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EFFECT OF SPACE CHARGE UPON TRANSPORT OF CHARGE CARRIERS

A.L. Ward

15 January 1964

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EFFECT OF SPACE CHARGE
UPON TRANSPORT OF CHARGE CARRIERS

A. L. Ward

FOR THE COMMANDER:
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ABSTRACT

Numerical machine calculations have been made that determine the effect of space charge, composed of mobile charge carriers, on the drift and diffusion of those carriers in an electric field. An apparent diffusion of carriers arises from the difference equations used to solve the transport problem, even though no diffusion term is included in the transport equations. This calculated diffusion is shown to be exact in the absence of space charge and in the limit of infinitely small calculation intervals. Numerical results illustrating the effect of space charge upon apparent diffusion coefficients and drift velocities are given for a fictitious gas. Calculations show good agreement with experimental data taken in two other laboratories to measure attachment coefficients in gases. Exploratory calculations have indicated the usefulness of this model for calculations in solid-state transport.

1. INTRODUCTION

One method of measuring the mobility of electrons in a gas subject to an applied field utilizes short pulses of ultraviolet light incident upon the cathode. Successive pulses of electrons leave the cathode as a result of photons created mainly near the anode in the discharge and the photoelectric effect at the cathode. The mobility then may be deduced from the time between successive current peaks. In the course of calculations simulating these experimental conditions, it was found that the time between calculated current peaks was considerably greater than the electron transit time obtained directly from the mobility used. In seeking the explanation of this unexpected result, it was discovered that the difference equations used in the calculations introduced a "diffusion" of charge carriers down the steep concentration gradient that is created in the gap. This apparent diffusion appeared despite the fact that the diffusion terms had been omitted in the formulation of the problem.

This report will show that, in the absence of ionization and of space charge, the difference equations that were used actually give a correct solution of the diffusion equation in the limit of infinitely small calculation intervals. Illustrative calculations will show the effect of space charge due to injection of a large pulse of carriers upon the apparent mobility and diffusion of the pulse. Comparisons with experimental measurements used to determine attachment coefficients in gases show the usefulness of the calculations. It is suggested that the calculation technique will also be of value in studying transport properties in the solid state.

2. MATHEMATICAL TECHNIQUES

The one-dimensional continuity equations governing the transport of two types of carriers in a material are
\[ \frac{\partial \rho_+}{\partial t} = -\frac{\partial J_+}{\partial x} \quad (1) \]

and
\[ \frac{\partial \rho_-}{\partial t} = \frac{\partial J_-}{\partial x} \quad (2) \]

where
\[ J_- = \rho_- \mu_- E + eD_- \frac{\partial n_-}{\partial x} \quad (3) \]

and
\[ J_+ = \rho_+ \mu_+ E - eD_+ \frac{\partial n_+}{\partial x} \quad (4) \]

In these equations \( J \) and \( \rho = n e \) are the current density and the charge density of the carriers, respectively, \( \mu \) is the mobility, and \( D \) the diffusion coefficient of the charge carriers, and \( E \) is the electric field intensity. The negative and positive sign subscripts refer to carriers of indicated sign of charge. In the absence of space charge, the well known solution to these equations for an injected pulse of \( N_0 \) carriers per square centimeter at the appropriate electrode \((x = 0); t = 0\) is

\[ n(x, t) = \frac{N_0}{\sqrt{4\pi Dt}} \exp \left( -\frac{(x-\mu Et)^2}{4Dt} \right) \quad (5) \]

The formulation used to compute the temporal growth of current in a gas has been presented previously (ref 1). Detailed consideration has also been given to the errors, the stability, and convergence properties of the difference equations used for machine computation (ref 2). In brief, (1) and (2) with added ionization terms but neglecting diffusion are solved together with Poisson's equation

\[ \frac{dE}{dx} = \frac{e}{\epsilon_0} (n_+ - n_-) \quad (6) \]

and suitable initial and boundary conditions.

