Aust. J. Phys., 1981, **34**, 677–88

The Effect of Diffusion on the Analysis of Pulsed Radiolysis Drift Tube Experiments

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Abstract

Electron drift velocities have previously been calculated from the transient waveforms recorded with a pulsed radiolysis drift tube (PRDT) using a first order theory in which it is assumed that diffusion during the drift of the electrons to the anode effectively increases the drift distance. In this paper the modifications to the transient waveforms caused by diffusion have been analysed more accurately by using a model representation of a group of electrons drifting and diffusing in a uniform electric field between plane, parallel absorbing electrodes. It is shown that, when account is taken of loss of electrons to the electrodes by diffusion, the correction factor differs in both magnitude and sign from that assumed in the first order theory.

1. Introduction

Electron mobilities have been determined from the transient waveforms recorded with a pulsed radiolysis drift tube (PRDT) (Wada and Freeman 1981). With this technique an X-ray pulse produces electrons uniformly between two plane parallel electrodes in a cell filled with gas at a known pressure. The passage of the electron group in the uniform field between the cathode and the anode results in a displacement current in the external circuit. The voltage pulse across a load resistance is measured with an amplifier and an oscilloscope, and is used to determine the electron mobility.

Under most conditions the effects of diffusion are small and have no effect on the transient waveform, but at low electric field strengths and high temperatures the effects of diffusion cannot be neglected.

Previously, the analysis of the transient waveforms was based on a first order theory where it is assumed that the effect of diffusion during the drift of the electrons to the anode effectively increases the drift distance (Wada and Freeman 1979). In the present work the modifications to the transient waveforms caused by diffusion have been analysed in more detail using a model representation developed by Lowke (1962) and Huxley (1972) of a group of electrons drifting and diffusing in a uniform electric field between plane, parallel absorbing electrodes. The model representation has been extended to describe the case of a PRDT experiment in order to develop a more accurate method of determining mobilities from the observed transient waveforms.

In Section 2 the number density distribution of a swarm of electrons drifting and diffusing between two absorbing electrodes is derived from the distribution for electrons travelling in free space. The effects of the cathode and anode on the behaviour of such a swarm are first considered separately and are then combined.

In Section 3 a theoretical description of a PRDT transient is developed from the number density distribution derived in Section 2. The influence of diffusion on the transient waveform observed in this type of experiment is discussed and a method of analysis proposed. Sections 4 and 5 discuss the importance of errors due to diffusive effects in determining drift velocities from the transient waveforms.

2. Travelling Group of Electrons

Number Density Distribution

The number density distribution of an isolated group of n_0' electrons drifting and diffusing in a gas under the influence of a uniform electric field may be represented by (see e.g. Huxley and Crompton 1974)

$$n(x,y,z,t) = \frac{n_0'}{(4\pi D_T t)(4\pi D_L t)^{\frac{1}{2}}} \exp\left(-\frac{x^2+y^2}{4D_T t}\right) \exp\left(-\frac{(z-v_{dr}t)^2}{4D_L t}\right), \qquad (1)$$

where the electric field is taken to be in the z direction, D_L is the longitudinal coefficient of diffusion, D_T is the lateral coefficient of diffusion and v_{dr} is the drift velocity. At time $t = 0$ the electron group is concentrated in an infinitesimal volume at the coordinate origin. In using this equation it is assumed that the electrons are released in the gas with the steady state energy distribution.

When the group extends uniformly to infinity in the xy plane this equation reduces to

$$n(z,t) = \frac{n_0}{(4\pi D_L t)^{\frac{1}{2}}} \exp\left(-\frac{(z-v_{dr}t)^2}{4D_L t}\right), \qquad (2)$$

where n_0 is the number of electrons per unit area in the initial plane δ-function distribution.

The number density distribution for electrons drifting and diffusing in a uniform electric field may be disturbed by the presence of absorbing electrodes. Here equation (2) is modified to describe the case of a group of electrons travelling between two infinite, parallel, plane electrodes.

Electrons are lost from the group by back diffusion to the cathode thus shifting the position of the maximum of the electron density (hereafter called the peak position) further away from the cathode. To represent the effect of the cathode on the electron density within the group an image term may be added to the expression for $n(z,t)$ (Lowke 1962) such that the number density is zero at the cathode.

