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EQUATIONS FOR THE KINETIC MODELING OF SUPERSONICALLY FLOWING ELECTRICALLY EXCITED LASERS

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EQUATIONS FOR THE KINETIC MODELING OF SUPERSONICALLY FLOWING ELECTRICALLY EXCITED LASERS

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ABSTRACT

The equations for the kinetic modeling of a supersonically flowing electrically excited laser system are presented. The work focuses on the use of diatomic gases, in particular carbon monoxide mixtures. The equations presented include the vibrational rate equation - which describes the vibrational population distribution, the electron, ion and electronic level rate equations, the gasdynamic equations for an ionized gas in the presence of an applied electric field, and the free-electron Boltzmann equation including flow and gradient coupling terms. The model developed accounts for vibration-vibration collisions, vibration-translation collisions, electron-molecule inelastic excitation and superelastic de-excitation collisions, charged particle collisions, ionization and three body recombination collisions, elastic collisions, and radiative decay, all of which take place in such a system. A simplified form of the free-electron Boltzmann equation is developed and discussed with emphasis placed on its coupling with the supersonic flow. A brief description of a possible solution procedure for the set of coupled equations is then discussed.

INTRODUCTION

The concept of a fast flow laser system is not new[1]. It has been demonstrated for electric discharge CO_2 laser mixtures, in both cw and pulsed operation, that a considerable increase in power can be achieved with the use of fast flow[2-11]. The addition of fast flow gives several attractive features: (a) the power output scales with the mass flow rate - this can represent up to a factor of 10^5 increase in power over that obtainable from conventional diffusion controlled laser systems, (b) the translational temperature of the gas is maintained at a low level by the convection which prevents the lower laser level for CO_2 systems from becoming populated to such an extent that the inversion is destroyed, and is very important for diatomic laser systems, which we shall mention below.

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To understand the importance of low translational temperatures for diatomic laser systems the mechanisms responsible for diatomic laser action will briefly be mentioned. When considering diatomic molecules, the anharmonic structure, i.e. the small decrease in spacing between vibrational energy states with increasing quantum number, introduces a new and crucial factor that leads to the processes which can ultimately produce laser action. Treanor et.al.[12] have shown that during the collision of two such anharmonic diatomic molecules the subsequent exchange of vibrational energy (V-V exchange) can lead to significant departures from a Boltzman distribution of vibrational energy. Specifically, in Ref. 12 it has been shown that under the conditions of a low translational temperature together with a high degree of vibrational excitation, population inversions between the combined vibration-rotation levels of adjacent vibrational states can occur. Such inversions then provide the basic mechanism by which diatomic lasers operate. In addition, to maximize the radiative gain on a particular vibration-rotation transition, once the inversion has been achieved, the number of molecules at the level in question must be maximized. This occurs when the molecules are preferentially populating the lower rotational levels, which occurs for low translational temperatures (assuming rotation is in equilibrium with translation).

The conditions of high vibrational excitation and low translational temperature occur naturally in the supersonic expansion of a gas from a hot reservoir. The occurance of these conditions in such gasdynamic expansions led McKenzie[13] to develop the CO gasdynamic laser. Defining efficiency, for the gasdynamic laser, as the ratio of laser power output to input enthalpy flux, where the latter is the power used to produce the heated reservoir and associated supersonic flow, McKenzie obtained efficiencies on the order of a few tenths of a percent for the CO system.

On the other hand, electric discharge lasers without flow have very high efficiencies but low power. For a CO system Bhaumik et.al.[14] has recently obtained 46% efficiency for conversion of electric power to laser power. This is the highest efficiency demonstrated for any laser system, polyatomic or diatomic. For such a system the laser gas is essentially in a static condition, cooled by liquid nitrogen, and excited by a glow discharge. The reason such high efficiencies are possible is that the input electrical power goes predominately into exciting the vibrational levels of the gas by electron-molecule collisions. This leads to the condition of high vibrational excitation, while the liquid nitrogen cooling provides the low translational temperature. However, since this is a static discharge laser, and consequently diffusion controlled - i.e. removal of heated gas is by diffusion to the walls, the advantages of increased power levels with fast flow rates are not utilized.

Consideration of these facts indicates that the use of electric discharge excitation combined with fast flow rates could potentially lead to highly efficient high power lasers. This is based on the separate advantages of each, and assuming that when combined they do not adversely effect each other.

Recently, laser power, using two different schemes but employing the features of electric discharge excitation and fast flow in CO mixtures has been demonstrated. First, Rich et.al.[15] (and later Kan et.al.[16]) excited a CO mixture with a glow discharge in the plenum chamber of a supersonic nozzle and then allowed the excited mixture to expand to supersonic speeds. It is clear that such a scheme produces the necessary conditions mentioned before for diatomic laser operation. However, this scheme produced a relatively inefficient laser with efficiencies of the order of a percent. This is due to the fact that much of the vibrational excitation produced in the plenum is lost to heating the gas in the subsonic portion of the expansion. The second scheme, developed by Kan et.al.[17], is essentially a direct extension of the liquid nitrogen cooled static electric discharge mentioned previously, whereby a fast flow rate of CO is now employed. This scheme used subsonic flow rates and relied on liquid nitrogen cooling and thus did not utilize a supersonic expansion to give the low temperature, and the concurrent further increase in power that would result from such an increased speed. However, this scheme did achieve efficiencies up to 26%.

These two schemes, representing initial approaches to combining fast flow and electric discharge excitation in diatomic gases have certain disadvantages, as mentioned above. With the prospect of more fully utilizing the advantages of each feature the intent of this work will be to discuss the situation of electric discharge excitation occuring in a supersonic stream.

This leads to important questions as to the mechanisms taking place in such combined systems, and the result of using supersonic flow, with the discharge occuring in the flow. For the case of electric discharges in a supersonic stream, questions concerning the stability must also be answered. Here, we assume a priori that such a discharge is feasible.

With these ideas in mind it is the purpose of this note to develop a kinetic model for the case of a supersonically flowing CO mixture with a stable electric discharge established in the flow. This note is in the form of a summary of the work done to date which consists of a development of the equations relevant to the problem and a brief description of a possible solution procedure.

BASIC THEORETICAL MODEL

Physical Model

The geometry employed is that of a supersonic nozzle in which the flow is to be established (see Fig. 1). In some region of the nozzle, electrodes are situated such that a discharge, alligned with the flow can be produced. The laser power is then extracted transverse to the flow and discharge direction. In the sketch shown, the discharge is located in a region of uniform flow properties, although it may be located in any portion of the

