description of the heavy species is always maintained, we are characterizing the ion energy as a mean value, even at the electrodes. Our 'mixed' hybrid is distinguished from conventional hybrid schemes, in the sense that the conventional use of the term 'hybrid' arises from the fact that electrons are treated differently than ions. Typically, electrons are treated kinetically while ions are treated as a fluid. In our 'mixed' scheme, we treat *electrons* alternately as either kinetic or fluid particles. It is this duality of the electrons that constitutes what we regard as our mixed hybrid.

We have, in fact, developed two distinct mixed hybrid methods. Both methods treat the heavy species hydrodynamically. The hybrids we will discuss refer to the mixed treatment of the *electrons*. The first is a Boltzmann-Equation/Fluid-Equation (BE/FE) procedure. It is fully self-consistent with the Poisson equation and alternately solves the Boltzmann and fluid equations for the electrons. Typically, the Boltzmann equation is solved for only a few rf cycles and generates rates and mobility constants which are then used in the fluid equations, which, in turn, are solved for hundreds of rf cycles, and so on.

Our second mixed hybrid code, which is used exclusively in this work, is referred to as a Boltzmann-Equation/Average-Equation (BE/AE) procedure. Here again, the electron Boltzmann equation is self-consistently solved with the Poisson equation and the heavy particle FE for only a few rf cycles. Based on information gained from the Boltzmann solution, a set of average equations (AE) is then used to advance only the heavy species in a fixed, time-averaged, effective electric field. Electrons are ignored in the AE - the electron density is simply increased or decreased with the change in positive ion density. The electron distribution function is allowed to readjust when the Boltzmann solution is restarted. The AE can be solved for many rf cycles before returning to the BE, but we have not found an automatic method for self-determination of the length of the AE intervals in the BE/AE hybrid.

2. Method of Solution

2.1 Boltzmann equation

At the heart of our calculations is an explicit time-dependent numerical solution of the electron Boltzmann equation[6,8]. We directly solve the Boltzmann equation in a three-dimensional phase space which includes one configuration-space and two velocity-space dimensions. The Boltzmann equation for electrons in this 1D-2V geometry is

$$\left[\frac{\partial}{\partial t} + v_z \frac{\partial}{\partial z} + \frac{qE}{m_e} \frac{\partial}{\partial v_z} \right] f_e(z, v_z, v_r, t) = \Gamma(z, v_z, v_r, t). \quad (1)$$

Here, $f_e(z, v_z, v_r, t)$ is the electron velocity distribution function (EVDF), and $\Gamma(z, v_z, v_r, t)$ is the collision operator, containing all of the electron scattering information[11]. Generally we will be investigating plasmas in which the fractional ionization of the gas is less than 0.0001 so that electron-ion and electron-electron collisions can

be ignored. Thus the binary collision assumption in the BE is assured and collective screening effects are negligible.

Γ consists of an in-scatter term Γ^+ , and an out-scatter term Γ^- which contain respectively the electron scattering rates into and out of a phase-space volume element located at (z, v_z, v_r) . Thus,

$$\Gamma(z, v_z, v_r, t) = \Gamma^+ - \Gamma^- \quad (2)$$

Γ^+ and Γ^- may each contain several components corresponding to each of the collision processes included in the model. The numerical evaluation of the collision integrals is simplified if we neglect the electron mass compared to the atomic mass, and also if we treat the differential cross sections as isotropic. The latter is a fair approximation for electron-neutral scattering if we use the momentum-transfer elastic cross section in place of the total elastic cross section. Explicit expressions for Γ^+ and Γ^- , under conditions of isotropic scattering, and a Lorentz gas (ie. limit of $m_e = 0$), can be written using the following definition of the angle-averaged EVDF,

$$\bar{f}(z, v, t) = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^\pi \sin(\theta) d\theta f = \frac{1}{2} \int_0^\pi \sin(\theta) d\theta f, \quad (3)$$

where θ is the scattering angle measured from the electric field direction $\hat{z}$.

For *elastic* scattering, the out- and in-scatter terms, Γ_{el}^- and Γ_{el}^+ are, respectively,

$$\Gamma_{el}^- = n_0 v \sigma_{mt}(v) f, \quad (4a)$$

and

$$\Gamma_{el}^+ = n_0 v \sigma_{mt}(v) \bar{f}. \quad (4b)$$

Here, n_0 is the neutral gas density and σ_{mt} is the momentum transfer scattering cross section. The momentum transfer cross section is used in order to obtain the correct lowest moment of the scattering integral when using isotropic cross sections. The above elastic scattering terms produce only angular relaxation of the EVDF. Electron energy relaxation is mainly driven by inelastic excitation processes, but there is a small correction due to atomic recoil in elastic scattering. This effect is important in the plasma bulk, where electron energies may fall below an eV. Electron cooling, to order m_e/M (the electron:atom mass ratio), due to elastic collisions is contained in the angle-averaged term [4]

$$\Gamma_{cool} = (m_e/M) n_0 v^{-2} \frac{\partial}{\partial v} (v^4 \sigma_{mt}(v) \bar{f}). \quad (5)$$

This cooling term is the leading correction to the Lorentz-gas approximation contained in Eqs.(4a) and (4b).