To account for the effect of an absorbing anode two further image terms are added, one arising from the original term (Lowke 1962) and the other from the cathode image term. If the cathode is situated at $z = 0$, the anode at $z = h$, and the group is released at z_0 at time t_0, the expression for the number density distribution becomes

$$n(z,z_0,t-t_0) = \frac{n_0}{\{4\pi D_L(t-t_0)\}^{\frac{1}{2}}} \left\{\exp\left(-\frac{\{z-z_0-v_{dr}(t-t_0)\}^2}{4D_L(t-t_0)}\right)\right.$$

$$\left. -\exp\left(-\frac{z_0 v_{dr}}{D_L}\right) \exp\left(-\frac{\{z+z_0-v_{dr}(t-t_0)\}^2}{4D_L(t-t_0)}\right)\right.$$

$$-\exp\left(\frac{(h-z_0)v_{dr}}{D_L}\right)\exp\left(-\frac{\{z-2h+z_0-v_{dr}(t-t_0)\}^2}{4D_L(t-t_0)}\right)$$

$$+\exp\left(\frac{hv_{dr}}{D_L}\right)\exp\left(-\frac{\{z-2h-z_0-v_{dr}(t-t_0)\}^2}{4D_L(t-t_0)}\right)\Bigg\}. \qquad (3)$$

This expression satisfies the anode boundary condition $n(h, z_0, t-t_0) = 0$. The anode correction terms perturb the cathode boundary condition $n(0, z_0, t-t_0) = 0$ but the effect is usually negligible. All the correction terms become negligible at points far removed from the electrodes.

Effect of Cathode

To consider the effect of the cathode we ignore the anode correction terms (i.e. the third and fourth lines) in the modified expression (3) for the number density distribution function and compare the development of a cathode affected electron group with a group released in free space at the same time and position.

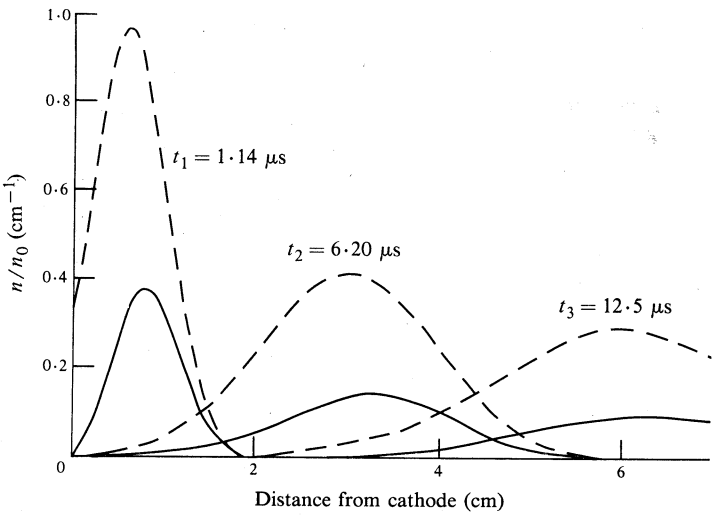

Fig. 1. Normalized electron density distribution viewed at three times for an electron group released 0·06 cm from the cathode in the absence of an anode. The drift velocity is $v_{dr} = 4{\cdot}74 \times 10^5$ cm s^{-1} and $D_L/v_{dr} = 0{\cdot}16$ cm. The solid curves are for a group affected by the cathode while the dashed curves are for a group travelling in free space. At time t_1 the pulse is losing electrons to the cathode but this loss has ceased by time t_2.

The curves labelled t_1 to t_3 in Fig. 1 show the effect of the cathode on an electron group drifting in nitrogen at a pressure of 5 Torr (1 Torr ≡ 133 Pa) with $E/N = 1{\cdot}2$ Td (1 Td ≡ 10^{-17} V cm^2), an example considered by Lowke (1962). The group was released 0·06 cm from the cathode at time $t = 0$, and v_{dr} and D_L are taken to be $4{\cdot}74 \times 10^5$ cm s^{-1} and $7{\cdot}46 \times 10^4$ cm^2 s^{-1} respectively ($D_L/v_{dr} = 0{\cdot}16$ cm). The solid curves represent the distributions for the cathode affected electron group while the dashed curves are for the group travelling in free space. At time t_1 electrons are being lost to the cathode by back diffusion, the effect of this loss being to displace

the position of maximum electron density further away from the cathode. At time t_2, back diffusion has effectively ceased and diffusion within the group has given it a gaussian shape. The peak is now travelling with the velocity v_{dr}, but its position is displaced relative to the group travelling in free space.

