This is to certify that the

thesis entitled

THEORY AND MODELING OF
NONEQUILIBRIUM ELECTRON-MOLECULE
INTERACTION IN HYDROGEN

presented by

Terrence Joseph Morin

has been accepted towards fulfillment
of the requirements for

Masters degree in Chemical Engineering

Martin C Hawley
Major professor

Date May 6, 1982

THEORY AND MODELING OF NONEQUILIBRIUM ELECTRON-MOLECULE INTERACTION IN HYDROGEN

By

Terrence Joseph Morin

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemical Engineering

1982

ABSTRACT

THEORY AND MODELING OF NONEQUILIBRIUM ELECTRON-MOLECULE INTERACTION IN HYDROGEN

By

Terrence Joseph Morin

Calculations of kinetic rate coefficients for ionization of ground state H_2, dissociation by transition to the first triplet state and one quantum excitation from the vibrational ground state in a high frequency, bounded electrical discharge are made based on a solution of the Boltzmann transport equation. Experimental cross-sections for specific vibrational and electronic transitions are used to specify the collision operator and then the Boltzmann equation is solved by the method of a spherical harmonic expansion. The distribution functions and associated inelastic excitation rate coefficients are calculated for a range of electric field strength, pressure and discharge geometry. The electric field strengths at breakdown are also calculated and the calculated values reproduce experimental results. Calculated average electron energies are linear in the electric field strength to pressure ratio. Also developed are means to analyze Langmuir double probe results to determine the average electron energy in laboratory discharges.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the financial support of the NASA-Lewis Research Center and the encouragement and assistance of Dr. Martin C. Hawley.

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NOTATION

Greek letters

α_1, α_2, α_3	distribution function parameters
β_1, β_2	distribution function parameters
γ	collision frequency (s^{-1})
δ	dirac delta distribution
ε	energy (ev)
ε_{j1}	threshold energy of type j collision
ε_{j2}	energy transferred in type j collision
ε_{ion}	energy of new electrons resulting from ionization of neutral molecule
μ	mobility (kg. $c^{-1} \cdot s^{-1}$)
ν	collision frequency (s^{-1})
σ	cross-section (m^2)
ω	frequency (s^{-1})
Ω	volume of phase space

a_0	Bohr radius of H atom (m)
e	electronic charge (c)
E	electric field strength ($V \cdot m^{-1}$)
f	distribution function ($ev^{-3/2}$)
F	force (N)
ℓ	mean free path (m)
m	electron mass (kg)

M	neutral mass, Mach number (kg)
n	electron number density (m^{-3})
N	neutral number density (m^{-3})
P_k	Legendre polynomial
$\underset{\hat{}}{r}$	spatial coordinate (m)
R	radius (m)
t	time (s)
v	velocity ($m \cdot s^{-1}$)
$\underset{\hat{}}{v}$	velocity coordinate ($m \cdot s^{-1}$)
$\underset{\hat{}}{\nabla}_r$	gradient operator in position space
$\underset{\hat{}}{\nabla}_v$	gradient operator in velocity space

INTRODUCTION

The energetic non-equilibrium environment of a low pressure gas discharge is characterized by nonlinear kinetic and transport phenomena and multiple channel energy transfer. It is this multichannel transfer feature that is often exploited in the application of gas discharge technology. For example, molecules of a diatomic gas may be excited to non-equilibrium distributions over rotational, vibrational and electronic states, including dissociation through several pathways. Atomic recombination processes may involve three collision partners. It is therefore of fundamental importance that the relative roles of each of the energy transfer mechanisms be determined. Equally important is the identification of the principal determinants of the product species and energy distributions.

In analysis of energy transfer in a weakly ionized pure diatomic gas the two fluid model is a useful conceptual framework within which to develop a calculational approach. The two fluid model, as an idealization of the transport phenomena in a stream of weakly ionized "heavy molecules" (hereafter referred to as the background gas), separates the gas stream into a background component, molecules and ions, and an electron gas component. Collisional and radiative interaction of each fluid with the other and with the environment is described in appropriate terms in the single component linear momentum and energy balance equations and/or appropriate collision integrals of the Boltzmann equation. Radiative transfer excluded, intracomponent transfer in the electron gas is by long range coulombic interaction. Intercomponent electron-background collisional energy transfer mechanisms may be divided into elastic, superelastic and inelastic. For weakly ionized gases, electron-ion scattering is generally neglected. Intracomponent transfer in the background gas is by short range elastic and inelastic collisions. For the electron gas, energy transfer with the environment is through the external electric field and boundary effects. Boundary effects and radiative transfer are the mechanisms for interaction between the background gas and environment.

Once the form of the kinetic expressions and coefficients are specified the balance equations may be solved to give information concerning energy transfer in a gas discharge.

Of specific interest are answers to the following questions.

a) How do individual energy transfer rates, e.g. rotational, vibrational, electronic excitation rates, depend on each other and what dependence do they exhibit on observable system variables e.g. gas pressure, electric field strength?

b) What experiments, experimental techniques or applications are suggested?

In progressing toward satisfactory resolution of these issues several tasks are undertaken. First, the possible collision processes are discussed and evaluated in light of their role as energy transfer pathways. Important collision processes are selected on this basis and calculational approaches are reviewed.

Second, the Boltzmann equation, with the collision terms previously determined, is solved and inelastic collision rates are calculated for the case of a high frequency bounded discharge in H_2.

These individual collision rate coefficients may then be used in a macroscopic model which includes relaxation and transport processes. Model performance may be used to analyze the potential of a high frequency bounded discharge in H_2 to couple energy to the rotational, vibrational, electronic or translational reservoirs.

TRANSFER IN THE ELECTRON GAS

A. Review of collision processes

1. Electron-electron interaction

Electron pair interactions are generally divided into binary close encounters and distant coulomb encounters. The close encounters are those collisional processes which occur within the strong interaction radius*, a distance much less than the interelectron distance. The long range coulomb encounters are those interactions which occur within a Debye radius**, and although are often modeled as binary encounters they involve many electrons and ions. Both types of electron pair interactions are randomizing processes. That is, an initially mono-energetic electron beam is which these pair interactions take place will, in the course of time, be characterized by a distribution of electron energies. For any initial distribution, the influence of the pair interactions is to "Maxwellianize" the distribution of energies. So the electron energy distribution in a discharge dominated by electron pair interaction would be close to a Maxwellian distribution.

For low density plasmas, where the strong interaction distance is much less than the interelectron distance, the close encounters may be neglected. The role of far encounters is determined by the

---

*The strong interaction radius is equal to the distance from the electron at which the interaction energy is twice the value of the electron kinetic energy.

**The Debye radius is equal to the distance from the electron at which the interaction energy and kinetic energy are equal magnitude of the electron particle density and the transport cross-section. Simple expressions for the transport cross-section may be derived with the assumption of a central coulomb potential. For small deflection encounters the quantum mechanical and classical approaches give identical results. Far encounters are predominantly characterized by small deflections and this feature is often exploited in solution of the Boltzmann equation describing particle transport in the electron gas. The integrand of the collision operator is expanded in terms of $(\Delta\varepsilon/\varepsilon)$ and the Fokker-Planck equation results if no other collisional processes are included.

Hazeltine (1939) was one of the first to examine the relative significance of electron pair far encounters and electron-background elastic scattering. Assuming a shielded Coulomb potential Hazeltine derives the electron pair interaction differential cross-section from quantum-mechanical considerations. He then determines the energy distribution functions corresponding to two extreme cases.

1) Electron pair interactions are dominant. The derived cross-section is used.
2) Electron-neutral elastic scattering is dominated. A velocity independent transport cross-section is assumed.

For the first case a Maxwellian electron energy distribution results; for the second case a Druyvestuyn distribution results. So it may be expected that the transition from case two to case one is accompanied by a "Maxwellianization" of the distribution function. Hazeltine then presents criteria for determining when exclusion of electron pair interactions is a justified simplification of the collision operator. For N_2 or Ne the assumption in case two of a velocity independent transport cross-section is realistic. For H_2 and He and characteristic electron energies above lev the transport cross-section is inversely related to electron energy resulting in a constant elastic collision frequency. The distribution function is Maxwellian rather than the Druyvestuyn and so no real change in the distribution is effected by the transition from case two to case one. Hazeltine's analysis does not include inelastic collision processes. Dreicer (1960) and more recently, Rockwood (1974) have investigated the relative roles of electron-neutral elastic, inelastic scattering and electron-electron coulomb interaction. Both Dreicer and Rockwood are concerned with d.c. gas discharges and both report a numerical solution of the Boltzmann equation. Dreicer concludes that the evolution of the distribution function from that characteristic of a Lorentizian gas to the equilibrium distribution occurs roughly over four orders of magnitude of the ionization fraction (10^{-6} - 10^{-4}). The distribution function is relatively insensitive to the electron density and strongly non-Maxwellian, indicating that the inelastic collision processes are dominant. Rockwood does a similar analysis for the effect of electron pair interaction and electron-ion interaction in Hg, $CO_2/N_2/He$ and CO/N_2 mixtures. Rockwood takes into consideration electron-neutral elastic and inelastic scattering and coulomb interactions, described by the Fokker-Planck equation. For atomic gases Rockwood concludes that electron pair interaction effects alter the distribution function to the largest extent when E/N and/or ε is small. If furthermore, there is a low-energy region free of inelastic cross-sections, then electron-electron interaction can alter transport phenomena.

For molecular gas discharges where there are large inelastic cross-sections below the first ionization potential Rockwood concludes that electron pair interactions are quite ineffective in maintaining a Maxwellian distribution.

For low electron density discharges in molecular gases like H_2, N_2, CO the contribution of electron pair interaction to energy transport may be justifiably neglected.

2. Electron-background interaction

Like intracomponent transfer in the electron gas, intercomponent transfer between electron gas and background gas may be separated into several regimes. Close encounters of electrons with neutral atomic and molecular species may be classed as elastic, inelastic or superelastic. For singly charged molecular and atomic ions the electron and ion densities are approximately equal in the bulk discharge and so for weakly ionized discharges the coulomb interaction between electrons and ionic species would not significantly effect intercomponent energy transfer. A third mechanism for intercomponent energy transfer is ion-electron recombination in the bulk discharge and at boundaries.

The relative significance of collisional transfer by elastic, inelastic or superlastic collisions depends on the magnitude of the total cross-sections for each process. Swarm experiments using the method of Ramsauer (1921) have been applied to the determination of the total cross-section of H_2 toward slow electrons. The coarse structure of the cross-section is representative of electron-neutral elastic scattering and indicates that below 1 ev the cross-section is velocity independent; above 1 ev it is inversely proportional to electron velocity. The same is true of atomic hydrogen. The differential cross-section for H_2 in slow electrons has been measured by Shyn and Sharp (1981) and the total collision frequency may be calculated from the cross-section in the following way.

$$\nu(v) = N\,v\,\sigma(v)$$

where:

$\nu(v) \equiv$ total collision frequency
$v \equiv$ electron velocity
$N \equiv$ scattering center density
$\sigma(v) \equiv$ collision cross-section (Fig. 1)

So for elastic electron-H,H_2 scattering the collision frequency is electron velocity independent above 1. ev.

The fine structure of the total cross-section gives some information concerning cross-sections for collisional excitation of rotational and vibrational states. Detailed calculated cross-sections were obtained by Engelhardt and Phelps (1963) by assuming trial forms for the inelastic cross-sections, solving the Boltzman equation and then comparing the experimental and the calculated diffusion coefficient, electron mobility and ionization frequency. The method is repeated until acceptable agreement is obtained. Cross-sections for $v = 0 \rightarrow v = 1$ and $v = 0 \rightarrow v = 2$ direct impact vibrational excitation have been measured by Schultz (1964) (Figure 2).

Cross sections for dissociation of molecular hydrogen by direct electron impact excitation of ground state H_2 to the lowest triplet state have been measured by Corrigan (1965) (Fig. 3). The total ionization cross-section has been measured by Rapp and Englander-Golden (1965) (Fig. 4).

Energy transfer by superelastic collisions i.e. from background to electrons, in weakly ionized H_2 is not significant in comparison with inelastic transfer, i.e. to rotational, vibrational or electronic energy, for two reasons. First the characteristic energy of the electron gas is much

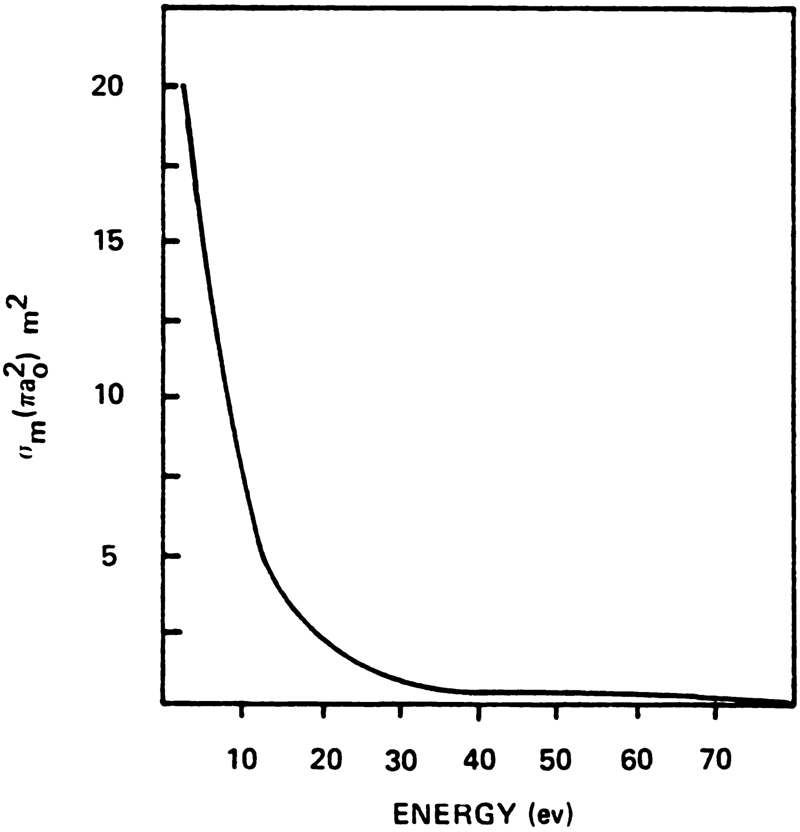


Figure 1. Momentum transfer cross-section of H_2.
Shyn and Sharp (1981)

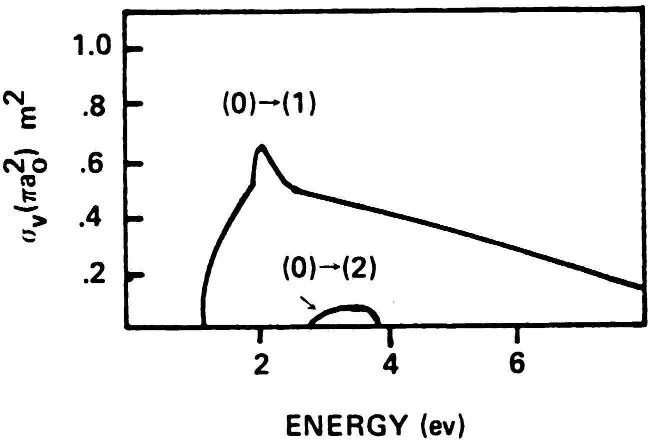


Figure 2. Cross-section for (0→1), (0→2) vibrational excitation of H_2. Schulz (1964)

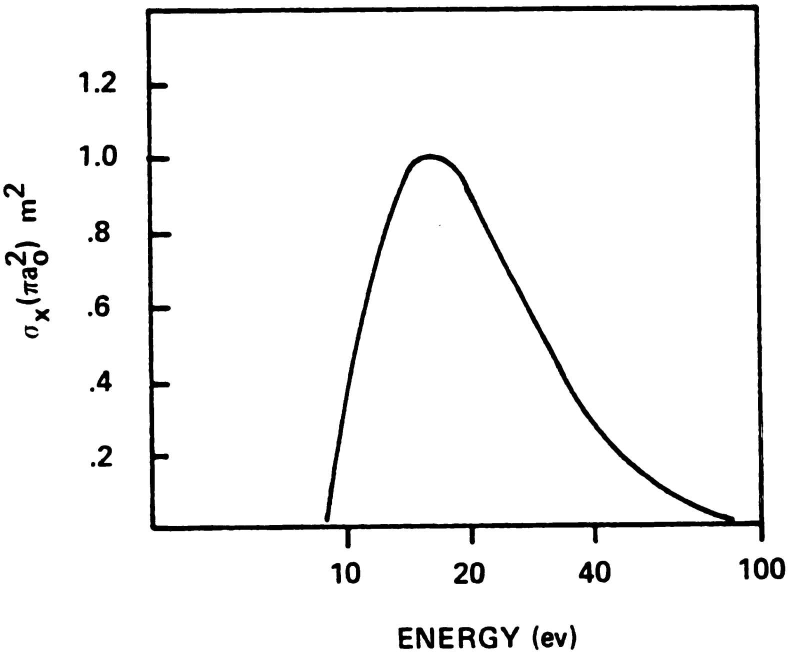


Figure 3. Cross-section for dissociation of H_2 by electronic excitation. Corrigan (1965)

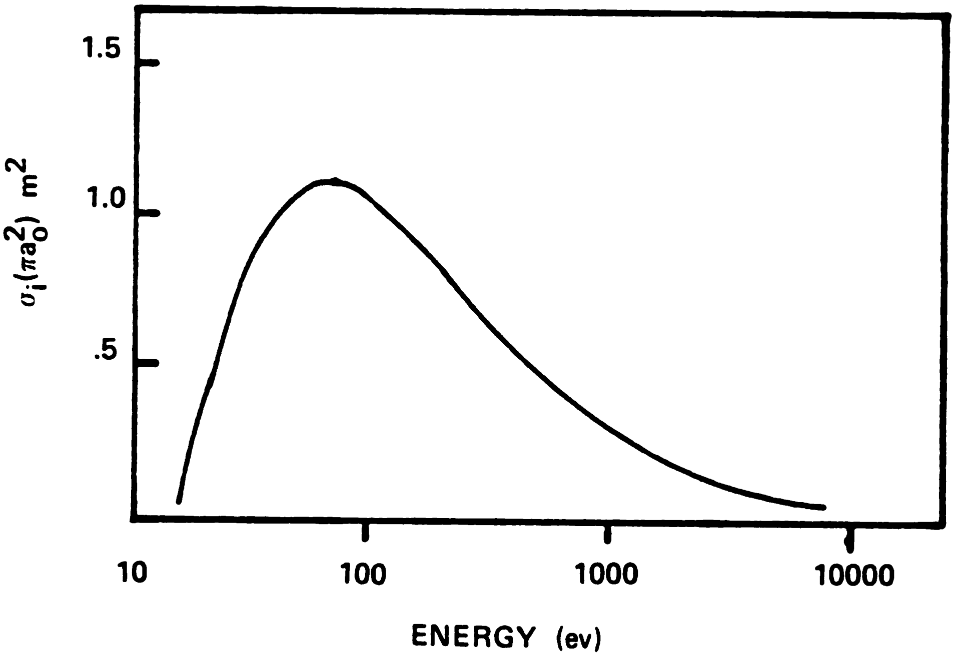


Figure 4. Total ionization cross-section for production of H_2^+. Rapp and Englander-Golden (1965)

greater than that of the background, and secondly because of the very low concentration of metastable species.