For *inelastic* collisions, the out-scatter term for atomic transitions $i \rightarrow j$ is

$$\Gamma_{ij}^- = n_i v \sigma_{ij}(v) f. \quad (6a)$$

The corresponding in-scatter term is

$$\Gamma_{ij}^+(v) = n_i (v'^2/v) \sigma_{ij}(v') \bar{f}(v'), \quad (6b)$$

where,

$$v'^2 = v^2 + (2/m_e)(W_j - W_i).$$

Here, W_i and n_i are, respectively, the energy and density associated with the i th atomic level and σ_{ij} is the cross section for the $i \rightarrow j$ transition. Note that these relations are valid for inelastic and superelastic transitions. Detailed balance is used to relate the upwards and downwards cross sections.

The out-scatter term due to ionization of the i th atomic level is

$$\Gamma_i^- = n_i v \sigma_i^{ion}(v) f, \quad (7a)$$

where σ_i^{ion} is the cross section for ionization of the i th atomic level. We use an approximation for the ionization inscatter term that assumes the ejected electron and the scattered incident electron share the available energy with a fixed partitioning. With this assumption, the associated in-scatter term has two components, taking account of the incident electron and the secondary electron produced during the ionization.

$$\begin{aligned} \Gamma_i^+ = & n_i \frac{v'^2}{(1-\chi)v} \sigma_i^{ion}(v') \bar{f}(v') \\ & + n_i \frac{v''^2}{\chi v} \sigma_i^{ion}(v'') \bar{f}(v''), \end{aligned} \quad (7b)$$

with

$$v'^2 = \frac{v^2}{(1-\chi)} + \frac{2}{m_e} W_i,$$

and,

$$v''^2 = \frac{v^2}{\chi} + \frac{2}{m_e} W_i,$$

where W_i is the threshold energy for ionization of the i th atomic level. The final

electron energies have been partitioned into fractions χ and $1 - \chi$ of the available energy. In all of the calculations reported here, we have set χ equal to 0.8, and found that variation of χ about this value does not greatly affect the results.

Using the collision terms described above, we perform numerical solutions of the Boltzmann equation for an EVDF by time integration. The EVDF supplies an electron density per $(length \times velocity)^3$ and is a continuous function of z, v_z and v_r . Its values are stored discretely in a 3D array in phase space. Continuous values are obtained via interpolation of the array, as will be described in detail later. We solve the BE numerically by combining a method of characteristics with a finite difference treatment of the collision integral. The Vlasov operator (LHS of Eq. (1)) is solved exactly by displacement along the *characteristic curves* or trajectories in phase space. This may be written as

$$f_e(z, v_z, v_r, t + \Delta t) = f_e(z - \Delta z, v_z - \Delta v_z, v_r, t), \quad (8)$$

where

$$\begin{aligned} \frac{d\Delta z}{dt} &= v_z, \\ \frac{d\Delta v_z}{dt} &= a = \frac{qE}{m_e}, \end{aligned}$$

are the equations of motion defining an electron trajectory in an external field producing acceleration a . In Eq.(8) the quantities Δt , Δz , and Δv_z are not restricted to be small increments. We combine this time evolution with an incremental, first order (Eulerian) advance for the collision term and have

$$f_e^{temp}(z, v_z, v_r, t) = f_e(z, v_z, v_r, t) + \Gamma(z, v_z, v_r, t)\Delta t, \quad (9a)$$

$$f_e(z, v_z, v_r, t + \Delta t) = f_e^{temp}(z - \Delta z, v_z - \Delta v_z, v_r, t) \quad (9b)$$

where we use an integration algorithm correct to second order for the trajectory (assuming time-independent acceleration due to the local field),

$$\Delta z = v_z \Delta t - \frac{1}{2} a(z, t)(\Delta t)^2,$$

and

$$\Delta v_z = \frac{1}{2} \left[a(z, t) + a(z - \Delta z, t) \right] \Delta t.$$

In this form, the time step Δt is not limited by the Courant condition and enables much larger time steps to be used than are permitted by finite-difference solutions.

The time step is, however, limited by other factors such as the collision and plasma periods. The terms on the right-hand side of Eq.(9a) are computed by an on-grid advance of the collision term, followed by the displacement along the characteristics of the Vlasov operator, which we discuss in the following section B.

Note that Eqs. (8) and (9) are written in such a manner that, as it is advanced in time from $t \rightarrow t + \Delta t$, each of the electron trajectories can be chosen to *terminate* exactly on a grid point in phase space (see Fig. 1.) In general the *initial* point (at time t) of each trajectory will not lie on a grid point. Thus, the density at the initial point of each trajectory must be interpolated from nearby points in phase space of the EVDF at time t . This scheme, which we refer to as Back-Interpolation (BI), can be contrasted with a Forward-Distribution (FD) moving algorithm in which trajectories *begin* on grid points and are terminated by distributing the densities among the phase space grid points nearest the trajectory terminus[7].

As the BE is advanced in time, the EVDF can be used to evaluate the time and space dependent rates of electron driven processes such as excitation and ionization. For instance, the excitation rate associated with the atomic transition $i \rightarrow j$ is

$$R_{ij}(z, t) = 4\pi \int_0^{\infty} v^2 dv [n_i v \sigma_{ij}(v)] \bar{f}(z, v, t). \quad (10)$$

The rate of ionization of the i th atomic level is

$$R_i^{ion}(z, t) = 4\pi \int_0^{\infty} v^2 dv [n_i v \sigma_i^{ion}(v)] \bar{f}(z, v, t). \quad (11)$$