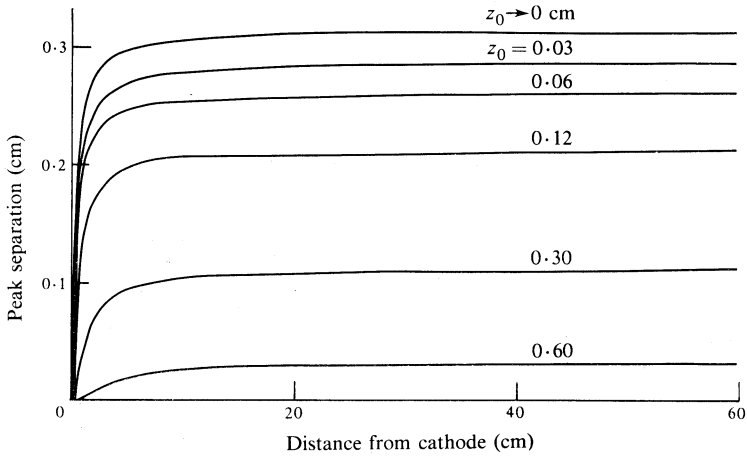

Fig. 2. Difference in peak position between the cathode affected and free space electron groups as a function of distance from the cathode for six release positions ($D_L/v_{dr} = 0{\cdot}16$ cm as in Fig. 1).

At a given time after the release of the group the difference in peak position between the cathode affected group and the group released in free space depends on the release position z_0. Fig. 2 shows this difference plotted as a function of distance from the cathode for various release positions, again for the case $D_L/v_{dr} = 0{\cdot}16$ cm. The closer the release position is to the cathode the greater the number of electrons lost from the trailing edge of the group by back diffusion, and hence the greater the shift in the group peak position, as can be seen from the figure.

Effect of Anode

The effect of the anode can be seen by ignoring the cathode correction terms in equation (3) (i.e. the second and fourth lines) and considering the first term and its corresponding anode image term. Again it is useful to compare the electron distribution with the distribution for a group travelling in free space.

Fig. 3 shows the development of a pulse released 3·6 cm from the anode for the condition $D_L/v_{dr} = 0{\cdot}16$ cm. The solid curves show the anode modified distribution while the dashed curve shows the distribution for a pulse travelling in free space. The electron groups are shown at three times after release.

The separation between the two peak positions for various release positions has been plotted in Fig. 4 against the distance of the peak from the anode for the group travelling in free space. Note that for an electron group released far from the anode the curve becomes approximately linear for small values of the ordinate (for example, corresponding to the peak being within 0·3 cm of the anode for a pulse released 6 cm from the anode). This indicates that the peak of the group affected by diffusion to the anode attains a stable position (although its magnitude decreases with time).

Similarly the peak of a pulse released close to the anode eventually attains a stable position although this position may be further from the anode than the release position. Note also that since the leading edge of the pulse loses electrons to the anode for a longer period of time the further away it is released, the separation increases as the distance between the release position and the anode increases.

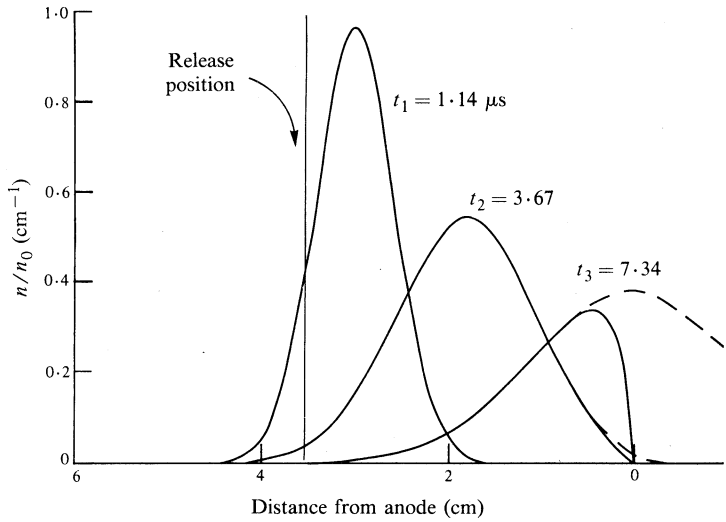

Fig. 3. Normalized electron density distribution viewed at three times for an electron group released 3·6 cm from the anode with $D_L/v_{dr} = 0{\cdot}16$ cm and $v_{dr} = 4{\cdot}74 \times 10^5$ cm s^{-1}. The solid curves represent the anode affected distributions and the dashed curve represents the free space distribution.