Energy transfer by electron-ion recombination is a density dependent process and the bulk phase recombination is generally neglected in weakly ionized discharges.

3. Interaction with environment

While bulk phase electron-ion recombination is not a significant energy transport mechanism in weakly ionized discharges the electron-ion recombination at surfaces is a dominant electron capture process and an important mechanism for energy transfer to the boundary of the discharge. Transport of electrons to the boundary is generally diffusive in the absence of an external magnetic field or collective large scale plasma oscillations. The diffusion of electrons is retarded by the sheath potential and so the electrons escaping to the boundary are characterized by energies above the sheath potential.

B. Review of methods to calculate energy transfer rates from electron to background gas.

Both transport theory and calculational approaches for electrons in a weakly ionized gas are based on the Boltzmann equation, which describes the electron distribution function in configuration and velocity space.

$$\frac{\partial f}{\partial t}(\underset{\wedge}{r},\underset{\wedge}{v},t) = -\underset{\wedge}{v}\cdot\underset{\wedge}{\nabla}_r f(\underset{\wedge}{r},\underset{\wedge}{v},t) - \frac{\underset{\wedge}{F}}{m}\cdot\underset{\wedge}{\nabla}_v f(\underset{\wedge}{r},\underset{\wedge}{v},t) + S(f(\underset{\wedge}{r},\underset{\wedge}{v},t))$$

The time rate of change of the distribution of electrons in phase space is equal to the sum of three terms. The first term is the particle "source" term due to electron motion. The second term is the source term due to applied and induced forces. The third term is the Boltzmann collision operator and is the particle source due to binary encounters between electron pairs, electron-neutral, and electron-ion pairs.

For electrons in a weakly ionized gas the Lorentz force relation is assumed.

$$\underset{\wedge}{F} = -e\,(\underset{\wedge}{E} + \underset{\wedge}{v} \times \underset{\wedge}{B})$$

Generally, there is no external magnetic field and so the Boltzmann equation may be written.

$$\frac{\partial f}{\partial t}(\underset{\wedge}{r},\underset{\wedge}{v},t) = -\nabla_{\underset{\wedge}{r}} \cdot \underset{\wedge}{v} f(\underset{\wedge}{r},\underset{\wedge}{v},t) + \nabla_{\underset{\wedge}{v}} \cdot \frac{e\underset{\wedge}{E}}{m} f(\underset{\wedge}{r},\underset{\wedge}{v},t) + S[f(\underset{\wedge}{r},\underset{\wedge}{v},t)]$$

For binary encounters between electrons and particles possessing internal structure the Boltzmann collision operator may be represented in terms of the electron distribution function, particle distribution function, F, differential cross sections for each type of encounter, and relative velocities.

$$S = \sum_{j,j'} \int_{v_2}\int_{\Omega} [f(\underset{\wedge}{r},\underset{\wedge}{v}_1',t)\, F_{j'}(\underset{\wedge}{r},\underset{\wedge}{v}_2',t) - f(\underset{\wedge}{r},\underset{\wedge}{v}_1,t)\, F_j(\underset{\wedge}{r},\underset{\wedge}{v}_2,t)]$$
$$|\underset{\wedge}{v}_1 - \underset{\wedge}{v}_2|\, \sigma_j^{j'}(|\underset{\wedge}{v}_1 - \underset{\wedge}{v}_2|,\theta)\, d\Omega\, d^3v_2$$

The term $\sigma_j^{j'}(|\underset{\wedge}{v}_1 - \underset{\wedge}{v}_2|,\theta)$ is the differential cross-section for a binary encounter of an electron and a particle of internal state j resulting in an electron and a particle of internal state j′. Solution of the Boltzmann equation in this form requires knowledge of the differential cross-section for each encounter, the distribution functions of the neutral and ion gases and an assumption concerning the relationship between point sources and electric field strength. Such detailed differential cross-section data is not available for even simple systems. For weakly ionized gases the neutral species distribution function is often assumed to be the product of a maxwellian velocity distribution and a Boltzmann distribution over each internal degree of freedom.

Methods for explicit calculation of the electron distribution function and electron-neutral energy transfer rates may be divided in two groups. The first method involves assumption of a semi-empirical parameterized distribution. Energy balance relations are then written in terms of the distribution parameters, temperature for example, instead of the distribution itself. This method is used in conventional discharge theory and as the basis for some plasma diagnostic techniques. The second method is that of direct solution of the Boltzmann equation, for which there are several approaches.

1. Assumption of a parameterized distribution

The most oftenly assumed velocity distribution is of the form

$$f\ (\varepsilon) = \alpha_1 \exp(-\alpha_2 \varepsilon)$$

and is the maxwellian distribution. This distribution function is the dominant term in a series solution of the Boltzmann equation for at least three special cases.

(i) Time independent, spatially homogeneous plasma, no external forces (exact solution given by maxwellian distribution)

(ii) Time independent, spatially homogenous plasma, Lorentz force, elastic electron-neutral interaction with cross-section inversely proportional to electron velocity, superelastic and inelastic interaction neglected.

(iii) Time independent, spatially homogeneous plasma, Lorentz force, electron pair encounters only with cross-section independent of electron velocity.

The assumed distribution is applied in discharge afterglows by analogy to case (i); in weakly ionized inert gas discharges by analogy to case (ii); in high electron density discharges by analogy to case (iii). The application made of this distribution is far wider than the limited scope defined by these three cases. The Maxwellian distribution forms the basis of much of conventional gas discharge analysis including the work of VonEngel (1965) on the relationship between electron density, discharge geometry and average electron energy; the work of Bell (1970, 1972, 1973) on calculation of dissociative excitation rates in H_2 and O_2, and development of energy and momentum balance equations in terms of an electron "temperature".

The electric probe technique, introduced by Langmuir (1924), is often used to measure electron density and average energy by relating these variables to the current-voltage characteristic curve of the probe measurement. The relationship so developed assumes a Maxwellian velocity distribution, thus restricting application of the probe technique to the special cases mentioned above. For other applications the theory should consider the effect of non-Maxwellian velocity distributions. (See Appendix B).

The probe technique may also be applied in some discharges to determine the electron velocity distribution from the current-voltage characteristic curve. Boyd and Twiddy (1959, 1960) have applied this technique in the low pressure (1 - 13 Pa) positive column of d.c. discharges in hydrogen and argon. They report a bimodal distribution for electrons in hydrogen and a closely Druyvestuyn distribution for argon; both are strongly non-Maxwellian. In view of these experimental indications the assumption of a Maxwellian velocity distribution in a weakly ionized discharge is suspect at best.

The Druyvestuyn distribution is another often assumed solution of the Boltzmann equation and is of the form

$$f(\varepsilon) = \alpha_1 \exp(-\alpha_2 \varepsilon^2)$$

The Druyvestuyn distribution is the dominant term of a series solution of the Boltzmann equation for the case of a time independent, spatially homogeneous d.c. discharge in which elastic electron-neutral collisions are dominant and have a velocity independent cross-section. This assumption of a velocity independent cross-section results in the characteristic "depleted tail" of the Druyvestuyn distribution. Ionization rates calculated from the Maxwellian and Druyvestuyn distributions greatly differ.

Other assumed distributions are the composite Maxwellian-Druyvestuyn of Haseltine (1939) and the two and three electron group models of Vriens (1973, 1974, 1977). Haseltine examines the relative role of electron pair interaction and electron-neutral elastic scattering assuming a velocity independent cross-section for the elastic process and a derived cross-section for the coulomb interaction. The composite Maxwellian-Druyvestuyn distribution, of the form

$$f(\varepsilon) = \alpha_1 \exp(-(\alpha_2 \varepsilon^2 + \alpha_3 \varepsilon))$$

is used to describe the continuous transition of the distribution from Maxwellian to Druyvestuyn as the dominant energy transfer mechanism shifted from coulomb interaction to electron-neutral elastic scattering. Haseltine does not consider the effect of inelastic collision processes in the analysis, restricting application of the work to gases which do not have significant inelastic cross-sections in the energy range below the first ionization potential. The composite distribution also results from a series solution of the Boltzmann equation for the case of a spatially homogeneous a.c. discharge in which elastic electron-neutral scattering is dominant and is characterized by a velocity independent cross-section.

The assumed distribution functions for the two and three electron group models of Vriens are characterized by two and three electron temperatures, respectively. A Maxwellian distribution is assumed over each of several subsets of the entire energy range and each range is characterized by a temperature. Balance equations for each group of electrons are written in terms of electron temperatures and densities. Application of the technique has been made to Ar, Cs-Ar and Hg-Ar discharges.

2. Direct solution

Three general approaches are taken in direct solution of the Boltzmann equation and Table 1 gives a summary of previous calculations of electron distribution functions in H_2. Each approach involves some degree of simplification as will be pointed out in the discussion to follow.

TABLE 1. Summary of previous calculations in H_2.

Worker	Calculational Approach	Collision processes included	External field	Boundary effects	Space charge
MacDonald & Brown (1949)	2-term spher. harm.	lumped electronic	a.c.	yes	no
Allis & Brown (1952)	2-term spher. harm.	lumped electronic	a.c.	yes	no
Rose & Brown (1955)	2-term spher. harm.	lumped electronic	a.c.	yes	yes
Dreicer (1960)	numerical	lumped electronic	d.c.	no	no
Frost & Phelps (1962)	2-term/numerical	rotational, vibrational, electronic	d.c.	no	no
Engelhardt & Phelps (1963)	2-term/numerical	rotational, vibrational, electronic	d.c.	no	no
Baraff & Buchsbaum (1963)	numerical	rotational, vibrational, electronic	a.c.	yes	no
Garscadden & Bailey (1981)	2-term/numerical	rotational, vibrational, electronic	d.c.	no	no

(a) Expansion in spherical harmonics

The expansion of the distribution function in spherical harmonics may be thought of as a perturbation expansion in which an isotropic distribution is the reduced term of the expansion. The higher order terms are increasingly anisotropic. For a close to isotropic distribution the series converges rapidly.

Without further assumptions the velocity distribution is expanded in spherical harmonics in velocity space by substitution of the following series expansion.

$$f_v\,(\hat{r},\hat{v},t) \;=\; \sum_{k=o}^{\infty} f_k(\hat{r},\hat{v},t)\; P_k(\cos\theta)$$

$P_k(\cos\theta)$ ≡ Legendre polynomials

θ ≡ angle between $\hat{v}$ and $\hat{z}$

The first few terms are -

$$f_v(\hat{r},\hat{v},t) \;=\; f_o(\hat{r},v,t) + f_1(\hat{r},v,t)\cos\theta + \frac{1}{2} f_2(\hat{r},v,t)\;[3\cos^2\theta - 1]$$

Substitution of the infinite series into the Boltzmann equation yields an infinite set of coupled integro partial differential equations of a finite number of terms. The first three equations are given below. (See Appendix A).

$$\frac{\partial f_0}{\partial t} + \frac{v}{3}\frac{\partial f_1}{\partial z} - \frac{eE_z}{m\,3}\,\frac{1}{v^2}\,\frac{\partial}{\partial v}\,(v^2 f_1) \;=\; S_0$$

$$\frac{\partial f_1}{\partial t} + v\,[\frac{\partial f_0}{\partial z} + \frac{2}{5}\frac{\partial f_2}{\partial z}] - \frac{eE_z}{m}\,[\frac{\partial f_0}{\partial v} + \frac{2}{5v^3}\,\frac{\partial}{\partial v}\,(v^3 f_2)] = S_1$$

$$\frac{\partial f_2}{\partial t} + v[\frac{2}{3}\,\frac{\partial f_1}{\partial z} + \frac{3}{7}\frac{\partial f_3}{\partial z}] - \frac{eE_z}{m}\,[\frac{2}{3}\frac{v\partial}{\partial v}\,(\frac{f_1}{v}) + \frac{3}{7}\frac{1}{v^4}\,\frac{\partial}{\partial v}\,(v^4 f_3)] = S_2$$

Expansion of the terms in the collision operator results in the following form for S_k.

$$S_k = \sum_{j,j'} \int_{v_2} d\underset{\hat{}}{v}_2 \int_{\Omega} d\Omega\,\sigma_j^{j'}(|v_2-v_1|,\Omega)\;|v_2-v_1|\;\{f_k(\underset{\hat{}}{r},\underset{\hat{}}{v}',t)\;F_{j'}(\underset{\hat{}}{r},\underset{\hat{}}{v}',t)$$

$$P_k(\cos\theta) - F_j(\underset{\hat{}}{r},\underset{\hat{}}{v},t)\;f_k(\underset{\hat{}}{r},\underset{\hat{}}{v},t)\}$$

Now it is assumed that the randomizing effect of collisional processes results in a close to isotropic velocity distribution, so that the entire distribution may be approximated by the first two or three terms.

The two term approximation is known as the Lorentz approximation and is much used. The validity of the assumption concerning the number of terms retained is verified a posteriori by comparison of the magnitude of the terms. Ginzburg and Gurevich (1960) and Ferrari (1975, 1977) have presented various criteria for determining the range of applicability of the Lorentz approximation. That of Ginzburg et al., is rather general. Ferrari however develops an a posteriori technique which makes use of the ratio of the sum of the inelastic collision frequencies to the elastic collision frequency (ξ_1) and the ratio of the sum of the effective inelastic collision frequencies to the effective elastic collision frequency (η_1). Ferrari draws on equivalence between the expansion in spherical harmonics and a perturbation expansion in powers of ξ_1, η_1. For ξ_1, η_1 of the same order of magnitude as (m/M), the Lorentz approximation is valid. For ξ_1, η_1 of the same order of magnitude as $(m/M)^{\frac{1}{2}}$ the three term approximation is necessary for an accurate solution. For ξ_1, η_1 of order unity, use of another approach is required as no approximation using a small number of terms is valid.

Morse et al. (1935) introduced the approximate method of Lorentz, originally developed for electron conduction in metals, to transport theory of electrons in d.c. electric discharges. Elastic scattering of electrons in a background of stationary neutral gas molecules was considered for a spatially homogeneous weakly ionized gas. A velocity independent transport cross-section was assumed and the resulting distribution was that of Druyvestuyn. Had Morse et al. used a transport cross-section inversely proportional to velocity a Maxwellian distribution would have resulted. Such a cross-section is representative of low atomic weight gases such as H_2, He. Although the velocity averaged transport coefficients do not differ greatly from the Maxwellian to the Druyvestuyn distributions, the fraction of electrons having energies associated with the high energy tail are significantly different. The excitation and ionization rates calculated from a Maxwellian distribution are many times greater than those from a Druyvestuyn distribution. Holstein (1946) extends the work of Morse and reformulates the problem to include the effect of inelastic collision processes.

Holstein derives the integrodifferential Boltzmann equation for the most general case of a time dependent, spatially inhomogeneous plasma in which elastic and inelastic scattering occurs. He assumes the Lorentz approximation and also assumes two simple models for collision processes. The cross-section for elastic transfer is velocity independent and the total inelastic cross-section is velocity independent above a threshhold and equal to zero below it. No application to a specific gas species is made in Holstein's analysis.

