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THE BOLTZMANN EQUATION IN GAS DISCHARGES, WITH SOME APPLICATION TO SF_6

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AUTHORS:P.K.Milsom and E.K.Gorton

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SUMMARY

We describe the behaviour of the electrons in a gas discharge by using the Boltzmann equation and Fermi golden rule ideas. The resulting equations are applied to Sulphur Hexafluoride and electron energy distribution functions are calculated. The distributions are shown to be in close agreement with those of a Monte-Carlo simulation. The ideas developed here should be easily extended to solve anisotropic scattering problems and may also make use of the pseudopotentials which are now becoming available in the literature.

Keywords: gas discharge lasers, hot electrons, uniform steady state, electron equations, Great Britain, (KR)

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1 INTRODUCTION

In Gas Discharge Lasers the molecular energy levels are excited by hot electrons which are accelerated to high speeds by the applied electric field. In order to appreciate and improve the efficiency of these systems it is necessary to understand the details of this process. The statistical nature of the scattering events means that the electrons in the electron swarm have a distribution of energies, in this report we concern ourselves with the evaluation of this distribution.

There are two established methods for tackling this problem. The first[1], which we will consider in detail, introduces a distribution function at line one. The distribution, which describes the probability of finding an electron in phase space, obeys the Boltzmann transport equation, which may be solved approximately in a simple regime.

The second method[2] treats the electrons individually and keeps track of their phase space trajectories. This method is exact and extremely useful for understanding spatial and magnetic field effects in gas discharges, however such calculations use large amounts of computer time and usually generate much more information than is needed for the type of problem which concerns experimental workers at the present time. Nevertheless the Monte-Carlo is a valuable tool in so far as it is exact and serves as a useful touchstone for Boltzmann equation results. For the present we concern ourselves with the Boltzmann equation and uniform, steady-state electron distributions. The Monte-Carlo method will be applied to dynamic non-uniform situations in a later document.

In Section 2 we introduce the electron distribution function and show that it obeys the Boltzmann equation. We decompose the distribution into s and p-like behaviour and use this to give two coupled equations.

In Section 3 we evaluate the s-type collision term derived in Section 2 for recoil scattering and inelastic scattering. Our method is different from the usual technique employed in gas systems, we use Fermi-Golden rule ideas to relate the transition rate to the scattering cross-section. Although our results are the same as those usually presented we feel that in view of pseudo-potential data now becoming available for gas atoms[4], the method is the natural one to use.

In Section 4 the p-type collision term is considered and a momentum relaxation time is introduced. The equations derived in Section 2 are then decoupled. We indicate how the equation dealing with the s-type part of the distribution is modified for a gas mixture. This equation is the working equation for the gas discharge system.

In Section 5 the working equation derived in Section 4 is solved under special conditions to give the Maxwell-Boltzmann and Druyvestyn distributions. In Section 6 we describe two general numerical methods for solving the Boltzmann equation when both recoil scattering and inelastic scattering are important. In Section 7 we reconsider the relaxation time approximation and introduce a modification to the equations presented in Section 6. This method is then used to calculate the electron distribution function in SF_6 and this is briefly compared to the exact results calculated by Monte-Carlo simulations. For completeness we consider distributions with the same average energy and we present a graph showing the difference between Maxwell-Boltzmann, Druyvestyn and the SF_6 distribution. In Section 8 we present a few concluding remarks.

2 THE BOLTZMANN EQUATION

We start by introducing a distribution function $f(\underline{k}, \underline{r}, t)$ which is defined as the probability of finding an electron with wavevector $\underline{k}$ at position $\underline{r}$ at time t with spin up. The growth of $f(\underline{k}, \underline{r}, t)$ is determined by the current of electrons into the six-dimensional phase space element. The electrons move in $\underline{r}$ space by virtue of their velocity, whilst motion in momentum space is due to the force acting on them. In the absence of scattering we equate the growth of $f(\underline{k}, \underline{r}, t)$ to the divergence of this six dimensional current.

$$\frac{\partial f}{\partial t}(\underline{k},\underline{r},\underline{t}) = -\underline{\nabla} \cdot (f\underline{v}) - \underline{\nabla}_{\underline{k}} \cdot (f\underline{F}) = -\underline{v} \cdot \underline{\nabla} f - \underline{F} . \nabla_{\underline{k}} f , \tag{1}$$

where

$$\underline{F} = \frac{-e}{\hbar} \left[\underline{E} + \underline{v} \times \underline{B} \right] = \frac{d\underline{k}}{dt} . \tag{2}$$

In the absence of applied fields and concentration gradients $\frac{\partial f}{\partial t}(\underline{k},\underline{r},\underline{t})$ is determined solely by collisions

$$\frac{\partial f}{\partial t}(\underline{k},\underline{r},t) = \left[\frac{\partial f}{\partial t}(\underline{k},\underline{r},t) \right]_{coll} . \tag{3}$$

The Boltzmann equation combines these two processes,

$$\frac{\partial f}{\partial t}(\underline{k},\underline{r},t) = -\underline{\nabla} \cdot (f\underline{v}) - \underline{F} \cdot \nabla_{\underline{k}} f + \left[\frac{\partial f}{\partial t} \right]_{coll} . \tag{4}$$

We shall examine the simplest case when $\underline{B} = 0$ and spatial gradients are unimportant. We shall also be concerned with the steady state. Then from equations 4 and 2 we have

$$\frac{-e}{\hbar} \underline{E} \cdot \nabla_{\underline{k}} f(\underline{k}) = \left[\frac{\partial f}{\partial t}(\underline{k}) \right]_{coll} \tag{5}$$

where $f(\underline{k})$ is now a function of $\underline{k}$ alone. Because the momentum-transfer cross-section is large and the scattering event is velocity randomising $f(\underline{k})$ will tend to be isotropic, however we know that the electron swarm must drift under the applied electric field so there must also be an anisotropic contribution to f which weights the distribution in the direction of the electrostatic force. In general $f(\underline{k})$ can be expanded in terms of the spherical harmonics

$$f\,(\underline{k}) = \sum_{n=0} f_n\,(k)\,P_n\,(\cos\psi), \tag{6}$$

where ψ is the angle between the electric field and the $\underline{k}$ vector direction. We assume only the first two terms are significant (the Lorentz approximation). Hence,

$$f\,(\underline{k}) = f_o\,(k) + \cos\psi\, f_1\,(k)\ . \tag{7}$$

on inserting 7 into 5 we see

$$\frac{-e}{\hbar}\, E\, \frac{\partial}{\partial k_z}\,(f_o\,(k) + \cos\psi\, f_1\,(k))$$

$$= \left[\frac{\partial f_o}{\partial t}\right]_{coll} + \cos\psi \left[\frac{\partial f_1}{\partial f}\right]_{coll}\ , \tag{8}$$

where the axes have been chosen so that $\underline{k}_z$ is in the direction of $\underline{E}$, (see Fig 1).

Coverting to polars we write,

$$\frac{\partial}{\partial k_z} = \frac{-\sin\psi}{k}\,\frac{\partial}{\partial\psi} + \cos\psi\,\frac{\partial}{\partial k}\ . \tag{9}$$

Hence,

$$\frac{-e}{\hbar}\, E \left[\frac{\sin^2\psi}{k}\, f_1 + \cos^2\psi\,\frac{\partial f_1}{\partial k} + \cos\psi\,\frac{\partial f_o}{\partial k}\right] =$$

$$\left[\frac{\partial f_o}{\partial t}\right]_{coll} + \cos\psi \left[\frac{\partial f_1}{\partial t}\right]_{coll}\ . \tag{10}$$

Multiplying equation 10 by sin ψ and integrating from 0 to π gives

$$\frac{-e}{\hbar}\, E \left[\frac{2}{3k}\, f_1 + \frac{1}{3}\,\frac{\partial f_1}{\partial k}\right] = \left[\frac{\partial f_o}{\partial t}\right]_{coll}\ . \tag{11}$$

Multiplying equation 10 by cos ψ and integrating from 0 to π gives

$$\frac{-e}{\hbar} E \frac{\partial f_o}{\partial k} = \left[\frac{\partial f_1}{\partial t} \right]_{coll} . \tag{12}$$

We see that we have separated equation 10 into two equations by considering s and p-type behaviours. The collision terms still need to be considered in some detail before the coupled equations 11 and 12 can be solved.