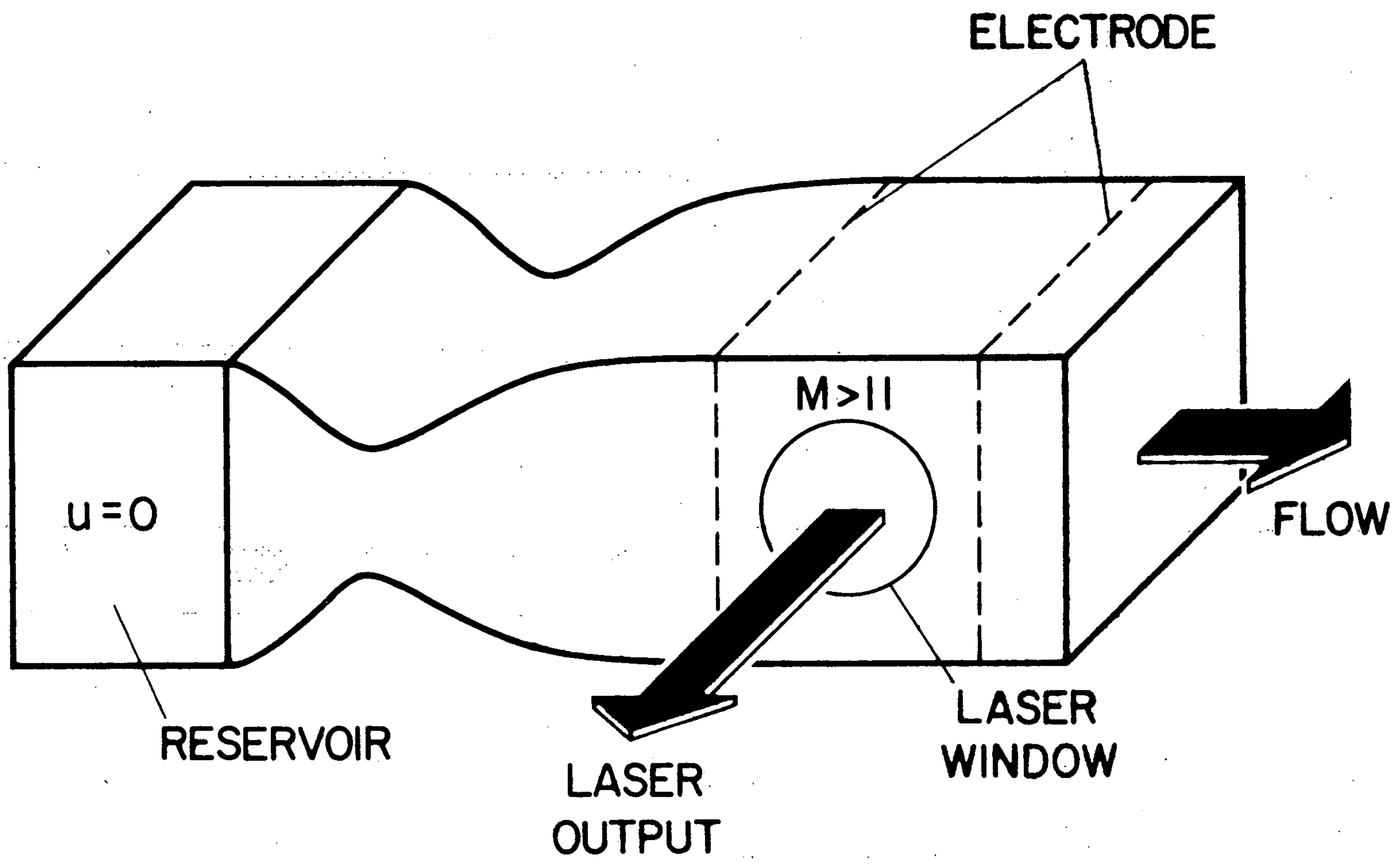

Fig. 1 Schematic of supersonically flowing electrically excited laser

nozzle; even the reservoir, as in Rich's[15] experiment.

For efficient excitation of the vibrational levels of a gas by electron collisions the average electron energies are those conveniently obtained in the positive column of a normal glow discharge (around 1 ev). We shall, therefore, consider only glow discharges, assumed to be fully established in the flow, and then attempt to model the ensuing positive column region. The questions of instability of the discharge are not considered. Such questions are, of course, important but can be investigated separately. (See Ecker et.al.[18] and Nighan et.al.[19]). By limiting the modeling to the positive column the space charge effects at the electrodes can be neglected. They are crucial to the establishment of a stable glow discharge, but unimportant in the physics of the positive column. The problem will also be assumed to be convectively controlled (see Section 3); thus the effects of diffusion to the walls will be considered negligible and the standard Schottky[20,21] type analyses are not relevant.

The gas is further assumed to enter the discharge region in a preionized state. Preionization has an important effect on efficient laser operation. Ordinarily, without preionization, the glow discharge is required to be self-sustaining. Then, ionization, produced by electron-molecule collisions at a rate sufficient to balance the loss mechanisms present, takes place within the discharge itself to keep the gas conductive. However, schemes that separate the above function of ionization from the concurrent vibrational excitation (crucial to producing the inversion needed for lasing) have been shown[22,23] to considerably increase laser performance. This is because the electrons in the discharge that are produced by an external means, can be of lower energy than that required to sustain the discharge. In fact, by proper tailoring of the discharge voltage, the electrons in the discharge can then be used for efficient vibrational excitation exclusively.

The emphasis of this work is thus to model the interaction of a (preionized) supersonic flow with the plasma of a positive column to study its effects on the resulting vibrational population distributions.

Energy Transfer Mechanisms

In a discharge of the type considered, several collisional and radiative energy exchange mechanisms take place. These transfer mechanisms are conveniently modeled by a division into six energy modes, consisting of a free-electron mode, an anharmonic oscillator mode of neutral particles, a bound-electron mode of neutral particles, a kinetic mode of heavy particles, and a UV and IR-photon mode (see Fig. 2). Details of the resulting model are similar in some parts, to the models described in Ref. 24, 25, 26.

Referring to Fig. 2 we assume that the free electrons, accelerated by the applied electric field, participate in the (numbered) energy transfer mechanisms of: (1) inelastic excitation and superelastic de-excitation collisions with the vibrational and electronic levels, (2) elastic