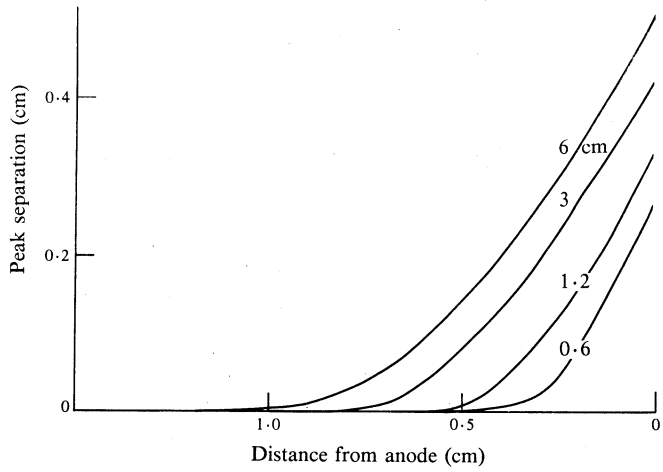

Fig. 4. Difference in peak position between the anode affected and free space groups as a function of free space peak position for groups released 0·6, 1·2, 3 and 6 cm from the anode ($D_L/v_{dr} = 0{\cdot}16$ cm).

Combined Effects of Cathode and Anode

We now consider the combined effect of the two electrodes and thus use all four terms in equation (3) to describe the electron density distribution. In the discussion we will take the electrode separation h to be 6 cm. We will again take $D_L/v_{dr} = 0{\cdot}16$ cm and consider the case of an electron group released $0{\cdot}06$ cm from the cathode (i.e. $z_0 = 0{\cdot}01h$) at time $t = 0$. The development of the pulse with time is shown in Fig. 5. As in Fig. 1 the solid curves represent the distributions for the electrode affected electron group while the dashed curves represent the distributions for the group travelling in free space. At time t_1, electrons are being lost to the cathode by back diffusion, but by time t_2 back diffusion to the cathode has ceased and the group has acquired a gaussian form travelling with the drift velocity (as was the case when there was no anode—see Fig. 1). The electrode affected group then leads the free space group. However, at time t_3 loss of electrons to the anode has begun and the position of the peak now lags behind the corresponding maximum for a group travelling in free space.

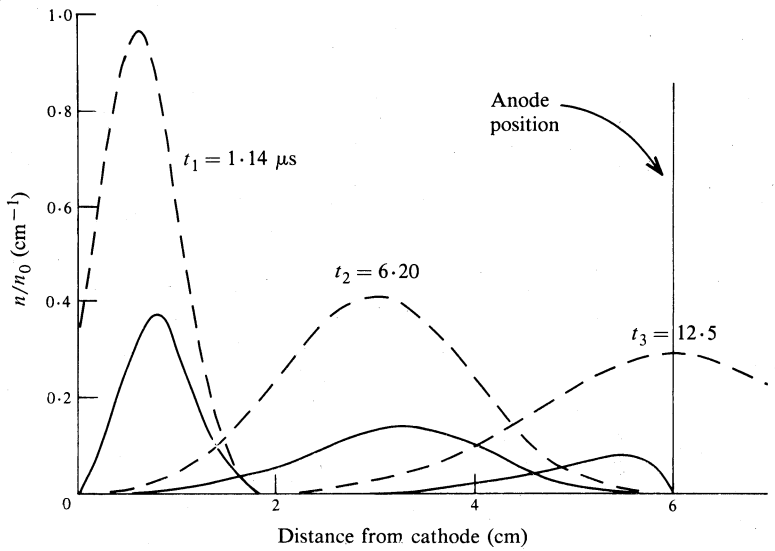

Fig. 5. Normalized electron density distribution viewed at three times for an electron group released at $z_0 = 0{\cdot}06$ cm with $D_L/v_{dr} = 0{\cdot}16$ cm, $v_{dr} = 4{\cdot}74 \times 10^5$ cm s^{-1} and $h = 6$ cm. The solid curves are for a group affected by electrodes while the dashed curves are for a free space group. At time t_1, the group shows the effects of loss of electrons to the cathode. Neither electrode is influencing the electron group at time t_2, but by time t_3 loss of electrons to the anode has begun to modify the profile of the group.