Effects due to radiative decay and radiation trapping[12] are also included in the R_{ij} rates. Meanwhile, the neutral and ionic atomic species are advanced in time in accordance with these rates and the following two-moment (continuity and momentum) fluid equations:

$$\frac{\partial n_j}{\partial t} = \sum_i R_{ij} + D_j \frac{\partial^2 n_j}{\partial z^2} \quad (12)$$

$$\frac{\partial n^{ion}}{\partial t} + \frac{\partial \phi^{ion}}{\partial z} = \sum_i R_i^{ion} \quad (13)$$

$$\phi^{ion} = n^{ion} v^{ion} \quad (14)$$

$$\frac{dv^{ion}}{dt} + v^{ion} \frac{dv^{ion}}{dz} = \frac{e}{m_{ion} \mu^{ion}} \left[\mu^{ion} E - v^{ion} - D^{ion} \frac{\partial n^{ion}}{n^{ion} \partial z} \right] \quad (15)$$

FIGURE 1. Vlasov Moving Operator. The dots represent the fixed grid of discrete coordinates in z , v_z phase space for which the electron density is stored. For clarity, the v_r component has been omitted from the figure. The curved line represents a particle trajectory in phase space. At each time step, trajectories are advanced in such a manner that they terminate on each of the discrete coordinates. The initial point for a trajectory will not, in general, lie on one of these points. Thus, the density of the initial point will have to be interpolated from the values of the surrounding points at the earlier time.

Here, n_j and n^{ion} are the densities of the j th atomic level and the ions, respectively. ϕ^{ion} is the ion flux, and D^{ion} and μ^{ion} are the ion diffusion and mobility. D_j is the neutral diffusion constant. Note that the ion fluid velocity is integrated from an Euler-like equation of motion which is written in a form that allows the ion velocity to asymptotically approach the known ion mobility and diffusion when inertia is unimportant. This occurs as m_{ion} becomes small.

Ions and metastable atoms striking the electrodes produce secondary electrons which are distributed in a pre-defined energy distribution. Secondary electrons due to electron impact are included via an energy dependent reflection coefficient. Metastable-metastable annihilation is also included with the resulting unit yield of electrons distributed in a Gaussian profile centered on a specified energy.

The Poisson equation,

$$\frac{\partial^2}{\partial z^2} \Phi(z) = \frac{e [n_e(z) - n^{ion}(z)]}{\epsilon_0}, \quad (16)$$

is solved by tridiagonal (Thomas) inversion at each time step, based on charge densities on grid points between the electrodes. The potential at the grounded electrode is fixed at zero while the potential at the driven electrode is $\Phi_0 \sin(\omega t)$. The electric field is computed by central difference from the potential. The major spatial grid stores the EVDF, particle densities, charge, and potential. A midpoint grid distributed between the major grid points stores the electric field and particle fluxes. The use of the major grid and the midpoint grid facilitates the finite differencing of the spatial derivatives, and also suppresses the growth of error associated with the highest frequency spatial mode.

We use a non-uniform spatial grid in order to increase accuracy in the sheath regions. The velocity grid is either chosen to be uniform in the velocity components, or to be uniform in square root of component absolute value. The latter grid is sometimes necessary for describing high density plasmas with a large density of cold (sub eV) electrons serving as a background for a much smaller density of electrons with higher energy. All finite differencing is developed to be second-order accurate in phase space manipulations wherever possible.

2.2 The Back-Interpolation Algorithm

The Vlasov operator or 'moving algorithm' for the EVDF is described by Eq (9). We have cast Eq.(9) so that the density at a particular phase-space element in the EVDF is advanced in time by interpolating, along z and v_z , the EVDF of an *earlier* time. We refer to this as a 'back-interpolation' (BI) method as opposed to a forward-distribution (FD) method[7] which advances the EVDF by taking a particular phase-space density from the *earlier* EVDF and distributing it over various phase-space elements of the *later* EVDF. The FD concept is present in all PIC methods[9], which allocate the predicted particle charge to space grids in order to solve Poisson's equation. Of course, this is not equivalent to redistributing the PIC particles themselves.

An important feature of our BI algorithm is that it allows one to easily use higher-order interpolation methods, unlike FD schemes which are usually linear. The use of higher order interpolation in the moving algorithm helps to reduce numerical diffusion, and enables one to resolve subtle effects such as electron energy loss due to momentum transfer collisions.

To illustrate this point, we have investigated a simple, homogeneous case sensitive to the momentum transfer energy loss. The electric field was fixed at 0.1 V/cm and the helium gas density was 1.0 Torr, giving a ratio of field strength to neutral density of $0.28 \times 10^{-17} \text{ Vcm}^2$, a value typical of the bulk region of our discharges. The initial electron energy distribution for each case was a Maxwellian with 0.2 eV mean energy. Two sets of calculations were made. One set used a four point bivariate (ie, in z and v_z) linear interpolation in the moving algorithm, and the other used a nine point bivariate interpolation, based on the 3 point Lagrange quadratic formula for each of the variables. In the quadratic interpolation, the nearest grid-point to the trajectory start was chosen to be the center point of the nine point cluster. Within each set of calculations, we varied the number of velocity points, or equivalently, the velocity resolution. The two sets of calculations were integrated for a given interval of time, with the *only* difference being the accuracy of the interpolation algorithm. A comparison of the calculated average energies vs velocity resolution was made and the results are presented in the form of a Richardson plot[13] in Fig.2. As the velocity resolution Δv approaches zero, the calculated energies from both the linear and quadratic codes approach the same value. The quadratic code clearly demonstrated electron momentum transfer cooling (Eq.(5)) and yielded results within a few percent of the extrapolated value with a modest number of velocity points. On the other hand, the cooling of the electrons in the code using *linear* interpolation is dominated by numerical

FIGURE 2. Richardson Extrapolation of BI Algorithm. Two back-interpolation (BI) algorithms for the method of characteristics in the Boltzmann equation (BE) integration. The four-point bivariate interpolation has much greater error than the nine-point bivariate (quadratic in each variable). The average energy is evaluated after a fixed interval of time evolution with all quantities held fixed except the velocity gridding. The extrapolation of a Richardson plot to zero increment (the ordinate) corresponds to an infinite grid density and an estimate of the exact result. The slope of the curve reveals the order of the cumulative truncation error in the finite difference approximation.

diffusion and actually *heats* the electrons. Using linear interpolation, cooling does not take place without a very high density of velocity points. This effect is important in the bulk region of the plasma, where conditions are very similar to these.

