



Space charge effects in high pressure mass spectrometry sources
by Mark Busman

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Chemistry

Montana State University

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Abstract:

Ion transport in unipolar mass spectrometry ion sources like corona API and electrospray has been studied theoretically. Unlike previous work in this area, the study has been done with the consideration of space charge effects. Analytic solutions of the space charge problem have been obtained for simple ion geometries, including the cases of infinite parallel planes, concentric cylinders of infinite length, and concentric spheres. These analytic solutions allow, for their respective geometries, the calculation of electric field, potential, ion density distributions, and ion residence times. It is shown that for typical operating conditions, the minimum potential required to overcome the space charge effect in corona API, or electrospray ion sources, constitutes a dominant or significant fraction of the total applied voltage. Further, the electric field, in the region of the ion sampling orifice and the ion residence time in the ion source are determined mainly by the space charge. Extending the approach to more general geometries, absolute sensitivities of corona API ion sources were calculated using a geometry independent treatment of space charge. Also, general geometries were modelled by a simulation calculation. The calculation was based on a computer program written to model ion flow in various ion sources having different geometries. Finally, the space charge influenced ion drift in a drift tube-type apparatus was modelled, as a function of time.

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MASS SPECTROMETRY SOURCES

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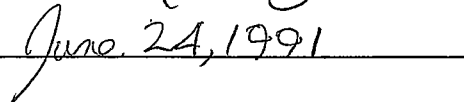


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ABSTRACT

Ion transport in unipolar mass spectrometry ion sources like corona API and electrospray has been studied theoretically. Unlike previous work in this area, the study has been done with the consideration of space charge effects. Analytic solutions of the space charge problem have been obtained for simple ion geometries, including the cases of infinite parallel planes, concentric cylinders of infinite length, and concentric spheres. These analytic solutions allow, for their respective geometries, the calculation of electric field, potential, ion density distributions, and ion residence times. It is shown that for typical operating conditions, the minimum potential required to overcome the space charge effect in corona API, or electrospray ion sources, constitutes a dominant or significant fraction of the total applied voltage. Further, the electric field, in the region of the ion sampling orifice and the ion residence time in the ion source are determined mainly by the space charge. Extending the approach to more general geometries, absolute sensitivities of corona API ion sources were calculated using a geometry independent treatment of space charge. Also, general geometries were modelled by a simulation calculation. The calculation was based on a computer program written to model ion flow in various ion sources having different geometries. Finally, the space charge influenced ion drift in a drift tube-type apparatus was modelled, as a function of time.

INTRODUCTION

In the last half century, mass spectrometry has gradually evolved from being an interesting tool for the mass measurement of relatively small ions, into a vital area of analytical chemistry. This evolution has followed the development of creative techniques for the introduction of molecules into an ion source for mass analysis, and achieving their ionization.

The ion sources used in mass spectrometry can be classified according to source pressures. Sources operated at pressures 1 torr and below can be considered to be low pressure ion sources. Low pressure sources include sources for many of the more commonly used mass spectrometry techniques: electron impact ionization (EI),^{1,2} chemical ionization (CI),³ and fast atom bombardment (FAB).⁴ High pressure ion sources can be thought to be those that operate in the pressure range between 1 torr and atmospheric pressure, and perhaps beyond. High pressure sources include the sources used for atmospheric pressure ionization (API),⁵ thermospray ionization (TSP),⁶ and electrospray ionization (ES).^{7,8} The ion sources in both of these categories have been studied to establish appropriate parameters for their operation. Much has been written with

respect to the mechanisms pertinent to the operation of these sources.

In mass spectroscopy, the understanding of the production of ions in the ion source is an important aspect of understanding the technique. Further, understanding the processes behind introducing the ions into the mass resolution part of the instrument is vital for insight into the identities and quantities of ions available for detection. The goal of this work is to evaluate certain aspects of ion transport in high pressure mass spectrometry sources with regard to the performance of these sources.

Ion Transport

In the ion source of the mass spectrometer ions are produced from existing molecules. These ions are then driven toward an aperture separating the high-pressure ion source from the low-pressure mass analyzer section of the mass spectrometer, where they can travel towards the detector. The processes causing the ions to leave the ion source can be of the following types of transport: convective, diffusive, and electrostatic.