There are two contributions to $\left[\frac{\partial f}{\partial t} (\underline{k}) \right]_{coll}$,

the growth of f($\underline{k}$) is due to transitions from all other $\underline{k}$' states into $\underline{k}$, minus a term due to electrons leaving $\underline{k}$.

So,

$$\left[\frac{\partial f}{\partial t} (\underline{k}) \right]_{coll} = \int \left[f(\underline{k}') P(\underline{k}', \underline{k}) - f(\underline{k}) P(\underline{k}, \underline{k}') \right] \frac{V}{8\pi^3} d^3k' . \tag{13}$$

where P ($\underline{k}$', $\underline{k}$) is the probability per unit time of a transition from a full state at $\underline{k}$' to an empty state at $\underline{k}$. The V/8π^3 factor is the density of states in $\underline{k}$ space.

Substituting equation 7 into 13 we obtain

$$\left[\frac{\partial f_o}{\partial t} (k) \right]_{coll} + \cos\psi \left[\frac{\partial f_1(k)}{\partial t} \right]_{coll} =$$

$$\int \left[f_o(k') P(\underline{k}', \underline{k}) - f_o(k) P(\underline{k}, \underline{k}') \right] \frac{V}{8\pi^3} d^3k'$$

$$+ \int \left[\cos\psi' f_1(k') P(\underline{k}'\underline{k}) - \cos\psi f_1(k) P(\underline{k}, \underline{k}') \right] \frac{V}{8\pi^3} d^3k' . \tag{14}$$

We assume that $P(\underline{k},\underline{k}')$ depends on k,k' and the scattering angle (γ) and not on the absolute orientation of the vectors in space.

It is, therefore convenient to evaluate the d^3k' integrals in a frame which has the k_z directed along the initial $\underline{k}$ direction. In this case

$$\cos\psi' = \cos\psi \cos\gamma + \sin\theta \sin\gamma \cos\beta \ , \tag{15}$$

where β is the azimuthal angle, (for details see Holtstein[3])

Substituting (15) into (14) and carrying out the integrals to separate the two contributions we obtain

$$\left[\frac{\partial f_1}{\partial t} (k) \right]_{coll} = \int \left[\cos\gamma \, f_1(k')P(\underline{k}',\underline{k}) - f_1(k)P(\underline{k},\underline{k}') \right] \frac{V}{8\pi^3} d^3k' \tag{16}$$

and

$$\left[\frac{\partial f_o}{\partial t} (k) \right]_{coll} = \int \left[f_o(k')P(\underline{k}',\underline{k}) - f_o(k)P(\underline{k},\underline{k}') \right] \frac{V}{8\pi^3} d^3k' \ , \tag{17}$$

These are still formal equations, in the next section we look at the influence of recoil scattering and inelastic scattering on equation 17 and in the following section we examine equation 16.

3 COLLISION PROCESSES

So far we have said nothing about the details of the microscopic events which remove energy from the electron distribution. These fall into two main categories, recoil and inelastic scattering. Under normal circumstances recoil scattering has little direct effect on energy relaxation as only a small amount of energy is removed in each scattering event, however it can be important at low electric fields when the second process, molecular excitation is unimportant because the electrons have not yet got enough energy.

In this section we evaluate the s-type part of the collision term by considering a Fermi-Golden Rule approach. Smith and Thompson[1] used hand waving arguments in their derivation and rigorous derivations seem in the main to be absent from the literature although Holstein's[3] method is correct. Our method relates the transition rate to the potential responsible for the scattering and in view of the pseudo-potentials now available[4] in the literature for calculating scattering rates by just such a route it seems like a worthy one to pursue. We start by quoting Fermi's Golden rule:-

Given an electron in state $\underline{k}$, the transition rate to an empty state $\underline{k}'$ is given by Fermi's golden rule.

$$P(\underline{k},\underline{k}') = \frac{2\pi}{\hbar} \left|\langle \underline{k}\right| eV(\underline{r}) \left| \underline{k}'\rangle\right|^2 \delta\,(\epsilon(\underline{k}) - \epsilon(\underline{k}') - \Delta(\underline{k},\underline{k}')), \tag{18}$$

where $\Delta(\underline{k},\underline{k}')$ is the energy lost by the electron in the transition and $V(\underline{r})$ is the perturbing potential due to the atom.

We now examine the two types of scattering process.

3.1 Recoil Scattering

We assume for the moment that all the atoms are at rest before a collision happens ie temperature = 0. Any energy dumped into the molecular system is also assumed to be removed instantaneously. So energy from the molecular system may not feed into the electron system. The scattering rate is usually written as

$$\Gamma = nQv, \tag{19}$$

where Q is the cross-section, v is the speed of the electron and n is the number of scatterers per unit volume. If the nature of $V(\underline{r})$ is known we may also evaluate $\Gamma(\underline{k})$ through the relation

$$\Gamma(\underline{k}) = \int P(\underline{k},\underline{k}') \frac{V}{8\pi^3} d^3k' \tag{20}$$

and equation 18.

Now for electrons with an energy less than 30 eV we shall assume that the scattering centre is much smaller than the wavelength of the electron. (Typically only ~ 10 times smaller). This allows us to replace the potential $V(\underline{r})$ with

$$V(\underline{r}) = S_0\delta(\underline{r}-\underline{r}_0), \tag{21}$$

where S_0 is the scattering strength.

If we treat the collision as elastic then we may easily evalulate the scattering rate $\Gamma(\underline{k})$

$$\Gamma(\underline{k}) = \int \frac{2\pi}{\hbar} S_o^2\, n\delta\,(\epsilon(\underline{k}) - \epsilon(\underline{k}')) \frac{V}{8\pi^3} d^3k'$$

$$= S_o^2 \frac{n\,m^2}{\pi\hbar^4} v, \tag{22}$$

where m is the mass of the elctron and we have used equations 18, 20 and 21.

So we see

$$Q = \frac{S_o^2 \; m^2}{\pi \hbar^4} , \tag{23}$$

where

$$S_o = \int V(\underline{r}) \; d^3r \tag{24}$$

If V($\underline{r}$) is finite in extent then it can be shown by partial wave analysis that equations 23 and 24 still hold approximately if the spread of V($\underline{r}$) is much smaller than the electron wavelength[5]. Experimentally however Q is dependent on energy. This dependence is due to the failure of our sharp potential assumption. Indeed the Ramsauer–Townsend minima in experimentally measured Q(ϵ) values is a manifestion of resonant tunnelling through the potential barrier due to the size of the atom[4]. To include the energy dependence in a simple way and still retain the isotropic scattering ideas we write the transition rate as

$$P(\underline{k}',\underline{k}) = \frac{2\pi}{\hbar} A(\epsilon') \, \delta \, (\epsilon'-\epsilon - \Delta) , \tag{25}$$

where Δ is the energy lost in a transition from $\underline{k}'$ to $\underline{k}$ and A(ϵ') is a function of the initial energy of the electron. Then

$$A(\epsilon) = \frac{\hbar^4 n}{V} \; \frac{Q(\epsilon)\,\pi}{m^2} . \tag{26}$$

We have retained the isotropic scattering approximation whilst incorporating the energy dependence of Q(ϵ). In reality anisotropic scattering and the energy dependence of Q(ϵ) are inextricably linked to the failure of the notion of delta function scattering centres. As we are mainly interested in the energy dependence of the electron distribution function it is hoped that such an approximation will not lead to large errors in calculated excitation rates.

In view of our preliminary remarks we note that recoil collisions can only remove energy from the electron system. Hence the first term in equation 17 which is the scattering in term (scattering into $\underline{k}$) must have k < k', similarly the second term has k' < k as electrons can only be removed from $\underline{k}$ by a decrease in energy.