A slight complication arises from the back-interpolation method when the initial phase-space point is projected to lie beyond the electrodes. In such cases, the source of the electron is assumed to be at the electrode, but from a slightly advanced point in time. The density is obtained by interpolating in time, at the electrode, between an updated and previously stored EVDF. Scattering conditions at the electrodes specify the outgoing part of the EVDF in terms of the incident part at any given time. These boundary conditions for the BE are simple to implement and rigorous[11].

2.3 Boltzmann-Equation/Average-Equation Hybrid

Our calculations in this paper focus on results obtained from our BE/AE hybrid code. As was mentioned above, a purely Boltzmann solution is prohibitively time-consuming, suggesting that some fluid-like solution might be better suited for the task. Recall that we are treating the heavy particle dynamics by two-moment fluid equations throughout. Only the electrons are treated by the Boltzmann equation. Fluid equations are "fast" because they do not solve for a velocity distribution function, but without an EVDF, they cannot predict many of the parameters which they require in order to be accurate. This suggests, then, that some combination of the predictive properties of the Boltzmann equation and the efficiency of the fluid equations might be formed to produce a satisfactory solution.

One such alliance of the BE/FE, which we will only mention *briefly*, is one in which the BE for the electrons is used, periodically, to provide averaged rates, mobility, and diffusivity for electrons. This allows us to integrate a fully self-consistent set of FE (including the electrons) coupled with the Poisson equation for many rf cycles before returning to the BE, whereupon the BE for the electrons is restarted and new electron properties are recalculated. The time-averaged, space-dependent quantities are calculated according to

$$\overline{g(z)} = \frac{1}{\tau} \int_t^{t+\tau} g(z, t') dt', \quad (17)$$

where g is the quantity to be averaged, and τ is, typically, 1 or 2 rf periods. The electron mobility and diffusivity are spatially averaged across the discharge gap in addition to the time average.

This scheme offers a considerable speed improvement over a purely BE solution, but it has some limitations. Our experience has shown that the FE can require a time step smaller than that which is used in the BE, at least with our explicit method of integration. The smaller time step limits the speed of the FE to about 100 times faster than the BE with a nominal velocity grid on our computers. Of course a more global limitation is that the FE must resolve the applied rf time scale, which is considerably less than the time scales associated with ion and neutral motion. Although the BE/FE offers a significant improvement in speed, it still falls short of what is required for discharges that require tens of thousands of rf cycles before reaching steady state. An additional problem with the BE/FE hybrid is that the cycle-averaged quantities that determine the behavior of the electron fluid, ie. the mobility and diffusivity, may cause the electron fluid solution to deviate from the kinetic BE solution in such a manner that the BE/FE hybrid does not converge to a "nice" steady state, but settles into a quasi-steady state which differs somewhat in the BE and FE intervals. This might be improved by the use of a space-dependent mobility and diffusivity for the electron fluid, but we have not investigated this aspect of the BE-to-FE calibration.

In response to these difficulties, we have developed a second mixed hybrid method. Here, the FE equations for electrons are abandoned, and a set of equations that advance *only* the heavy species, in a *fixed* field with *fixed* electron-produced rates, are used. We refer to this as a Boltzmann-Equation/Average-Equation (BE/AE) hybrid. In the AE intervals, the equations of motion for the heavy species in the plasma are exactly Eqs.(12)-(14) with R_{ij} replaced by $\bar{R}_{ij}$, and Eq. (15) replaced by

$$v^{ion} = (E\mu)_{fi} - D_{fi} \frac{\partial n^{ion}}{n^{ion} \partial z}. \quad (15b)$$

Here, $(E\mu)_{fi}$, and D_{fi} , are computed in the last BE cycle and are defined below. The time-cycle-averaged $\bar{R}_{ij}$ are computed as in Eq.(17) from the distribution function and cross sections. The rates are chosen to remain fixed during the AE. As we are not treating the electron dynamics or the applied rf field during the AE, we must decide how to approximate the electric field acting on the charged ions. We could use an averaged field, $\bar{E}$, or attempt to evaluate a dynamic field from the Poisson equation assuming some prescribed variation in the electron charge density during the AE. By observation of the BE solutions themselves, we have found that it is best to assume the electric field is invariant in time, which implies that the electron density variation in the AE should track the positive ion density variation, giving a constant charge density, potential, and field. We also have found that the transition from BE to AE and

back is much more stable if we reduce the size of the directly-averaged field and balance the decrease by an increased ion diffusion constant, very much motivated by ambipolar diffusion analysis.

Physically, the reasons for this ambipolar correction to the averaged field can be understood by considering that, in the bulk, the electron and ion densities are nearly identical and that the sheath has shielded out most of the electric field. Furthermore, it must be remembered that the 'real' field is oscillatory and that, although the electric field averaged over a single cycle may have some small finite value, fixing the bulk field to this value for thousands of equivalent average periods may exaggerate the small bias in the ion motion.