Convective Transport

The ion source is often at much higher pressure than the mass analyzer region. The ions will be carried along with the gas stream down the pressure gradient. The study of

how ions can flow along with a moving gas is an important area in fluid dynamics.⁹

Diffusive Transport

In many ion sources, ions are not formed throughout the source, but, instead, are formed in a small volume in the ion source. Here, the concentration of ions may be very high. The ions tend to diffuse out of the areas of high concentration into areas of lower concentration. The mathematical treatment of the diffusion of ions in gases is well developed.^{10,11}

Electrostatic Transport

Ions, as charged species, will drift in existing fields. An ion will drift in the direction of existing electrical fields. The drift velocity depends on the field's intensity. Again, the mathematical treatment of ionic drift has already been developed.^{9,11} Ion drift will now be discussed in more detail.

MATHEMATICAL TREATMENT OF ION TRANSPORT

The application of electrostatics to charged particle flow and, in particular, ion flow has been important to physics for many years. The analysis ion flow has been based on Coulomb's and Maxwell's equations.¹² It is these equations that make the analysis of ion drift in the mass spectrometer ion source possible.

Drift Equation

Using appropriate laws of electrostatics, one can predict the magnitude and direction of the forces acting upon ions at specific locations in the source. Moreover, assuming certain characteristics of both the ions, and the neutral gas inside the source, one can predict a velocity for an ion under the influence of a given field. This velocity, the drift velocity, v , can be given as a function of electric field strength, E , by the drift equation,

$$v = \kappa \cdot E, \quad (1)$$

where κ is the ion mobility, a constant, dependent on both the characteristics of the ion and its surrounding gas, and generally assumed to be independent of field strength.^{10,13}

The drift equation is essentially an empirical equation that summarizes a large amount of experimental data. It has been shown to be applicable at high pressures (above 1 torr). The mobility, κ , is the empirical constant in the equation. The mobility constant's magnitude is dependent on the charged particle's response to an electric field and to the collisions with the neutral bath gas that the particle will experience. Compilations of mobility data have been published, most notably by McDaniel.¹³

Laplacian Field

An ion source often has several electrically insulated components that have different applied potentials. From the geometry of the ion source, it is possible, in theory, to map out the electric fields in the source, that result from the application of the potentials to the various source components.¹⁴ Generally, it is assumed that the field strength at any point in the source is dependent on only the external applied field. The field strength at any point is determined by the source geometry and the respective applied voltages on various source components. This external field is commonly called the Laplacian field.¹¹

Space Charge Field

As ion densities in the source increase, the coulombic forces between the ions will increasingly modify the

Laplacian electrical fields experienced by ions. In the source the conduction of current will be unipolar. By saying that the current is unipolar, it is meant that particles of only one polarity exist in the source, and that the ion flow can be considered accordingly. The ions in the ion source, traveling at finite velocities, experience a mutual coulombic repulsion during the time that they transit the gap between electrodes, thus forming their own electric field. The Laplacian field is combined with the field caused by the moving charge, the space charge field. This combination is the actual field experienced by the ions. In the extreme, the space charge field, from the unipolar current, can be so large that it completely dominates any applied field.

Historical Background

The modification of Laplacian fields by space charge was noticed many years ago by workers studying electrical currents between charged plates. As they attempted to increase the current between these charged plates by changing the conditions between the plates, they found that it was not possible to increase the current beyond a certain limiting current. This was explained by the modification of the fields between the plates, by the current flow.^{15,16,12}

The mathematical picture of space charge was initially developed by Child, in 1908, to model the evaporation of

calcium ions from a heated plate.¹⁵ Unaware of Child's work, Langmuir, in 1913, independently developed a similar model to describe the behavior of thermionic currents from filaments.¹⁶ In 1914, Townsend described the space charge influenced currents in terms of the mobilities of the charge carriers. It became common for the maximum currents, as allowed by the space charge, to be called space charge limited.^{12,11,10}