For recoil scattering the initial and final energies are related through the equation 1

$$\epsilon' - \epsilon = \frac{m}{M} (\epsilon + \epsilon') - \frac{m^2}{M} \sqrt{\frac{2\epsilon'}{m}} \sqrt{\frac{2\epsilon}{m}} \cos \gamma , \tag{27}$$

where ϵ' is the energy of the initial state $\underline{k}'$, ϵ that of the final state $\underline{k}$, γ is the scattering angle and M is the mass of the recoiling atom.

Defining

$$g(\epsilon',\epsilon) = \epsilon' - \epsilon - \frac{m}{M}(\epsilon + \epsilon') + \frac{m}{M}\sqrt{2\epsilon'}\sqrt{2\epsilon}\cos\gamma\ , \qquad (28)$$

we may write

$$P(\underline{k}',\underline{k}) = \frac{2\pi}{\hbar} A(\epsilon')\,\delta\,(g\,(\epsilon',\epsilon)) \qquad (29)$$

We may now re-write equation 17 solely in terms of energy

$$\left[\frac{\partial f_o}{\partial t}\right]_{coll} = \int\int \left[f_o(\epsilon')\frac{2\pi}{\hbar}A(\epsilon')\delta(g(\epsilon',\epsilon)) - f_o(\epsilon)\frac{2\pi}{\hbar}A(\epsilon)\delta(g(\epsilon,\epsilon'))\right]$$

$$\frac{V}{8\pi^3}\sqrt{\frac{2m\epsilon}{\hbar^2}}\ \frac{m}{\hbar^2}\ d(\cos\gamma)\ d\theta\ d\epsilon' \qquad (30)$$

we note that $g\,(\epsilon',\epsilon) = 0$ is approximately satisfied by $\epsilon = \epsilon'$.

We use the property of the delta function

$$\delta(g(x)) = \sum_n \frac{1}{|g'(x_n)|}\,\delta\,(x-x_n) \qquad (31)$$

where the x_n are the set of numbers which satisfied $g(x) = 0$.

Now,

$$\left| g'\,(\epsilon',\,\epsilon)\right| \sim 1 - \frac{m}{M}(1 - \cos\gamma) \qquad (32)$$

and

$$\left| g'\,(\epsilon,\,\epsilon')\right| \sim 1 + \frac{m}{M}(1 - \cos\gamma) \qquad (33)$$

Hence we obtain,

$$\left[\frac{\partial f_o}{\partial t}\right]_{\mathrm{recoil}} = \int \left[f_o\,(\epsilon+\Delta)\,\frac{2\pi}{\hbar}\,A\,(\epsilon+\Delta)\,\frac{\sqrt{(\epsilon+\Delta)}}{1-\frac{m}{M}\,(1-\cos\gamma)} - f_o(\epsilon)\,\frac{2\pi}{\hbar}\,A\,(\epsilon-\Delta)\,\frac{\sqrt{\epsilon-\Delta}}{1+\frac{m}{M}\,(1-\cos\gamma)} \right] \frac{V}{8\pi^3}\,\sqrt{\frac{2m}{\hbar^2}}\,\frac{m}{\hbar^2}\,d\,(\cos\gamma)\,d\theta \tag{34}$$

now $\epsilon + \Delta \approx \frac{1}{2}\, m\, (v + \alpha v)^2$

where v is the speed of an electron with energy ϵ and

$$\alpha = \frac{m}{M}\,(1 - \cos\gamma). \tag{35}$$

Writing everything in terms of speed,

$$\left[\frac{\partial f_o}{\partial t}\,(v)\right]_{\mathrm{recoil}} = \int \left[f_o\,(v+\alpha v)\,\frac{2\pi}{\hbar}\,A\,(v+\alpha v)\,\frac{\sqrt{\frac{m}{2}}\,(v+\alpha v)}{1-\alpha} - f_o(v)\,\frac{2\pi}{\hbar}\,A\,(v-\alpha v)\,\frac{\sqrt{\frac{m}{2}}\,(v-\alpha v)}{1+\alpha} \right]$$

$$\frac{V}{8\pi^3}\,\sqrt{\frac{2m}{\hbar^2}}\,\frac{m}{\hbar^2} \times 2\pi\,d\,(\cos\gamma)\,, \tag{36}$$

where we have integrated over θ.

Expanding, integrating and using equation 26 we find

$$\left[\frac{\partial f_o(v)}{\partial t}\right]_{\text{recoil}} = \frac{1}{mv^2}\frac{\partial}{\partial v}\left[\frac{m^2}{M} NQv^4 f_o\right] \tag{37}$$

converting to an energy derivative,

$$\left[\frac{\partial f_o}{\partial t}\right]_{\text{recoil}} = \frac{1}{v}\frac{\partial}{\partial \epsilon}\left[\frac{4NQ\epsilon^2}{M} f_o\right] . \tag{38}$$

This result along with the equation derived in the next section will allow us to complete equation 11.

3.2 Inelastic Scattering

As well as being able to reduce its energy by increasing the kinetic energy of the surrounding gas molecules an electron may excite the gas molecule by changing either its vibrational state or by forcing an electron transition. This is usually the dominant process for energy relexation in a typical discharge as these transitions relax large amounts of energy (typically ~10 eV). In this section we consider how this scattering mechanism influences the s-type part of the collision term.

We shall assume that the transition rate may again be written in the form

$$P\ (\underline{k},\underline{k}') = \frac{2\pi}{\hbar}\ A(\epsilon)\ \delta\ (\epsilon-\epsilon' - \Delta), \tag{39}$$

where Δ is now a constant corresponding to an excitation energy in the gas molecule and $P(\underline{k},\underline{k}')$ takes an electron to a reduced energy. Evaluation of the scattering rate $\Gamma(\underline{k})$ gives

$$\Gamma(\underline{k}) = \int P\ (\underline{k},\ \underline{k}')\ \frac{V}{8\pi^3}\ d^3k'$$

$$= \frac{A(\epsilon)}{\hbar^4}\ \frac{V}{\pi}\ m\ \sqrt{2m\ (\epsilon-\Delta)}\quad . \tag{40}$$

equating Γ with NQv we find

$$A(\epsilon) = NQ(\epsilon) \frac{\pi}{V} \frac{\hbar^4}{m^2} \frac{\sqrt{\epsilon}}{\sqrt{(\epsilon-\Delta)}} . \tag{41}$$

We now examine the $\left[\partial f_o/\partial t \right]_{coll}$ due to inelastic collisions

$$\left[\frac{\partial f_o(k)}{\partial t} \right]_{inel} = \int \left\{ f_o(k') P(\underline{k}', \underline{k}) - f_o(k) P(\underline{k}, \underline{k}') \right\} \frac{V}{8\pi^3} d^3k' \tag{42}$$

substituting equation 41 into 42 gives

$$\left[\frac{\partial f_o(k)}{\partial t} \right]_{inel} = \int \left\{ f_o(k') A(\epsilon')\delta(\epsilon-\epsilon'+\Delta) - f_o(k) A(\epsilon)\delta(\epsilon-\epsilon'-\Delta) \right\}$$

$$\frac{V}{\pi} \sqrt{2m\epsilon'} \frac{m}{\hbar^4} d\epsilon'$$

$$= \left[f_o(k') A(\epsilon+\Delta) \sqrt{\epsilon+\Delta} - f_o(k) A(\epsilon) \sqrt{\epsilon-\Delta} \right] \frac{V}{\pi} \sqrt{2m} \frac{m}{\hbar^4} \tag{43}$$

where k' is now the solution of $\frac{\hbar^2 k'^2}{2m} = \epsilon + \Delta$

substituting (41) into (43) gives

$$\left[\frac{\partial f_o}{\partial t} \right]_{inel} (\epsilon) = \left[f_o(\epsilon+\Delta) NQ(\epsilon+\Delta)(\epsilon+\Delta) - f_o(\epsilon) NQ(\epsilon) \epsilon \right] \sqrt{\frac{2}{m\epsilon}} \tag{45}$$

This result completes equation 11, however before the coupled equations 11 and 12 can be solved, we need to calculate $\left[\frac{\partial f_1}{\partial t} \right]_{coll}$.