McDonald and Brown (1949) apply a similar approach to hydrogen. Empirical inelastic excitation efficiencies, taken from the experimental work of Ramien (1931), are used to model the ionization and unspecified excitation processes. Individual excitation processes are not examined. The ionization frequency and diffusion coefficient of electrons in hydrogen are calculated from the derived distribution function and compared with experimental results.

The results of the analysis predict breakdown electric fields in good agreement with experimental results. Allis and Brown (1952) derive a simpler solution to the problem addressed by MacDonald and Brown by neglect of the electron free diffusion term with respect to inelastic transfer in the high energy region of the distribution function. The result of Allis and Brown accurately predicts breakdown fields in hydrogen over a wider range in pressure than does the result of MacDonald and Brown. The work of Rose and Brown (1955) generalizes the two earlier works to include the effect of space charge. In all three works inelastic processes below 8.9 ev are neglected and the inelastic processes in the energy range 8.9 - 16. ev are described by a single excitation frequency calculated from the work of Ramien. The works also share the maximum energy loss assumption in common. This assumption models electron-molecule collisions as events in which electrons transfer all of their kinetic energy to the molecular partner. This assumption significantly alters the form of the collision term in the Boltzmann equation. All electrons which transfer kinetic energy to a gas molecule through collision then reappear at the origin in energy space.

The three works also neglect electron pair interactions. Dreicer (1960) examines the intermediate case of the strongly ($n/N > .01$) but not completely ionized hydrogen d.c. discharge. His treatment of inelastic collision terms in the Boltzmann equation is like that of MacDonald and Brown. The d.c. unbounded discharge is also modeled by Frost and Phelps (1962) and Engelhardt and Phelps (1963).

In developing a set of inelastic excitation cross-sections Frost and Phelps obtain a solution of the Boltzmann equation for the two term approximation. In an iterative procedure, an assumed set of cross-sections is included in the Boltzmann collision operator and the isotropic portion of the distribution function is calculated from which the electron diffusion coefficient and mobility are calculated. These calculated values are compared with experimental values of the coefficients. Assumed cross-sections are varied until good agreement over a wide range of d.c. electric field strength and neutral gas pressure is made.

Cross-sections of single and multi-quantum vibrational excitation in H_2 were not available at the time Frost and Phelps (FP) and Engelhardt and Phelps (EP) developed their results. Schultz (1964) compares experimental cross-sections with those calculated by FP, EP and finds major disagreement both in threshold energy and the energy at which a maximum in cross-section occurs. EP predict a threshold of 0.53 ev and a maximum at 4.35 ev. Schultz measured a cross-section for (v=0) → (v=1) with threshold of 1.0 ev and a maximum at 2.0 ev. Over the low energy range of 0-10 ev the predicted cross-section is much larger than the measured one. This would indicate that a larger than expected vibrational excitation cross-section is required in order to obtain good agreement between calculated and measured transport coefficients. Allis and Brown (1952) note however, that if vibrational excitation cross-sections are included in the calculation of breakdown field strength, agreement cannot be obtained between calculated and measured values.

A more recent approach to the problem is that of Allis and Haus (1974), who introduce simplified models of inelastic collision processes and obtain a closed form analysis of the electron distribution in CO, CO_2 and a CO_2;N_2 mixture. From examination of the Boltzmann equation Allis and Haus identify the electron fluxes in energy space that result from the applied field and from the inelastic collision processes. The collision operators for each of the inelastic processes are written in terms of excitation frequencies. If (n) collision processes are included, the approach results in an algebraic relation for the distribution function given in terms of (n+1) constants. Application of the normalization condition reduces the number of constants by one. Other assumptions and/or relations are necessary to uniquely specify the electron distribution. Unlike other workers Allis and Haus use the resulting distribution function to calculate kinetic constants for inelastic processes other than ionization.

Recent work by Garscadden and Bailey (1981) studies the effect of non-equilibrium populations of vibrationally excited H_2 on the rate of dissociative attachment in d.c. unbounded discharges.

(b) Perturbation expansion

In a weakly ionized gas the intercollisional energy transfer from electric field to electron and the ratio of electron mean free path to characteristic length are small. Bernstein (1969) takes direct advantage of this in constructing a perturbation expansion of the Boltzmann equation in terms of these small parameters. In expanding the collision operator Bernstein includes only electron-neutral elastic encounters but comments on extension of the technique to include inelastic electron-neutral encounters and electron-electron encounters.

Van de Water (1976) extends the work of Bernstein to the case of an instationary ($M \gg 1$), inhomogeneous neutral gas but assumes close to local thermodynamic equilibrium between the neutral gas and electron gas and only electron-neutral elastic encounters. No application of the technique is made to a specific neutral species.

(c) Direct numerical simulation

Baraff and Buchsbaum (1963) solve the Boltzmann equation for an unbounded electron gas in hydrogen, taking into account vibrational and electronic excitation. No assumption regarding angular dependence is made and the distribution function is given as a function of electron energy and angle with respect to the field orientation. The result of their analysis is an upper bound on the effective electric field strength to gas pressure ratio. Baraff and Buchsbaum (BB) show that above this bound the distribution function is sufficiently anisotropic that the Lorentz approximation cannot represent it. This poses no problem for most cases of interest in weakly ionized gases. EP report that the upper bound of BB corresponds to a situation in which upwards of 10% of the input energy is tranferred through ionization processes. There is a major problem with the analysis of BB however, the cross-sections used are those calculated by EP using the Lorentz approximation. As noted by EP, the calculated set of cross-sections is not unique. They should therefore not be used in an evaluation of the Lorentz approximation. The work of BB is an analysis then of the Lorentz approximation <u>and</u> the degenerate set of collision cross-sections calculated by EP. BB do not calculate values for the individual, distribution averaged excitation frequencies.

Rockwood (1974) presents a numerical solution of the Boltzmann equation for an electron gas in both mercury and molecular gas mixtures. Coulomb interactions are included and the calculated distribution function, drift velocity and transport coefficients are given for fractional ionizations below .001. The major results of Rockwood's work have been discussed earlier.

3. Summary of Approaches

An evaluation of the four approaches taken in analysis of gas discharges is based on the following questions.

(a) How much of the physics of the discharge is retained?

(b) How applicable is the result? Is the range of applicability determined *a priori*?

(c) What information is required for the analysis and what information is generated?

(d) Is the approach computationally flexible?

The basic question in mind as these approaches are evaluated is, "Will it describe how individual energy transfer rates (rotational, vibrational, electronic, elastic excitation and de-excitation rates) depend on each other and the dependence they exhibit on observable system variables (gas pressure, external field strength)"? None of the works reviewed provide an answer to this fundamental question for high frequency self-sustained discharges in a bounded region.

The assumption of a solution is the simplest approach. The physics of the problem is imposed by the solution assumed rather than extracted from a consideration of the important collisional processes. To the extent that there exists strong correspondence between the physics of the assumed solution and that of the problem, the approach may be said to retain the essential character of the problem. Generally though, the range of physical circumstances in which this strong correspondence exists cannot be determined *a priori*. The range of applicability may then be determined either "intuitively" or on the basis of a more accurate analysis. Often the value of the more accurate analysis lies in defining those regions where simpler models are sufficient (Dang and Steinberg, 1980). Computationally, all three popular assumed solutions are simple and flexible. Only physical constants for the particular species of interest are required. No information concerning the boundary or collisional processes is required. Each assumed solution, of course, generates the distribution function for the electron gas. Transport and kinetic coefficients may be derived from velocity averages of the distribution function and appropriate cross-sections.

In most cases of interest in weakly ionized discharges, where the range of applicability of the assumed distribution is unknown, the assumption of a distribution function is at best, an empirical approach.

For those approaches in which direct solution of the Boltzmann equation is required, the physics of the problem is reflected in formulation of the collision integral and in the boundary effects. As can be seen from the review of previous work for hydrogen discharges the treatment of the collision integral is varied and sometimes curious. The spherical harmonic expansion, perturbation methods and direct numerical simulation all admit more rigorous formulation of the collision integral for binary point collisions than is generally done.

For the spherical harmonic expansion the range of applicability is determined by comparison of relative order of magnitude of the terms retained in the expansion to those neglected. Comparison of $|f_0|$ and $|f_1|$ would give an estimate of the range of applicability for the Lorentz approximation. Although this is an a posteriori approach it does not require a more complex analysis (i.e. three term expansion) to provide the bounds.

The variable range over which a perturbation expansion may be applied is determined by the number and type of perturbation variables as well as by the local behavior of the function.

The spherical harmonic expansion may be thought of as a perturbation expansion in which the reduced term is the isotropic distribution. As referred to earlier Ferrari has demonstrated an equivalence between a perturbation expansion in mass ratios and the expansion in spherical harmonics. For the perturbation expansion the reduced term is usually the Maxwellian distribution and so it inherently preserves less information about the collision processes than does the reduced term of the expansion in spherical harmonics.

The range of applicability of a strictly numerical approach is generally only limited by the stability and convergence properties of the numerical technique.

For all three approaches which involve direct solution of the Boltzmann equation, collision cross-sections for dominant collisional processes are required. In the case of molecular hydrogen, experimental cross-sections exist for one quantum vibrational excitation, dissociative excitation via $b^3\Sigma_u^+$ and ionization. If boundary effects are considered then some information concerning the geometry and boundary conditions is required.

For computational flexibility the assumed solution approach is most flexible and the numerical and pertubation schemes the least flexible.

The two term expansion in terms of Legendre polynomials (special case of spherical harmonics) is the basis of the approach taken in this analysis of a high frequency, self-sustained bounded discharge in H_2. The following factors support this choice.

1) The reduced term is isotropic though non-equilibrium and retains more information concerning collision and boundary effects than a perturbation scheme.

2) A posteriori calculation of the range of applicability is possible.

3) It is computationally more flexible than either a perturbation or numerical scheme.

C. Development of Model

The Boltzmann equation, derivable from application of balance principles to electrons in phase space, may be written as following.

$$\frac{\partial f}{\partial t}(\underset{\wedge}{r},\underset{\wedge}{v},t) + \underset{\wedge}{v} \cdot \underset{\wedge}{\nabla}_r f(\underset{\wedge}{r},\underset{\wedge}{v},t) + \underset{\wedge}{F} \cdot \underset{\wedge}{\nabla}_v f(\underset{\wedge}{r},\underset{\wedge}{v},t) = S(\underset{\wedge}{r},\underset{\wedge}{v},t)$$

The two tasks involved in obtaining a solution are to specify the form of the collision integral and to expand the equation in spherical harmonics and collect terms.

First note that for non-equilibrium plasmas the average electron energy is generally much larger than the average background gas energy. So in developing the collision integral the assumption is made that the background gas molecules are stationary with respect to the electrons. Four basic collision processes are considered: elastic transfer between electrons and molecules, one quantum vibrational excitation, dissociation of the diatomic species via excitation to a repulsive electronic state and single step ionization.

Consider an element in velocity space, $d\Omega$, in which electrons are entering and exiting through point collisions with the stationary background. The rate at which electrons are removed from the volume element by a type-j collision may be stated in the following integral.

$$R^- = N(\underset{\wedge}{r},t) \int_\Omega v\, \sigma_j(v,\theta)\, f(v,\theta,\phi,t,\underset{\wedge}{r})\, d\Omega$$

where

$N(\underset{\wedge}{r},t)$ = background density

$\sigma_j(v,\theta)$ = cross-section for collision of type-j

$d\Omega$ = $v^2 \sin\theta\, d\theta\, d\phi\, dv$

The rate of appearance of electrons in the volume element by collision of an electron with velocity v´ with a background molecule is also given in terms of an integral.

$$R^{+} = N(\underset{\wedge}{r},t) \int_{\Omega} v' \sigma_j(v',\theta') \; f(v',\theta',\phi',t,\underset{\wedge}{r}) \; d\Omega$$

So the net rate of change of the electron density may be written as the difference of these two terms.

$$R = N(\underset{\wedge}{r},t) \int_{\Omega} \{ v'\sigma_j(v',\theta') \; f(v',\theta',\phi',t,\underset{\wedge}{r}) \; (\frac{d\Omega'}{d\Omega})$$

$$- v\sigma_j(v,t) \; f(v,\theta,\phi,t,\underset{\wedge}{r}) \} \; d\Omega$$

First, note that $(d\Omega'/d\Omega) = (v'^2 dv'/v^2 dv)$. For point collisions the relationship between v´ and v is defined by momentum and energy conservation considerations. For elastic collisions:

$$v' = v/[(1-\frac{m}{M}) \; (1 - \cos\theta)]$$

$$\frac{dv'}{dv} = \frac{v'}{v}$$

$$(\frac{d\Omega'}{d\Omega}) = (\frac{v'}{v})^3$$

So the collision integral becomes:

$$R = N(\underset{\wedge}{r},t) \int_{\Omega} \{ \frac{v'^4}{v^3} \sigma_{el}(v',\theta') f(v',\theta',\phi',t,\underset{\wedge}{r})$$

$$- v\sigma_{el}(v,\theta) f(v,\theta,\phi,t,\underset{\wedge}{r})\} \quad d\Omega$$

For inelastic collisions where some discrete energy loss, v_j^2, of the electron is involved $v'^2 = v^2 + v_j^2$.

$$\frac{dv'}{dv} = \frac{v}{v'}$$

$$(\frac{d\Omega'}{d\Omega}) = \frac{v'}{v}$$

and the integral becomes:

$$R = N(\underset{\wedge}{r},t) \int_{\Omega} \{\frac{v'^2}{v} \sigma_j(v',\theta') f(v',\theta',\phi',t,\underset{\wedge}{r})$$

$$- v\sigma_j(v,\theta) f(v,\theta,\phi,t,\underset{\wedge}{r})\} \quad d\Omega$$

This rate of appearance is velocity averaged, but a velocity dependent source term is the desired quantity. So we let $R = \int_{\Omega} S \; 4\pi v^2 dv$. So for elastic collisions

$$S_{el} = \frac{N(\underset{\wedge}{r},t)}{4\pi} \int_{\theta,\phi} \{\frac{v'^4}{v^3} \sigma_{el}(v',\theta') f(v',\theta',\phi,t,\underset{\wedge}{r})$$

$$- v \; \sigma_{el}(v,\theta) f(v,\theta,\phi,t,\sigma)\} \quad d\omega$$

Where $d\omega = \sin\theta \, d\theta \, d\phi$

And for inelastic collisions the source term has the form:

$$S_j = \frac{N(\hat{r},t)}{4\pi} \int_{\theta,\phi} \{\frac{v'^2}{v} \sigma_i(v',\theta) \, f(v',\theta,\phi,t,\hat{r})$$

$$-v \, \sigma_i(v,\theta) \, f(v,\theta,\phi,t,\hat{r})\} \, d\omega$$

Now we take advantage of the property of elastic collisions that $|v'-v|$ is small. The distribution function is expanded in a Taylor series about v.

$$v'^4 \sigma_{el}(v',\theta) \, f(v',\hat{Y}) = v^4 \, \sigma_{el}(v,\theta) \, f(v,\hat{y}) + \frac{\partial}{\partial v}(v^4 \, \sigma_{el}(v,\theta)$$

$$f(v,\hat{y})) \, (v'-v)$$

$$+ \frac{1}{2} \frac{\partial^2}{\partial_v^2} (v^4 \, \sigma_{el}(v,\theta) \, f(v,\hat{y})) \, (v'-v)^2 + \ldots$$

The first two terms of this expansion are substituted for the integrand in the integral for S_{el}. So the integral for S_{el} becomes

$$S_{el} \cong \frac{N(\hat{r},t)}{4\pi} \int_{\theta,\phi} \frac{1}{v^3} \frac{\partial}{\partial v} (v^4 \, \sigma_{el}(v,\theta) \, f(v,\hat{y})) \, (v'-v) \, d\omega$$

$$\approx \frac{N(\hat{r},t)}{4\pi} \int_{\theta,\phi} \frac{1}{v^2} \frac{m}{M} (1-\cos\theta) \frac{\partial}{\partial v} (v^4 \, \sigma_{el}(v,\theta) \, f(v,\hat{y})) \, d\omega$$

$$S_{el} = \frac{N(r,t)}{4\pi} \frac{1}{v^2} \frac{\partial}{\partial v} \{v^4 \frac{m}{M} \int_{\theta,\phi} (1-\cos\theta)\ \sigma_{el}(v,\theta)\ f(v,\underset{\wedge}{y})\ d\omega\}$$

This result is the same as that used in the work of Holstein, Allis and others. It is in the development of the inelastic source terms that this analysis differs from others.