Our prescription for determining the field to be used in the AE can be motivated by examining the drift-diffusion equation for the ion flux and its ambipolar form,

$$v^{ion} n^{ion} = \mu^{ion} n^{ion} E - D^{ion} \frac{\partial n^{ion}}{\partial z} \approx -D_{amb} \frac{\partial n^{ion}}{\partial z}. \quad (18)$$

This, of course, involves the assumption of equal electron and ion fluxes, resulting in the electron-and-ion-dependent D_{amb} . [14] What we have found to work successfully is to assume that all ion motion in the center of the plasma is the result of ambipolar diffusion, not mobility. The spatially-independent ion diffusion constant that accomplishes this is computed from quantities that have been cycle-averaged in the last rf cycle of the BE, namely, $\overline{n^{ion}}$ and $\overline{\mu^{ion} E}$:

$$D_{fit} = \frac{\overline{n^{ion}} (\overline{\mu^{ion} E})'}{(\overline{n^{ion}})''}, \quad (19)$$

where the primes denote space derivatives and all quantities are evaluated at the mid-point (center of symmetry) of the plasma. Eq.(19) is obtained by applying L'Hospital's rule to the ambipolar diffusion relation. If D_{fit} is larger than D_{amb} , based on the ambient electron and ion mean energies, we use D_{amb} in place of D_{fit} . The use of D_{fit} in Eq.(15) is compensated by a reduction in E , just as the use of D_{amb} implies total neglect of E in the drift-diffusion relation of Eq.(18). The residual electric field is found from

$$[E \mu(z)]_{fit} = \overline{v^{ion}}(z) + \frac{D_{fit}}{\overline{n^{ion}}(z)} \frac{\partial \overline{n^{ion}}(z)}{\partial z}, \quad (20)$$

for all z . By inspection of computed values, this field is close to the direct cycle average of E , except in the bulk, where it is considerably weaker. Thus what we accomplish is a replacement of weak electric-field-driven ion flux by a diffusion-driven flux

in the bulk. The heavy particle densities and fluxes are also cycle-averaged in the last BE cycle and these averages are used as initial conditions for the AE integration. We save the ratio of the instantaneous densities to the cycle-average densities (as a function of z) at this point for use in the restarting of the BE. The result of using this averaging procedure is illustrated in Fig. 3, showing how the ion flux varies with time and space during the BE and AE periods. The results of Fig. 3 are near steady-state equilibrium, and there is very little change to be seen in the 4000 cycles of AE integration.

During the AE, the motion of the electrons is ignored, but the ions are allowed to continue to evolve. The electric field is fixed to a time-averaged, space-dependent value given by $(E\mu)_{fit}$ from Eq.(20). Upon finishing the AE interval of integration, the ion density may be different than it was at the beginning of the AE interval. The question then arises, how to adjust the electron density to be consistent with the new ion distribution. This is accomplished, when re-entering the BE, by increasing or decreasing the electron density and EVDF (at each space point) by the amount of change in ion density produced during the AE integration. This maintains the relative electron-ion charge balance, which is assumed to be constant during the AE integration. The AE densities are also multiplied by the ratio of instantaneous to average densities that were saved from the previous BE interval. This helps smooth the transition from the AE back to the BE. The electrons quickly readjust to the new plasma conditions, sometimes acquiring energy high enough to affect the rates in the BE. Ionization is temporarily suppressed to avoid these spurious ion peaks. Typically, the electrons require several nanoseconds to readjust. This BE/AE procedure has similarities to one method described by Sommerer and coworkers[2,7] for the acceleration of plasma simulations.

The BE/AE has some important advantages over the BE/FE. Since the AE interval does not advance electrons, calculate self-consistent electric fields, or respond to the rf frequency, the whole procedure is more stable, runs faster, and can accept much larger time-steps. Furthermore, the BE/AE closely approaches the same steady state as the BE because the AE are based on direct numerical averages of quantities evaluated in the BE. This is contrasted to the BE/FE hybrid where one is basing the acceleration algorithm on a different physical description, namely the fluid equations for the electrons. The only further important observation to be made is that the BE/FE and the BE/AE display almost identical convergence properties when solving the plasma from startup conditions. However we cannot prove that the overall time dependence is exact because of the many time scales involved in the plasma dynamics. We feel that

FIGURE 3. Ion Drift Velocity in Space and Time. The time-interval plotted here includes both BE and AE periods. The Boltzmann equation was solved for three rf cycles. The drift velocity during the BE clearly reflects the oscillations of the applied rf potential. During the AE, this oscillatory motion is averaged out as the ions respond to a time-averaged, effective electric field. Here, the AE equations were solved for 4000 rf cycles. The variation in spacing that is evident in the spatial dimension of the grid work is due to the non-uniform grid as discussed in the text.

certain plasma *transients* might be better described by the BE/FE hybrid.