The concept of space charge has been used for a wide range of application. From the initial use for currents between charged plates, the space charge concept has been used in electronics for the design of tube-type electronic components,¹⁷ in meteorology to model lightning strikes, in aircraft design to evaluate charge buildup on various airplane structural components,⁹ in industry for the design and maintenance of electrostatic precipitators,¹⁸ and in the modelling of fields surrounding high voltage, direct current power transmission lines.¹⁷

As the field of mass spectroscopy developed, it was natural for the concept of space charge to be applied to the emerging technique. However, early workers correctly assumed that they were working with ion currents and ion densities that were too low for space charge to be important. The combinations of source conditions and ionization techniques being utilized made the modifications

of the Laplacian fields in the sources, by the space charge, insignificant.¹⁹

Recent years have seen a continual evolution of the mass spectroscopy field. New techniques for ionization have changed the conditions in the ionization source considerably. The atmospheric pressure ionization (API)⁵ and the electrospray ionization (ESI)⁷ techniques have utilized sources that have particularly deviated from the conventionally expected conditions of high vacuum and low ion densities. So, it can be argued that an assessment of the importance of space charge in the sources of some of these newer techniques is due. Notable in displaying the use of space charge analysis in high pressure mass spectrometry, is the ECD model by Gobby, Grimsrud and Warden.²⁰

Mathematical Background

To evaluate space charge effects in these newer sources, use of the previously developed methodology for determining space charge influenced fields must be made. However, early work with space charge was restricted to the analysis of simple geometries. Due to the difficulty of the mathematics involved, workers would idealize their experimental apparatus as either infinite parallel planes, concentric cylinders of infinite length, or concentric spheres.¹⁷ These geometries were amenable to mathematical analysis, yielding data appropriate to the individual

worker's needs. The computation of space charge influences in these geometries was based on the Poisson equation,

$$-\nabla \cdot \vec{E} = \frac{\rho}{\epsilon}, \quad (2)$$

where $\nabla \cdot \vec{E}$ is the gradient of the electric field, ρ is the space charge density in terms of charge per unit volume, and ϵ is electrical permittivity; and the continuity equation,

$$\left[\frac{\partial \rho}{\partial t} \right] + \nabla \cdot \vec{J} = 0, \quad (3)$$

where t is time. When considering stable ion source conditions, the steady state form of the continuity equation,

$$\nabla \cdot \vec{J} = 0, \quad (4)$$

can be used by assuming $(\partial \rho / \partial t) = 0$.

Here, \vec{J} is the ion current density. As was discussed earlier, the ion current will have contributions from diffusion, convection, and electrostatic transport. This dependence of \vec{J} can be mathematically stated as

$$\vec{J} = \kappa \rho \vec{E} - D \nabla \rho + \vec{F}, \quad (5)$$

where D is the diffusion constant and \vec{F} is the gas flow vector. The first term relates to the ion drift contribution to the current density vector, while the second and third terms indicate the effects of diffusion and convection, respectively.¹⁰ Diffusion and convection terms

are important only in some very special situations, and are not treated in this work.

Beyond this point the mathematics will be expressed in scalar notation, instead of the previously used vector notation.

Analytic Solutions

For this work, the Poisson and continuity equations were utilized to predict electric fields, space charge densities, potentials, ion transit times, etc. for ion sources with certain assumed operating parameters. Given the wide variation in the geometries of real ion sources, all three simple geometries, amenable to giving analytical solutions, were considered. Similar analyses have previously been described, for use in discharge physics, by Townsend¹² and Chapman.²¹ Descriptions of these analyses, for each of the three geometries, follow.

Planar

In this geometry, shown in Figure 1, two planes of infinite area are placed parallel to each other at some finite distance, l . A potential difference, V_0 , exists between the two plates. A current, i , is assumed to flow between the two plates. Furthermore, all of this current is carried by one type of charged particle, with a mobility, κ . The unipolar current originates at one surface, and terminates at the other.

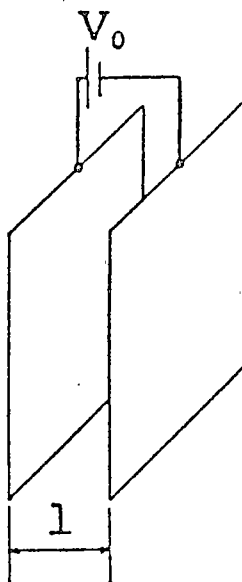


Figure 1. Planar Geometry, infinite parallel planes.