The complete form of the collision integral is the sum of the integrals for the four collision processes considered. With the collision term specified it remains to approximate the distribution function by an expansion in spherical harmonics, that is:

$$f(v,\theta,\phi,t,\underset{\wedge}{r}) = \sum_{k=0}^{\infty} P_k(\cos\theta)\ f_k(v,\underset{\wedge}{r},t)$$

Substitution of the expansion and utilization of addition theorems and orthogonality properties of the Legendre polynomials yields an ordered, infinite set of equations. This ordered set is further divided by expansion of each $f_k(v,\underset{\wedge}{r},t)$ in a Fourier series in time, that is:

$$f_k(v,\underset{\wedge}{r},t) = \sum_{-\infty}^{\infty} f_k^{\ell}(v,\underset{\wedge}{r}) \exp(j\ell\omega t).$$

In both expansions the series is truncated after the second term. The series expansion is then reduced to the form:

$$f(v,\theta,\phi,t,\underset{\wedge}{r}) = f_0^0(v,\underset{\wedge}{r}) + f_0^1(v,\underset{\wedge}{r}) \exp(j\omega t) + \cos\theta\{f_1^{\,0}(v,\underset{\wedge}{r})$$

$$+ f_1^1(v,\underset{\wedge}{r})\}\exp(j\omega t)$$

The time dependent isotropic term, f_0^1, is discarded as being physically unreasonable. By construction, the isotropic portion of the distribution function is not disturbed by the electric field so one would not expect an induced time dependence.

The three remaining equations may be written as follows.

$$v \underset{\wedge}{\nabla} f_0^0 = \underset{\wedge}{S}_1^0$$

$$j\omega \underset{\wedge}{f}_1^1 - \frac{2e\underset{\wedge}{E}}{m} \frac{\partial f_0^0}{\partial v} = \underset{\wedge}{S}_1^1$$

$$\frac{v}{3} \underset{\wedge}{\nabla} \cdot \underset{\wedge}{f}_1^0 - \frac{e\underset{\wedge}{E}}{3m} \cdot \frac{1}{v^2} \frac{\partial}{\partial v} (v^2 \underset{\wedge}{f}_1^1) = S_0^0$$

Before the equations are simplified further, the series expansion is substituted in the collision integrals to give the following expressions. (See Appendix A for details)

$$S_{0,el}^0 = \frac{m}{M} \frac{1}{v^2} \frac{\partial}{\partial v} [v^3 \gamma f_0^0]$$

$$\underset{\wedge}{S}_1^0 = - \gamma \underset{\wedge}{f}_1^0$$

$$\underset{\wedge}{S}_1^1 = -\gamma \underset{\wedge}{f}_1^1$$

The form of $S_{0,in}^0$ will be developed later.

The collision expressions are substituted into the previous set of differential equations and an uncoupled set of three differential equations results after some rearrangement.

The differential equations for the f_1^0, f_1^1 terms are given in terms of the lead term.

$$-\frac{v^2}{3\gamma}\nabla_r^2 f_0^0 - \frac{2}{3}\frac{|E|^2 e^2 \gamma}{m^2(\gamma^2+\omega^2)}\frac{1}{v^2}\frac{\partial}{\partial v}\left[v^2 \frac{\partial f_0^0}{\partial v}\right] - \left(\frac{m}{M}\right)\gamma\frac{1}{v^2}\frac{\partial}{\partial v}\left[v^3 f_0^0\right]$$

$$- S_{0,in}^0 = 0$$

$$\underset{\wedge}{f}_1^1 = -\frac{v}{\gamma}\underset{\wedge}{\nabla}_r f_0^0$$

$$\underset{\wedge}{f}_1^1 = \frac{\gamma e E}{m(\gamma^2+\omega^2)}\frac{\partial f_0^0}{\partial v}$$

where:

$|E|$ ≡ r.m.s. $\underset{\wedge}{E}$ field magnitude

m ≡ electron mass

M ≡ background gas mass

γ ≡ collision frequency for momentum transfer, constant with respect to v

$S_{o,in}^0$ ≡ collision integrals for inelastic process with $f = f_0^0$

For convenience the independent variable is changed from velocity to energy. Let $\varepsilon = \frac{1}{2} mv^2/e$.

$$\varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial \varepsilon} \left(\varepsilon^{3/2} \frac{\partial f_0^{\,0}}{\partial \varepsilon}\right) + \frac{3m^2(\gamma^2+\omega^2)}{ME^2 e} \varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial \varepsilon} \left(\varepsilon^{3/2} f_0^{\,0}\right) + \frac{(\gamma^2+\omega^2)}{E^2\gamma^2} \varepsilon \nabla_{\underset{\wedge}{r}}^{2} f_0^{\,0}$$

$$+ \frac{3(\gamma^2+\omega^2)}{E^2\gamma\left(\frac{2e}{m}\right)^{\frac{1}{2}}} S_{0,in}^{\,0} = 0$$

Note that the r.m.s. value of the electric field has been replaced by the peak value. For a type - j collision the collision integral may be written as: (See Appendix A for details)

$$S_{0,j}^{\,0} = N(\underset{\wedge}{r},t) \left\{\frac{(\varepsilon+\varepsilon_{j2})}{\varepsilon^{\frac{1}{2}}} \sigma_j(\varepsilon+\varepsilon_{j2}) f_0^{\,0}(\varepsilon+\varepsilon_{j2}) - \varepsilon^{\frac{1}{2}}\sigma_j(\varepsilon) f_0^{\,0}(\varepsilon)\right\}$$

where: $\varepsilon_{j2} \equiv$ energy transfer in collision.

This form may be used for one quantum vibrational excitation, dissociation through electronic excitation and ionization. Assuming that all ionizing collisions result in a singly ionized molecule with ejection of a new, low energy free electron, a different type of collision term is required for the electron flux in energy space due to production of free electrons by such collisions.

$$S_{0,ion}^{\,0} = N(\underset{\wedge}{r},t)\, \varepsilon^{\frac{1}{2}} \sigma_{ion}(\varepsilon)\, f_0^{\,0}(\varepsilon,\underset{\wedge}{r})$$

From balance principles and the assumption of single ionization we require that the net rate of production of free electrons be equal to the net ionization frequency. This requirement determines the value of $\sigma_{ion}(\varepsilon)$. These collision terms are substituted into the differential equation for the lead term of the series expansion to give the following equation.

$$\varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial\varepsilon} \left(\varepsilon^{3/2} \frac{\partial fo^{0}}{\partial\varepsilon}\right) + \alpha_1 \varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial\varepsilon} \left(\varepsilon^{3/2} f_0^{\;0}\right) + \alpha_2 \varepsilon \nabla^2_{\underset{\wedge}{r}} f_0^{\;0}$$

$$+ \alpha \quad \varepsilon^{-\frac{1}{2}} N(\underset{\wedge}{r},t) \left[\sum_j \{ (\varepsilon+\varepsilon_{j2}) \sigma_j(\varepsilon+\varepsilon_{j2}) f_0^{\;0}(\varepsilon+\varepsilon_{j2},\underset{\wedge}{r}) - \varepsilon \sigma_j(\varepsilon) f_0^{\;0}(\varepsilon,\underset{\wedge}{r})\} + \varepsilon \sigma_{ion} (\varepsilon) f_0^{\;0} (\varepsilon,\underset{\wedge}{r})\right] = 0$$

Two conditions apply on the behavior of $f_0^{\;0}$ in energy space.

(1) $f_0^{\;0} (0,\underset{\wedge}{r})$ is bounded, $f_0^{\;0} (\varepsilon,\underset{\wedge}{r}) \to 0$, for $\varepsilon \to \infty$

$$\int_0^\infty \varepsilon^{\frac{1}{2}} f_0^{\;0} (\varepsilon,\underset{\wedge}{r}) d\varepsilon = n(r)$$

The second condition is a normalization condition and results from the definition of the distribution function.

Taking the first moment of the distribution results in:

$$\int_0^\infty \alpha_2 \varepsilon^{3/2} \nabla_r^{\;2} f_0^{\;0} d\varepsilon + \alpha_3 \int_0^\infty N \varepsilon \sigma_{ion}(\varepsilon) f_0^{\;0} d\varepsilon = 0$$

$$\alpha_2 \nabla_r^{\;2} \int_0^\infty \varepsilon^{3/2} f_0^{\;0} d\varepsilon = -\alpha_3 N \int_0^\infty \varepsilon \sigma_{ion}(\varepsilon) f_0^{\;0} d\varepsilon$$

Now the right hand side is proportional to the ionization frequency and the integral on the left hand side is the product of the average energy and the electron density.

$$\alpha_2 \bar{\varepsilon} \nabla^2 n(\underset{\wedge}{r}) = -\frac{\alpha_3 \nu_i n(\underset{\wedge}{r})}{(\frac{2e}{m})^{\frac{1}{2}}} \quad ; \quad \nu_i = N\nu_i^{\,0}$$

$$\nabla^2 n(\underset{\wedge}{r}) = -\frac{\alpha_3 \nu_i \, n(r)}{\alpha_2 \bar{\varepsilon} (\frac{2e}{m})^{\frac{1}{2}}} ; \quad \frac{\alpha_3}{\alpha_2} = 3\,(\gamma\Lambda)^2 \,(\frac{m}{2e})^{\frac{1}{2}}$$

$$= -\frac{\nu_i}{D}\, n(\underset{\wedge}{r}) \quad ; \quad D = \frac{2e\,\bar{\varepsilon}}{3\gamma m}$$

$$\underset{\wedge}{\nabla}^2 n(\underset{\wedge}{r}) = -\frac{1}{\Lambda^2}\, n(\underset{\wedge}{r}) \quad ; \quad \frac{1}{\Lambda^2} = \frac{\nu_i}{D}$$

So $f_0^{\,0}(\varepsilon,\underset{\wedge}{r})$ may be written as the product of a function $f_0^{\,0}(\varepsilon)$ and $n(\underset{\wedge}{r})$ where the following condition on $f_0^{\,0}(\varepsilon)$ applies.

$$\int_0^\infty \varepsilon^{\frac{1}{2}} f_0^{\,0}(\varepsilon)d\varepsilon = 1.$$

Therefore we may write the spatial divergence, $\underset{\wedge}{\nabla}^2 f_0^{\,0}(\varepsilon,\underset{\wedge}{r})$ as $-\frac{1}{\Lambda^2} f_0^{\,0}(\varepsilon)\, n(\underset{\wedge}{r})$. The electron density may be factored out of the other terms to give an ordinary differential equation in energy space.

$$\varepsilon^{-\frac{1}{2}} \frac{d}{d\varepsilon} (\varepsilon^{3/2} \frac{df_0^{\,0}(\varepsilon)}{d\varepsilon}) + \alpha_1 \varepsilon^{-\frac{1}{2}} \frac{d}{d\varepsilon} (\varepsilon^{3/2} f_0^{\,0}(\varepsilon)) - \alpha_2 (\frac{1}{\Lambda^2})\, \varepsilon f_0^{\,0}(\varepsilon)$$

$$+ \alpha_3 \varepsilon^{-\frac{1}{2}} N(\underset{\wedge}{r},t) \, [\sum_j \{(\varepsilon+\varepsilon_{j2})\, \sigma_j(\varepsilon+\varepsilon_{j2})\, f_0^{\,0}(\varepsilon+\varepsilon_{j2}) - \varepsilon\sigma_j(\varepsilon) f_0^{\,0}(\varepsilon)\}$$

$$+ \varepsilon\sigma_{ion}(\varepsilon)\, f_0^{\,0}(\varepsilon)] = 0$$

The value of $(1/\Lambda^2)$ is not variable but is related to physical boundary conditions and geometry through solution of the diffusion equation.

Solution of the diffusion equation is given in Appendix D.

This last ordinary differential equation is the starting point for many of the previous workers. Engelhardt, Frost and Phelps neglect the diffusion and ionization terms in their iterative fitting of cross-sections to transport coefficients. If the entire equation is multiplied through by $\varepsilon^{\frac{1}{2}}\, d\varepsilon$ and integrated and the diffusion and ionization terms neglected, the following results:

$$\frac{df_0^{\,0}}{d\varepsilon} + \alpha_1 f_0^{\,0} = -\alpha_3 N(\underset{\wedge}{r},t) \int_0^{\varepsilon} \varepsilon^{-3/2} \sum_j \{(\varepsilon + \varepsilon_{j2})\, \sigma_j(\varepsilon+\varepsilon_{j2})\, f_0^{\,0}(\varepsilon+\varepsilon_{j2})$$

$$- \varepsilon\sigma_j(\varepsilon)\, f_0^{\,0}(\varepsilon)\}\, d\varepsilon$$

In the work of Allis and Haus the right hand side is approximated in terms of constants which correspond roughly to excitation frequencies. So a first order differential equation results, whose solution has N + 1 undetermined constants where N is the number of inelastic processes considered. One of the constants is determined from the normalization condition but the others must be determined by imposition of additional conditions on the solution. If the inelastic processes are neglected the solution is Maxwellian, with $f_0^{\,0} = C_1 \exp(-\alpha_1\varepsilon)$.

In the series of papers by Allis <u>et al</u>. the expression for the collision terms is replaced by the following expression:

$$\alpha_3 \, N(\underset{\wedge}{r},t) \, [\sum_j (- \varepsilon^{\frac{1}{2}}\sigma_j(\varepsilon) \, f_0^{\,0}(\varepsilon)) + q \, \delta(o) \, f_0^{\,0}(\varepsilon)]$$

Where $\delta(o)$ ≡ Dirac delta distribution

q ≡ electron flux in energy space due to collisions in which electrons lose all their energy and reappear at $\varepsilon = 0$.

Allis _et_ _al_. consider dissociative excitation and ionization but not vibrational excitation. A single cross-section, combining the effects of dissociation and ionization, is obtained from the work of Ramien. Therefore, separate excitation frequencies for dissociation and ionization were not reported and indeed, could not be calculated from this cross-section.

In order to specify the differential equation for the lead term of the series expansion, the form of the cross-section must be specified and the relationship between $f_0^{\,0}(\varepsilon+\varepsilon_{j2})$ and $f_0^{\,0}(\varepsilon)$ must be specified or approximated.

In hydrogen the cross-sections for one quantum vibrational excitation and dissociative excitation, available from experiment, rise sharply beyond a threshold, peak very near to the threshold and then fall of at least as quickly as the total cross-section. For these two collision processes then a suitable model for the cross-section is given by:

$$\sigma_j(\varepsilon) = \sigma_j \, \varepsilon^{-\frac{1}{2}} \, S(\varepsilon-\varepsilon_{j1})$$

Where σ_j $\equiv$ proportional to the peak value of $\sigma_j(\varepsilon)$

$S(\varepsilon-\varepsilon_{ji})$ $\equiv$ unit step function

ε_{j1} $\equiv$ threshold energy for j-type collision.

The cross-section for production of positive molecular ions in hydrogen is also available from experiment. Above a threshold at 16 ev the cross-section is almost linear in electron velocity out to 80 ev. A suitable model for this cross-section is given by:

$$\sigma_i(\varepsilon) = \sigma_i \, \varepsilon^{-\frac{1}{2}} (\varepsilon-\varepsilon_{i1}) \, S(\varepsilon-\varepsilon_{i1})$$

The form of $f_0^{\,0}(\varepsilon+\varepsilon_{j2})$ is approximated by a three term Taylor expansion and the series is substituted into the collision terms. The resulting equation is of the form:

$$(a_0\varepsilon+b_0) \frac{d^2 f_0^{\,0}}{d\varepsilon^2} + (a_1\varepsilon+ b_1) \frac{df_0^{\,0}}{d\varepsilon} + (a_2\varepsilon+b_2) f_0^{\,0} = 0$$

$$a_0 = 1 + N(\underset{\wedge}{r},t) \frac{\alpha_3}{\gamma} \sigma_i' \frac{\varepsilon_{i2}^2}{2}$$

$$b_0 = \frac{N(\underset{\wedge}{r},t)\alpha_3}{\gamma} \{\sigma_v' \frac{\varepsilon_{v2}^2}{2} + \sigma_x' \frac{\varepsilon_{x2}^2}{2} - \sigma_i' \frac{\varepsilon_{i2}^2}{2} (\varepsilon_{i1}-\varepsilon_{i2})\}$$

$$a_1 = \alpha_1 + \sigma_i' \varepsilon_{i2} N(\underset{\wedge}{r},t) \frac{\alpha_3}{\gamma}$$

$$b_1 = 3/2 + \frac{N(\underset{\wedge}{r},t)\alpha_3}{\gamma} \{\sigma_v' \varepsilon_{v2} + \sigma_x' \varepsilon_{x2} - \sigma_i' \varepsilon_{i2} (\varepsilon_{i1}-\varepsilon_{i2})\}$$

$$a_2 = \frac{N(\underset{\wedge}{r},t)\alpha_3}{\gamma} (\sigma_i' - \sigma_i) - \alpha_2$$

$$b_2 = \frac{3}{2}\alpha_1 + N(\underset{\wedge}{r},t)\,\frac{\alpha_3}{\gamma}\{\sigma_{ion} + (\sigma_v' - \sigma_v) + (\sigma_x' - \sigma_x)$$

$$- \sigma_i' \varepsilon_{i1} + \sigma_i' \varepsilon_{i2} + \sigma_i \varepsilon_{i1}\}$$

The primes identify cross-sections corresponding to net production at ε due to a j-type collision taking place at $\varepsilon + \varepsilon_{j2}$.