Summarizing, the BE/AE is comprised of the following steps:

1. The numerical solutions of the electron-Boltzmann and ion-fluid equations are carried out, self-consistently with the Poisson equation, for some prescribed interger number of RF cycles, as described in section II.A.
2. During the last BE cycle, space-dependent, time-averaged electron driven rates and neutral species diffusion constants are calculated using Eq. (17). The diffusion constant and the effective $E\mu$ product for the ions and are computed via Eqs. (17),(19) and (20). The space-dependent, time-averaged electron densities are computed and saved for re-entry into the BE. The instantaneous electron densities at the end of the BE cycle are also saved.
3. The heavy species are advanced for several RF cycles according to the modified versions of Eqs. (12)-(14) and (15b), where the appropriate time-averaged quantities have been substituted for the instantaneous values. Electron dynamics are not treated.
4. When the prescribed number of RF periods have been completed with the AE equations, the electron densities have to be updated before re-entering the BE integration. The average electron densities are scaled up (or down) by the net change in ion density over the AE period. Then the average electron densities are scaled at each space point by the ratio of instantaneous to average density which was computed at the beginning of the AE period.
5. Return to step 1, entering the BE integration at the same phase in the RF cycle as when it was left.

3. Simulations for He Plasma

3.1. Helium Model

We have modified our BE/AE code to incorporate a realistic model for simulating low-temperature He discharges. Fig. 4 illustrates the five level model we have developed for electron/helium collisions. In the figure, solid lines indicate inelastic (up arrow) or superelastic (down arrow) transitions. Wavy lines indicate radiative decay, and boxed areas depict composite levels. The singlet and triplet composite states include the $n=2 \rightarrow 10$, levels of the s, p, and d orbitals, except for the $1s2s^1S$

FIGURE 4. Helium Model Atomic Levels. This figure illustrates the model of atomic levels and transition for He used in our studies. The circled numbers label the five populations that are followed in the rate equations. The solid arrows label all transitions that are computed from the electron distribution function and cross sections. The wavy arrows label the two radiative transitions that are included, both of which have radiative trapping. The boxed levels (polygons) denote the collections that are grouped together for the purposes of excitation from the ground state. The level spacing is not to scale.

metastable state, which is treated individually. Transitions from the ground state to these composites use cross sections that are summed over the grouped levels. Cross sections for momentum transfer and ionization from the ground state were taken from Hayashi[15] and Rapp, Englander-Golden[16], respectively. The $1s2s^3S \rightarrow 1s2s^1S$ cross section was fitted to the data of Fon, *et. al.* [17] All other cross sections were from Janev[18]. The singlet composite levels decay to the $1s2p^1P$ which decays to both the $1s2s^1S$ metastable and the ground level. The triplet composite levels all decay to the $1s2s^3P$ metastable. Effective lifetimes due to radiation trapping for the $1s2p^1P \rightarrow 1s2s^1S$ and the $1s2p^1P \rightarrow 1s^2$ transitions were also included[12].

Additional processes which produce electrons include metastable-metastable annihilation and secondary electron emission due to ions or metastables impacting on the electrodes. Electrons produced from a metastable-metastable annihilation are distributed isotropically within a Gaussian shaped energy band having a half-width of 1.0 eV, and centered on 9.54 eV. Here, we used a reaction rate constant of $2.0 \times 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. Our value is about twice the average of all the experiments done on this quantity. The destruction coefficient for metastable-metastable collisions, which is defined to be twice the metastable-metastable reaction rate coefficient, is given with critical discussion in: R.H.Neynaber, *et. al.* [19]. Our value is also in rough agreement with the value used by Sommerer, *et.al.* [7], who apparently made the same error in interpretation of the reported rates, due to the confused definition of the rate constant. Electrons produced via ion or metastable impact on the electrodes are also distributed isotropically, with energies evenly distributed between 2.0 and 13.0 eV. The secondary electron coefficients γ_{ion} and $\gamma_{metastable}$ are 0.28[20] and 0.29[21], respectively. Electrons impacting on the electrodes were specularly reflected with an energy dependent scattering coefficient of the form

$$\gamma_e = 1.03 \exp \left[- \left[\frac{\log \frac{\epsilon}{400}}{1.1634} \right]^2 \right], \quad (21)$$

where ϵ is the energy of the incident electron in eV. Eq.(21) was obtained by fitting to the measured data[22]. A point that we have ignored because of a lack of information is the energy spectrum of the electron- produced secondary electrons.

The ion motion, described by Eq. (15), requires ion mobility and diffusion constants μ^{ion} and D^{ion} . The ion mobility is not a constant, but dependent on the local electric field by way of an empirical formula given by Ward[23]. The diffusion

constant was obtained via the Einstein relation, $D^{ion} = T(eV)\mu[14]$. The diffusion constant for helium neutral species was $450 \text{ Torr cm}^2\text{sec}^{-1}[24]$.

3.2. Convergence of the BE/AE Scheme

As we have indicated in the Introduction, plasmas in the GEC cell may require several tens of thousands of rf cycles, or several milliseconds, to reach a steady state. This requires as many as 10^8 BE time steps before convergence. Our BE/AE scheme, which we have described above, can reduce the number of calculations required by more than 3 orders of magnitude.

The ability of our BE/AE hybrid to converge on a steady state solution for arbitrarily chosen initial conditions is illustrated in Fig. 5. It shows, as a function of time, the electron, triplet and singlet metastable, and current densities at the midpoint of the discharge. The conditions for which these results were obtained were for a 0.5 Torr, 100 Volt amplitude, helium plasma operating at 13.56 MHz and with an electrode separation of one inch. The initial conditions for the simulation consisted of spatially uniform electron and ion densities of $5.0 \times 10^8 \text{ cm}^{-3}$. The initial Maxwellian electron distribution had a mean energy of 3.0 eV. The initial metastable and excited state densities were zero.