The mathematical analysis of the planar geometry gives electric field strength and ion density as a function of distance, x , from the source plate. A detailed derivation of the equations shown here is presented in Appendix A. The equations for field strength and space charge density are

$$E = \left(\frac{2i}{K \epsilon_0} x + E_0^2 \right)^{1/2} \quad (6)$$

$$\rho = \frac{i}{K} \left[\frac{2i}{K \epsilon_0} x + E_0^2 \right]^{1/2}. \quad (7)$$

Here E_0 is the field strength at the source plate ($x=0$). Graphs of the functions for certain sets of initial conditions are given in Figures 2, 3, 4, and 5. The Figures show the remarkable modification of the conditions in the source, in the space charge dominated (SCD) case. Especially noteworthy is the decrease in the electric field strength and the increase in the ion density in the area near the source plate.

Cylindrical

In this geometry, shown in Figure 6, a cylinder of radius, r_0 , is enclosed by a concentric cylinder of radius, r_1 . The surface of the inner cylinder acts to supply a current of charged particles that flow to the outer cylinder. These concentric cylinders are assumed to be of infinite length. Again, a potential difference exists between the two cylinders and the current is completely carried by charged particles of mobility, κ . The field strength is E_0 at the surface of the inner electrode ($r=r_0$).

The mathematical analysis of the cylindrical geometry gives electric field strength and ion density in terms of distance, r , from the axis at the center of the two