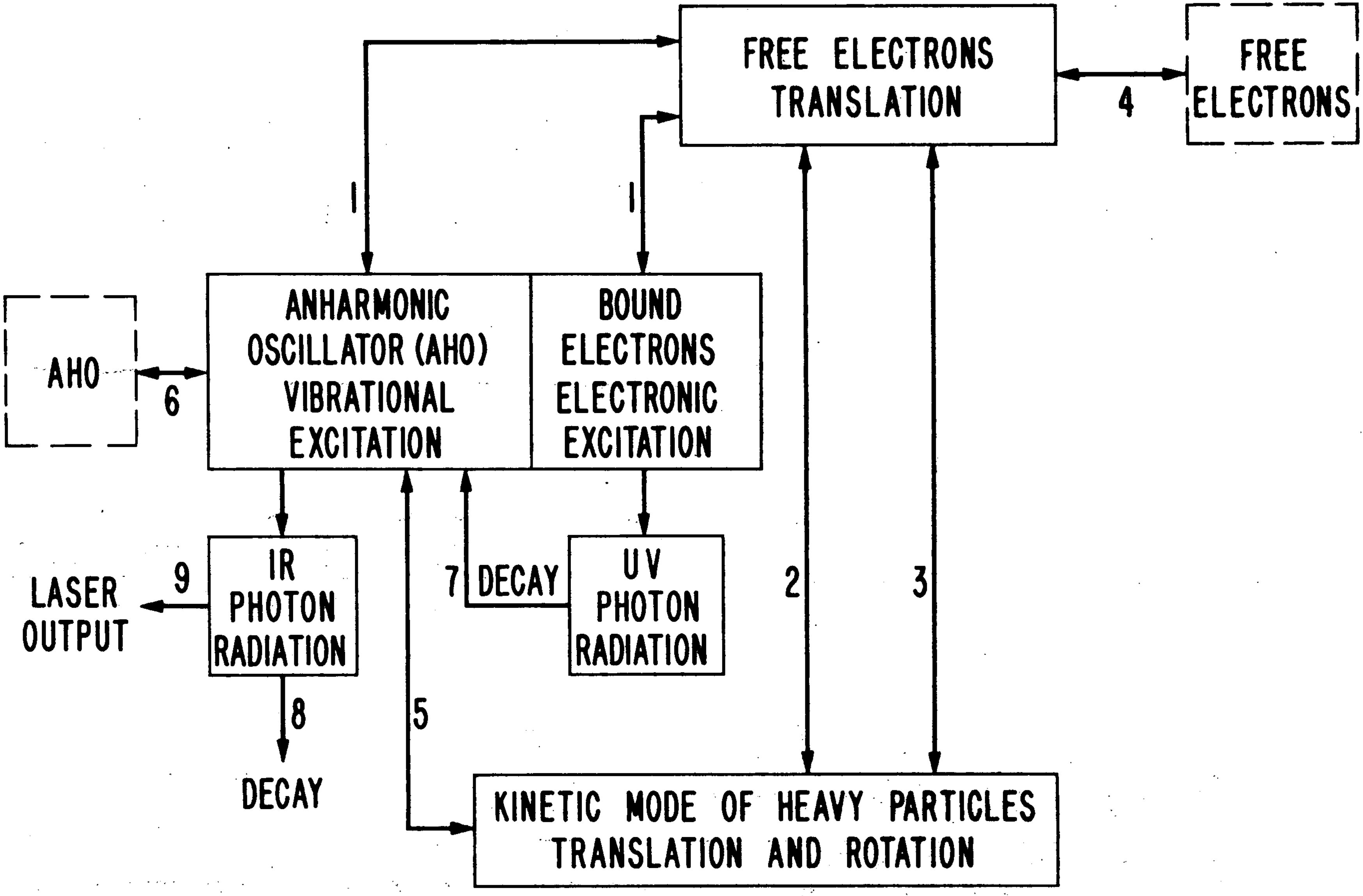

Fig. 2 Energy Flow Diagram

collisions with heavy particles, (3) ionization and three-body recombination collisions, and (4) electron-electron collisions. This energy distribution is subsequently redistributed by: (5) vibration-translation collisions, (6) vibration-vibration collisions, (7) radiative decay of electronic levels (8) radiative decay of vibrational levels and finally, (9) possible induced radiative transitions between vibrational levels. Several assumptions are implicit in this model: (a) the gas mixture consists of electrons, singly charged ions, and nuetrals - of which several monatomic and diatomic species are allowed, (b) translation and rotation are in equilibrium at the temperature T, (c) the excitation of ion electronic states is negligible, (d) the ions are in kinetic equilibrium with the neutral particles, (e) dissociation is ignored, and (f) photoionization and two-body recombination are negligible.

One further simplification will be to neglect at the outset the effect of stimulated emission (process 9) since we are only interested here in the calculation of radiative gain prior to the introduction of any laser applications.

The free electrons in this model are not expected to be in a Boltzmann distribution. In fact, for conditions typical of CO and CO_2 lasers, it has been shown theoretically[27] and experimentally[28,29], the distribution is profoundly non-Maxwellian and is strongly affected by the electron-molecule energy processes discussed above. Since the electron-molecule collision rates (needed to determine the vibrational population distribution), the electron temperature, the heat conduction, and the current density, are all averages over the distribution of electron energy it is clear that a knowledge of this distribution is needed for an accurate representation of the model.

In summary, the energy transfer mechanisms discussed above, together with an appropriate development of the free-electron-Boltzmann equation are postulated to sufficiently model the combined flowing gas-electric discharge situation under consideration. In Section 3 to follow, the necessary rate equations for the model are given. Section 4 presents the standard gasdynamic equations for an ionized gas in the presence of an applied electric field. Finally, in Section 5 the free-electron Boltzmann equation is developed and certain simplifications are then made that are appropriate to the present model.

RATE EQUATIONS

The equation necessary to describe the vibrational population distribution of the laser gas mixture is the species continuity[30,31] equation for the vibrational levels. For a general unsteady flow problem this equation is

$$\frac{\partial n_s^k}{\partial t} + \nabla \cdot (n_s^k \vec{v}_s) = \dot{n}_s^k \qquad k = 0,1,2 \ldots N_s \, , \qquad (1)$$

where n_s^k is the number density of species s in level k, $\vec{v}_s$ is the species velocity and, $\dot{n}_s^k$ is the net rate of production of species s in level k to be determined from a consideration of the energy transfer processes described previously.

Before proceeding with the expression for $\dot{n}_s^k$ the conditions that insure a convectively controlled problem will be presented. We find, after an examination of the left-hand side of Eq. (1), that two conditions must be satisfied. These are:

$$u_o >> \frac{L}{d^2} D_{amb} , \tag{2}$$

and

$$u_o >> V_F , \tag{3}$$

where u_o, V_F, L, d, and D_{amb} are: characteristic flow velocity, electron diffusion velocity in the supersonic flow direction, discharge axial length, discharge transverse length, and ambipolar diffusion coefficient*.

Each condition can easily be checked once a solution is known. In fact, values for V_F can be calculated exactly from the formulation to be discussed in Section 5.

For the present problem we assume that the above conditions are satisfied and thus Eq. (1) can be written for each vibrational level k, for steady one-dimensional flow, as follows:

$$\rho u \frac{d}{dy}\left(\frac{n_s^k}{\rho}\right) = \dot{n}_s^k \qquad k = 0,1,2\ldots N_s , \tag{4}$$

where y is the coordinate in the one-dimensional flow direction, ρ is the average density, and u is the mass average velocity.

To determine the expression for the production of excited vibrational levels, $\dot{n}_s^k$, we take into account certain of the energy transfer processes described in Fig. 2. These consist of the following collisional and radiative processes:

(i) Inelastic and superelastic collisions with electrons - process 1.
(ii) Vibration-translation collisional exchange with the various constituents - process 5.
(iii) Vibration-vibration collisional exchange within the laser gas and other diatomic constituents - process 6.
(iv) Excitation due to the spontaneous emission from the excited electronic level - process 7. We assume here that only one electronic level ($a^3\Pi$) is excited sufficiently to participate in the energy transfer processes.

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*The development of these conditions follows a discussion given by Hassan and Bordeaux[32]. Here, however, the diffusion to the walls takes place by electron-ion ambipolar diffusion[33].

(v) Spontaneous emission - process 8.

(vi) Possible ionization and 3-body recombination effects.

In addition, the modeling includes the following features:

(vii) The vibrational quantum states of the diatomic gas are treated as those of a Morse anharmonic oscillator[34]:

$$\epsilon_s^k = \kappa \, \theta_s \, k \left[1 - \Delta_s (k+1) \right] , \tag{5}$$

where

θ_s = characteristic vibrational temperature,

Δ_s = small anharmonic oscillator parameter,

κ = Boltzmann constant,

ε_s^k = energy of the k vibrational state of species s.

(viii) With the exception of vibrational transitions induced by electron collisions, only single quantum transitions are allowed.

(ix) The free electrons in the discharge are <u>not</u> assumed to be in a Maxwell-Boltzmann distribution and consequently several parameters will be needed to characterize their properties.

(x) For the excited electronic state its ground vibrational level is the only level assumed to be populated.

Combining these various features of the model with Eqs. (4) and defining the mole fraction of species s in level k as

$$x_s^k \equiv \frac{n_s^k}{\sum\limits_{s,k} n_s^k} , \tag{6}$$

we obtain the following vibrational rate equations for x_s^k:

$$\begin{aligned} u \frac{dx_s^k}{dy} = \sum_p Z_{sp} Q_{sp}^k + x_e \Bigg\{ & \sum_{\ell=0}^{k-1} x_s^\ell R_s^{\ell k} + \sum_{\ell=k+1}^{N_s} x_s^\ell R_s^{\ell k} \\ & - x_s^k \sum_{\ell=0}^{k-1} R_s^{k\ell} - x_s^k \sum_{\ell=k+1}^{N_s} R_s^{k\ell} - x_s^k R_s^{k\lambda} + x_s^I x_e R_s^{\lambda k} \Bigg\} \\ & - x_s^k A_s^{k,k-1} + x_s^{k+1} A_s^{k+1,k} + x_s^E A_s^{Ek} , \qquad k = 0,1,2 \ldots N_s . \end{aligned} \tag{7}$$

In this equation the first term on the right-hand side accounts for vibration-vibration (V-V) and vibration-translation (V-T) collisions and is given, between species s and p, by McKenzie[34] as follows:

$$
\begin{aligned}
Z_{sp} &= \text{average collision rate} \\
&= \frac{\rho}{m}\, d_{sp}^2 \sqrt{\frac{8\pi\kappa T}{\mu_{sp}}}\,, \qquad (8)
\end{aligned}
$$

where d_{sp}^2 = average collision cross section for encounters between species s and p,