3. Description of a PRDT Experiment

Development of Description

The time dependent current density $i(t)$ in a PRDT due to a pulse of ionizing radiation is given by

$$i(t) = N(t)\, e v_{dr}, \tag{4}$$

where e is the electron charge and $N(t)$ is the total number of electrons in a column of unit area in the gap. An expression for $N(t)$ due to a pulse which *instantaneously* and uniformly illuminates the gap can be obtained by integrating expression (3) for the number density distribution over all z_0 ($0 \leqslant z_0 \leqslant h$) and z ($0 \leqslant z \leqslant h$). For an irradiating pulse of duration τ a third integration over release times t_0 is needed.

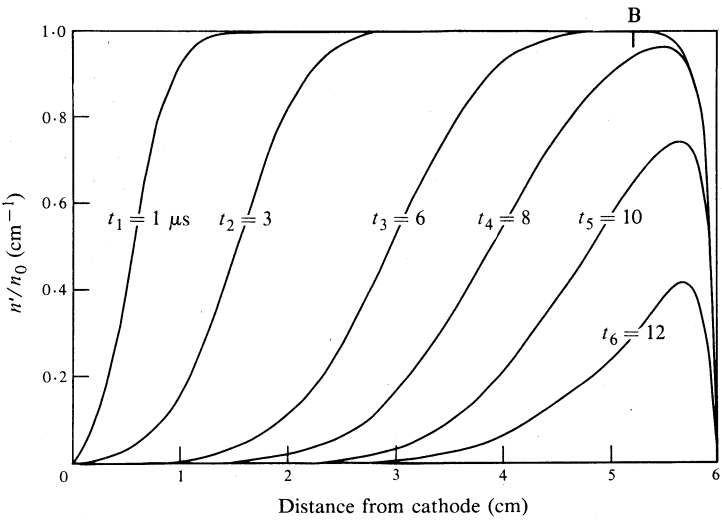

Fig. 6. Normalized number density distribution in the gap for $D_L/v_{dr} = 0{\cdot}11$ cm, $h = 6$ cm, uniform instantaneous irradiation and six observation times after irradiation.

Integrating the expression for the number density distribution over all release points z_0 gives the number density profile at a given time t due to uniform, instantaneous irradiation at t_0 ($t > t_0$). Thus we have

$$n'(z, t-t_0) = \int_0^h n(z, z_0, t-t_0)\, dz_0 . \tag{5}$$

Fig. 6 shows the distribution of n' in the gap at a series of times t_1 to t_6 after the initial time of irradiation t_0 for $D_L/v_{dr} = 0{\cdot}11$ cm and $h = 6$ cm. As the electron swarm drifts away from the cathode the loss of electrons to the cathode by back diffusion decreases until it effectively stops. The trailing edge of the swarm broadens due to diffusion as it approaches the anode but for most of the time loss of electrons to the cathode does not affect the total loss rate. Near the anode the density profile quickly attains a steady state shape which it keeps until the trailing edge, broadened by diffusion, reaches the point B in Fig. 6.

Integrating $n'(z, t-t_0)$ over all z gives the total number of electrons N in a column of unit area at a given time t for instantaneous irradiation ($\tau = 0$) at time t_0:

$$N_{\tau=0}(t-t_0) = \int_0^h n'(z, t-t_0)\, dz , \tag{6}$$

and plots of $N_{\tau=0}$ against time give curves of the form shown in Fig. 7. The curve shows an initial sharp decrease, a linear decay region, and a tail at longer times. The initial sharp decrease results from diffusion to the electrodes in the period before

back diffusion has ceased and the anode edge of the swarm has reached a steady shape. The linear decay region of the curve occurs after these conditions have been met. During the period of linear decay the loss of electrons from the gap occurs at a rate which is directly proportional to the drift velocity v_{dr}. The tail occurs when the trailing edge of the swarm reaches the vicinity of the anode and modifies the electron density distribution in that region.