Because each cross-section has a discontinuity at its threshold, the domain is sectioned into regions which differ in that the coefficinets of the differential equation change. The general solution is of the form:

$$f_0^{\,0}(\varepsilon) = \exp(h\varepsilon)\,\{\phi^1 M[a,c,\xi] + \phi^2\, \xi^{1-c}\, M[a-c+1,\ 2-c,\xi]\}$$

Where $h = -\dfrac{a_1}{2a_0} - \dfrac{1}{2a_0}\sqrt{a_1^{\,2} - 4a_0a_2}$

$\phi^1,\ \phi^2 \equiv$ coefficients to be determined from conditions imposed on solution space

$a = [b_o h^2 + b_1 h + b_2] \ / \ [2a_o h + a_1]$

$c = [a_0 b_1 - a_1 b_0] \ / \ a_0^{\,2}$

$\xi = (\varepsilon + {}^{b_0}/_{a_0})\ \sqrt{a_1^{\,2} - 4\,a_0 a_2} \ / \ a_0$

$M[\alpha,\beta,\lambda] =$ confluent hypergeometric function.

The domain is sectioned into seven intervals described in the following table.

Table 2. Subregions of energy domain

Interval	Left Endpoint	Right Endpoint
0	0.	ε_{ion}
1	ε_{ion}	$\varepsilon_{i1}-\varepsilon_{i2}$, $\varepsilon_{xi}-\varepsilon_{x2}$
2	$\varepsilon_{i1}-\varepsilon_{i2}$	$\varepsilon_{v1}-\varepsilon_{v2}$
3	$\varepsilon_{v1}-\varepsilon_{v2}$	ε_{v1}
4	ε_{v1}	ε_{x1}
5	ε_{x1}	ε_{i1}
6	ε_{i1}	∞

The particular solution is constructed by applying the boundedness condition on $f_0^{0}(\varepsilon)$ at $\varepsilon = 0$ and then equating the values of $f_0^{0}(\varepsilon)$ and $d\, f_0^{0}(\varepsilon)/d\varepsilon$ at the endpoints. The second constant is determined from the normalization condition for $f_0^{0}(\varepsilon)$.

In the interval $[0, \varepsilon_{ion}]$ there are no inelastic effects and it can be shown that the second term of the general solution is inversely proportional to $\xi^{\frac{1}{2}}$. Requiring $f_0^{0}(0)$ to be bounded requires that ϕ_0^{2} be set to zero. All the other values of ϕ_j^{1}, ϕ_j^{2} may be calculated now in terms of ϕ_0^{1}. Finally, ϕ_0^{1} may be calculated with the normalization condition.

From the resulting expression for the distribution function the electron-neutral binary diffusion coefficient, electron mobility, and velocity averaged collision frequencies for inelastic collisions may be calculated.

The diffusion coefficient may be calculated from the expression for the electron flux in terms of the anisotropic portion of the distribution function and a constitutive model.

$$\underset{\wedge}{J} = \underset{\wedge}{\overline{v}}\, e = - e\, \underset{\wedge}{\nabla} (D\, n_e)$$

For an electric field oriented parallel with $\underset{\wedge}{z}$, we have for $\underset{\wedge}{J} \cdot \underset{\wedge}{z}$

$$J_z = n_e\, \overline{v \cos \theta}\; e = - e \frac{d}{dz} (D_z n_e)$$

$$n_e\, \overline{v \cos \theta} = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} v \cos \theta\, (f_0(v,\underset{\wedge}{r}) + \cos \theta\, f_1(v,\underset{\wedge}{r}))\; v^2 \sin \theta\, d\theta\, d\theta\, dv$$

Noting that $f_1^0(v,\underset{\wedge}{r}) = f_1^0(v)\, n_e = - v/\gamma\, d(nf_0^0)/dz$ we arrive at the familiar expression for the diffusion coefficient of a dilute gas.

$$D = \frac{2e\, \overline{\varepsilon}}{3\gamma m}$$

where

$\overline{\varepsilon}$ ≡ average energy of electron gas

γ ≡ electron-neutral collision frequency

For a Maxwellian distribution $\overline{\varepsilon} = 3\ kT/2e$ and $D = kT/\gamma m$.

From the anisotropic time dependent term $f_1{}^1(v,\underset{\wedge}{r})$, the time dependent velocity term may be calculated and thus the electron mobility may be calculated.

$$\underset{\wedge}{\overline{v}_1} = \mu \underset{\wedge}{E}$$

When the average fluctuating velocity is calculated the following form results for the electron mobility.

$$\mu = \frac{e\gamma}{m(\gamma^2+\omega^2)}$$

The inelastic collision excitation frequencies may be calculated in the usual manner.

$$\overline{\nu_i} = \int_0^\infty \int_0^{2\pi} \int_0^\pi \nu_1(v)\ f_0{}^0(v,\underset{\wedge}{r})\ v^2 \sin\theta\ d\theta\ d\theta\ dv$$

In a discharge the diffusion mode shifts from free diffusion at breakdown toward ambipolar diffusion at steady state operation. The ambipolar diffusion coefficient is also calculated from the average energy of the electron gas.

$$D_A = \frac{2e\ \overline{\varepsilon}}{3\gamma m_i}$$

Where: $\bar{\varepsilon} \equiv$ average energy of electron gas

$\overline{m_i} \equiv$ ion mass

D. Discussion of the form of the distribution function

The form of the derived distribution function may be explored by examining its behavior near several regions.

First, consider the case of an unbounded plasma in which elastic interaction is the dominant mechanism for energy exchange. The derived distribution function collapses to the Maxwellian distribution, as we would intuitively expect. The average energy for this distribution is given as:

$$\bar{\varepsilon}_m = \left(\frac{Me}{2m^2}\right)\left(\frac{E^2}{\gamma^2+\omega^2}\right)$$

In the derivation of the distribution function it is assumed that the total collision cross-section is inversely proportional to electron velocity. If the distribution function is derived assuming that the total cross-section is constant with respect to electron velocity the following distribution results.

$$f(\varepsilon) = \frac{\left(\frac{\beta_1\beta_2}{E^2}\right)^{3/4} \exp\left\{-\frac{\beta_2}{E^2}\left(\varepsilon^2\frac{\beta_1}{2} + \omega^2\varepsilon + \frac{\omega^4}{4\beta_1}\right)\right\}}{\Gamma(3/2)\, U\left\{1, \frac{\omega^2}{E}\sqrt{\frac{\beta_1}{\beta_2}}\right\}}$$

where $\beta_1 \equiv 2e/m\ell^2$

$\beta 2 \equiv 3m^2/Me$

$\ell \equiv$ mean free path for electron-neutral elastic encounter

$\Gamma(\alpha) \equiv$ gamma function

$U(\alpha,\delta) \equiv$ parabolic cylinder function

This distribution was derived assuming that elastic interaction dominate energy exchange between electron gas and background gas. This distribution is similar to that of Druyvestuyn. If we set the driving frequency, ω, to zero, the distribution function becomes exactly that of Druyvestuyn. The average energy for this distribution is given as:

$$\bar{\epsilon}_D = \frac{3}{2}\left(\frac{E^2}{\beta_1\beta_2}\right)^{\frac{1}{2}} \frac{U\{2, \frac{\omega^2}{E}\sqrt{\beta_2/\beta_1}\}}{U\{1, \frac{\omega^2}{E}\sqrt{\beta_2/\beta_1}\}}$$

For the case where $\omega = 0$, the average energy is given by:

$$\bar{\epsilon}_{D,0} = \frac{\Gamma(5/4)}{\Gamma(3/4)}\left(\frac{2E^2}{\beta_1\beta_2}\right)^{\frac{1}{2}}$$

E. Calculations and Results

The assumed forms of the inelastic collision cross-sections were fit to experimental values (see Fig. 2-4). The following cross-sections resulted.

$$\sigma_v(\varepsilon) \;=\; 8.485(10^{-21})\ \varepsilon^{-\frac{1}{2}} \cdot S(\varepsilon-2.)\ \ m^2/s$$

$$\sigma_x(\varepsilon) \;=\; 2.647(10^{-20})\ \varepsilon^{-\frac{1}{2}} \cdot S(\varepsilon-9.)\ \ m^2/s$$

$$\sigma_i(\varepsilon) \;=\; 1.9\ \ (10^{-21})\ \varepsilon^{-\frac{1}{2}}\,(\varepsilon-16.) \cdot S(\varepsilon-16.)\ \ m^2/s$$

where $S(\varepsilon-\varepsilon_0) \equiv$ unit step function.

The remaining cross-section to be specified is that corresponding to the electrons introduced near $\varepsilon = 0$ from ionization of H_2. This cross-section must be determined through iterative calculation. A value of the cross-section is estimated, the distribution function is calculated and the ionization frequency is calculated. From the ionization frequency the value of the cross-section is calculated and then compared with the estimate.

Iterative calculation is also required to determine the electric field strength for a given geometry and pressure. The diffusion length calculated from integral properties of the distribution function must match that calculated from the geometry of the discharge. The relation between the diffusion length and geometry is determined from a solution of the diffusion-reaction equation.

The results of the calculations are summarized in several sets of figures. The computational procedures are given in Appendix E.

Figure 5 illustrates the relationship between effective electric field strength, background pressure and geometry at the breakdown condition. Experimental data for a wide range of frequency, geometry and pressure are also plotted. The calculated points represent a narrow selection of pressure (100-600 N/m^2), geometry (Λ = .0013-.0002 m) and frequency ($\gamma/\omega = 1$). All pressures are normalized to 300 K.

For gas discharges of interest the mass transfer rate of electrons is bounded above by free diffusion and bounded below by ambipolar diffusion. With increasing electron number density the discharge shifts from the free diffusion regime to the ambipolar regime. Accompanying this drop in the effective diffusion coefficient is a drop in the effective electric field from its breakdown value.

Figure 6 illustrates the change in the distribution averaged electron energy as the ratio of effective electric field to pressure shifts from its breakdown value to the ambipolar limit. The average electron energy is useful in calculating the electron diffusion coefficient and in estimating the energy transfer rates for elastic binary enounters.

In Figures 7 through 9 plots of sample electron energy distribution functions are given. The three calculated distribution functions correspond to the ambipolar limit ($E_e/p = 75$), breakdown ($E_e/p = 175$) and an intermediate value ($E_e/p = 125$). Each calculated distribution is accompanied by two other plotted distributions. One is the Maxwellian distribution resulting from a solution of the Boltzmann equation with inelastic encounters not included. The second is a Maxwellian distribution of the same average energy as the calculated distribution. The first is a solution of the Boltzmann equation, the

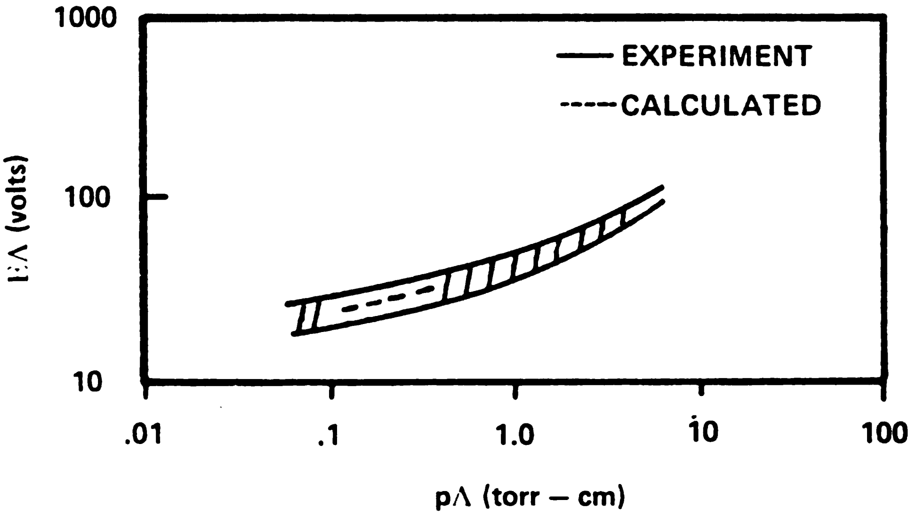


Figure 5. Comparison of calculated and experimental breakdown field strengths for 2.47 GHz in H_2.

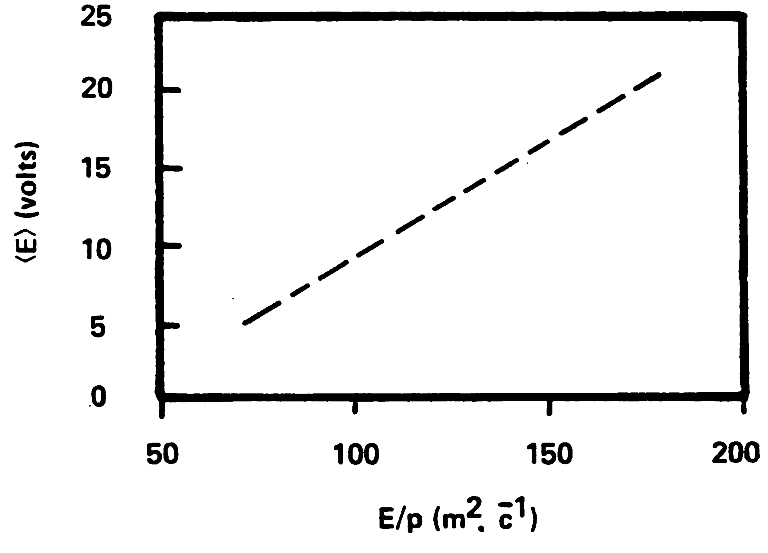


Figure 6. Average electron energy calculated for E/p = 75 - 175 $m^2 \cdot c^{-1}$.

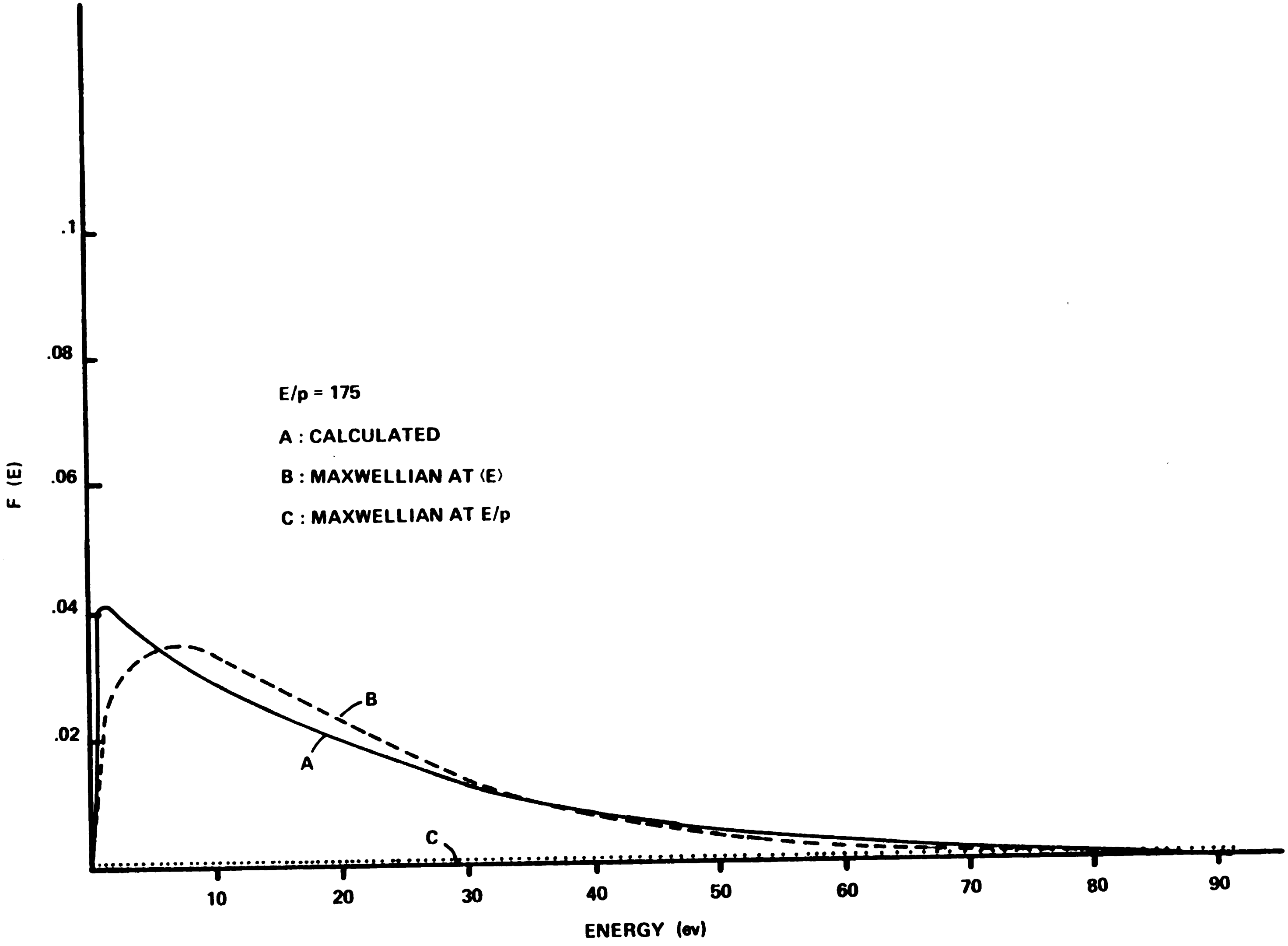


Figure 7. Calculated electron distribution functions for E/p = 175. $m^2 \cdot c^{-1}$.