μ_{sp} = reduced mass,

m = molecular mass,

$$= \sum_s m_s\,, \qquad (9)$$

Q_{sp}^k = molar production per collision

$$= [Q_{sp}^k]_{V\text{-}V} + [Q_{sp}^k]_{V\text{-}T}\,, \qquad (10)$$

where

$$
\begin{aligned}
[Q_{sp}^k]_{V\text{-}V} = \sum_{\ell} \Bigg\{ & P_{sp}\begin{pmatrix}\ell,\ell+1\\ k,k-1\end{pmatrix}\left[x_s^{k-1}\, x_p^{\ell+1} \exp\left(\frac{\epsilon_p^{\ell+1,\ell}}{\kappa T} - \frac{\epsilon_s^{k,k-1}}{\kappa T}\right) - x_s^k\, x_p^\ell\right] \\
& + P_{sp}\begin{pmatrix}\ell,\ell+1\\ k+1,k\end{pmatrix}\left[x_s^{k+1}\, x_p^{\ell} - x_s^k\, x_p^{\ell+1} \exp\left(\frac{\epsilon_p^{\ell+1,\ell}}{\kappa T} - \frac{\epsilon_s^{k+1,k}}{\kappa T}\right)\right]\Bigg\}, \qquad (11)
\end{aligned}
$$

and

$$
\begin{aligned}
[Q_{sp}^k]_{V\text{-}T} = \left(\sum_{\ell'} x_p^\ell\right) \Bigg\{ & P_{sp}^{k,k-1}\left[x_s^{k-1} \exp\left(\frac{-\epsilon_s^{k,k-1}}{\kappa T}\right) - x_s^k\right] \\
& + P_{sp}^{k+1,k}\left[x_s^{k+1} - x_s^k \exp\left(\frac{-\epsilon_s^{k+1,k}}{\kappa T}\right)\right]\Bigg\}. \qquad (12)
\end{aligned}
$$

In the above notation $P_{sp}^{a,b}$ is the V-T probability per collision that species s will make the transition from vibrational quantum state a to b as a result of an encounter with species p. Similarly $P_{sp}\binom{m,n}{a,b}$ is the V-V probability per collision that an encounter between species s and p will cause an a to b transition in species s and a simultaneous

m to n transition in species p.

It is beyond the scope of this paper to discuss in detail the appropriate expressions for the above transition probabilities and consequently we will briefly describe those to be used and cite references for the interested reader. For the V-T probabilities, which are reasonably well established, the functional form given by Schwarz, Slawsky, and Herzfeld[35], modified by Keck and Carrier[36] and normalized to fit the data of Millikan and White[37] are to be used. The expressions obtained in this manner can be found in McKenzie and also Rich et.al.[25] The V-V probabilities to be used include contributions from a short range interaction as done by Rapp-Englander-Golden[38] and a long range interaction important at low temperature as treated by Sharma and Brau[39]. A detailed discussion of the expressions obtained from such considerations is given by Jeffers and Kelley[40] and also by Rockwood [41].

For the remaining terms in Eq. (7) the following definitions apply:

x_e = mole fraction of electrons,

x_s^I = mole fraction of ions of species s,

x_s^E = mole fraction of neutrals of species s in the ground vibrational level of the excited electronic state, where the excited electronic state is denoted by E,

A_s^{ab} = Einstein A coefficient (sec^{-1}) for spontaneous emission for species s, obtained from Penner[42] for a Morse oscillator and is given by:

$$A_s^{k,k-1} = \left(\frac{\epsilon_s^k - \epsilon_s^{k-1}}{\epsilon_s^1}\right)^3 \left|\frac{R_s^{k,k-1}}{R_s^{10}}\right|^2 A_s^{10}, \tag{13}$$

where

$$\frac{R_s^{k,k-1}}{R_s^{10}} = -\left(\frac{1}{A_s} - 2\right)\left[\frac{\left(\frac{1}{A_s} - 1\right)}{\left(\frac{1}{A_s} - 3\right)\left(\frac{1}{A_s} - 5\right)}\right]^{1/2} \frac{(-1)^{2k-1}}{\left(\frac{1}{A_s} - 2k\right)}\left[\frac{k\left(\frac{1}{A_s} - 2k-1\right)\left(\frac{1}{A_s} - 2k-3\right)}{\left(\frac{1}{A_s} - k\right)}\right]^{1/2} \tag{14}$$

A_s^{Ek} = Rate coefficient (sec^{-1}) for spontaneous emission from the ground vibrational level of the excited electronic state to vibrational level k of the ground electronic state of species s[43],

$$= \frac{64\pi^4}{g_k\, 3h^4\, c^3} (\epsilon_s^{kE})^3 \,|\,\overline{R}_{es}\,|^2\, q_s^{ok}, \tag{15}$$

$R_s^{k\ell}$ = electron-molecule vibrational excitation rate (sec^{-1})

$$= \frac{\rho}{m} \int_{\epsilon_s^{k\ell}}^{\infty} \left(\frac{2}{m_e}\right)^{1/2} \epsilon f^o(\epsilon,y)\, S_s^{k\ell}(\epsilon)\, d\epsilon, \tag{16}$$

R_s^k = inverse electron-molecule de-excitation rate

$$= \frac{\rho}{m} \int_{\epsilon_s^{k\ell}}^{\infty} \left(\frac{2}{m_e}\right)^{1/2} \epsilon S_s^{k\ell}(\epsilon) f^o(\epsilon - \epsilon_s^{k\ell}, y)\, d\epsilon \,, \qquad (17)$$

R_s^k = collisional ionization rate coefficient

$$= \frac{\rho}{m} \int_{\epsilon_s^{k\lambda}}^{\infty} \left(\frac{2}{m_e}\right)^{1/2} \epsilon f^o(\epsilon, y) S_s^{k\lambda}(\epsilon)\, d\epsilon \,, \qquad (18)$$

R_s^k = rate coefficient for inverse three-body recombination process

$$= \left(\frac{\rho}{m}\right)^2 \frac{1}{2g_{s\lambda}} \left(\frac{2}{m_e}\right)^{1/2} \left(\frac{h^2}{2\pi m_e}\right)^{3/2} \int_0^{\infty} \epsilon f^o(\epsilon - \epsilon_s^{k\lambda}, y)\, d\epsilon \;\cdot \qquad (19)$$

where

$$\int_0^{\epsilon - \epsilon_s^{k\lambda}} \frac{\sqrt{\pi}}{2} S_s^{k\lambda}(\epsilon, \epsilon_b) \frac{f^o(\epsilon_b, y)\, f^o(\epsilon - \epsilon_s^{k\lambda} - \epsilon_b, y)}{f^o(\epsilon - \epsilon_s^{k\lambda}, y)}\, d\epsilon_b \,,$$

q_s^{ok} = Frank-Condon factor for transition from ground vibrational level of excited electronic state to vibrational level k of ground electronic state,

$|\bar{Re}_s|^2$ = electronic transition moment,

ε_s^{kE} = energy difference from vibrational level k of ground electronic state to ground vibrational state of excited electronic state,

ε = free-electron energy (ev),

$f^o(\varepsilon, y)$ = energy and spatially dependent isotropic electron distribution function (to be discussed in Section 5),

$S_s^{k\ell}(\varepsilon)$ = energy-dependent collisional cross section for vibrational excitation of species s,

$S_s^{k\lambda}(\varepsilon)$ = energy-dependent collisional ionization cross section of species s,

$\epsilon_s^{k\ell} = \epsilon_s^{\ell} - \epsilon_s^{k}$,

$\epsilon_s^{k\lambda} = \epsilon_s^{\lambda} - \epsilon_s^{k}$,

where ε_s^{λ} is the ionization energy.

In the above expressions detailed balance has been used to relate the inverse processes[44]. The spectroscopic constants needed can be found in Herzberg[43] or in the NBS[45] tables.

We note that if the electron distribution function is Maxwellian at a temperature T_e then the inverse rates are simply related as follows:

$$R_s^{\ell k} = \bar{R}_s^{k\ell} \exp\left(\frac{\epsilon_s^{k\ell}}{\kappa T_e}\right), \tag{20}$$

and

$$R_s^{\lambda k} = \bar{R}_s^{k\lambda} \frac{1}{2g_{s\lambda}} \left(\frac{h^2}{2\pi m_e \kappa T_e}\right)^{3/2} \exp\left(\frac{\epsilon_s^{k\lambda}}{\kappa T_e}\right), \tag{21}$$

where the barred rate coefficients are calculated for a Maxwellian distribution.