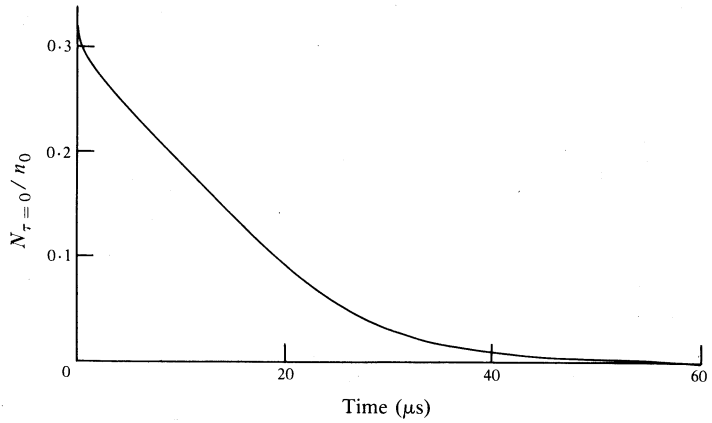

Fig. 7. Total number of electrons $N_{\tau=0}$ in a column of unit area normalized with respect to the number of electrons per unit area in a plane δ-function distribution at time $t = 0$: $v_{dr} = 1\times10^4\,\mathrm{cm\,s^{-1}}$, $D_L = 160\,\mathrm{cm^2\,s^{-1}}$ and $h = 0{\cdot}32\,\mathrm{cm}$.

To extend the case of instantaneous ionizing irradiation to that of an irradiating pulse of uniform intensity of duration τ, it is assumed that the pulse is equivalent to a number of identical instantaneous pulses occurring successively such that the time intervals between pulses are equal and infinitesimally short. Hence, the total number of electrons in the gap due to a uniform irradiating pulse of duration τ is

$$N_\tau(t) = \int_0^\tau N_{\tau=0}(t-t_0)\,\mathrm{d}t_0\,. \tag{7}$$

The current flowing in the gap due to the pulse is proportional to $N_\tau(t)$ (as in equation 4). Consequently, $N_\tau(t)$ has the form of the experimentally measured transient waveform which is represented schematically in Fig. 8.

Where there is no diffusion ($D_L = 0$) it is possible to obtain analytical expressions for the transient waveforms (Wada and Freeman 1979). For an interelectrode spacing h, we have

$$N_\tau(t) = n_0 ht(1-t/2t_d) \qquad 0 \leqslant t \leqslant \tau, \tag{8a}$$

$$= n_0 h\tau(t_d+\tfrac{1}{2}\tau-t)/t_d \qquad \tau < t \leqslant t_d, \tag{8b}$$

$$= n_0 h(t_d+\tau-t)^2/2t_d \qquad t_d < t < t_d+\tau, \tag{8c}$$

$$= 0 \qquad t \geqslant t_d+\tau, \tag{8d}$$

where $t_d = h/v_{dr}$ is the time taken for an electron group drifting in free space to travel the distance h. The increase in $N_\tau(t)$ at times $t \leqslant \tau$ is not linear since electrons are being removed by drift to the anode while the irradiating pulse is still present. The

waveform peaks at time τ when the irradiating pulse is removed and then decays linearly until time t_d when the electrons created at $t = 0$ have all been lost from the gap. Thereafter the rate of electron loss decreases, giving a tail to the waveform. As before, this nonlinearity is due to the fact that electrons were being lost while the irradiating pulse was present.

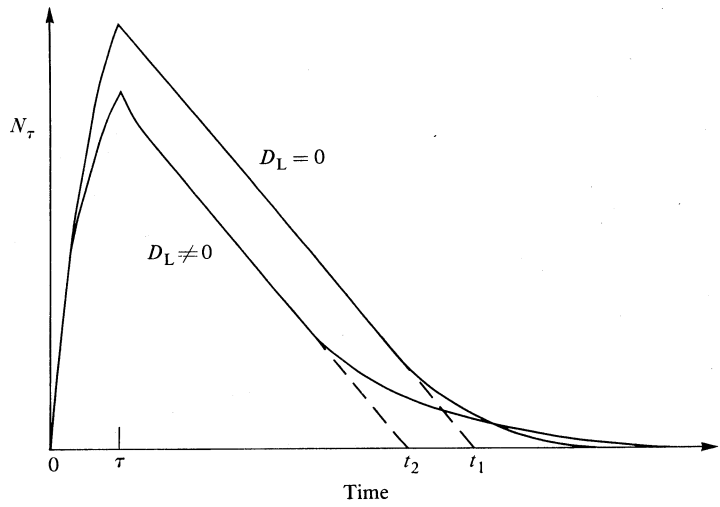

Fig. 8. Schematic diagram of the total number of electrons N_τ in a column of unit area in the gap as a function of time when the gap is irradiated for a time interval τ. Two cases are illustrated, one with and one without diffusion. The experimentally observed transient waveform takes the same form as the curve for N_τ. The dashed lines are the linear regions of the decay curves extrapolated to the time axis to give intercepts t_1 and t_2 for the cases $D_L = 0$ and $D_L \neq 0$ respectively.