Omitting the ionization terms, the difference equations used for the numerical computations are

\[ \frac{n_-(x_k, t_n + \Delta t) - n_-(x_k, t_n)}{\Delta t} = -v_- \left[ \frac{n_-(x_k, t_n) - n_-(x_k - \Delta x, t_n)}{\Delta x} \right] \quad (7) \]

and

\[ \frac{n_+(x_k, t_n + \Delta t) - n_+(x_k, t_n)}{\Delta t} = v_+ \left[ \frac{n_+(x_k, t_n) - n_+(x_k + \Delta x, t_n)}{\Delta x} \right] \quad (8) \]

where
\[ x_k = k\Delta x; \quad k = 0, 1, 2, \ldots, M \]
\[ t_n = n\Delta t; \quad n = 0, 1, 2, 3, \ldots \]
Here the number of calculation intervals across the gap of distance \( d \) is \( M \), i.e., \( d = M\Delta x \), and the drift velocities are given by equations of the form \( v = \mu \dot{E} \). The difference equations were chosen unsymmetrical with respect to \( x \) for reasons of stability (ref. 2). The time interval is chosen by the use of the input parameter, \( F \), and the equation

\[
\Delta t = F \frac{\Delta x}{\max \{v_-(x,t), v_+(x,t)\}}
\]

where stability conditions require \( F \) to be less than unity and \( v_- \) and \( v_+ \) to be non-negative (ref. 2). We will assume the usual case that \( v_+ > v_- \) and set \( p = F, q = 1 - F, p^* = F^* = \mu_+ F/\mu_- \) and \( q^* = 1 - p^* \). Then in the absence of space charge, (7) and (8) becomes, using (9)

\[
n_-(k, n + 1) = p n_-(k - 1, n) + q n_-(k, n)
\]

\[
n_+(k, n + 1) = p^* n_+(k + 1, n) + q^* n_+(k, n)
\]

Each equation describes the intact movement of the distribution through a distance given by the fraction, \( p \) or \( p^* \), of one distance grid point in the appropriate direction for each time step. Owing to the similarity of these two equations, only one needs to be considered, and (10) is chosen.

Before the rigorous mathematical derivation, it will be helpful to go through the actual steps the computer would use for a simple problem. The initial condition is illustrated in the first diagram in figure 1, labeled \( n = 0 \), corresponding to \( t = 0 \). The density \( N(k, n) \) is unity for \( k = 1 \) and zero elsewhere, as shown by the solid line. For \( F \) (or \( p \)) = 1/2, this triangular distribution moves intact one-half grid space, as shown by the dashed curve. However, the computer only records data at each grid point, hence the density is 1/2 at grid points \( k = -1 \) and \( k = 2 \) and zero elsewhere. This trapezoid is then the initial condition for the second time step, shown in the second diagram, labeled \( n = 1 \). This process is repeated for each time step. The fit to the normal distribution becomes better each time step, as shown by the lower diagrams where the normal distributions are shown as dashed curves.

The mathematical derivation may now be continued. For initial and boundary conditions, let

\[
n_-(0, 0) = N'_0, \quad n_-(1, n) = 0, \quad \text{and} \quad n_-(k = 0, 0) = 0
\]

then

\[
n_-(k, n) = N'_0 \frac{n!}{k! (n-k)!} \frac{p}{q}^k \frac{n-k}{q} = b(k; n, p) N'_0
\]
Figure 1: Graphical representation of apparent diffusion due to finite difference equation.
where \( b(k; n, p) \) is the binomial distribution (ref 3). Now, according to the De Moivre-Laplace limit theorem

\[
\lim_{n, k \to -} b(k; n, p) = \frac{1}{\sqrt{2\pi npq}} \exp\left(-\frac{(k - np)^2}{2npq}\right)
\]

(13)

providing

\[
\lim_{n, k \to -} \frac{x_k}{n}^3 = 0, \quad \text{where} \quad x_k = \frac{k - np}{n}
\]

and \( h^3 = npq \).