Equation (7) is written for diatomic gases of species s. If a monatomic gas is also employed in the mixture then an appropriate rate equation, taking into account electronic excitation, ionization, and possibly spontaneous emission is required. This is easily obtained from Eq. (7) by setting the first and last terms on the right-hand-side to zero and interpreting the indicies of the remaining terms as associated with electronic levels of the monatomic gas. It is clear, however, that with the magnitude of the electron energies that are dealt with in this model only one or two electronic levels will be excited, with the preponderance of the atoms being in their ground electronic state.

In addition to the vibrational rate equation, rate equations for the excited electronic level, the ions, and the electrons are also required. For the present model these equations are:

electronic level rate

$$u \frac{dx_s^E}{dy} = -x_e x_s^E R_s^{Eo} + x_e\left(\sum_k x_s^k\right) R_s^{oE} - x_e x_s^E R_s^{E\lambda} + x_e^2 x_s^I R_s^{\lambda E} - x_e x_s^E \sum_k A_s^{Ek}, \tag{22}$$

ion rate

$$u \frac{dx_s^I}{dy} = x_e \sum_k x_s^k R_s^{k\lambda} - x_e^2 x_s^I \sum_k R_s^{\lambda k} + x_e x_s^E R_s^{E\lambda} - x_e^2 x_s^I R_s^{\lambda E} \equiv \dot{w}_s^I, \tag{23}$$

electron rate

$$u \frac{dx_e}{dy} = \sum_s (\dot{w}_s^I), \tag{24}$$

where

R_s^{Eo} = rate coefficient for de-excitation by electron collision to ground electronic state-assumed independent of vibrational states.

GASDYNAMIC EQUATIONS

To determine the flow and thermodynamic properties the overall mass, momentum, energy, and the equation of state are needed. For the reader

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who may be interested in problems other than the steady quasi-one-dimensional model employed here, the mass, momentum, and energy equations will first be written in general form and then specialized to the present model. Assuming an inviscid flow in the presence of an electric field with no imposed magnetic field these equations are[30,31]:

overall mass

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{u}) = 0 , \tag{25}$$

overall momentum

$$\rho \frac{D\vec{u}}{Dt} + \nabla p = \rho_e \vec{E} , \tag{26}$$

overall energy

$$\rho \frac{D}{Dt}\left(\frac{1}{2}u^2 + h\right) - \frac{\partial p}{\partial t} = -\nabla \cdot \vec{q} + \vec{E} \cdot \vec{J} + \dot{Q}_{IN} , \tag{27}$$

where

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{u} \cdot \nabla ,$$

p = static pressure of mixture,

ρ_e = free charge density = $(\sum_s n_s^I - n_e)e$, e electron charge magnitude,

h = total enthalpy of mixture,

$\vec{q}$ = heat conduction,

$\vec{J}$ = total current density = $\rho_e \vec{u} + e(\sum_s n_s^I \vec{V}_s^I - n_e \vec{V}_e)$,

$\vec{V}_s^I$ = ion diffusion velocity,

$\vec{V}_e$ = electron diffusion velocity,

$\dot{Q}_{IN}$ = heat added per unit volume due to inelastic effects,

$\vec{E}$ = electric field strength.

We now specialize these equations to steady quasi-one-dimensional flow, add the equation of state, and make the additional assumptions of (i) neutral plasma, (ii) mixture of perfect gases, and, (iii) no heavy particle heat conduction, to obtain the following:

overall mass

$$\frac{d}{dx}(\rho A u) = 0 , \tag{28}$$

overall momentum

$$\rho u \frac{du}{dx} + \frac{dp}{dx} = 0, \tag{29}$$

overall energy

$$\rho u \frac{d}{dx}\left(\frac{1}{2}u^2 + h\right) = \frac{\partial q_e}{\partial x} + EJ + \dot{Q}_{IN}, \tag{30}$$

state

$$p = \frac{\rho}{m}\left\{x_e \boldsymbol{\kappa} T_e + \boldsymbol{\kappa} T\,[x_e + \sum_{s=d}(x_s^E + \sum_k x_s^k) + \sum_{s=m}(\sum_k x_s^k)]\right\}, \tag{31}$$

$$\begin{aligned} h = \frac{P}{\rho} + \frac{1}{m}\Bigg\{ & \frac{3}{2}x_e \boldsymbol{\kappa} T_e + \frac{3}{2}x_e \boldsymbol{\kappa} T + \sum_{s=d}\,[x_e \boldsymbol{\kappa} T + \frac{5}{2}\boldsymbol{\kappa} T(\sum_k x_s^k) + \sum_k x_s^k \epsilon_s^k + x_s^E \epsilon_s^E] \\ & + \sum_{s=m}\,[\frac{3}{2}\boldsymbol{\kappa} T(\sum_k x_s^k) + \sum_k x_s^k \epsilon_s^k]\Bigg\}, \end{aligned} \tag{32}$$

where the nomenclature used is:

d = diatomic constituents,

m = monatomic constituents,

A = A(x) cross sectional area,

$\varepsilon^k_{s=m}$ = electronic energy of the kth level of monatomic species s,

and

$$\begin{aligned} \dot{Q}_{IN} = \frac{\rho}{m}\sum_s\Bigg[x_e\Bigg\{ & \sum_k^{N_s-1}\sum_{\ell=k+1}^{N_s}[x_s^\ell R_s^{\ell k} - x_s^k R_s^{k\ell} + x_s^k A_s^{\ell k}]\,\epsilon_s^{k\ell} \\ & + [(\sum_k x_s^k) R_s^{0E} - x_s^E R_s^{Eo}]\,\epsilon_s^{oE} + \sum_k[-x_s^k R_s^{k\lambda} + x_e x_s^I R_s^{\lambda k}]\,\epsilon_s^k \\ & + [-x_s^E R_s^{E\lambda} + x_e x_s^I R_s^{\lambda E}]\,\epsilon_s^{E\lambda}\Bigg\} + \sum_{\substack{k \\ k \neq k-1}}\sum_p(Z_{sp} Q_{sp}^k \epsilon_s^{k\ell})\Bigg]. \end{aligned} \tag{33}$$

To complete the formulation expressions for the current density J, electron heat conduction q_e, and electron temperature T_e are needed.

The current density for a neutral plasma is given by the conduction current density as

$$J = e(\sum_s n_s^I V_s^I - n_e V_e). \tag{34}$$

But for the case where the electron energy is much greater than that of the heavy particles, such as is found in glow discharges $V_s^I/V_e \ll 1$, therefore the current is carried by the electrons only and is given by

$$J \approx -en_e V_e \, . \tag{35}$$

The electron diffusion velocity V_e is calculated from an integral of the electron distribution function as follows[46]:

$$V_e = \frac{1}{3}\left(\frac{2}{m_e}\right)^{1/2} \int_0^\infty \epsilon f'(\epsilon,y)\, d\epsilon \, . \tag{36}$$

The same is true for T_e and q_e and they are given by[46]:

$$T_e = \frac{2}{3}\,\frac{1}{\kappa} \int_0^\infty \epsilon^{3/2} f^o(\epsilon,y)\, d\epsilon \, , \tag{37}$$

and

$$q_e = \frac{\sqrt{2}}{3}\,\frac{\rho}{m}\,\frac{1}{\sqrt{m_e}}\, x_e \int_0^\infty \epsilon^2 f'(\epsilon,y)\, d\epsilon \, . \tag{38}$$

In these expressions, as well as the rate coefficients discussed in the previous section (Eqs. 16–19), the functions $f^o(\varepsilon,y)$ and $f'(\varepsilon,y)$ appear. These functions represent the first two terms of a series expansion of the free-electron velocity distribution function. (The procedure by which they are obtained, and the equations governing them will be given in the next section.) They are obtained from a solution of the free-electron Boltzmann equation which is itself coupled to the gasdynamic equations.