4 THE RELAXATION TIME APPROXIMATION

In the presence of an applied electric field the distribution function $f(\underline{k})$ contains an anisotropic contribution $f_1(k)\cos\theta$ which would decay if the field was turned off. We model this decay with the ansatz.

$$\left[\frac{\partial f_1}{\partial t} (k) \right]_{coll} = - \frac{f_1(k)}{\tau (k)} \tag{46}$$

where $\tau(k)$ is a momentum relaxation time which is a function of k alone.

If we assume that the main contribution to the relaxation rate is due to quasi-elastic scattering through the recoil scattering process then

$$P(\underline{k},\underline{k}') \approx P(\underline{k}',\underline{k}) \text{ and } f_1(k') \approx f_1(k)$$

Substituting 46 into 16 we find,

$$- \frac{f_1 (k)}{\tau (k)} \approx \int (\cos\gamma - 1)\ f_1(k)\ P\ (\underline{k}',\underline{k})\ d^3k', \tag{47}$$

which gives the momentum relaxation rate,

$$\frac{1}{\tau (k)} = \int (1-\cos \gamma)\ P\ (\underline{k}',\ \underline{k})\ d^3k' \quad . \tag{48}$$

For isotropic scattering the momentum relaxation rate equation 48 and the scattering rate equation 20 are identical. In this case

$$\frac{1}{\tau} = \Gamma = NQv \tag{49}$$

In general this expression will only be a valid representation of the momentum decay process when the scattering rate due to recoil scattering is much larger than that due to inelastic cross-sections. Many authors have considered the breakdown of Boltzmann calculations in a gas to be due to the truncation of the series, however the validity of the relaxation time approximation has not been investigated. We shall assume that we are working at an electric field where equation 49 is valid, then equation 12 becomes

$$\frac{-e}{\hbar}\ E\ \frac{\partial f_o}{\partial k} = - f_1\ NQv \tag{50}$$

Similarly for equation 11

$$\frac{-\,e^2E^2}{3m^2}\;\frac{1}{v^2}\;\frac{\partial}{\partial v}\left[\frac{v}{NQ}\;\frac{\partial f_o}{\partial v}\right] = \left[\frac{\partial f_o}{\partial t}\right]_{coll}, \tag{51}$$

or in terms of energy,

$$\frac{-e^2E^2}{3m}\;\frac{1}{v}\;\frac{\partial}{\partial \epsilon}\left[\frac{2\epsilon}{NQ}\;\frac{\partial f_o}{\partial \epsilon}\right] = \left[\frac{\partial f_o}{\partial t}\right]_{coll}. \tag{52}$$

Hence from equations 38 and 45

$$\frac{-e^2E^2}{3m}\;\frac{1}{v}\;\frac{\partial}{\partial \epsilon}\left[\frac{2\epsilon}{NQ}\;\frac{\partial f_o}{\partial \epsilon}\right] = \frac{1}{v}\;\frac{\partial}{\partial \epsilon}\left[\frac{4NQ\;\epsilon^2}{M}\;f_o\right]$$

$$+\left[f_o\,(\epsilon+\Delta)\;NQ\;(\epsilon+\Delta)\;(\epsilon+\Delta)\;-\;f_o(\epsilon)\;NQ\;(\epsilon)\;\epsilon\right] \tag{53}$$

Making the change of variables $\epsilon = eu$, we obtain

$$\frac{E^2}{3}\;\frac{\partial}{\partial u}\left[\frac{u}{NQ}\;\frac{\partial f_o}{\partial u}\right] + \frac{2m}{M}\;\frac{\partial}{\partial u}\left[NQ\;u^2\;f_o\right]$$

$$+\left[f_o\,(u+\Delta)\;NQ\;(u+\Delta)\;(u+\Delta)\;-\;f_o\,(u)\;NQ\;(u)\;u\right] = 0\,. \tag{54}$$

This is the working equation for the single component gas when the temperature is small and the relaxation time approximation is valid

We are usually concerned with a gas mixture at finite temperatures, then the equation is modified to give[1]

$$
\begin{aligned}
&\frac{E^2}{3}\frac{\partial}{\partial u}\left[u\left[\sum_k N_k Q_m^k\right]^{-1}\frac{\partial f_o}{\partial u}\right] + 2m\frac{\partial}{\partial u}\left[u^2\left[\sum_k \frac{N_k Q_m^k}{M_k}\right] f_o\right] \\
&+ \frac{2mK_BT}{e}\frac{\partial}{\partial u}\left[u^2\left[\sum_k \frac{N_k Q_m^k}{M_k}\right]\frac{\partial f_o}{\partial u}\right] \qquad (55) \\
&+ \sum_j\sum_k \left[\left[u + u_{jk}\right] f_o\left[u + u_{jk}\right] N_k^o\, Q_j^k \left[u + u_{jk}\right] - uf_o\left[u\right] N_k^o\, Q_j^k \left[u\right] \right] \\
&+ \sum_j\sum_k \left[\left[u - u_{jk}\right] f_o\left[u - u_{jk}\right] N_k^j\, Q_j^k \left[u - u_{jk}\right] - uf_o\left[u\right] N_k^j\, Q_j^k \left[u\right] \right] = 0 ,
\end{aligned}
$$

where k labels the gas species and j corresponds to the j-th excitational state, whilst $Q_j^k(u)$ is the corresponding cross-section. N_k is the total number of k-type molecules whilst N_k^o is the number of k-type molecules in the ground state and N_k^j is the number of k-type molecules in the j-th excited state.

Before we proceed to a full numerical solution of equation 55 we examine an analytical limit.

5 THE MAXWELL-BOLTZMANN AND DRUYVESTYN DISTRIBUTIONS

There are two well established distributions which may be used as best first guesses to the electron distribution when some quantity such as the average energy is known and others need to be estimated. The Maxwell-Boltzmann distribution is the well known thermal equilibrium distribution. The Druyvestyn distribution is less well known and is relevant to the high field regime, when thermal effects are less important. To derive both and consider the transition from one to the other we consider a single component gas when inelastic scattering is unimportant and the momentum transfer cross-section is independent of energy, then the Boltzmann equation reads.

$$
\begin{aligned}
&\frac{E^2}{3}\frac{\partial}{\partial u}\left[u\left[N\,Q_m\right]^{-1}\frac{\partial f_o}{\partial u}\right] + 2m\frac{\partial}{\partial u}\left[u^2\left[\frac{N\,Q_m}{M}\right] f_o\right] \\
&+ \frac{2mK_BT}{e}\frac{\partial}{\partial u}\left[u^2\left[\frac{N\,Q_m}{M}\right]\frac{\partial f_o}{\partial u}\right] = 0, \qquad (56)
\end{aligned}
$$

integrating twice we find

$$f_o(u) = \left[\frac{-u}{\beta}\right] \left[1 + \frac{\beta}{\alpha}u\right]^{\alpha/\beta^2} , \tag{57}$$

where

$$\alpha = \left[\frac{E}{N}\right]^2 \frac{M}{6mQ_m^2} ,$$

$$\text{and} \quad \beta = \frac{K_B T}{e} , \tag{58}$$

and we have dropped the k-label as it is now superfluous. Under weak electric field conditions, when alpha is small, the shape of the distribution is dominated by the temperature of the gas molecules, giving a Maxwell-Boltzmann distribution,

$$f_o = \exp\left[\frac{-u}{\beta}\right] . \tag{59}$$

In the field dominated regime we may consider beta to be small, giving the Druyvestyn distribution,

$$f_o = \exp\left[\frac{-u}{2\alpha}\right] . \tag{60}$$

The characteristic energy of the electron gas ϵ_k (eV) is given by the ratio of the diffusion coeffcient to the mobility.

$$\epsilon_k \equiv \frac{D}{\mu} ,$$

where

$$D = \frac{1}{3N} \left[\frac{2e}{m} \right]^{1/2} \int_o^\infty \frac{uf_o}{Q_m} du, \qquad (61)$$

and

$$\mu = \frac{1}{3N} \left[\frac{2e}{m} \right]^{1/2} \int_o^\infty \frac{u}{Q_m} \frac{\partial f_o}{\partial u} du \ . \qquad (62)$$

On evaluating the integrals, we find that in the temperature dominated regime

$$\epsilon_k = \frac{K_B T}{e} \ , \qquad (63)$$

which is a restatement of the Einstein relation for a non-degenerate electron gas.