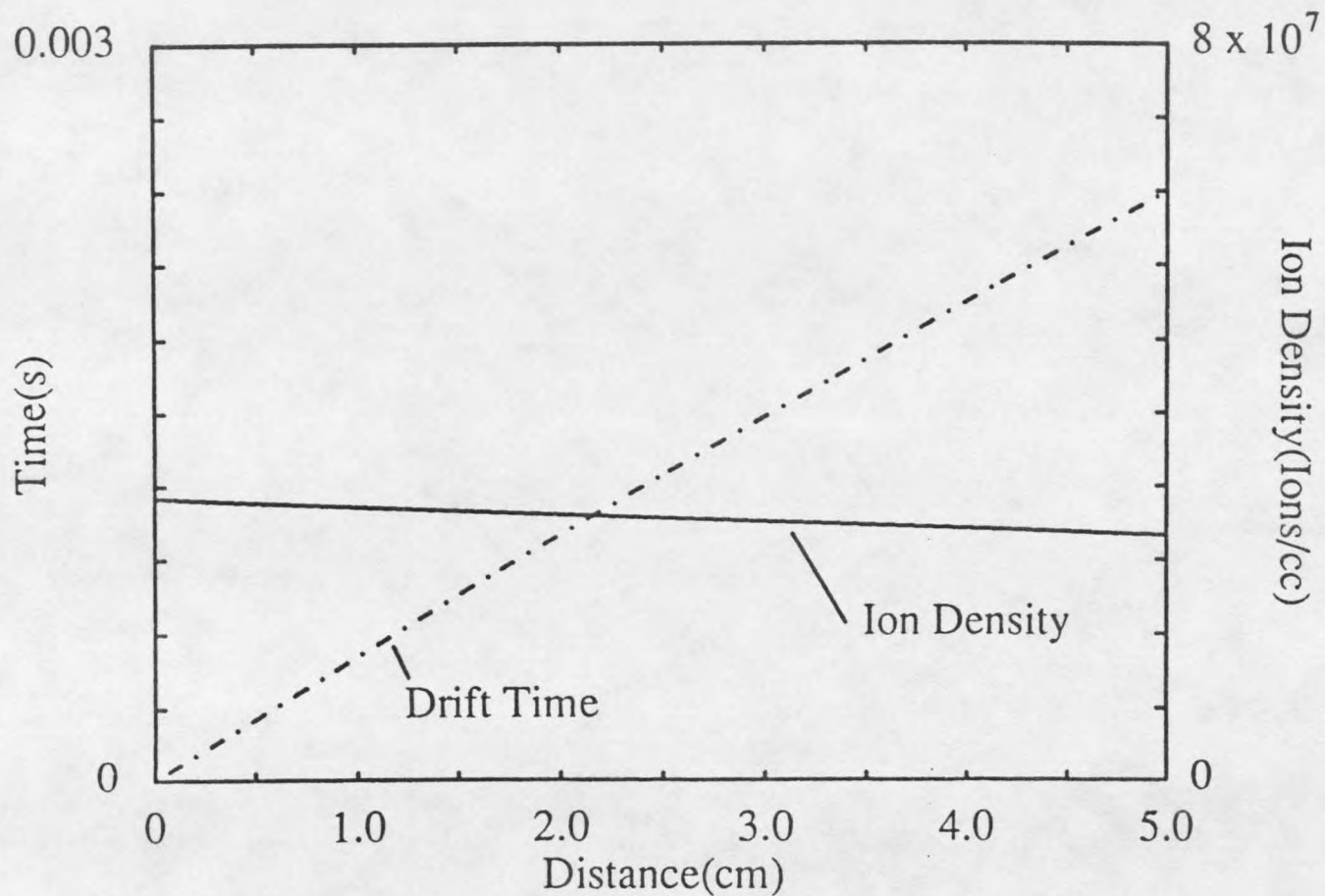


Figure 2. Non-space charge dominated residence times and space charge densities, in the planar geometry, as a function of distance. The current density is 1.0×10^{-8} A/cm²; the total applied potential, $V_0=10,000$ V; and the ion mobility, $\kappa=1 \times 10^{-4}$ m²/V·s.