For the present discharge model we will be concerned with weakly ionized plasmas, that is

$$x_e / \sum_{s,k} x_s^k \ll 1 \, .$$

For this condition we find, after a comparison of the various cross sections that appear in the rate equations, that all three-body recombination terms can be neglected. This, coupled with the assumption of a neutral plasma eliminates the necessity of determining the mole fraction of ions so that the ion rate equation can be dropped from the system of equations.

We thus have a system of $8 + s(1+N_s)$ coupled equations consisting of Eqs. (7), (22), (24), and (29) through (32), and the equations for $f^o(\varepsilon,y)$ and $f'(\varepsilon,y)$ (see Eqs. (42) and (43) of the next section) together with auxiliary equations, for the system of unknowns: ρ, u, T, p, h, x_e, x_S^E, x_S^k, $f^o(\varepsilon,y)$ and $f'(\varepsilon,y)$.

Finally, when this system of equations is solved and with the solution for the vibrational population distribution known, the small signal gain can be calculated. A detailed derivation of the necessary gain equation for the case of Doppler and pressure broadened lines for a diatomic gas is given by McKenzie* and will not be repeated here.

ELECTRON KINETICS

Boltzmann Equation

As previously mentioned the free electrons in the discharge are generally in a non-Maxwellian distribution. The fundamental equation governing this distribution is the Boltzmann equation. Analysis of various features of this equation have been done in the past[27,44,46,48-54] however, it is convenient here to summarize those features appropriate to the present model.

In a frame of reference moving with the mass average velocity of the fluid, the electron velocity distribution function $f(\vec{c},\vec{x},t)$ satisfies the equation[46]

$$\frac{D}{Dt}(n_e f) + \vec{c}\cdot\nabla_x(n_e f) - \left(\frac{e\vec{E}}{m_e} + \frac{D\vec{u}}{Dt}\right)\cdot n_e\nabla_c f - \vec{c}\cdot\nabla_x\vec{u} - n_e\nabla_c f = \frac{\partial f}{\partial t}\bigg|_{COLL}\ , \qquad (39)$$

where ∇_x and ∇_c are the gradients with respect to the spatial coordinates and electron velocity, respectively. The right hand side of Eq. (39) represents the rate of change of $f(\vec{c},\vec{x},t)$ in a series as follows:

$$f(\vec{c},\vec{x},t) = f^o(c,\vec{x},t) + \frac{\vec{c}}{c}\cdot\vec{f}\,'(c,\vec{x},t) + \dots\ , \qquad (40)$$

where

$$|\vec{f}\,'(c,\vec{x},t)| << f^o(c,\vec{x},t)\ . \qquad (41)$$

The function f^o represents the isotropic contribution, and $\vec{f}\,'$ gives the small anisotropic contribution to the velocity distribution function.

Substitution of Eq. (40) into Eq. (39), and successive integration of the velocity moments of the resulting equation[46], yields a sequence of coupled equations for f^o, $\vec{f}\,'$. . . . . Transforming this set of equations to the independent variable ε, the electron energy $\varepsilon = 1/2\ m_e c^2$; using the condition of Eq. (41) and assuming that $|u| \leq c$, we obtain two coupled equations for $f^o(\varepsilon,\vec{x},t)$ and $\vec{f}\,'(\varepsilon,\vec{x},t)$ as follows:

$$\left(\frac{\epsilon m_e}{2}\right)^{1/2}\frac{D}{Dt}(n_e f^o) + \frac{\epsilon}{3}\nabla_x(n_e\vec{f}\,') - \frac{n_e e\vec{E}}{3}\frac{\partial}{\partial\epsilon}(\epsilon\vec{f}\,')$$
$$- n_e\left(\frac{m_e}{3}\right)\frac{D\vec{u}}{Dt}\cdot\frac{\partial}{\partial\epsilon}(\epsilon\vec{f}\,') - n_e\frac{(2m_e)^{1/2}}{3}\epsilon^{3/2}\nabla_x\vec{u}\,\frac{\partial f^o}{\partial\epsilon} = \frac{\partial f^o}{\partial t}\bigg|_{COLL}\ . \qquad (42)$$

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*In McKenzie's derivation the expression for $A_S^{k,k-1}$ should be replaced by that given by Eq. (13).

and
$$\left(\frac{m_e}{2\epsilon}\right)^{1/2} \frac{D}{Dt}(n_e \vec{f}\,') + \nabla_x (n_e f^o) - n_e e \vec{E}\, \frac{\partial f^o}{\partial \epsilon} - n_e m_e \frac{D\vec{u}}{Dt}\frac{\partial f^o}{\partial \epsilon} = \frac{\partial \vec{f}'}{\partial t}\Big|_{COLL}\, , \qquad (43)$$

where f is normalized such that
$$\int_0^\infty \epsilon^{1/2} f^o(\epsilon,\vec{x},t)d\epsilon = 1\, . \qquad (44)$$

With this normalization, if the distribution were Maxwellian, at temperature $T_e(\vec{x},t)$, under the present approximation the distribution function would be given by
$$f^o_{max}(\epsilon,\vec{x},t) = \frac{2}{\sqrt{\pi}}\frac{1}{(\kappa T_e)^{3/2}} \exp(-\epsilon/\kappa T_e)\, . \qquad (45)$$

Note that from Eqs. (42) and (43) the conservation equations of electron energy and momentum can be derived. To obtain the electron energy equation multiply Eq. (42) by $(\frac{2}{me})^{1/2}\varepsilon d\varepsilon$ and integrate over all electron energy. With the electron energy equation written in such a form it is then possible to obtain the fraction of power transferred by the electrons to the various modes of the gas, in particular, to the vibrational levels. In this way the parameters in the problem can be adjusted to maximize the amount of power transfered to the vibrational levels and concurrently the laser efficiency. Such an analysis has been carried out for a static discharge by Nighan[27]. To obtain the momentum equation multiply Eq. (43) by $2/3\ \varepsilon^{3/2}d\varepsilon$ and integrate over all electron energy.

Collision Terms

The remaining expressions required are those for the collision terms. Considerable simplifications arise in these terms because the electron mass is much smaller than that of the heavy particles, causing the heavy particle speed to be much smaller than that of the electrons even for high supersonic speeds. Thus, the collision operators can be approximated by the operators occuring in a plasma of motionless heavy particles and moving electrons. For the energy transfer mechanisms included in this model the collision operator consists of a sum of four contributions accounting for elastic-heavy particle collisions, $\partial f/_{\partial t|eh}$, ionization and three-body recombination collisions, $\partial f/_{\partial t|ion}$, charged particle collisions $\partial f/_{\partial t|e-e}$, and most importantly, inelastic and superelastic excitation and de-excitation collisions $\partial f/_{\partial t|ex}$. Expressions for the collision terms for these types of collisions employing the small electron mass approximation have been developed in the past[44,48,51,54] and those appropriate to the present case will be given. For the f^o operators we have:

$$\left.\frac{\partial f^o}{\partial t}\right|_{eh} = n_e \sum_s \frac{2m_e}{m_s}\frac{\partial}{\partial \epsilon}\left\{\epsilon^2 n_s Q_s^{\ell h}(\epsilon)\left[f^o(\epsilon) + kT\,\frac{\partial f^o(\epsilon)}{\partial \epsilon}\right]\right\}, \qquad (46)$$

$$\begin{aligned}\left.\frac{\partial f^o}{\partial t}\right|_{ion} = n_e \sum_s \sum_{k=0}^{N_s} \Bigg\{ & \epsilon C_{s_k} n_s^I n_e \int_0^{\epsilon-\epsilon_s^{k\lambda}} S_s^{k\lambda}(\epsilon,\epsilon_b) f^o(\epsilon_b)\cdot f^o(\epsilon-\epsilon_b-\epsilon_s^{k\lambda})\,d\epsilon_b \\ & - \epsilon n_s^k f^o(\epsilon) S_s^{k\lambda}(\epsilon) + 2n_s^k \int_0^{\infty} \epsilon_i f^o(\epsilon_i) S_s^{k\lambda}(\epsilon_i,\epsilon)\,d\epsilon_i \\ & - 2n_s^I n_e C_{s_k} f^o(\epsilon) \int_0^{\infty} \epsilon_i f^o(\epsilon_i-\epsilon-\epsilon_s^{k\lambda}) S_s^{k\lambda}(\epsilon_i,\epsilon)\,d\epsilon_i \Bigg\}, \qquad (47)\end{aligned}$$