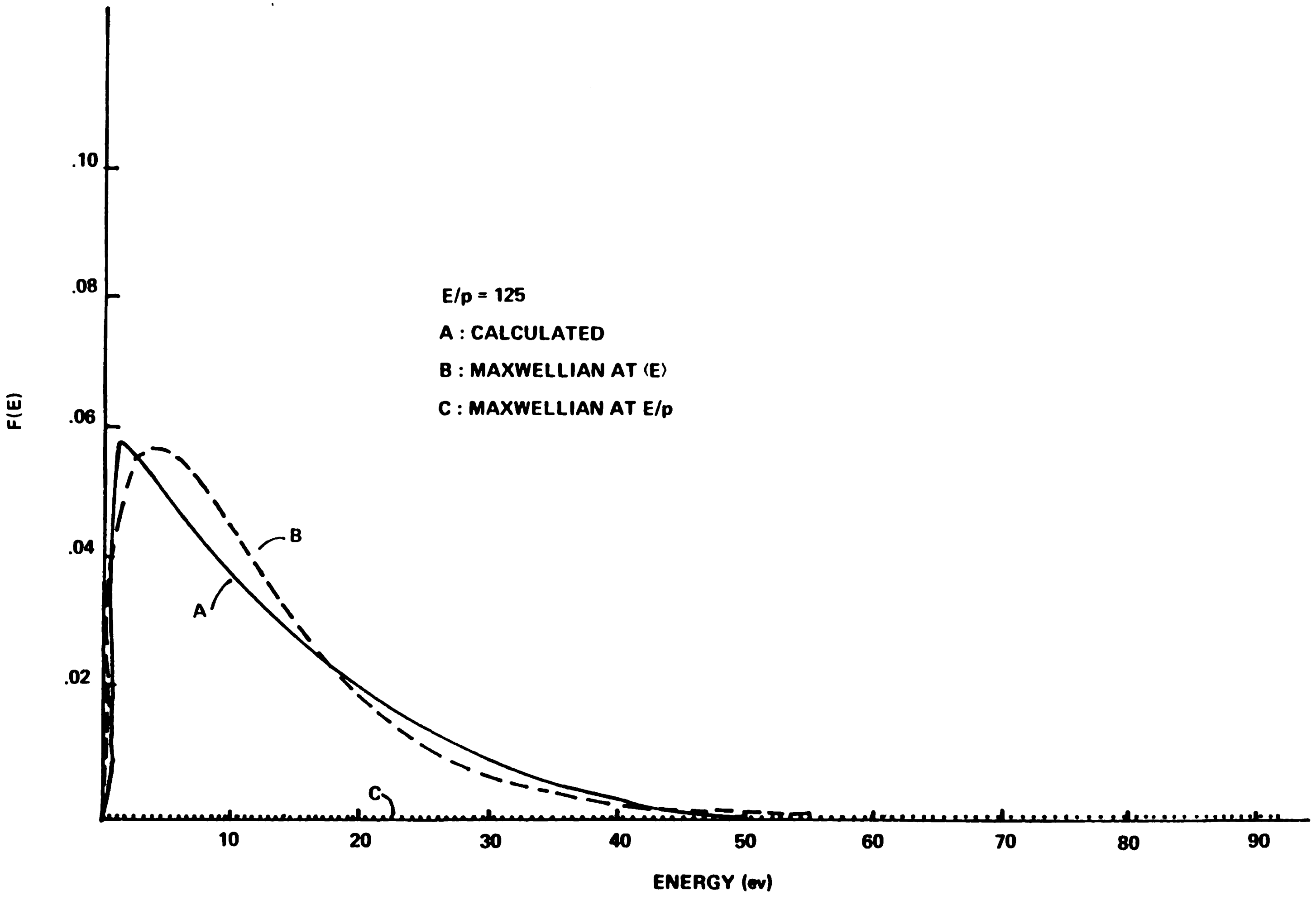


Figure 8. Calculated electron distribution functions for E/p = 125. $m^2 \cdot c^1$.

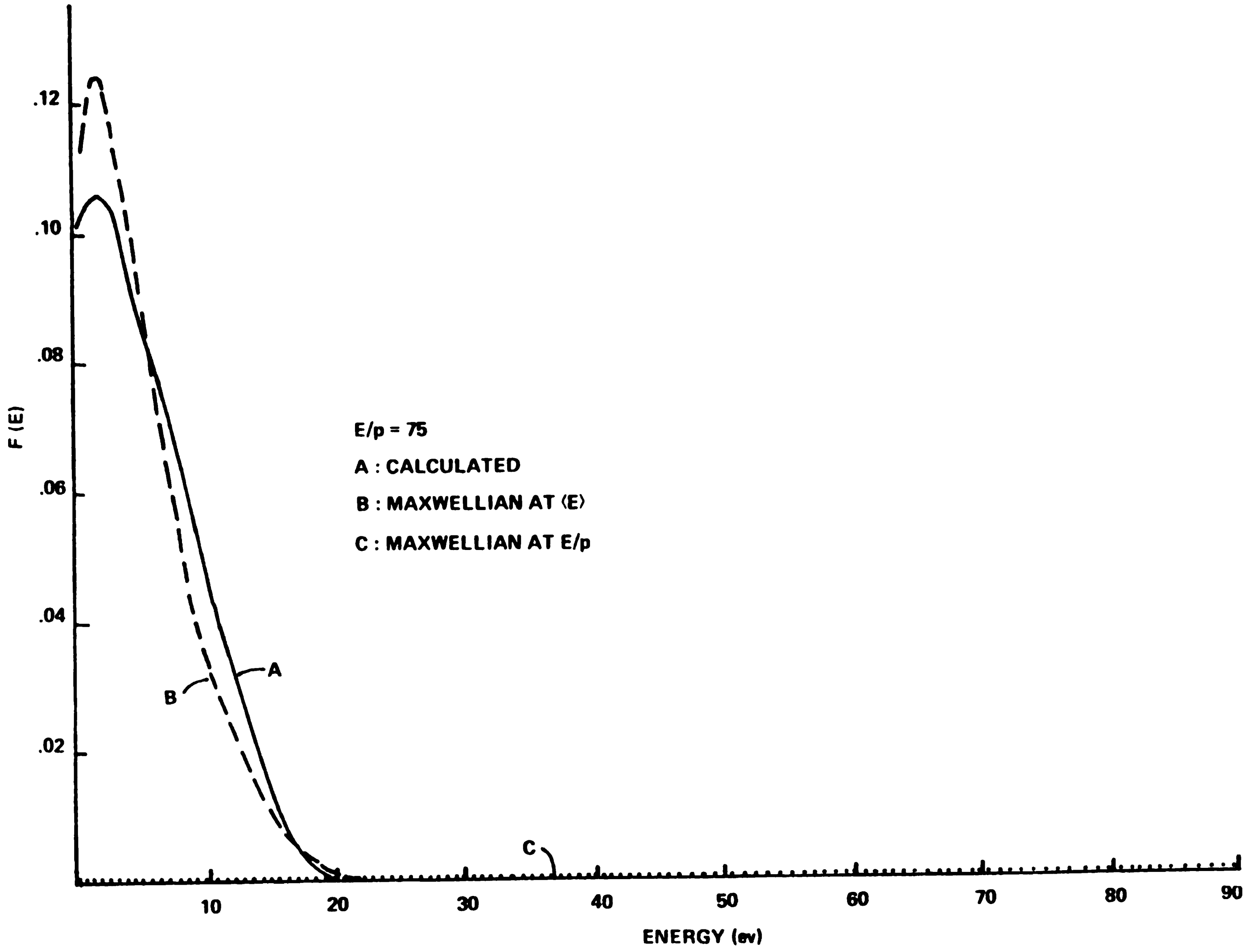


Figure 9. Calculated electron distribution functions for $E/p = 75. m^2 \cdot c^{-1}$.

second is a Maxwellian curve fit. This distinction is important.

Figure 10 presents the ratio of calculated inelastic collision frequencies to the frequency for momentum transfer as a function of the ratio of effective electric field strength to gas pressure. The calculated inelastic collision frequencies are compared with inelastic collision frequencies calculated from a Maxwellian distribution at the same average energy.

F. Discussion

Experimental measurements of breakdown field strength as a function of gas pressure and field frequency for a given geometry have been made by Githens (1940), MacDonald and Brown (1949) and MacDonald, Gaskell and Gitterman (1963). The experimental measurements are made for a range of pressure (13. - 13,300. Pa), diffusion length (5.(10^{-4}) - .0151 m), and frequency (.5 - 10 GHz).

These experimental results are plotted in Figure 5 and are represented by the cross-hatched band. Predicted breakdown field vs gas pressure is also plotted in Figure 5. The plot illustrates several points to be made.

First, the predicted breakdown fields are in close agreement with experimental results over the range of values included. The range of discharge conditions considered is, 100-600 Pa, Λ = 2.(10^{-4}) - 1.3(10^{-3}), (γ/ω) = 1. (The value of the ratio of the elastic collision frequency to angular field frequency is fixed at 1. because breakdown fields are at a minimum at this value).

This agreement bears on the conclusion of Allis and Brown (1952) that such agreement cannot be obtained if vibrational excitation of

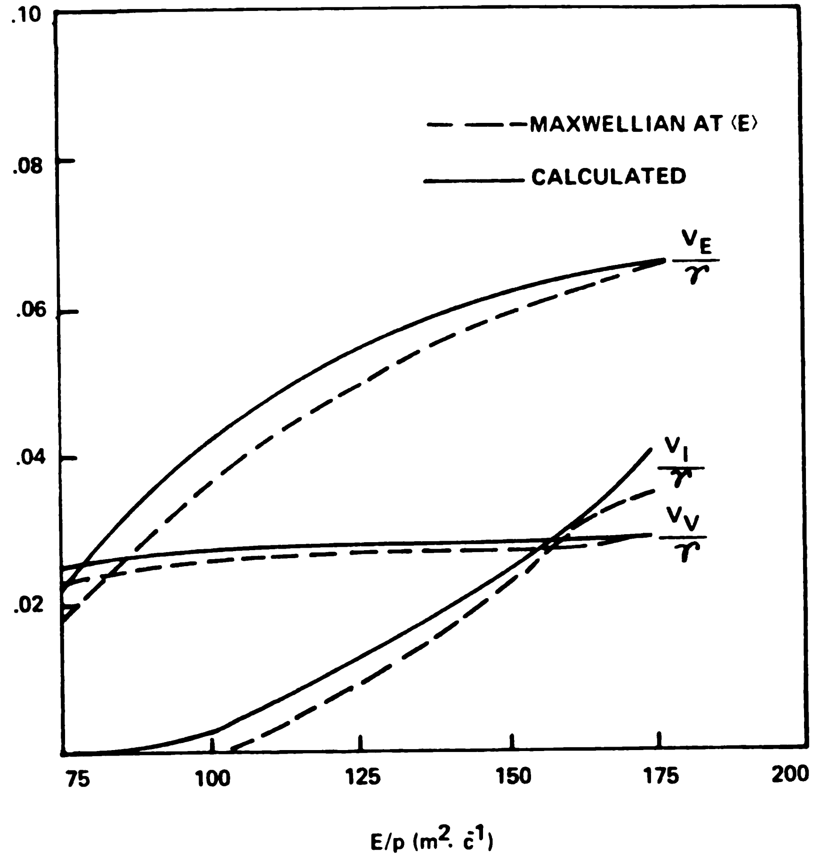


Figure 10. Calculated collision efficiencies for vibrational and electronic excitation for E/p = 75 - 175 $m^2 \cdot c^{-1}$.

H_2 (ground state) by electrons is included in the analysis.

Two features of the analysis done by Allis and Brown which may explain their conclusion are the maximum energy loss assumption and the cross-sections used in the calculations. In formulation of the collision terms of the Boltzmann equation Allis and Brown assumed that electrons transfer all their kinetic energy to the gas. This assumption reduces the collision term significantly, and the result of the assumption is to greatly increase the rate of energy transfer from the electron to the background gas. Second, the cross-section for ionization of H_2 used in the calculation of Allis and Brown is roughly twice the experimental values of Rapp and Englander-Golden. These two features would result in over-estimation of dissociation and ionization rates and so it is not surprising that the collision terms for vibrational excitation of the diatomic molecules were excluded in order to fit the predicted breakdown fields to the experimental values.

The cross-sections used by Allis and Brown were obtained from the work of Ramien. Since the work of Allis and Brown, more accurate and detailed experimental total cross-sections have become available.

Figure 6 illustrates the dependence of the distribution averaged electron energy on the ratio of effective electric field to gas pressure. The relationship is linear over a wide range of (E_e/p). This functional dependence is in marked contrast to the Maxwellian distribution, in which the average energy is proportional to the square of (E_e/p). Experimental results of Varnerin and Brown (1950) at $(E_e/p) < 75.$ also exhibit a linear relationship between $\bar{\varepsilon}$ and (E_e/p).

The next three figures (Figures 7, 8, 9) illustrate the progression from the breakdown condition to the ambipolar limit. In each of the three figures the maximum of the Maxwellian distribution corresponding to the same value of (E_e/p) is far off scale. The Maxwellian distribution corresponding to the same value of (E_e/p) is the solution of the Boltzmann equation under the assumption that energy transfer from the electron gas takes place only by elastic interaction of the electron and background gas. In this sense then, the distribution is strongly non-Maxwellian over the range of (E_e/p) of interest here.

As expected, the distribution function falls off rapidly as the electric field strength drops from its maximum at breakdown to a minimum at the ambipolar limit.

As a solution to the Boltzmann equation the Maxwellian distribution function is clearly unsuitable. However, the simple closed form expression for the Maxwellian distribution is attractive and useful in analysis of experimental results (e.g. Langmuir probe data) and calculation of excitation rate coefficients. In each of the three figures the calculated distribution function is compared with a Maxwellian "curve fit". The Maxwellian distribution is of the same average energy as the calculated distribution function. In all three figures this Maxwellian curve fit falls off more rapidly than the calculated distribution. All plotted distribtuions are normalized.

Rarely is the distribution function used directly in analysis of experimental results. More often it is a few integral properties of the distribution that are of interest (e.g. diffusion coefficient, rate coefficients for excitation processes). Figure 10 is a comparison of rate coefficients for (0) → (1) vibrational excitation, dissociation and ionization calculated from the two distribution functions. The rate coefficients are plotted as ratios of the excitation frequency to the total collision frequency for momentum transfer.

The rate coefficients for (0) → (1) vibrational excitation calculated from the two distributions are close in magnitude near breakdown and diverge slowly near the ambipolar limit. The difference between the two curves does not exceed 10% over the range of (E_e/p) considered. So for gas discharges in hydrogen with average energies between 5 and 20 ev, a curve fit Maxwellian distribution gives values of the (0) → (1) vibrational excitation rate coefficient comparable to those calculated from a full solution of the Boltzmann equation.

Such close agreement is not obtained for dissociation and ionization rate coefficients. So, once an average electron energy is determined, the vibrational excitation rate may be calculated from a Maxwellian curve fit. To determine the rates of dissociation and ionization, the value of (E_e/p) is read from the plot of $\bar{\varepsilon}$ vs (E_e/p) and the solution to the Boltzmann equation corresponding to this (E_e/p) is determined and used to calculate the rate coefficients. The average energy of the electron gas may be calculated from Langmuir double probe data by the technique illustrated in Appendix B.

CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. Solution of the Boltzmann equation for a bounded plasma by a spherical harmonic expansion, in which electron-molecule energy transfer takes place by (0) → (1) vibrational excitation, excitation of the first repulsive triplet state of H_2 and ionization of ground state H_2, results in breakdown electric fields which reproduce experimental values.
2. Calculated electron distribution functions are strongly non-Maxwellian.
3. Vibrational excitation rates may be reasonably predicted from a Maxwellian "curve fit" using an experimental value for the average energy. Excitation rate coefficients for electronic excitations (e.g. dissociation, ionization) cannot be calculated via this approach.
4. The average energy of the electron gas should depend in a linear fashion on the value of (E_e/p). This manner of dependence is consistent with experimental results.
5. A method is developed to determine the average electron energy from Langmuir double probe data.

B. Recommendations

1. Model development

(a) Cross-sections for electronic excitation of atomic hydrogen (e.g. excitations with resulting transitions giving Lyman, Balmer lines, ionization) are on the order of πa_0^2 in the energy range 1. - 100. ev. Electron-atom interaction should be included in the analysis. From an energy efficiency point of view, the presence of radiative transitions is discouraging. However, the presence of such transitions gives the experimenter a tremendous diagnostic advantage.

(b) Plasmas are fertile environments for propagation of fluctuations and a host of unstable phenomenon. The model response to perturbations in initial or boundary conditions begs to be considered. Penrose (1960) derived stability criteria for a uniform non-Maxwellian plasma based on the Vlasov equation (collisionless Boltzmann equation). Extension of the criteria to a uniform non-Maxwellian plasma described by a solution of the Boltzmann equation would be very useful.

2. Laboratory experiments

(a) Interpretation of Langmuir probe results is highly dependent on the velocity distribution assumed. From the electron distributions calculated here, the probe characteristic curves could be analyzed to give the average energy of the distribution and possibly the electron number density.