The curve for $N_\tau(t)$ is modified by the presence of diffusion ($D_L \neq 0$) for two reasons: more electrons are lost in the interval 0 to τ as there is now a reduction in $N_\tau(t)$ due to diffusion to both electrodes, as well as drift to the anode, and the reduction due to back diffusion to the cathode continues for a short time after time τ. Consequently, the peak value of N_τ is lower than in the diffusion-free case, and only at some time $t > \tau$ does the curve become linear and parallel to the previous curve (see Fig. 8). Even when diffusion loss to the cathode ceases, the trailing edge of the swarm continues to broaden by diffusion and hence some electrons are resident in the gap for a longer period of time than in the diffusion-free case. As a consequence of the enhanced initial loss the transient breaks away earlier from its linear form, while the spreading of the trailing edge of the drifting swarm results in an extension of the tail at longer times.

Numerical Calculations

The three integrations needed to develop the description of the PRDT transient from the analytic expression (3) for the electron number density in an infinite xy plane were performed numerically on a UNIVAC 1100/82 computer.

The first integration (over all z_0) was performed using a method described by Patterson (1968) based on the optimum addition of points to the Gauss quadrature formulae. As expression (3) is the sum of four error functions, the results of this integration could be checked for convergence by comparing them with values derived from tables of integrals.

The second integration (over all z) was performed using Simpson's rule. The results were found to converge rapidly.

The final integration (over the irradiation time τ) was performed using the method of Gill and Miller (1972) based on third order finite-difference formulae. This third integration was checked by numerically integrating the analytic expression obtained for $N_{\tau=0}(t)$ in the absence of diffusion ($D_L = 0$) and comparing the results with the values given by the analytic expression for $N_\tau(t)$ (equations 8).

Analysis of Transient Waveform

In the absence of diffusion, electron mobilities may be inferred from the transient waveforms recorded in PRDT experiments using a method based on the analytic expressions (8) describing the waveforms. The linear decay section of the waveform for the $D_L = 0$ case (see Fig. 8) may be extrapolated to the time axis to obtain a time t_1. The time t_1 is related to the time t_d that the peak of an electron swarm drifting in free space would take to travel a distance h by

$$t_d = t_1 - \tfrac{1}{2}\tau, \tag{9}$$

and the mobility μ is then given by

$$\mu = v_{dr}/E = h^2/Vt_d, \tag{10}$$

where V is the potential difference between the electrodes (Wada and Freeman 1979).

When analysing their transient waveforms Wada and Freeman obtained a time t_1' which they used in equations (9) and (10). They accounted for the effect of diffusion (under conditions where the electrons are in thermal equilibrium with the gas) by assuming the effective length of the drift tube to be

$$h\{1+(2kT/eV)^{\frac{1}{2}}\}, \tag{11}$$

where T is the gas temperature and k is Boltzmann's constant. The term $h(2kT/eV)^{\frac{1}{2}} = (2Dt_d)^{\frac{1}{2}}$ is the r.m.s. displacement $\langle z^2\rangle^{\frac{1}{2}}$ of thermal electrons after a time t_d if they are released at a plane and diffuse in one dimension, the diffusion coefficient ($D_L = D$) being given by the Nernst–Townsend relation

$$D = (kT/e)\mu. \tag{12}$$

In making this correction it is assumed that the effect of diffusion on the electrons in the trailing edge of the swarm as it moves across the gap can be accounted for by increasing the drift distance by $\langle z^2\rangle^{\frac{1}{2}}$. When the expression for the drift distance is modified in this way equation (10) becomes

$$\mu = h^2\{1+(2kT/eV)^{\frac{1}{2}}\}/Vt_d. \tag{13}$$

The present work shows that an iterative technique should be used to determine the drift velocity from the transient waveform. Extending the linear decay section of the waveform to the time axis gives an intercept t_2 which can be used to calculate

an initial value for the drift velocity. Using this first estimate of v_{dr} and the corresponding value of D calculated from the Nernst–Townsend relation, we can predict the transient waveform with the procedure described in this section. This transient may then be analysed in the same manner as the experimental waveform to obtain a time intercept t_2'. The difference between the times t_2 and t_2' indicates the error in the first order estimate of the drift velocity. The value of the drift velocity is decreased accordingly and the simulation procedure repeated. If necessary, these steps can be repeated until a converged value for the drift velocity is obtained. The theoretical waveform obtained using this converged drift velocity should, of course, give a value for the time axis intercept which equals the experimental result.