$$\begin{aligned}\left.\frac{\partial f^o}{\partial t}\right|_{e-e} = n_e \sum_s \frac{\partial}{\partial \epsilon}\Bigg\{ & 3n_e(\kappa T_e)^2 Q_s^{e-i}\Bigg[I_0^o f^o(\epsilon) + \frac{2}{3}\epsilon\cdot \\ & \frac{\partial f^o(\epsilon)}{\partial \epsilon}(I_2^o + J_{-1}^o)\Bigg]\Bigg\}, \qquad (48)\end{aligned}$$

$$\begin{aligned}\left.\frac{\partial f^o}{\partial t}\right|_{ex} = n_e \sum_s \sum_{k=o}^{N_s-1} \sum_{\ell=k+1}^{N_s} \Bigg\{ & (\epsilon+\epsilon_s^{k\ell}) S_s^{k\ell}(\epsilon+\epsilon_s^{k\ell}) n_s^k\cdot \\ & \left[f^o(\epsilon+\epsilon_s^{k\ell}) - \frac{g_s^k}{g_s^\ell}\frac{n_s^\ell}{n_s^k} f^o(\epsilon)\right] + n_s^k \epsilon S_s^{k\ell}(\epsilon)\cdot \\ & \left[f^o(\epsilon-\epsilon_s^{k\ell})\frac{g_s^k}{g_s^\ell}\frac{n_s^\ell}{n_s^k} - f^o(\epsilon)\right]\Bigg\}, \qquad (49)\end{aligned}$$

$$C_{s_k} = \frac{g_s^k}{2g_s^\lambda}\left(\frac{h^2}{2\pi m_e}\right)^{3/2}\sqrt{\frac{\pi}{2}},$$

where $f^o(\varepsilon,\vec{x},t)$ is written as $f^o(\varepsilon)$ for convenience.

Here the sum in Eq. (46) includes all heavy particle species, and $\varepsilon_i=\varepsilon_s^{k\lambda}+\varepsilon_b+\varepsilon$ is the energy of the incident ionizing electron. The following definitions also apply:

$Q_s^{eh}(\varepsilon)$ = energy-dependent electron-heavy-particle momentum transfer cross section,

Q_s^{ei} = energy average electron-ion cross section,

= $6\Pi(e^2/12\Pi\varepsilon_o kTe)^2 \ell n\Lambda$,

C_{s_k} =

g_s^k = degeneracy of level k of species s; unity for vibrational levels,

$S_s^{k\lambda}(\varepsilon,\varepsilon_b)$ = Cross section for ionization of a particle in the kth level by an electron of energy ε which results in an electron of energy ε_b. It is related to the conventional ionization cross section $S_s^{k\lambda}(\varepsilon)$ as follows:

$$S_s^{k\lambda}(\epsilon) = \int_0^{\epsilon-\epsilon_s^{k\lambda}} S_s^{k\lambda}(\epsilon,\epsilon_b)d\epsilon_b \ ,$$

$$I_p = \frac{1}{\epsilon^{p/2}} \int_0^{\epsilon} \epsilon^{\frac{1}{2}(p+1)} f^{\ell}(\epsilon)d\epsilon \ ,$$

$$J_p = \frac{1}{\epsilon^{p/2}} \int_{\epsilon}^{\infty} \epsilon^{\frac{1}{2}(p+1)} f^{\ell}(\epsilon)d\epsilon \ .$$

Note that these expressions are written for a general level k. In other words, with the proper interpretation of the cross sections, the equations apply for either rotational, vibrational or electronic level excitations. However, to apply them to situations which involve all three processes simultaneously, it must be assumed that the cross section for each process is independent of the other. In this way each process can be described by equations written in the above form and each expression can then be added to obtain the total contribution.

To determine the expressions for the $\vec{f}'$ collision operator, Refs. 44 and 46 show that only the elastic collision term is important. This is a consequence of the fact that the electron-heavy-particle momentum transfer cross section is larger than any of the other cross sections. With this we find that the $\vec{f}'$ operator can be written in the following simple form:

$$\left.\frac{\partial \vec{f}^1}{\partial t}\right|_{COLL} = -\, n_e \left[\sum_s n_s Q_s^{eh}(\epsilon)\right] \vec{f}^1(\epsilon,\vec{x},t) \ , \qquad (50)$$

where the sum includes all heavy particles.

The necessary expressions for the collision terms have now been developed for the Boltzmann equation and, by making certain order of magnitude arguments applicable to the present model, certain simplifications are possible. By a comparison of the magnitudes of the various cross sections (the sources of these cross sections will be given latter), we find, for the weakly ionized gas assumed here, with $m_e \ll m_s$, and for the average electron energies involved, that: a) the elastic collision term Eq. (46) can be neglected, b) the first and fourth terms in Eq. (47), which represent recombination terms can be neglected, and c) the charged-particle collision term Eq. (48) can be neglected.

Simplified Equations

We seek to further simplify Eqs. (42) and (43) by examining the various terms on the lef-hand side of the equations, where we now specialize to a steady one-dimensional case. To facilitate this we introduce the following non-dimensional variables:

$$\bar{u} = \frac{u}{u_o}, \bar{\rho} = \frac{\rho}{\rho_o}, \bar{\epsilon} = \frac{\epsilon}{\frac{1}{2} m_e c_o^2}, \bar{y} = \frac{y}{L}$$

$$\bar{\lambda}_s^{k\ell} = \frac{\lambda_s^{k\ell}(\epsilon)}{\lambda_R}, \; \bar{\lambda}^{eh} = \frac{\lambda^{eh}(\epsilon)}{\lambda_R}, \; \bar{\lambda}_s^{k\lambda} = \frac{\lambda_s^{k\lambda}(\epsilon_i, \epsilon)}{\lambda_R (\frac{1}{2} m_e c_o^2)},$$

$$\bar{F} = \frac{F}{\rho_o (\frac{1}{2} m_e c_o^2)^{-3/2}},$$

where $\lambda_s^{k\ell}(\epsilon) \equiv \dfrac{1}{S_s^{k\ell}(\epsilon)\rho/m}$ is an inelastic collision

mean free path, $\lambda^{eh}(\epsilon) \equiv \dfrac{1}{\sum_s n_s Q_s^{eh}}$ is an elastic collision

mean free path, and $F = \rho x_e f$. The above normalization is chosen such that the barred variables are of order unity with the exception of $\bar{F}$, where $\bar{F}' \ll \bar{F}^o$. With this normalization Eqs. (42) and (43) become, after substitution of the simplified collision terms, the following:

$$\left(\frac{\lambda_R}{L}\frac{u_o}{c_o}\right)\bar{\epsilon}^{1/2}\bar{u}\frac{\partial \bar{F}^o}{\partial \bar{y}} + \left(\frac{\lambda_R}{L}\right)\frac{1}{3}\bar{\epsilon}\frac{\partial \bar{F}^1}{\partial \bar{y}} - \frac{1}{3}\left(\frac{2eE\lambda_R}{m_e c_o^2}\right)\frac{\partial}{\partial \bar{\epsilon}}(\bar{\epsilon}\bar{F}^1)$$
$$-\left(\frac{\lambda_R}{L}\right)\left(\frac{u_o}{c_o}\right)^2 \frac{2}{3}\bar{u}\frac{d\bar{u}}{d\bar{y}}\frac{\partial}{\partial \bar{\epsilon}}(\bar{\epsilon}\bar{F}^1) - \frac{2}{3}\left(\frac{\lambda_R}{L}\frac{u_o}{c_o}\right)\bar{\epsilon}^{3/2}\frac{d\bar{u}}{d\bar{y}}\frac{\partial \bar{F}^o}{\partial \bar{\epsilon}} = \left.\frac{\partial \bar{F}^o}{\partial t}\right|_{COLL}, \tag{51}$$