In the field dominated regime we find

$$\epsilon_k = \frac{\frac{E}{N}}{\sqrt{\frac{3m}{M}} Q_m} \ . \qquad (64)$$

In general the momentum transfer cross-section is a function of energy and inelastic scattering is important. In the next two sections we describe how general solutions may be found for a gas mixture.

6.1 CALCULATING THE ELECTRON DISTRIBUTION BY GAUSS-SEIDEL ITERATION

We consider equation 55 and make the transformations $n(u) = \eta u^{\frac{1}{2}} f_{o(u)}$, where η is the normalisation. After some manipulation we find

$$-\frac{\partial}{\partial\epsilon}\left[\frac{2Ne^2\left[\frac{E}{N}\right]^2\epsilon}{3m\left[\frac{\nu}{N}\right]}\left[\frac{n}{2\epsilon}-\frac{\partial n}{\partial\epsilon}\right]\right]-\frac{\partial}{\partial\epsilon}\left\{\bar{\nu}\left[n\left[\frac{K_BT}{2}-\epsilon\right]-K_BT\epsilon\frac{\partial n}{\partial\epsilon}\right]\right\}$$

$$+\sum_j\sum_k N_k\left[R_{jk}(\epsilon+\epsilon_{jk})\,n\,(\epsilon+\epsilon_{jk})-R_{jk}(\epsilon)\,n\,(\epsilon)\right]$$

$$+\sum_j\sum_k N_k\,\Delta_{jk}\left[R'_{jk}(\epsilon-\epsilon_{jk})\,n\,(\epsilon_{jk})-R'_{jk}(\epsilon)\,n\,(\epsilon)\right]=0 \qquad (65)$$

where ϵ_{jk} is the energy needed to take a k-type species into its j-th excited state,

$$\frac{\nu}{N}=\nu\,(\epsilon)\sum_k Q_m^k\,(\epsilon)\,\frac{N_k}{N},$$

$$\bar{\nu}=2m\,N\nu\,(\epsilon)\sum_k\frac{Q_m^k\,(\epsilon)}{M_k}\,\frac{N_k}{N},$$

$$R_{jk}=Q_j^k\,(\epsilon)\,\nu\,(\epsilon),$$

$$R'_{jk}=\left[\frac{\epsilon+\epsilon_{jk}}{\epsilon}\right]Q_j^k\,(\epsilon+\epsilon_{jk})\,\nu\,(\epsilon)=Q^k_{-j}(\epsilon)\,\nu\,(\epsilon),$$

$\nu(\epsilon)$ is the velocity of the electron and Δ_{jk} is the proportion of k-type gas molecules in excited state j.

We discretise by using the approximate derivative expressions

$$\frac{\partial n}{\partial\epsilon'}=\frac{n_{p+1}-n_{p-1}}{2\Delta\epsilon},$$

$$\frac{\partial^2 n}{\partial\epsilon'^2}=\frac{n_{p+1}-2n_p+n_{p-1}}{(\Delta\epsilon)^2},$$

where $\Delta\epsilon$ is chosen as the fundamental energy step. After some manipulation we find

$$
\begin{aligned}
& a_{p-1}\, n_{p-1} + b_{p-1}\, n_{p+1} - (a_p + b_p)\, n_p \\
& + \sum_j \sum_k N_k \left[R_{jk,p+m_{jk}}\, n_{p+m_{jk}} - R_{jk,p}\, n_p \right] \\
& + \sum_j \sum_k N_k\, \Delta_{jk} \left[R'_{jk,p-m_{jk}}\, n_{p-m_{jk}} - R'_{jk,p}\, n_p \right] = 0
\end{aligned}
\tag{67}
$$

where

$$b_{p+1} = \frac{2Ne^2 \left[\frac{E}{N} \right]^2}{3m \left[\frac{\nu}{N} \right]} \left[\frac{\epsilon\ (p)}{\Delta\epsilon} - \frac{1}{4\Delta\epsilon} \right] + \frac{\bar{\nu}}{2\Delta\epsilon} \left[\epsilon(p) - \frac{K_B T}{2} + \frac{2K_B T}{\Delta\epsilon}\, \epsilon(p) \right], \tag{68}$$

$$a_p = \frac{2Ne^2 \left[\frac{E}{N} \right]^2}{3m \left[\frac{\nu}{N} \right]} \left[\frac{\epsilon\ (p)}{\Delta\epsilon} - \frac{1}{4\Delta\epsilon} \right] + \frac{\bar{\nu}}{2\Delta\epsilon} \left[\frac{K_B T}{2} - \epsilon\ (p) + \frac{2K_B T}{\Delta\epsilon}\, \epsilon(p) \right], \tag{69}$$

and $\epsilon(p) = p\ \Delta\epsilon$

The a_k's and b_k's have physical interpretations as the rates at which electrons are upscattered and downscattered respectively. It follows from the definition of $n(\epsilon')$ and the finite nature of $f_0(0)$ that $b_1 = 0$ and $a_0 = 0$. Hence if the discrete Boltzmann equation is written down in matrix form then to ensure that electrons are not scattered to negative energies then certain of the elements are reduced in form.

In the absence of inelastic scattering the matrix is tridiagonal and a simple analytic recursion relation exists for n_p. With the boundary condition we find

$$b_2 n_2 = a_1 n_1$$

and

$$n_{p+1} = \frac{(a_p + b_p)\, n_p - a_{p-1}\, n_{p-1}}{b_{p-1}}\ . \tag{70}$$

the equation's are linear in n_p and the normalisation is still yet to be fixed we can choose n_1, then the recursion relation may be used to solve for n_p for elastic scattering given any form for $Q^k_m(\epsilon')$.

In general when excitation events are important solutions of equation 67 may be found by Gauss-Seidel iteration.

6.2 DIRECT SOLUTION BY ITERATION

The method quoted above can consume large amounts of computer time before convergence is achieved. In this section we consider a method which is quick when superelastic collisions are unimportant. We consider a direct solution of equation 55.

Equation 55 may be approximated by centred finite differences[6], with an energy step of Δu, to give,

$$(B-A)\, f_{i-1} = (A+B)\, f_{i+1} + (C-2A)\, f_i + S, \tag{71}$$

where

$$(\Delta u)^2 A = -\frac{1}{3}\left[\frac{E}{N}\right]^2_1 \frac{u}{Q} + \frac{2mkT}{Me}\, u^2\, Q_2, \tag{72}$$

$$2\Delta u B = \frac{1}{3}\left[\frac{E}{N}\right]\left[\frac{1}{Q_1} - \frac{u}{Q_1^2}\,\frac{dQ_1}{du}\right] + \frac{2m}{M}\, u^2 Q_2 \tag{73}$$

$$+ \frac{2mkT}{Me}\left[2uQ_2 + u^2\,\frac{dQ_2}{du}\right],$$

$$C = \frac{2m}{M}\left[2uQ_2 + u^2\,\frac{dQ_2}{du}\right], \tag{74}$$

$$S = \sum_{jk} (u + u_{jk})\, f_{i+\delta_{jk}}\, Q_j^k\, (u + u_{jk}) - u f_i \sum_{jk} Q_j^k\, (u)$$

$$+ \sum_{jk} \Delta_{jk}\, (u - u_{jk})\, f_{i-\delta_{jk}}\, Q^k_{-j} (u - u_{jk}) - u\, f_i \sum_{jk} \Delta_{jk}\, Q^k_{-j}\, (u), \tag{75}$$

and δ_{jk} is the nearest integer to $u_{jk}/\Delta u$. We have also detailed the following quantities

$$M = \sum_k M_{jk} N_{jk}, \qquad (76)$$

$$N = \sum_k N_k, \qquad (77)$$

$$Q_1(u) = \frac{\sum_k Q^k_m(u) N_k}{N}, \qquad (78)$$

and

$$Q_2(u) = \sum_k \frac{M Q^k_m(u) N_k}{N M_k} . \qquad (79)$$

In the absence of superelastic collisions $\Delta_{jk} = 0$, then equation 71 may easily be solved. A guess is made for the average energy of the electrons in the distribution. Typically this will be less than the threshold energy of the first inelastic cross-section. The maximum energy considered in this calculation is set at two or three times this value. $f_{I_{max}}$ and $f_{I_{max}+1}$ are set to finite but small values and the difference is chosen such that $f_{I_{max}} > f_{I_{max}+1}$ as we expect to be in the tail of the distribution. Values of $[f_N]_{N>I_{max}+1}$ are assumed to be sufficiently small so that electrons scattering down from higher energies have a tiny effect on the distribution function. Equation 71 is then iterated down to f_1.