The Boltzmann and average equations were alternately solved for various lengths of time. In the early stages of the simulation, the Boltzmann equation was solved for two rf cycles, after which the average equations were solved for 100 cycles. As the simulation progressed, changes in the plasma became more subtle, and it was possible to adjust the procedure to solving the AE for 4000 cycles for each two or three cycles using the BE. Different ratios of Boltzmann to average periods can also be used. Such differences, although not affecting the steady state values, may yield different transient behavior in the simulation. This is because the use of the BE/AE procedure may introduce spurious transient dynamics. Thus, it is important to point out that the time-dependence illustrated in the Fig. 5. is not *necessarily* a true picture of the time-dependence of the real plasma. We have, however, strived to select a program of alternating BE/AE periods which will yield reasonably accurate transient information while minimizing the computation time. This is done by adjusting the number of cycles over which the AE are solved, before returning to the BE to update the rates and the field. When the characteristics of the plasma are changing rapidly, the rates are updated more often by the BE. When changes in the plasma are slow, the AE are solved for longer periods of time before returning to the BE.

FIGURE 5. BE/AE Convergence. These calculations show the convergence of the BE/AE procedure when started from initial conditions that are not chosen in any special way. The abscissa is time, measured in rf cycles of about 74 ns. The units of the plotted quantities are given in the marker explanations for each curve. The lines are drawn to guide the eye. The final time of the simulation is 6 ms. The detail of the oscillatory transient is not necessarily real (see text), although the apparent characteristic time for convergence to steady state (about 1.5 ms) is quite real. This is the 0.5 Torr, 100V case.

The final test of convergence that we apply is that the densities should not change by more than a few percent on the final sequence on BE-AE-BE integrations, where the AE interval is of the order of the slowest time scale in the system (typically several thousand RF periods.) In this example, the convergence was better than 0.1% over 8000 RF periods.

3.3. Steady-State of a He RF Discharge

Because we have a rather complete kinetic model of the He plasma, we choose He as a test case for comparison to experiment[25]. There are a few case studies of rf-driven He plasmas in the literature[2], but these all have differing dimensions, pressures, and applied voltages, as well as different degrees of sophistication in the method of simulation. A calculation for the GEC reference cell [1] would seem to be most appropriate for our exercise. The GEC cell is a parallel plate, 13.56MHz, 1 in (2.54 cm) plate separation laboratory device with good diagnostics for electron and meta-stable densities. We choose to examine the 100 V amplitude, 1 Torr case and compare to experimentally measured quantities. The experimental measurements as well as additional simulations are being reported in separate publications[25,26] for a range of voltages and pressures.

The calculation proceeded through a series of BE/AE cycles, some of which required changes in grid density and time step to accommodate the increased plasma density and sheath structure, but this could have been avoided with judicious starting conditions. Our code has several processing subroutines which can revise the gridding and time steps when needed. The results reported here in fact originated as a completed steady-state run at another gas pressure or voltage. The total effective real time of BE/AE evolution is more than 1 ms, but the number of BE cycles is the order of several tens. The space grid increased from 0.01693 cm (2.54 cm/150) near the electrodes to 0.06773 cm. in the center, with a total of 91 points altogether. The velocity grid consisted of 65 points in each direction ($+v_z$, $-v_z$, v_r), distributed out to an energy of 100 eV. The time step was 0.02 ns. The moving was performed with the bivariate quadratic back interpolation, and the velocity gridding was uniform in $|v_i|^{1/2}$ as discussed earlier. The results are converged in time to better than a few percent in 8000 rf cycles, but a realistic limit on the numerical accuracy might be as large as 10-20% due to space and velocity gridding. In Table I, we give a comparison the experimental measurements of Greenberg and Hebner [25] under these conditions. There could be a question as to the meaning of a comparison of 1D calculations with experiment, but the unpublished results[25] show a fairly radially uniform (10% density variation)

plasma in the center of the reactor. Thus we feel these comparisons are meaningful.

The most noteworthy feature of the comparison is the agreement of the predicted quantities to better than about a factor of two with the measurements. The over-prediction of the singlet metastable density may be due to a high electron mean energy in the simulation. The presence of more sub-eV electrons would selectively de-excite the singlet metastable into the triplet, thus lowering the singlet density with very little noticeable effect on the triplet density. A hot electron distribution would tend to hold the triplet/singlet density ratio at 3, but neither the simulation nor the measurement shows this ratio precisely. We feel that the overall agreement with absolute measurements of plasma and atomic densities is quite encouraging.

Table I. Comparison with Experiment		
	Simulation	Experiment
Peak electron number density (10^{10}cm^3)	1.05	1.9
Peak triplet metastable density (10^{11}cm^3)	2.0	1.5
Center singlet metastable density (10^{10}cm^3)	5.6	2.3
Total current density (mA cm^{-2})	1.5	2.2
Center electron average kinetic energy (eV)	2.3	1.8 ^a

Table I. Comparison of our plasma data with the experimentally measured quantities from [25]. The conditions are 100 V amplitude driving voltage, 1 Torr He gas, and 2.54 cm. electrode separation. The electrode area is 81 cm^2 . Center refers to the mid-point between the electrodes, on-axis in the radial center.

^aThe mean energy for the experiment was not measured, but roughly deduced from data of Godyak, et al [27] in a different geometry discharge, using the current density from [25].

4. Summary

We have developed an efficient, numerical, mixed hybrid simulation of low-temperature rf plasmas in a 1D-2V geometry. Our method includes a fully self-consistent solution of the Boltzmann/Poisson equations and a set of time-averaged, fluid-like equations which are coupled to the Boltzmann/Poisson solution.