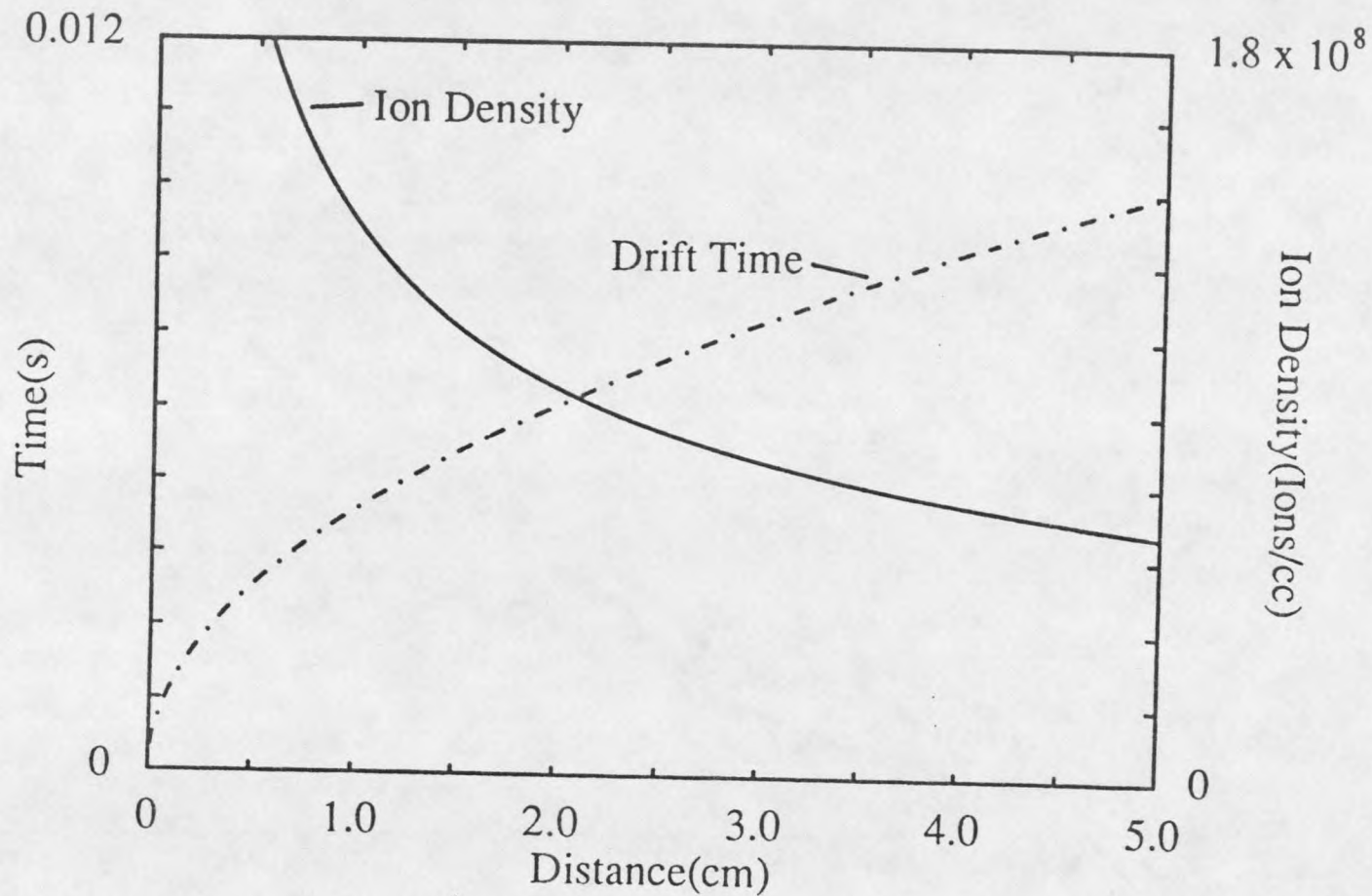


Figure 3. Space charge dominated residence times and space charge densities, in the planar geometry, as a function of position. The current density is 1.0×10^{-8} A/cm²; the applied potential, $V_0=3,600$ V; and the ion mobility, $\kappa=1 \times 10^{-4}$ m²/V·s.