This technique is much quicker than the Gauss-seidel method as the operation described above only has to be carried out I_{max} times whereas the Gauss-seidel technique scales as I^2_{max}.

7 APPLICATION TO A REAL GAS (SF_6)

The momentum relaxation time quoted in section 4 is only approximately correct, in general inelastic scattering will affect it in a none trivial way.

It has been suggested that the momentum relaxation rate should be proportional to the total cross-section rather than the momentum transfer cross-section. This approximation is incorrect in detail, ideally we should find a momentum relaxation time which is the self-consistent solution of equation 16. In the case of recoil scattering the quasi-elasticity of the process allows us to divide through by the p-like part of the distribution and remove it from the equation. Inelasticity on the other hand allows no such simplification and solutions of equation 16 should ideally be found by iteration.

However we have adopted the total cross-section method as a best first approach and treated the ionisation and attachment processes just as inelastic processes which removed energy from the electron bath. The only effect of these modifications was to adjust the first bracket in equation 55 so that the momentum transfer cross-section was replaced by the total cross-section.

We focussed our attention on SF_6 and taking the cross-sections supplied by Itoh[7] (See Fig 2) we used both numerical methods to produce electron distributions. Both techniques produced the same result giving us confidence in our computer code.

The E/N value was varied until the electron creation rate was the same as the annihilation rate.

ie

$$\int Q_{ion}(\epsilon)\,\epsilon f(\epsilon)\,d\epsilon = \int Q_{ATT}(\epsilon)\,\epsilon f(\epsilon)\,d\epsilon.$$

This gave us the stable working field. A Monte-Carlo program[9] was also run for this E/N value and the results were found to be in close agreement (See Figure 3).

For completeness we have compared the calculated SF_6 distribution to Maxwell-Boltzmann and Druyvestyn distributions with the same average energy, these results are presented in Figure 4. We see that the shape of the true result is more closely followed by the Druyvestyn distribution which falls off more quickly with energy than than the slowly decaying Maxwell-Boltzmann. We also note that neither of the analytical distributions reproduce the tail of the true distribution and the Boltzmann calculation is necessary if we are to estimate the excitation rates of higher lying energy levels with any accuracy.

CONCLUSIONS

We have used Fermi Golden rule ideas to derive the Boltzmann transport equation for a single component gas at low temperatures. A modified Boltzmann equation has been solved within the relaxation time approximation to give good agreement with an exact Monte-Carlo simulation for SF_6. The Boltzmann code is simple in form and may easily be used to consider gas mixtures and to evaluate stable working fields. We note however that the relaxation time approximation used in this report is inexact, it would be interesting to calculate a self-consistent relaxation time by an iterative procedure.

In the longer term Fermi's Golden rule and the gas pseudo-potentials which are now available (and shown to be accurate[4]) should make it possible to calculate the recoil cross-section for simple gases.

REFERENCES

1 Smith and Thomson "Computer modelling of Gas Lasers" Plenum Press. New York and London 1978.

2 K Satoh et al J Phys D Appl Phys 21, 1988, 931.

3 T Holstein Phys Rev 70 1946 367

4 B Plenkiewicz et al Phys Rev A 38, 1988, 4460

5 P Milsom Ph D Thesis Warwick University (1988)

6 T Johnson et al IEEE Journal of Quantum Electronics QE-15, 1979, 289

7 H Itoh et al, J Phys D Appl Phys 21, 1988, 922

8 A Rockwood Phys Rev A8, 2348 (1973)

9 P K Milsom RSRE Memo, (to be published)

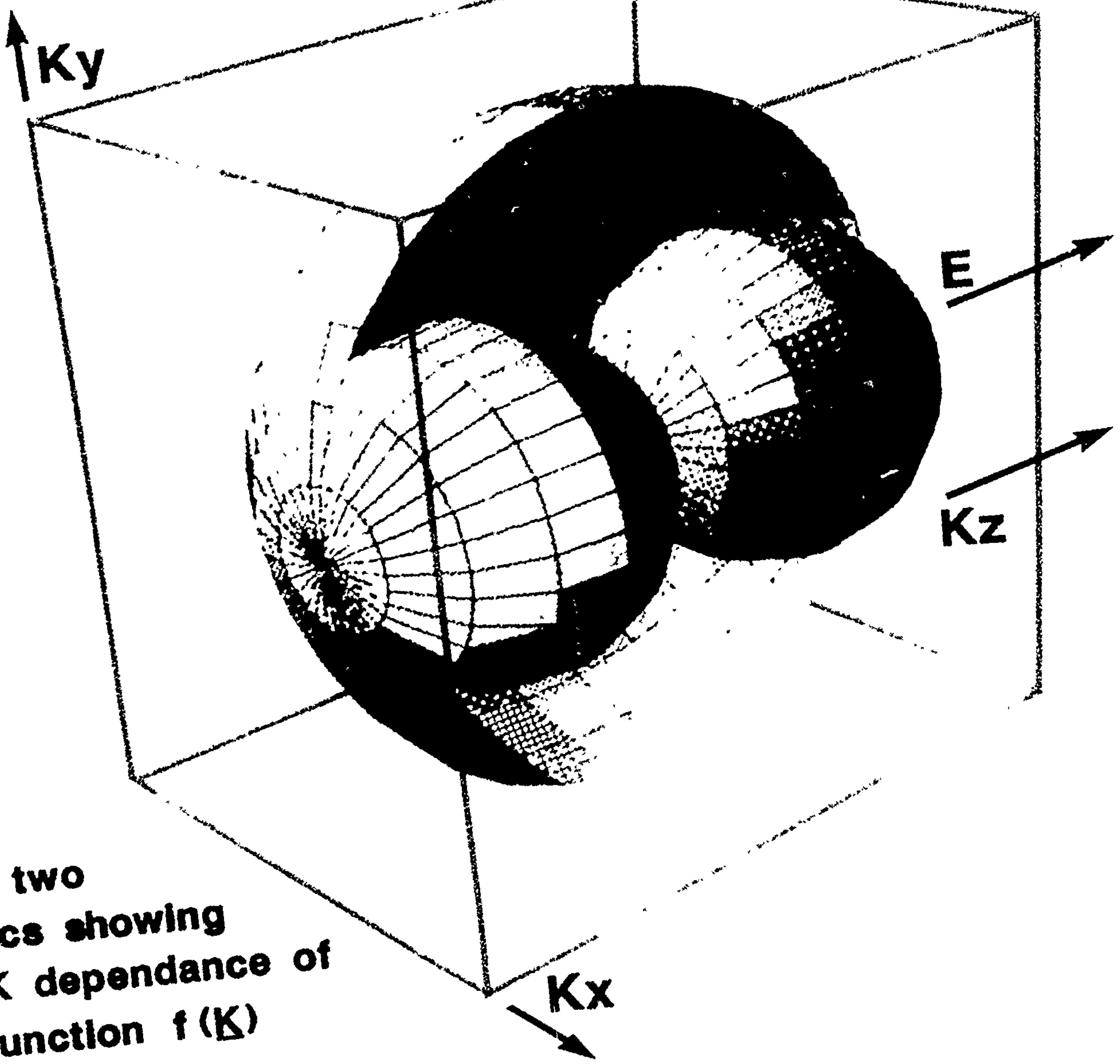

Figure 1 The first two spherical harmonics showing the form of the K dependance of the distribution function f ($\underline{K}$)