APPENDICES

APPENDIX A

Derivation of the Boltzmann Equation and Expansion in Spherical Harmonics

Consider a fixed volume element in phase space. Now apply the usual balance principle to the electron gas which fills the volume element.

Rate of accumulation of electrons in volume element in phase space = Net flux across boundary in position space + Net flux across boundary in velocity space

+ Collisional source rate

Specify the volume element in phase space by specifying an element in position space (R^3) and in velocity space.

$$\frac{\partial}{\partial t}\int_{V_R}\int_{V_v} F(\underset{\wedge}{r},\underset{\wedge}{v},t)\, d^3\underset{\wedge}{r}\, d^3\underset{\wedge}{v} = -\int_{V_v}\int_{A_R} (\underset{\wedge}{n}_R \cdot \underset{\wedge}{V}_r)\, F(\underset{\wedge}{r},\underset{\wedge}{v},t)\, d^2\underset{\wedge}{r}\, d^3\underset{\wedge}{v}$$

$$-\int_{V_R}\int_{A_v} (\underset{\wedge}{n}_v \cdot \underset{\wedge}{V}_v)\, F(\underset{\wedge}{r},\underset{\wedge}{v},t)\, d^2\underset{\wedge}{v}\, d^3r + \int_{V_R}\int_{V_v} S(\underset{\wedge}{r},\underset{\wedge}{v},t)\, d^3\underset{\wedge}{v}\, d^3\underset{\wedge}{r}$$

Noting that $\underset{\wedge}{V}_v = \underset{\wedge}{a}$ and making use of the divergence theorem:

$$\int_{V_R}\int_{V_v}\left\{ \frac{\partial F}{\partial t} + \nabla_{\hat{r}} \cdot \hat{v}F + \nabla_{\hat{v}} \cdot \hat{a}\, F - S\right\} \, d^3\hat{v}\, d^3\hat{r} = 0$$

And as our volume element was arbitrarity chosen:

$$\frac{\partial F}{\partial t} + \nabla_{\hat{r}} \cdot \hat{v}F + \nabla_{\hat{v}} \cdot \hat{a}F - S = 0$$

For cases in which there is no external magnetic field, we may write the following for electrons.

$$\frac{\partial F}{\partial t} + \hat{v} \cdot \nabla_{\hat{r}} F - \frac{e}{m}\hat{E} \cdot \nabla_v F = S$$

where: $e \equiv$ electronic charge

$m \equiv$ electron mass

$\hat{E} \equiv$ external electric field

Expansion of Boltzmann equation (see also Cherrington (1979)).

The Boltzmann equation may be written as:

$$\frac{\partial f}{\partial t} + \hat{v} \cdot \hat{\nabla} f - \frac{e}{m}\hat{E} \cdot \nabla_{\hat{v}} f = S$$

$$\text{Let } f(\hat{v},\hat{r},t) = \sum_{k=0}^{\infty} P_K(\cos\theta)\, f_K(v,\hat{r},t)$$

Let $\hat{E} = E_0 \exp(j\omega t)\,\hat{z}$. So $\hat{v} \cdot \hat{E} = v\,E\cos\theta$.

Substituting the expansion, we have,

$$\frac{\partial}{\partial t} \sum_0^\infty P_k f_k + \underset{\wedge}{v} \cdot \underset{\wedge}{\nabla} \sum_0^\infty P_k f_k - \frac{e}{m} \underset{\wedge}{E} \cdot \underset{\wedge}{\nabla}_v \sum_0^\infty P_k f_k = S$$

First note that the P_k's are not functions of time. To simplify the second term note that the Legendre polynomials in velocity space are independent of position, and also that the electric field has only one component.

$$\underset{\wedge}{v} \cdot \nabla \sum_0^\infty P_k f_k = \sum_0^\infty P_k (\underset{\wedge}{v} \cdot \nabla f_k)$$

$$= \sum_0^\infty P_k \, v \cos \theta \frac{\partial f_k}{\partial z}$$

To simplify the third term note that f_k is a function of v only and that P_k is a function of θ only.

$$\underset{\wedge}{\nabla}_v P_k f_k = \underset{\wedge}{\hat{v}} P_k \frac{\partial f_k}{\partial v} - \underset{\wedge}{\hat{\theta}} \frac{1}{v} f_k \sin \theta \frac{\partial P_k(\cos \theta)}{\partial(\cos \theta)}$$

$$\underset{\wedge}{E} \cdot \nabla_v P_k f_k = E \cos \theta \, P_k \frac{\partial f_k}{\partial v} + E \frac{1}{v} f_k \sin^2 \theta \frac{\partial P_k (\cos \theta)}{\partial(\cos \theta)}$$

Now to simplify the notation let $x = \cos \theta$.

$$\sum_0^\infty [P_k \frac{\partial f_k}{\partial t} + P \quad v x \frac{\partial f_k}{\partial z} - \frac{e}{m} E x P_k \frac{\partial f_k}{\partial v} - \frac{e}{m} E \frac{1}{v} f_k (1-x^2) \frac{\partial P_k}{\partial x} = S]$$

Now using addition theorems and recursion relations for Legendre polynomials:

$$\sum_{0}^{\infty} [P_k \frac{\partial f_k}{\partial t} + v\frac{\partial f_k}{\partial z} [\frac{k+1}{2k+1} P_{k+1} + \frac{k}{2k+1} P_{k-1}] - \frac{eE}{m} [(\frac{\partial f_k}{\partial v} - \frac{kf_k}{v}) \frac{k+1}{2k+1} P_{k+1}]$$

$$- \frac{eE}{m} [(\frac{\partial f_k}{\partial v} + \frac{k+1}{v} f_k) \frac{k}{2k+1} P_{k-1}]] = S$$

Note also that the Legendre polynomials are orthogonal. So we multiply through by P_j and integrate over θ and ϕ.

$$\text{Note that: } \int_0^{2\pi} \int_0^{\pi} P_k^{\,2} (\cos \theta) \sin \theta \, d\theta \, d\phi = \frac{4\pi}{2k+1}$$

$$\int_0^{2\pi} \int_0^{\pi} P_k (\cos \theta) P_j (\cos \theta) \sin \theta \, d\theta \, d\phi = 0, \; j \neq k$$

The final result:

$$\frac{\partial f_k}{\partial t} + v [\frac{k}{2k-1} \frac{\partial f_{k-1}}{\partial z} + \frac{k+1}{2k+3} \frac{\partial f_{k+1}}{\partial z}] - \frac{eE}{m} [\frac{k}{2k-1} v^{k-1} \frac{\partial}{\partial v} (\frac{f_{k-1}}{v^{k-1}})]$$

$$- \frac{eE}{m} [\frac{k+1}{2k+3} \frac{1}{v^{k+2}} \frac{\partial}{\partial v} (v^{k+2} f_{k+1})] = \frac{2k+1}{4\pi} \int_0^{2\pi} \int_0^{\pi} P_k \, S \sin \theta \, d\theta \, d\phi$$

So that first three equations may be written:

$$\frac{\partial f_0}{\partial t} + \frac{v}{3} \frac{\partial f_1}{\partial z} - \frac{eE}{3m} \frac{1}{v^2} \frac{\partial}{\partial v} (v^2 f_1) = \frac{1}{4\pi} \int_0^{2\pi} \int_0^{\pi} S \sin \theta \, d\theta \, d\phi$$

$$\frac{\partial f_1}{\partial t} + v\,\frac{\partial f_0}{\partial z} + v\,\frac{2}{5}\,\frac{\partial f_2}{\partial z} - \frac{eE}{m}\left[\frac{\partial f_0}{\partial v} + \frac{2}{5}\,\frac{1}{v^3}\,\frac{\partial}{\partial v}\,(v^3 f_2)\right] = \frac{3}{4\pi}\int_0^{2\pi}\int_0^{\pi} S\,\cos\theta\,\sin\theta\;d\theta\;d\phi$$

$$\frac{\partial f_2}{\partial t} + v\left[\frac{2}{3}\,\frac{\partial f_1}{\partial z} + \frac{3}{7}\,\frac{\partial f_3}{\partial z}\right] - \frac{eE}{m}\left[\frac{2}{3}\,v\,\frac{\partial}{\partial v}\left(\frac{f_1}{v}\right) + \frac{3}{7}\,\frac{1}{v^4}\,\frac{\partial}{\partial v}\,(v^4 f_3)\right]$$

$$= \frac{5}{4\pi}\int_0^{2\pi}\int_0^{\pi} S\,P_2\,(\cos\theta)\,\sin\theta\;d\theta\;d\phi$$

From the Lorentz approximation we assume that f_2, f_3... are negligible with respect to f_1, f_2. So the equations become:

$$\frac{\partial f_0}{\partial t} + \frac{v}{3}\,\frac{\partial f_1}{\partial z} - \frac{e}{3}\,\frac{E}{m}\,\frac{1}{v^2}\,\frac{\partial}{\partial v}\,(v^2 f_1) = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} S\,\sin\theta\;d\theta\;d\phi$$

$$\frac{\partial f_1}{\partial t} + v\frac{\partial f_0}{\partial z} - \frac{eE}{m}\,\frac{\partial f_0}{\partial v} = \frac{3}{4\pi}\int_0^{2\pi}\int_0^{\pi} S\,\cos\theta\,\sin\theta\;d\theta\;d\phi$$

Now we require expansions of the collision integral.

In general we may write:

$$S_{k,j} = \frac{2k+1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} P_k(\cos\theta) \frac{N}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} \{v'\sigma'_j(v') \sum_0^{\infty} f'_k P'_k \left(\frac{d\omega'}{d\omega}\right)$$

$$- v\,\sigma_j(v) \sum_0^{\infty} f_k P_k\} \sin\theta\, d\theta$$

To carry out the first integration we must relate the P'_k to P_k using an addition theorem for Legendre polynomials. From this we obtain:

$$S_{k,j} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} N \{v'\,\sigma_j(v')\, f_k(v')\, P_k(\cos\theta) \left(\frac{d\omega'}{d\omega}\right) - v\,\sigma_j(v) f_k(v)\} \sin\theta\, d\theta$$

To calculate $S_{0,el}$, the first term of the integrand is approximated using a two term Taylor series expansion.

$$S_{0,el} = \frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} N \frac{1}{v^2} \frac{\partial}{\partial v} \{v^4 \left(\frac{m}{M}\right) (1-\cos\theta)\, \sigma_{el}(v)\, f_0\} \sin\theta\, d\theta$$

$$S_{0,el} = N \frac{1}{v^2} \frac{\partial}{\partial v} \{v^4 \left(\frac{m}{M}\right) \sigma_{el}(v)\, f_0\}$$

To calculate $S_{1,el}$, the collision term corresponding to the second term of the expansion we again make use of the fact that $v' \rightarrow v$ and assume $\sigma(v') = \sigma(v)$, $f(v') = f(v)$ and $(d\omega'/d\omega) = 1$.

$$S_{1,el} = \frac{-1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} N\ v\ \sigma(v)\ f_1(v)\ (1-\cos\theta)\ \sin\theta\ d\theta$$

$$= -\ N\ v\ f_1(v)\ \{\frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} (1-\cos\theta)\ \sigma(v)\ \sin\theta\ d\theta\}$$

$$= -\ N\ v\ \sigma(v)\ f_1(v)$$

$$= \ -\gamma\ f_1(v) \quad \text{where } \gamma = N\ v\ \sigma(j)\ \equiv \ \text{collision frequency}$$

To calculate $S_{k,j}$ for inelastic collisions note that in general $P_k^{\,1} = P_k$ i.e. small scattering angle.

$$S_{k,j} = \frac{2k+1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} P_k(\cos\theta)\ \sin\theta\ d\theta\ \frac{N}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta\ d\theta$$

$$\{v'\ \sigma_j(v')\ \Sigma f_k'\ P_k\ (\frac{d\omega'}{d\omega})\ -\ v\ \sigma_j(v)\ \Sigma f_k P_k\}$$

$$S_{k,j} = \frac{2k+1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi} P_k(\cos\theta)\ \sin\theta\ d\theta N\{v'\ \sigma_j(v')\ f_0(v')\ (\frac{d\omega'}{d\omega})$$

$$-\ v\ \sigma_j(v)\ f_0\}$$

$$S_{k,j} = \begin{cases} N\ \{v'\ \sigma_j(v')\ f_0(v')\ (\frac{d\omega'}{d\omega})\ -\ v\ \sigma_j(v)\ f_0\} & \text{if } k = 0 \\ 0 & \text{if } k > 0 \end{cases}$$

Now with the collision integrals specified it remains to deal with the time dependence of the distribution. We have assumed an electric field of the form E_0 exp($j\omega t$) and make the further assumption that the anisotropic term of the distribution function may be decomposed into the sum of a time independent and time dependent term i.e. two term Fourier series.

$$f_1 = f_1^{\,0} + f_1^{\,1} \exp(j\omega t)$$

$$\frac{\partial f_1}{\partial t} = f_1^{\,1}\, j\omega \exp(j\omega t)$$

Recall also that:

$$\frac{\partial f_0}{\partial t} + \frac{v}{3}\frac{\partial f_1}{\partial z} - \frac{eE}{3m}\frac{1}{v^2}\frac{\partial}{\partial v}(v^2 f_1) - N\frac{1}{v^2}\frac{\partial}{\partial v}\left(v^4\left(\frac{m}{M}\right)\sigma_e(v)\, f_0\right) = S_{0,in}$$

$$\frac{\partial f_1}{\partial t} + \frac{v\partial f}{\partial z} - \frac{eE}{m}\frac{\partial f_0}{\partial v} = -\gamma f_1$$

If the assumed decomposition is substituted into the two relations, terms of like time dependence are equated, and the complex portion neglected the following equations result.

$$\frac{-v^2}{3\gamma}\frac{\partial^2 f_0}{\partial z^2} - \frac{2}{3}\frac{\bar{E}^2 e^2 \gamma}{m^2(\gamma^2+\omega^2)}\frac{1}{v^2}\frac{\partial}{\partial v}\left[v^2\frac{\partial f_0}{\partial v}\right] - \left(\frac{m}{M}\right)\frac{\gamma}{v^2}\frac{\partial}{\partial v}\left[v^3 f_0\right] - S_{0,in} = 0$$

$$f_1^{\,0} = -\frac{v}{\gamma}\frac{\partial f_0}{\partial z}$$

$$f_1^{\,1} = \frac{\gamma e|E|}{m(\gamma^2+\omega^2)}\;\frac{\partial f_0}{\partial v}$$

Now the coordinate transformation is made from velocity to energy space and the r.m.s. electric field strength is replaced by the peak field strength.

APPENDIX B

Derivation of characteristic curves for probe measurements in Maxwellian and nonMaxwellian electron gases.

Consider a plane probe in an electron gas:

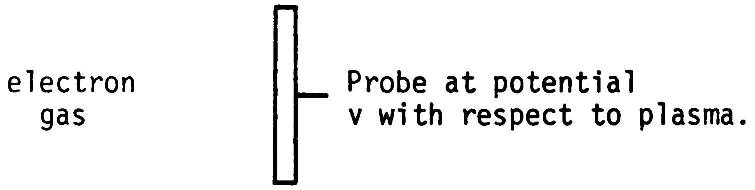


Figure 11. Sketch of a planar probe in an electron gas.

The flux of electrons to the probe due to electrons with velocity between $\underset{\wedge}{v}$ and $\underset{\wedge}{v} + d\underset{\wedge}{v}$ is given by:

$$dj = n_e \underset{\wedge}{v} \cdot \underset{\wedge}{z} \; 4\pi \; v^2 \; f(v) \; dv$$

$$= n_e \; v \cos\theta \; 4\pi v^2 \; f(v) \; dv$$

For each v, only electrons of $\theta < \theta^*$ are energetic enough to reach the probe.

Let $\phi = -2eV/m$. So $v \cos\theta^* = \phi^{\frac{1}{2}}$

$$j = n_e \int_{\phi^{\frac{1}{2}}}^{\infty} 4\pi v^2 f(v) \int_{0}^{\theta^*} \cos\theta \; 2\pi \sin\theta \; d\theta \; dv$$

$$j = 8\pi n_e \int_{\phi^{\frac{1}{2}}}^{\infty} v^3 f(v) \int_{1}^{\cos\theta^*} (-\cos\theta) \; d(\cos\theta) \; dv$$

$$j = -\, 8\pi n_e \int_{\theta^{\frac{1}{2}}}^{\infty} v^3 f(v) \left[\tfrac{1}{2}\cos^2\theta\right]_{1}^{\cos\theta^*} dv$$

$$j = -\, 4\pi n_e \int_{\phi^{\frac{1}{2}}}^{\infty} v^3 f(v) \left[\frac{\phi}{v^2} - 1\right] dv$$

Transform to energy variable.

$$j = 2\pi n_e \left(\frac{e}{2m}\right)^{\frac{1}{2}} \left[\int_{|v|}^{\infty} f(\varepsilon)\varepsilon \; d\varepsilon + v \int_{|v|}^{\infty} f(\varepsilon) \; d\varepsilon\right]$$

Now the electron flux to the probe is available in terms of certain integral properties of the distribution function.