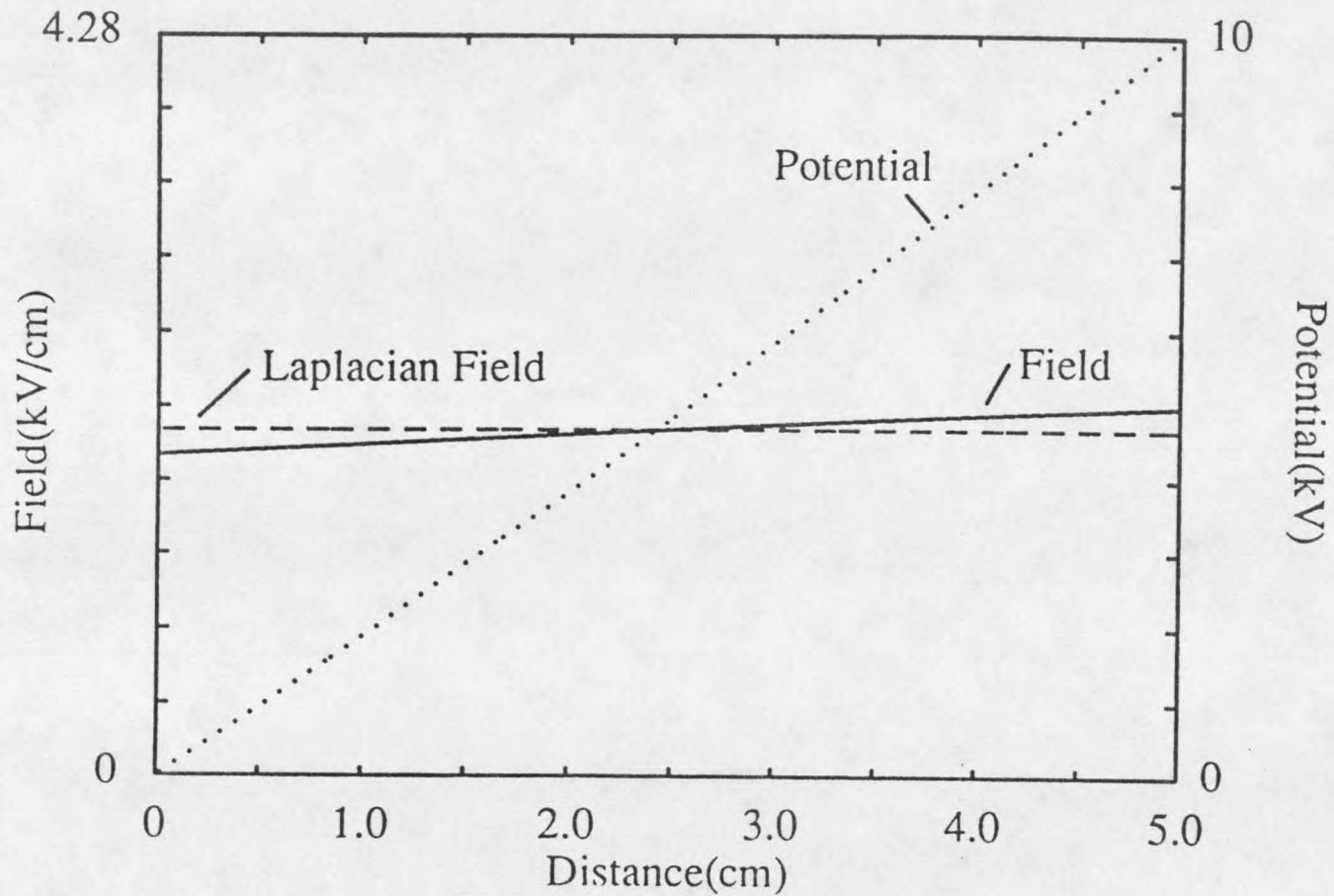


Figure 4. Non-space charge dominated potentials and fields, in the planar geometry, as a function of distance. Applied potential, current density, and ion mobility are as specified for Figure 2.