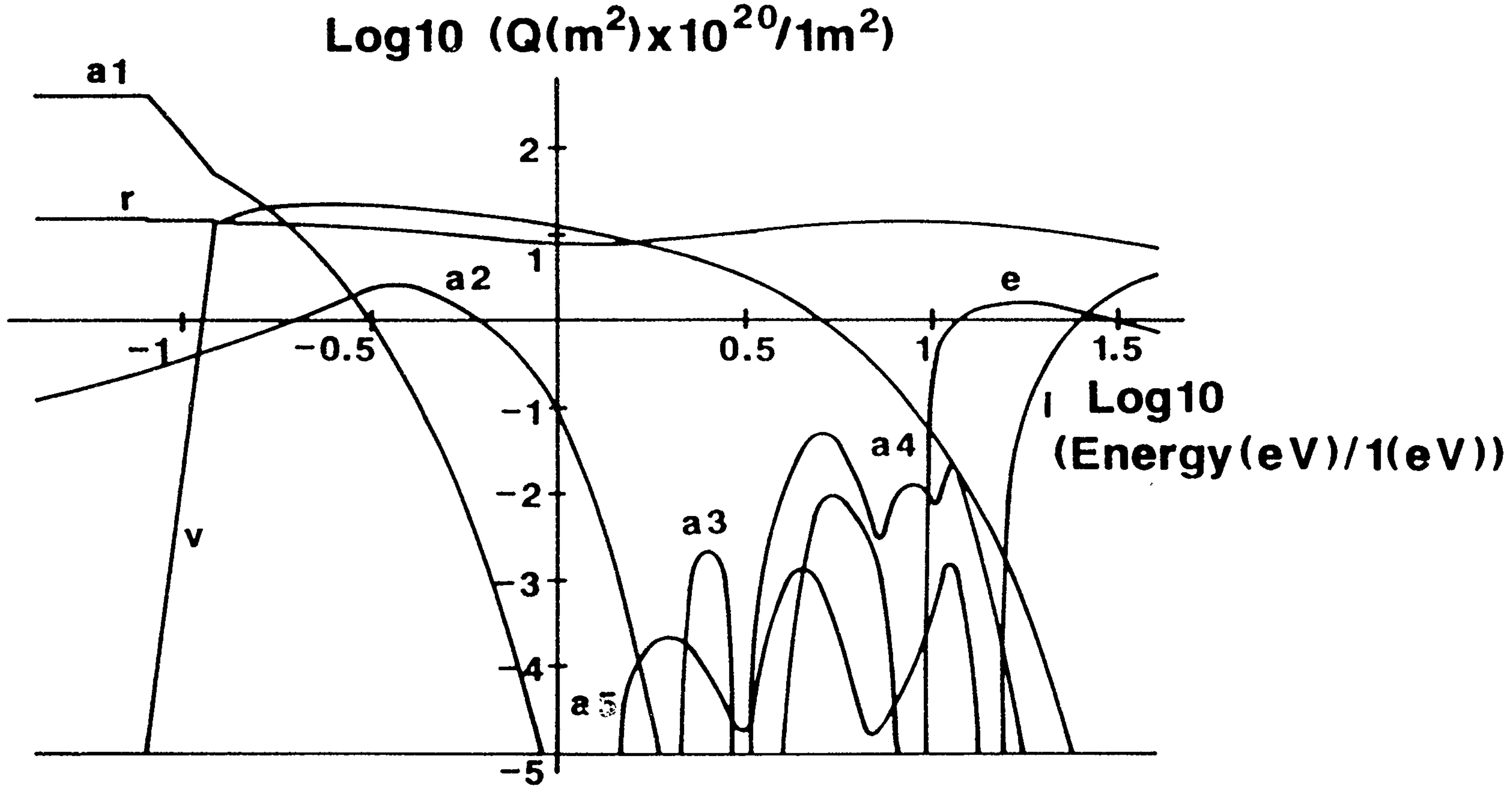

FIGURE 2

electron-SF_6 collision cross-sections on log/log scales.

r=recoil cross-section

v=a vibrational excitation cross-section

e=an electronic excitation cross-section

a=an attachment cross-section

I=an ionisation cross-section

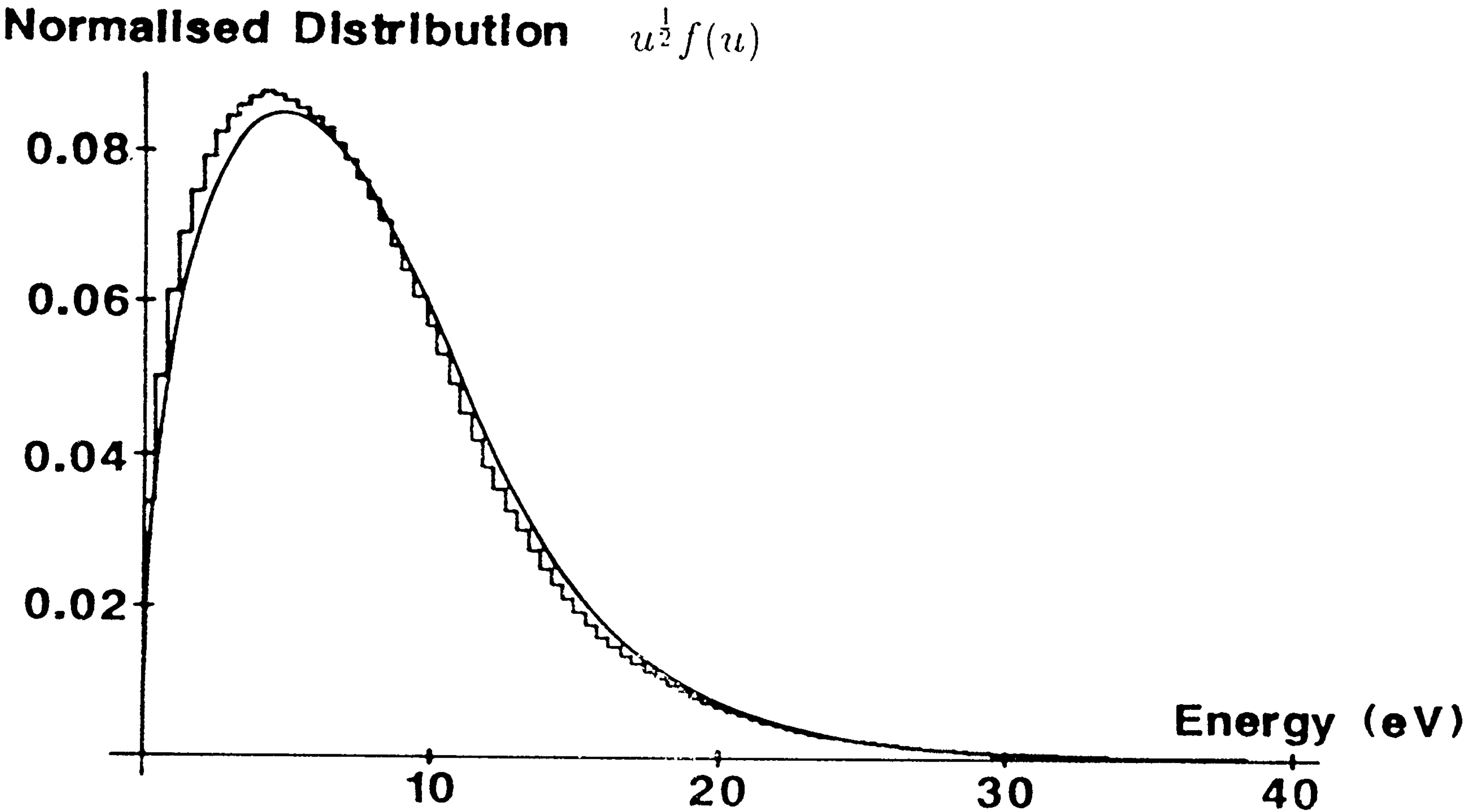

FIGURE 3

Steady-state electron energy distribution functions.
The Histogram is the result of a Monte-Carlo Simulation,
whilst the curve results from solving the Boltzmann equation.
(E/N =367Td)