4. Discussion

To illustrate the size of the diffusion correction when diffusion is significant, we consider a case already in the literature. Wada and Freeman (1981) measured the drift velocity of electrons in nitrogen over a wide temperature range, using for some of their experiments a fixed gas number density of $5{\cdot}7\times10^{19}$ mol cm^{-3} in an apparatus of drift distance 0·32 cm. When $E/N = 2{\cdot}7\times10^{-3}$ Td the drift velocity was reported to be approximately 10^4 cm s^{-1} at $T = 295$ K and 3×10^4 cm s^{-1} at $T = 79$ K. We have made calculations for their experimental drift distance of 0·32 cm and for a larger value of 1·60 cm which was chosen arbitrarily to demonstrate the effect of significantly increasing the drift length. The value of the diffusion coefficient at the two temperatures was calculated using the Nernst–Townsend relation. Table 1 shows the diffusion corrections predicted by the present analysis.

Table 1. Diffusion corrections determined from present analysis

T (K)	h (cm)	v_{dr} (cm s^{-1})	D (cm^2 s^{-1})	Correction for diffusion (%)	$4kT/eV$ (%)
295	0·32	1×10^4	160	11	10
295	1·60	1×10^4	160	2	2
79	0·32	3×10^4	133	2·8	2·8
79	1·60	3×10^4	133	0·44	0·56

As can be seen from the table, the diffusion corrections are smallest for the larger drift distance and the lower temperature. However, in all cases considered, diffusion corrections are significant. The data in the last column of the table show that a good estimate of the correction factor is $4kT/eV$, that is, the factor is approximately $2(D/\mu)/V$.

The detailed analysis presented in this paper enables us to make the following points:

(i) If loss of electrons by diffusion to the electrodes could be neglected, extrapolation of the linear section of the transient waveform to the time axis would lead to a value of t_d which could be used directly in equation (10) to give the mobility, that is, no further correction to the value of the mobility would be required. Diffusion in the trailing edge of the swarm as it crosses the gap extends the tail of the transient waveform but does not introduce any error into the mobility calculated in this way.

(ii) To analyse the transient waveforms correctly the effect of diffusion loss to the electrodes must be considered. The true electron mobility is smaller than that

determined from the transient waveform by an extrapolation technique because of the loss of electrons to both electrodes by diffusion. In the case of the cathode this loss occurs only while there is a significant electron density adjacent to it (that is, during the initial period of ionization and immediately following it), while there is a steady loss of electrons to the anode for most of the time $\tau + t_d$. As a consequence, electrons are swept from the gap more rapidly than would be the case if the only loss mechanism was drift* and the apparent drift velocity is therefore larger than the true drift velocity.

5. Conclusions

In the present work the effect of diffusion on the transient waveforms observed in PRDT experiments has been studied. It has been shown that loss of electrons by diffusion to the electrodes is the most important factor to be accounted for in analysing the transient waveforms.

Our analysis is based on the assumption that the electron density is zero at the cathode and anode boundaries and that the commonly used first order equation of continuity for the electron number density can be applied (see e.g. Huxley and Crompton 1974). This simple approach involves a number of approximations, the most significant being the use of spatially uniform and time independent transport coefficients throughout the whole drift space, it being assumed that the electrons are released with the steady state energy distribution. However, similar analyses have proved remarkably successful in predicting the correction factors that must be applied to allow for diffusion when calculating drift velocities from the transit times measured in other types of drift tube experiments (see e.g. Elford 1972). It therefore seems unlikely that a more detailed analysis based on a more exact treatment of the role of the boundaries (Braglia and Lowke 1979) would affect the conclusions of this paper.

Acknowledgment

I wish to thank Dr R. W. Crompton for suggesting this project and for his help, encouragement and guidance throughout this work and, in particular, for his comments and criticisms on the manuscript.

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Manuscript received 13 July, accepted 8 September 1981

* Once the loss of electrons by back diffusion to the cathode ceases, the further modification to the trailing edge of the swarm by diffusion has no influence on the value of t_d determined from the experimental waveform.