Case 1: Maxwellian distribution

$$f(\varepsilon) = \frac{2\alpha_1^{2/3}}{\sqrt{\pi}} \; e^{-\alpha_1 \varepsilon}$$

The integration results in the following expression for electron flux:

$$\ln j = \ln [4\, n_e (\frac{\pi e}{2\alpha_1 m})^{\frac{1}{2}}] - \alpha_1 V$$

This is the usual result exploited in interpretation of Langmuir probe data. The slope of ln j <u>vs</u> V gives α_1 which is directly related to the average energy of the electron gas.

Case 2: D.C. Druyvestuyn distribtuion

$$f(\varepsilon) = \frac{2(\frac{\beta_1\beta_2}{2E^2})^{3/4}}{\Gamma(3/4)} \exp(-\frac{\beta_1\beta_2}{2E^2}\varepsilon^2)$$

$$\text{Let } \alpha_0 = \frac{\beta_1\beta_2}{2E^2}$$

So then:

$$j = 4\pi n_e (\frac{e}{2m}) \frac{\alpha_0 3/4}{\Gamma(3/4)} [\frac{1}{2\alpha_0} \exp(-\alpha_0 v^2) - \frac{v}{2}\sqrt{\frac{\pi}{a_0}} \text{ erfc } (\sqrt{a_0} V)]$$

Case 3: A.C. Druyvestuyn distribution

$$f(\varepsilon) = \frac{(\frac{\beta_1\beta_2}{E^2})3/4 \exp[-(\frac{\beta_1\beta_2}{2E^2})\varepsilon^2 - (\frac{\beta_2\omega^2}{E^2})\varepsilon - \frac{\beta_2\omega^4}{4\beta_1 E^2}]}{\Gamma(3/2)\ U\{1, \frac{\omega^2}{E} \sqrt{\frac{\beta_2}{\beta_1}}\}}$$

For ease of notation, let:

$$a = \frac{\beta_1\beta_2}{\alpha E^2} ; \quad b = \frac{\beta_2\omega^2}{E^2} ; \quad c = \frac{\beta_2\omega^4}{4\beta_1 E^2}$$

$$f(\varepsilon) = \frac{(2a)^{3/4} \exp [- a\varepsilon^2 - b\varepsilon - c]}{\Gamma(3/2) \; U \{1,2\sqrt{c}\}}$$

$$j = \frac{2\pi n_e \left(\frac{e}{2m}\right)^{\frac{1}{2}} (2a)^{3/4}}{\Gamma(3/2) \; U \{1,2\sqrt{c}\}} \; [\frac{1}{2a} \exp [- (av^2 + bv + c)]$$

$$- \frac{b}{4a}\sqrt{\frac{\pi}{a}} \exp [\frac{-(b^2+ac)}{a}] \operatorname{erfc}[v\sqrt{a} + \frac{b}{\sqrt{a}}] - \frac{v}{2} \frac{\pi}{\sqrt{a}} \exp [\frac{-(b^2+ac)}{a}]$$

$$\operatorname{erfc} [v\sqrt{a} + \frac{b}{\sqrt{a}}]]$$

If $b = c = 0$, this expression reduces to that for the d.c. Druyvestuyn distribution, as expected.

APPENDIX C

Derivation of Maxwellian and Druyvestuyn distribution functions.

Maxwellian

Assume that elastic interactions dominate and that the collision frequency for momentum transfer is constant with respect to electron energy. Then the Boltzmann equation becomes:

$$\varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial\varepsilon} (\varepsilon^{3/2} \frac{\partial f}{\partial\varepsilon}) + \alpha_1 \varepsilon^{-\frac{1}{2}} \frac{\partial}{\partial\varepsilon} (\varepsilon^{3/2} f) = 0$$

$$\int_0^{\varepsilon} \frac{\partial}{\partial\varepsilon} (\varepsilon^{3/2} \frac{\partial f}{\partial\varepsilon}) \, d\varepsilon + \alpha_1 \int_0^{\varepsilon} \frac{\partial}{\partial\varepsilon} (\varepsilon^{3/2} f) \, d\varepsilon = 0$$

$$\frac{df}{d\varepsilon} + \alpha_1 f = 0$$

$$f(\varepsilon) = c_1 \exp(-\alpha_1 \varepsilon)$$

From the normalization condition we have:

$$C_1 \mathop{}\limits_{0}^{\infty} \exp(-\alpha_1 \varepsilon) \, \varepsilon^{\frac{1}{2}} \, d\varepsilon = 1.$$

So, $C_1 = 2\alpha_1^{3/2} / \sqrt{\pi}$

$$f(\varepsilon) = \frac{2\alpha_1^{3/2}}{\sqrt{\pi}} \exp(-\alpha_1\varepsilon) \quad ; \quad \alpha_1 = \frac{3m^2}{Me} \left(\frac{\gamma^2+\omega^2}{E^2}\right)$$

$$\bar{\varepsilon} = {}_0^{\infty} \varepsilon^{3/2} f(\varepsilon)\, d\varepsilon$$

$$\bar{\varepsilon} = \frac{2\alpha_1^{3/2}}{\sqrt{\pi}} \int_0^{\infty} \varepsilon^{3/2} \exp(-\alpha_1\varepsilon)\, d\varepsilon$$

$$\bar{\varepsilon} = \frac{3}{2\alpha_1}$$

Druyvestuyn

Assume that elastic interactions dominate and that the total elastic cross-section is constant with respect to electron energy.

Let $\ell = N \sigma_t v$

$= v/\ell$

where: $\ell \equiv$ mean free path

The Boltzmann equation takes the form:

$$\varepsilon^{\frac{1}{2}} \frac{\partial}{\partial\varepsilon} \left\{\frac{\varepsilon^2}{(\frac{2e}{m})\varepsilon + \omega^2\ell^2} \frac{\partial f}{\partial\varepsilon}\right\} + \frac{3m^2}{M\ell^2E^2e} \varepsilon^{\frac{1}{2}} \frac{\partial}{\partial\varepsilon} \{\varepsilon^2 f\} = 0$$

$$\frac{\partial f}{\partial \varepsilon} + \beta_2 \left(\frac{\beta_1 \varepsilon}{E^2} + \omega^2\right) f = 0 \; ; \qquad \beta_1 \equiv \frac{2e}{m\ell^2}$$

$$\beta_2 \equiv 3\, m^2/Me$$

$$f(\varepsilon) = f(0) \exp\left\{-\frac{\beta_2}{E^2}\left(\frac{\varepsilon^2 \beta_1}{2} + \omega^2 \varepsilon\right)\right\}$$

From normalization condition, we have that:

$$f(\varepsilon) = \frac{\left(\frac{\beta_1 \beta_2}{E^2}\right)^{3/4} \exp\left\{-\frac{\beta_2}{E^2}\left(\frac{\beta_1 \varepsilon^2}{2} + \omega^2 \varepsilon + \frac{\omega^4}{4\beta_1}\right)\right\}}{\Gamma(3/2)\; U\left\{1, \frac{\omega^2}{E} \sqrt{\frac{\beta_2}{\beta_1}}\right\}}$$

where: $U(\alpha,\beta) \equiv$ parabolic cylinder function

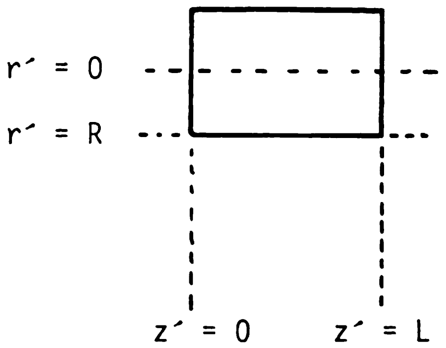
The average energy is given by:

$$\bar{\varepsilon} = \frac{\frac{3}{2}\left(\frac{E^2}{\beta_2 \beta_1}\right)^{\frac{1}{2}} U\left\{2, \frac{\omega^2}{E} \sqrt{\frac{\beta_2}{\beta_1}}\right\}}{U\left\{1, \frac{\omega^2}{E} \sqrt{\frac{\beta_2}{\beta_1}}\right\}}$$

APPENDIX D

A solution of the diffusion-reaction equation.

$$D\,\underset{\wedge}{\nabla}^2 n + \nu_i n = 0 \quad ; \qquad n\ (\text{boundary}) = 0$$



$$\frac{\partial n}{\partial r'}\,(r' = 0,\ z') = 0$$

$$\frac{\partial n}{\partial z'}\,(r',\ z' = \frac{L}{2}) = 0$$

Let $\Lambda^2 = \frac{D}{\nu_i}$; $r = \frac{r'}{R}$; $z = \frac{z'}{L}$

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial n}{\partial r}\right) + \left(\frac{R}{L}\right)^2 \frac{\partial^2 n}{\partial z^2} + \left(\frac{R}{\Lambda}\right)^2 n = 0$$

Assume that $n(r,z) = \sum_{\lambda} a_{\lambda}(r)\, b_{\lambda}(z)$

So:

$$\sum_{\lambda}\left(\frac{1}{r}\ \frac{\partial}{\partial r}\left(r\ b_{\lambda}\,\frac{\partial a_{\lambda}}{\partial r}\right) + \left(\frac{R}{L}\right)^2 a_{\lambda}\,\frac{\partial^2 b_{\lambda}}{\partial z^2} + \left(\frac{R}{\Lambda}\right)^2 a_{\lambda} b_{\lambda}\right) = 0$$

$$\Sigma\ b_{\lambda}\,\frac{\partial a}{\partial r}\,(r=0) = 0 \qquad \Sigma\ a_{\lambda}\,\frac{\partial b}{\partial z}\,(z = \tfrac{1}{2}) = 0$$

$$\Sigma\ a_{\lambda}\ (r=1)\ b_{\lambda} = 0 \qquad \Sigma\ a_{\lambda}\ b_{\lambda}(z=0) = 0$$

Let $\frac{\partial^2 b_\lambda}{\partial z^2} = -\lambda^2_n \, b_\lambda.$

So the equation becomes

$$b_\lambda \sum_\lambda \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial a_\lambda}{\partial r}\right) + \left(\left(\frac{R}{\Lambda}\right)^2 - \left(\frac{R}{L}\right)^2 \lambda_n{}^2\right) a_\lambda\right) = 0$$

$$r \frac{d^2 a_\lambda}{dr^2} + \frac{da_\lambda}{dr} + r\left(\left(\frac{R}{\Lambda}\right)^2 - \left(\frac{R}{L}\right)^2 \lambda_n{}^2\right) a_\lambda = 0$$

Applying boundary conditions, the solutions to the two ordinary differential equations are given by:

$$b_\lambda (z) = c_{1_{\lambda,n}} \sin (\lambda_n z) \qquad \lambda_n = n\pi \qquad n = 1,2,3...$$

$$a_\lambda (r) = c_{2_{\lambda,n}} J_0(\alpha_n r) \qquad \alpha_n = \text{zeroes of } J_0$$

where α_n is related to λ_n and geometry by:

$$\alpha_n{}^2 = \left(\frac{R}{\Lambda}\right)^2 - \left(\frac{R}{L}\right)^2 n^2 \pi^2$$

Only the lowest order eigenmodes are of physical interest here, so:

$$\frac{1}{\Lambda^2} = \left(\frac{\alpha_1}{R}\right)^2 + \left(\frac{\pi}{L}\right)^2$$

$$n(r,z) = N_0 \sin(\pi z)\, J_0(\alpha_1 r)$$

From the relation between the cylinder geometry and the diffusion length, Λ, the value of (D/ν_i) for which a nontrivial solution of the diffusion-reaction equation exists may be determined.

APPENDIX E

Calculational procedure for average energy, breakdown field and inelastic collision rate coefficients.

Given:

$$f_0°(\varepsilon) = \exp(h\varepsilon)\ \{\phi^1 M[a,c,\zeta] + \phi^2\ \zeta^{1-c}\ M[a-c+1,\ 2-c,\zeta]\}$$

and the values of h, a, c, ζ as functions of E, p, ω, Λ, cross-sections given on page 43. ϕ^1 and ϕ^2 are undetermined constants.

1. Specify the gas pressure, electric field angular frequency, diffusion length, collision cross-sections.
2. Estimate a value for the breakdown electric field strength. Experimental values may be a good place to begin.
3. Estimate a value for the electron flux due to ionization, σ_{ion}.
4. Calculate h, a, c using relations on pages 42-43. Also calculate the coefficients in the relation between ζ and ε. These values of h, a, c and coefficients in ζ will vary from region to region in the energy domain (Table 2). Seven sets of values for h, a, c and $\zeta(\varepsilon)$ will result.
5. Take the first derivative of $f_0°(\varepsilon)$ with respect to ε. This may be done explicitly.

Note that $f_0°$ and $df_0°/d\varepsilon$ may be written in the following way for each region--j.

$$f_0°(\varepsilon_i)_j = \phi_j^1\ A_j^1 + \phi_j^2\ A_j^2$$

$$\frac{df_0°}{d\varepsilon}\ (\varepsilon_i)_j = \phi_j^1\ B_j^1 + \phi_j^2\ B_j^2$$

A_j^1, A_j^2, B_j^1, B_j^2 are constants depending on h, a, c, $\zeta(\varepsilon_i)$ and ε_i.

As noted on page 44, in the first energy region the initial condition on $f_0{}^\circ(0)$ requires that $\phi_0{}^2 \equiv 0$.

The procedure to calculate the $\phi_j{}^1$, $\phi_j{}^2$ is outlined here for values of $\phi_1{}^1$, $\phi_1{}^2$.

The first boundary occurs at $\varepsilon = \varepsilon_{ion}$ ($\simeq$ .1 ev):

$$f_0{}^\circ(\varepsilon_{ion}) = \phi_0{}^1 A_0{}^1 = \phi_1{}^1 A_1{}^1 + \phi_1{}^2 A_1{}^2$$

$$\frac{df_0{}^\circ}{d\varepsilon}(\varepsilon_{ion}) = \underbrace{\phi_0{}^1 B_0{}^1}_{\substack{\text{region}\\0}} = \underbrace{\phi_1{}^1 B_1{}^1 + \phi_1{}^2 B_1{}^2}_{\substack{\text{region}\\1}}$$

These two equations may be rewritten as:

$$\begin{bmatrix} \phi_1{}^1 \\ \phi_1{}^2 \end{bmatrix} = \phi_0{}^1 \begin{bmatrix} A_1{}^1 & A_1{}^2 \\ B_1{}^1 & B_1{}^2 \end{bmatrix}^{-1} \begin{bmatrix} A_0{}^1 \\ B_0{}^1 \end{bmatrix}$$

So now $\phi_1{}^1$, $\phi_1{}^2$ are given in terms of $\phi_0{}^1$ and some constants depending on h, a, c, $\zeta(\varepsilon_{ion})$ and ε_{ion}. This procedure may be repeated at each boundary to give $f_0{}^\circ(\varepsilon)$ in terms of functions of h, a, c, $\zeta(\varepsilon)$, ε and the undetermined constant $\phi_0{}^1$.

$$f_0{}^\circ(\varepsilon) = \phi_0{}^1 g_0(\varepsilon)$$

$$\int_0^\infty \varepsilon^{\frac{1}{2}} f_0{}^\circ(\varepsilon)\, d\varepsilon = \phi_0{}^1 \int_0^\infty \varepsilon^{\frac{1}{2}} g_0{}^\circ(\varepsilon)\, d\varepsilon$$

But the left hand side is unity by normalization, so:

$$(\phi_0^1)^{-1} = \int_0^\infty \varepsilon^{\frac{1}{2}} g_0{}^\circ(\varepsilon)\, d\varepsilon$$

The integrations are carried out numerically by a modified Simpson's quadrature. So now the distribution function is given in terms of h, a, c, $\zeta(\varepsilon)$ and ε.

6. Calculate the rate coefficient for ionization as follows:

$$\nu_i = \int_0^\infty \nu_i(\varepsilon)\, f_0{}^\circ(\varepsilon)\, \varepsilon^{\frac{1}{2}}\, d\varepsilon$$

From this, calculate the electron flux due to ionization by equating the rate of ionization to the rate of electron production by ionization ($\nu_i = \sigma_{ion}$).

7. Compare the calculated rate to the estimated rate of electron production by ionization. If the two agree within acceptable limits, then calculate the average energy and diffusion length.

$$\Lambda^2 = \frac{2e\bar{\varepsilon}}{3m\gamma\nu_i} \quad ; \bar{\varepsilon} = \int_0^\infty f_0{}^\circ(\varepsilon)\, \varepsilon^{\frac{3}{2}}\, d\varepsilon$$

If the two rates do not agree then return to step 3.

8. Does the calculated diffusion length, Λ, match that specified in step 1? If no, return to step 2. If yes, calculate the remaining inelastic rate coefficients by the following integral.

$$\nu_j = \int_0^\infty \nu_j(\varepsilon)\, f_0{}^\circ(\varepsilon)\, \varepsilon^{\frac{1}{2}}\, d\varepsilon$$

The electric field strength at breakdown, average energy and inelastic rate coefficients resulting from these calculations are given in Figs. 5, 6, 10. Sample distribution functions are plotted in Fig. 7-9. These figures are plots of $f_0{}^\circ(\varepsilon)\, \varepsilon^{\frac{1}{2}}$, the density function, rather than $f_0{}^\circ(\varepsilon)$ itself.

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