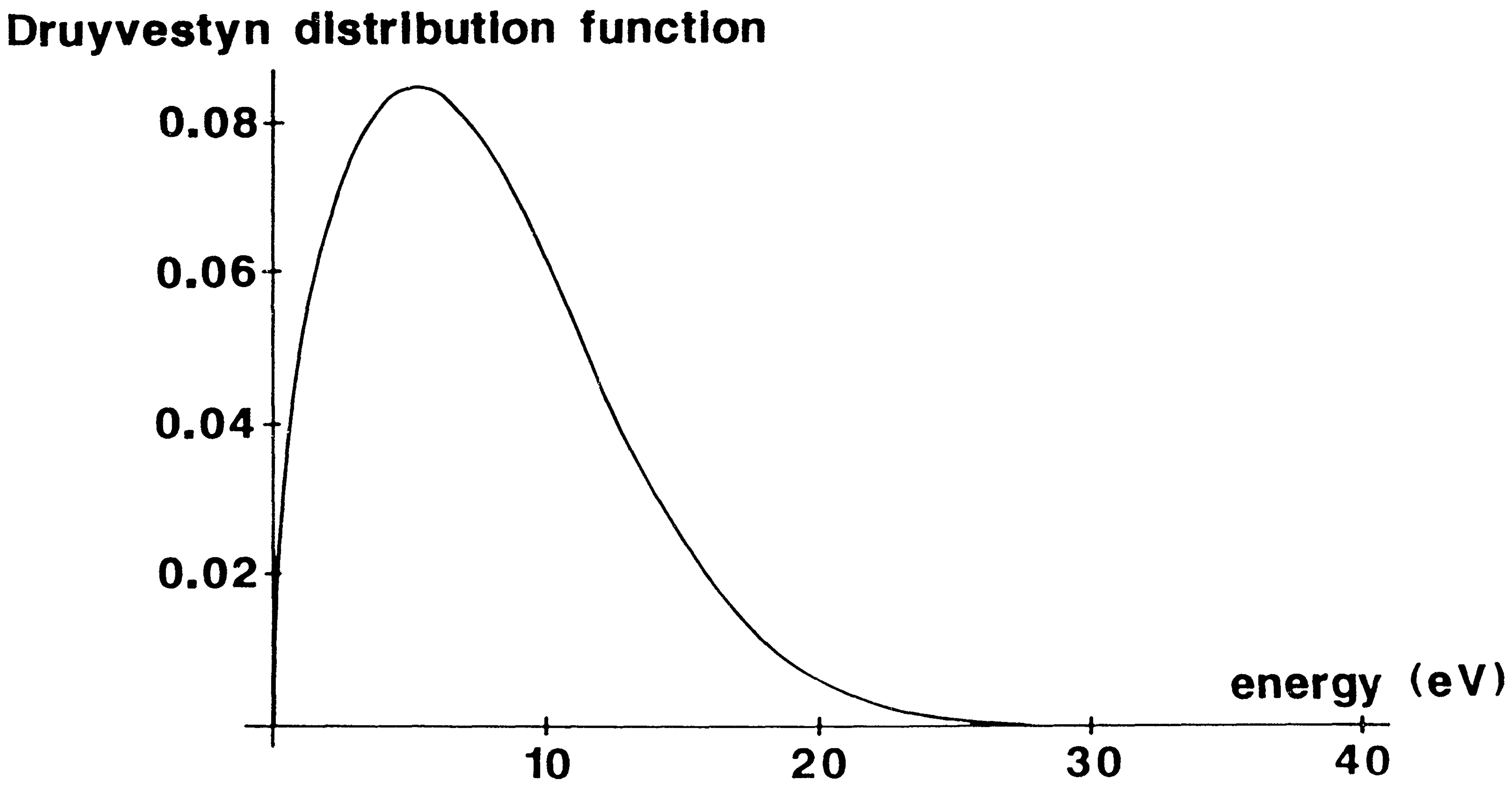

FIGURE 4(a)

A Druyvestyn distribution with the same average energy as the Boltzmann result in 3

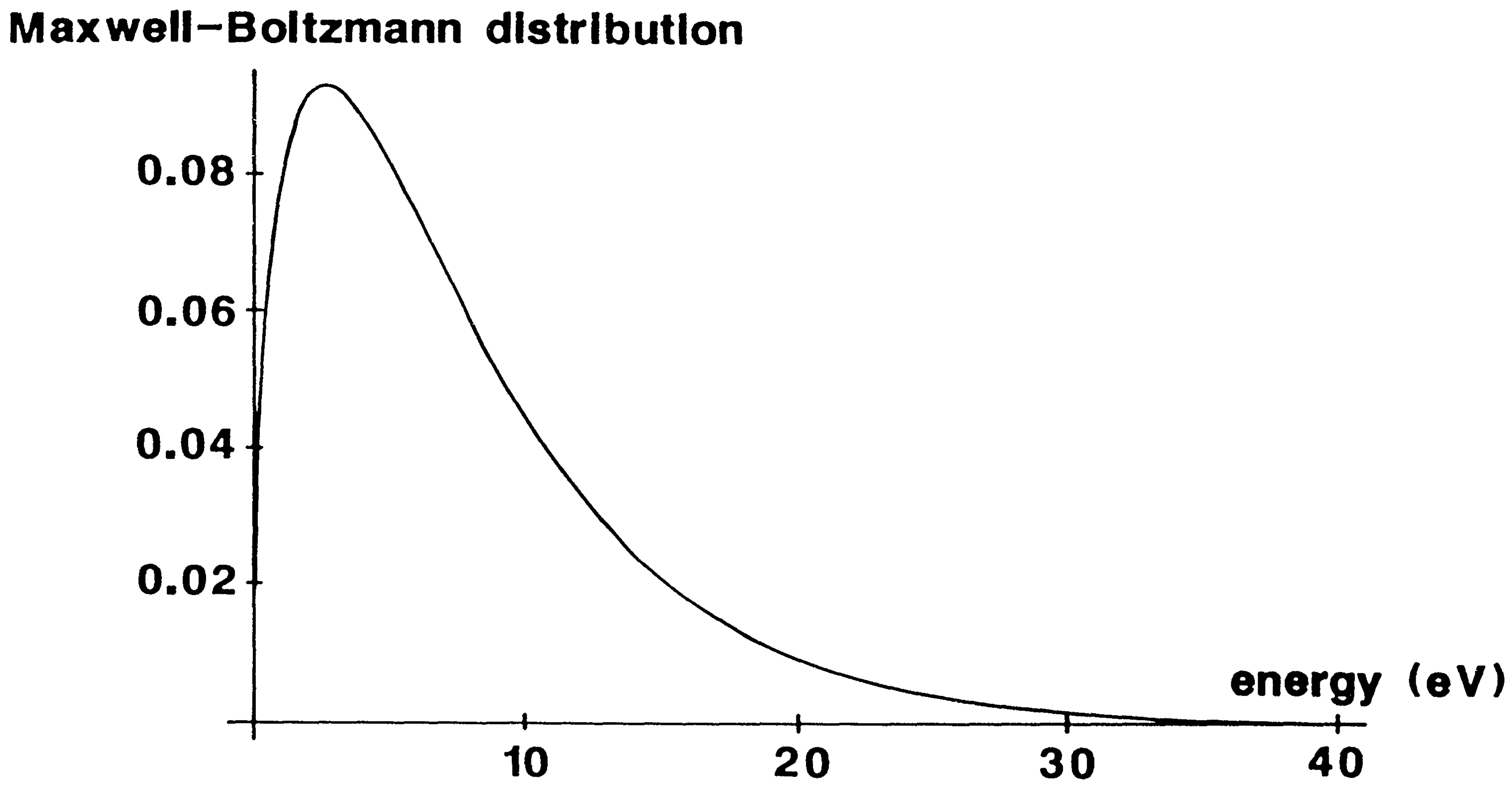

FIGURE 4(b)

A Maxwell-Boltzmann number density distribution with the same average energy as the Boltzmann result in FIGURE 3.

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Abstract

We describe the behaviour of the electrons in a gas discharge by using the Boltzmann equation and Fermi golden rule ideas. The resulting equations are applied to Sulphur Hexafluoride and electron energy distribution functions are calculated. The distributions are shown to be in close agreement with those of a Monte-Carlo simulation. The ideas developed here should be easily extended to solve anisotropic scattering problems and may also make use of the pseudopotentials which are now becoming available in the literature.

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