and

$$\left(\frac{\lambda_R}{L}\right)\left(\frac{u_o}{c_o}\right)\frac{\bar{u}}{\bar{\epsilon}^{1/2}}\frac{\partial \bar{F}^1}{\partial \bar{y}} + \left(\frac{\lambda_R}{L}\right)\frac{\partial \bar{F}_o}{\partial \bar{y}} - \left(\frac{2eE\lambda_R}{m_e c_o^2}\right)\frac{\partial \bar{F}^o}{\partial \bar{\epsilon}} - 2\left(\frac{u_o}{c_o}\right)^2\left(\frac{\lambda_R}{L}\right)\bar{u}\frac{d\bar{u}}{d\bar{y}}\frac{\partial \bar{F}^o}{\partial \bar{\epsilon}} \tag{52}$$
$$= -\bar{F}^1(\bar{\epsilon})/\bar{\lambda}^{eh},$$

where

$$\left.\frac{\partial \bar{F}^o}{\partial t}\right|_{COLL} = \sum_s \sum_{k=0}^{N_s-1} \sum_{\ell=k+1}^{N_s} \left\{ \frac{(\bar{\epsilon}+\bar{\epsilon}_s^{k\ell})}{\bar{\lambda}_s^{k\ell}(\bar{\epsilon}+\bar{\epsilon}_s^{k\ell})} x_s^k \left[\bar{F}^o(\bar{\epsilon}+\bar{\epsilon}_s^{k\ell}) \right.\right.$$
$$\left.\left. - \frac{g_s^k}{g_s^\ell}\frac{x_s^\ell}{x_s^k}\bar{F}^o(\bar{\epsilon})\right] + \frac{x_s^k \bar{\epsilon}}{\bar{\lambda}_s^{k\ell}(\bar{\epsilon})}\left[\bar{F}^o(\bar{\epsilon}-\bar{\epsilon}_s^{k\ell})\frac{g_s^k}{g_s^\ell}\frac{x_s^\ell}{x_s^k} - \bar{F}^o(\bar{\epsilon})\right]\right\} \tag{53}$$
$$+ 2\sum_s \left\{ -\frac{\bar{\epsilon} x_s^k \bar{F}^o(\bar{\epsilon})}{\bar{\lambda}_s^{k\lambda}(\bar{\epsilon})} + x_s^k \int_0^\infty \frac{\bar{\epsilon}_i \bar{F}^o(\bar{\epsilon})}{\bar{\lambda}_s^{k\lambda}(\bar{\epsilon}_i, \bar{\epsilon})} d\bar{\epsilon}_i \right\}.$$

Three parameters appear in these equations, namely

$$\frac{u_o}{c_o},\ \frac{2eE\lambda_R}{m_e c_o^2},\ \text{and}\ \frac{\lambda_R}{L}\ .$$

Upon estimating the magnitude of these quantities we find that for the average electron energies involved in this problem (1 ev) $u_o/c_o \ll 1$, and the ratio $\frac{2eE\lambda_R}{m_e c_o^2}$ is of order unity. The ratio λ_R/L, which is the Knudsen number, is in general less than one and we will exploit this by expanding the distribution function $\bar{F}^o$ in a series in $\lambda_R/L=\delta$. This expansion is given by:

$$\bar{F}^o = F_o+\delta F_1+ \ldots, \qquad (54)$$

where $\delta \ll 1$.

Thus, taking into account the above order of magnitudes, substituting Eq. (52) into Eq. (51) to obtain an equation for $\bar{F}^o$ alone, using the expansion (54) in the resulting equation, retaining only the first two terms of the expansion, we obtain the following two coupled equations for F_o and F_1 (dropping bars for convenience)

$$-\frac{1}{3}E_R^2\frac{\partial}{\partial\epsilon}\left\{\epsilon\lambda^{eh}\frac{\partial F_o}{\partial\epsilon}\right\} = \left.\frac{\partial F_o}{\partial t}\right|_{COLL}, \qquad (55)$$

$$\begin{aligned}-\frac{1}{3}E_R^2\frac{\partial}{\partial\epsilon}\left\{\epsilon\lambda^{eh}\frac{\partial F_1}{\partial\epsilon}\right\} &= \left.\frac{\partial F_1}{\partial t}\right|_{COLL}\\ &+\frac{2}{3}\left(\frac{u_o}{c_o}\right)\epsilon^{3/2}\frac{du}{dx}\frac{\partial F_o}{\partial\epsilon}-\left(\frac{u_o}{c_o}\right)\epsilon^{1/2}u\frac{\partial F_o}{\partial x}-\frac{1}{3}E_R^2\,\epsilon\frac{\partial}{\partial x}\left\{\lambda^{eh}\frac{\partial F_o}{\partial\epsilon}\right\}\\ &-\frac{1}{3}E_R^2\frac{\partial}{\partial\epsilon}\left\{\epsilon\lambda^{eh}\frac{\partial F_o}{\partial x}\right\},\end{aligned} \qquad (56)$$

where $\left.\frac{\partial F_o}{\partial t}\right|_{COLL}$ and $\left.\frac{\partial F_1}{\partial t}\right|_{COLL}$ are given by Eq. (53) with the appropriate substitution, and $E_R \equiv \frac{2eE\lambda_R}{m_e c_o^2}$. Finally, the equation for $\bar{F}'$, to consistent order in δ and u_o/c_o is given by:

$$F^1 = -\lambda^{eh}\left[-E_R\frac{\partial F_o}{\partial\epsilon}+\delta\left(\frac{\partial F_o}{\partial x}-E_R\frac{\partial F_1}{\partial\epsilon}\right)\right] \qquad (57)$$

Equations (54)-(57) give the solution to the free-electron Boltzmann equation provided the Knudsen number is small. This confines the region of applicability of these equations to situations where gradients in the flow are not large.

We see from these equations that the effects of gradients and flow velocity are demoted to second order. In fact, as one might expect for such a situation the equation for F_o, which gives the largest contribution to the distribution function, is the same as that for a stationary gas (see Nighan[27]). The difference here is that Eq. (55) is to be interpreted as being applied locally at each point in the discharge. In a gross sense, one can then say that to first order the presence of the discharge alters the flow, but the flow does not alter the electron distribution in the discharge.

To solve these equations the cross sections for electron-vibrational, electronic, and ionization collisions important to this problem must be known. A search of the literature gives many of these cross sections for various gases that might be employed and certain of these references are listed below:

CO: vibrational excitation (ref. 55), electronic excitation (ref. 56, 61), momentum transfer (ref. 56), ionization (ref. 62).

N_2: vibrational excitation (ref. 55, 57, 59) electronic excitation and momentum transfer (ref. 57), ionization (ref. 62).

He, Ar, Xe: electronic, ionization and momentum transfer (ref. 58, 60, 62).

For the crucial electron-vibrational collisions in CO only cross sections for excitation from ground state molecules are known (ref. 55). Thus, when including electron collisions with excited state molecules the cross sections must be estimated (see Abraham and Fisher[63] for one scheme of estimation).

Finally, in order to solve Eq. (55) (and(58)) which is a second-order ordinary differential-difference equation, a numerical technique is required. Several approaches have been used in the past[44,64,65] each with its own virtues and the interested reader can refer to the references cited for more information.

With a solution procedure for the free-electron Boltzmann equation chosen, the remaining question is the approach to be used to obtain the numerical solution of the coupled set of rate, gasdynamic, and electron kinetic equations. A possible scheme is to employ the method of Bailey[47] who obtained solutions for nozzle flows with chemical nonequilibrium. This scheme linearizes the gasdynamic and rate equations and then employs an implicit integration scheme to obtain the solution of these linearized equations. This method has been used successfully by McKenzie in his gasdynamic laser studies.

When using such a scheme the electron properties need not be considered as independent variables such as T, u, etc., and thus they become auxiliary quantities to be determined at each point. This implies that the free-electron Boltzmann equation solution also becomes an auxiliary calculation, and this can greatly reduce the complexity of the numerical calculations.

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