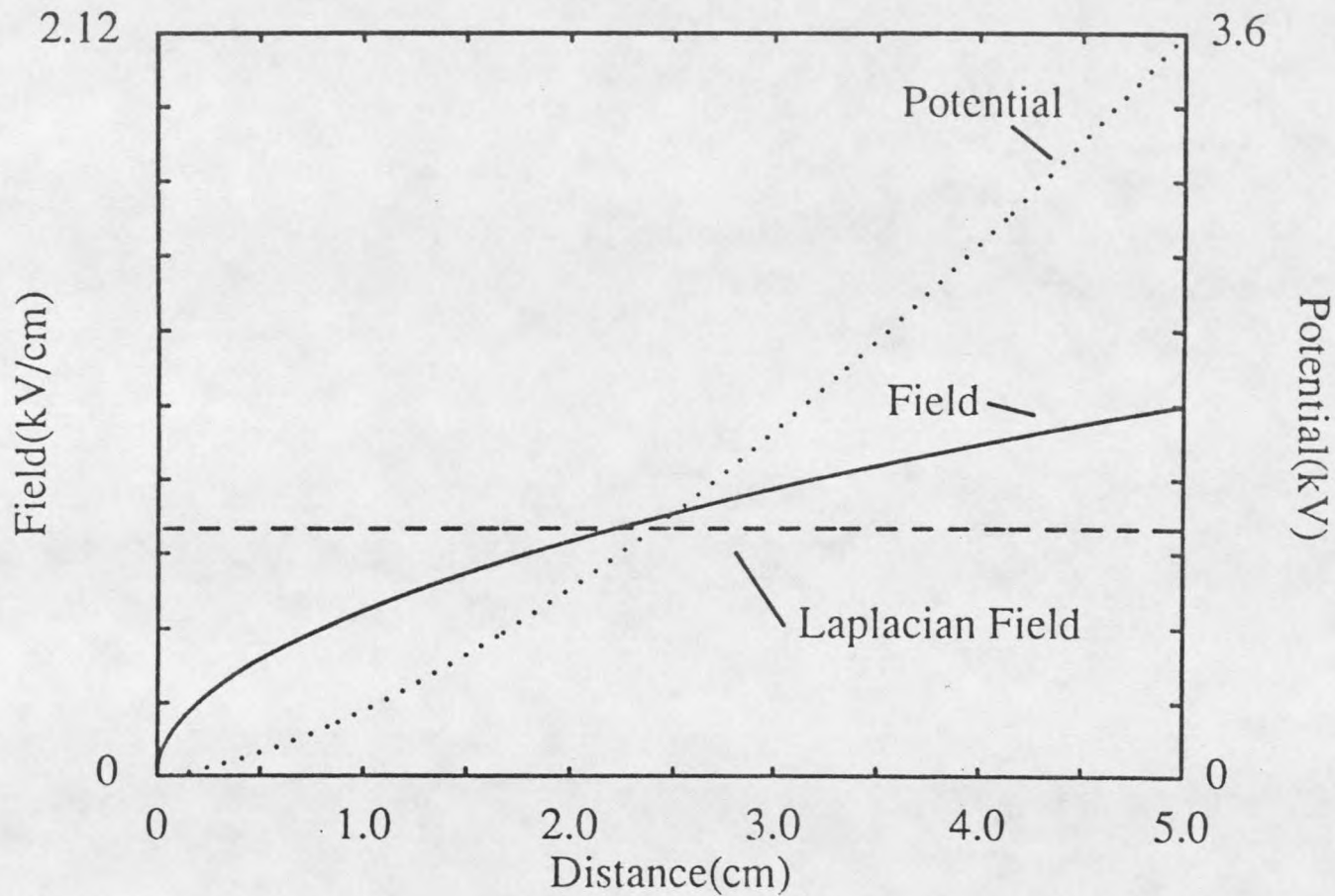


Figure 5. Space charge dominated potentials and fields, in the planar geometry, as a function of distance. Applied potential, ion current, and ion mobility are as specified for Figure 3.

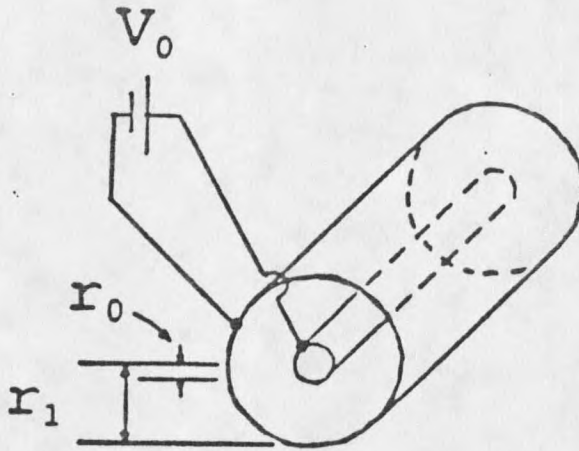


Figure 6. Cylindrical geometry, concentric cylinders of infinite length.

cylinders. Mathematically, the functions apply to the region between the concentric cylinders. A detailed derivation of the equations shown here is presented in Appendix A. The equations for field strength and space charge density are

$$E = \frac{r_0}{r} \left[\frac{i}{2\pi K \epsilon_0 r_0^2} (r^2 - r_0^2) + E_0^2 \right]^{1/2} \quad (8)$$

$$\rho = \frac{i}{2\pi r_0 \kappa} \left[\frac{i}{2\pi \kappa \epsilon_0 r_0^2} (r^2 - r_0^2) + E_0^2 \right]^{-1/2} \quad (9)$$

A graph of the functions for a certain set of initial conditions is given in Figures 7 and 8. Interestingly, in the space charge dominated case, the space charge density is independent of position. The cylindrical analysis was used by Shahin to model his cylindrical ion source. However, the dimensions of his source, as well as his low ion currents, made space charge influences negligible.¹⁹

Spherical

Analogous to the cylindrical case, this geometry, shown in Figure 9, involves concentric spheres. The inner sphere, which acts as an ion supply, is of radius, r_0 . The radius of the outer sphere is r_1 . The two spheres are separated by a potential difference, and current flows from the inner sphere to the outer sphere by the drift of charged particles of mobility, κ . The field strength is E_0 at the inner sphere surface ($r=r_0$).

The mathematical analysis of the spherical geometry gives field strength and ion density in terms of distance, r , from a point at the center of the two spheres. Mathematically, the functions are valid in the region between the concentric spheres. A detailed derivation of the