A unique feature of our Boltzmann solution is its Back-Interpolation algorithm. This algorithm improves both accuracy and efficiency of the calculation because it allows one to use higher order interpolation methods during advance of the electron densities in phase space. The higher order interpolation reduces numerical diffusion in the calculation and also reduces the density of points required for an accurate solution.

Our mixed hybrid method allows one to use information gained during a Boltzmann solution of only a few rf cycles, and incorporate this information into a fluid-like solution which very efficiently advances the heavy species in the plasma. The use of this mixed method can bring the calculation to a steady state in much less time than a purely electron-Boltzmann solution.

5. References

1. P.J.Hargis, Jr., K.E.Greenberg, P.A.Miller, J.B.Gerardo, J.R.Torczynski, M.E.Riley, G.A.Hebner, J.R.Roberts, J.K.Olthoff, J.R.Whetstone, R.J.Van Brunt, M.A.Sobolewski, H.M.Anderson, M.P.Splichal, J.L.Mock, P.Bletzinger, A.Garscadden, R.A.Gottscho, G.Selwyn, M.Dalvie, J.E.Heidenreich, J.W.Butterbaugh, M.L.Brake, M.L.Passow, J.Pender, A.Lujan, M.E.Elta, D.B.Graves, H.H.Sawin, M.J.Kushner, J.T.Verdeyen, R.Horwath, T.R.Turner, to appear in *The Review of Scientific Instruments*, Dec., 1993.
2. Methods and models for solution of low-temperature, rf-driven plasmas are given in the special April issue of *IEEE Trans. on Plasma Science*, Vol. 19, No. 2, 1991.
3. K. Kitamori, H. Tagashira and Y. Sakai, *J. Phys. D* 11, 283 (1978).
4. T. Holstein, *Phys. Rev.* 70, 367 (1946).
5. A.V. Phelps and L.C. Pitchford, *Phys. Rev. A* 31, 2932 (1985).
6. P.J. Drallos and J.M. Wadehra, *Phys. Rev. A* 40, 1967 (1989).
7. W.N.G. Hitchon, D.J. Koch, and J.B. Adams, *J. Comp. Phys.* 83, 79 (1989), and T.J. Sommerer, W.N.G. Hitchon, R.E.P. Harvey and J.E. Lawler, *Phys. Rev. A* 43, 4452 (1991).
8. P.J. Drallos and M.E. Riley, *Phys. Rev. A* 44, 1405 (1991).
9. C.K. Birdsall and A.B. Langdon, *Plasma Simulation via Computer Simulation*, McGraw-Hill, New York (1985), and R.W. Hockney and J.W. Eastwood, *Computer Simulations Using Particles*, I.O.P. Publishing, Bristol (1988).
10. M. Surendra, D.B. Graves, and G.M. Jellum, *Phys. Rev. A* 41, 1112 (1990).
11. The Boltzmann equation is discussed from a fundamental point of view in the following references: K.Kumar, H.R.Skullerud, and R.E.Robson, *Kinetic Theory of Charged Particle Swarms in Neutral Gases*, *Aust. J. Phys.* 33, 343 (1980); I.P.Shkarofsky, T.W.Johnson, and M.P.Bachynski, *The Particle Kinetics of Plasmas*, Addison-Wesley Pub. Co., Reading, MA (1966); J.O.Hirschfelder, C.F.Curtiss, and R.B.Bird, *Molecular Theory of Gases and Liquids*, John Wiley, NY,NY(1954); C.Cercignani, *Mathematical Methods in Kinetic Theory*, Plenum

Press, NY, NY (1969).

12. T.Holstein, Phys. Rev. 72, 1212 (1947).
13. L.F.Richardson, Phil. Trans. Roy. Soc. A-210, 307 (1910) and A-226, 300, (1927).
14. F.F. Chen, *Introduction to Plasma Physics*, Plenum Press, New York, NY (1974).
15. M. Hayashi, Internal Report IPPJ-AM-19, Nagoya Institute of Technology (1981).
16. D.Rapp and P.Englander-Golden, J. Chem. Phys. 43, 1464 (1965).
17. W.C.Fon, K.A.Berrington, P.G.Burke, and A.E.Kingston, J. Phys. B: At. Mol. Phys. 14, 2921 (1981).
18. R.K.Janev, W.D.Langer, K.Evans, Jr., D.E. Post, Jr., *Elementary Processes in Hydrogen-Helium Plasmas*, Springer-Verlag, Berlin (1987).
19. R.H.Neynaber, G.D.Magnuson, and S.Y.Tang, J. Chem. Phys. 68, 5112 (1978).
20. H.D.Hagstrum, Phys. Rev. 104, 672 (1956). Also see E.W.McDaniel, *Collision Phenomena in Ionized Gases*, Ch.13, Wiley & Sons, NY, NY 1964.
21. R.F.Stebbing, Proc. Roy. Soc.(London) A- 241, 270 (1957).
22. Von G.Blankenfeld, Ann. der Physik 9, 48 (1951) and I.M.Bronshtein, Bull. Acad. Sci. USSR 22, 442 (1958).
23. A.L.Ward, J. Appl. Phys. 33, 2789 (1962).
24. A.V.Phelps, Phys. Rev. 99, 1307(1955).
25. K.E.Greenberg, and G.A.Hebner, J. Appl. Phys., 73, 8130(1993).
26. M.E.Riley, K.E.Greenberg, G.A.Hebner, and P.J.Drallos, J. Appl. Phys., 75, 2789 (1994). July, 1993.
27. V.A.Godyak, R.B.Piejak, and B.M.Alexandrovich, Phys.Rev.Letts., 68, 40(1992).

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