The right-hand member of (13) is recognized as the normal distribution. Comparison of (12) with (5) shows that

\[
npq = 2Dt/(\Delta x)^2 \quad \text{and} \quad N = N'O \Delta x
\]

(14)

Changing back to the original notation, recalling that

\[
n = t/\Delta t, \quad k = x/\Delta x, \quad \Delta x = d/M, \quad p = F, \quad Q = 1 - F
\]

and

\[
\Delta t = Fd/M
\]

we find

\[
D_+ = (1 - F) v_d^2 / 2M
\]

This may be expressed also in terms of the gap voltage, \( V = Ed \), as

\[
\frac{D_+}{\mu_+} = \frac{(1 - F) V}{2M} \quad \text{and} \quad \frac{D_+}{\mu_-} = \frac{(1 - \mu_+ F/\mu_-) V}{2M}
\]

(15)

It is seen that the diffusion coefficients for the negative and positive charge carriers cannot be adjusted independently to fit experimental values. For gases where \( \mu_+ \ll \mu_- \), \( D_+ / \mu_+ \) calculated from (15) is much larger than \( D_- / \mu_- \), completely opposed to experimental observations. However, the computer program has an option to omit electron transport properties (ref 2), (1) then being replaced by the stationary ionization condition. In this case, the time step is determined solely by \( v(x, t) \) in (9). This allows larger time steps, and the positive ion diffusion coefficient is determined by \( F \) instead of \( F^* \), as is the case if \( \mu_+ > \mu_- \).

The limit on convergence for (13) is essentially that, \( F \) cannot be close to unity (the pulse being transported without change of shape if \( F = 1 \)) or to zero (no transport). A comparison of the maximum amplitude obtained by setting \( p = q = 1/2 \) in (12) with that for the normal
distribution shows that the approximate error is 50 $n^{-1}$ percent, where $n$ is the number of time calculations.

It is of course preferable to choose $F \approx 1/2$ to insure symmetry of diffusion in $x$. However, certain combinations of voltages, mobilities, and diffusion constants lead to values of $M$ too small for accuracy of calculations or too large to keep the computer time reasonable. Values of $M$ from 12 to 100 and of $F$ from 0.01 to 0.99 have been used thus far. The skewness of the binomial distribution is given by $(q-p)/(npq)^{1/2}$, which in the present notation becomes $(1-2F)/(nF(1-F))^{1/2}$, showing that the skewness decreases inversely as the square root of $n$, the number of calculation time steps. The possibility of simulating the effect of back diffusion to an electrode by using $F = 1/2$ is also suggested.

3. **ILLUSTRATIVE EXAMPLES FOR A FICTITIOUS GAS**

A number of calculations have been made to determine the effect of space charge upon the apparent mobility and diffusion of a fictitious gas. This fictitious gas has $\mu_p = 1 \times 10^6$ and $\mu_p = 5 \times 10^3$ cm$^2$/torr/sec. Calculations will be reported for a 1-cm gap, a gas pressure of 10 torr and an applied potential of 100 v. Values of $F$ and $M$, and therefore of $D = (1-F) \mu V/2M$, varied widely, $D_0$ being the diffusion coefficient in the absence of space charge as indicated by (15). Figure 2 shows the result of calculations for $M = 20$, $F = 0.5$, $n_{(0,0)} = 10^9$ cm$^{-3}$ ($N_0 = 5 \times 10^4$ cm$^{-3}$), and no ions in the gap. According to (15), this calculation pertains to 1.25-v electrons, and the number of charge carriers produces an initial field distortion, $\Delta E/E_o = [E_{(max)} - E_{(min)}]/E_{(ave)}$, of 0.09 percent. The fit to (5) using $D_0$ from (15) is excellent after only a few time steps. The pronounced effect of space charge distortion is shown in figure 3 for the same calculation parameters, but with $n_{(0,0)} = 10^9$ cm$^{-3}$, the initial field distortion then being 90.5 percent. An apparent diffusion coefficient, $D^*$, defined from $D^* = r^2/4t$, where $r$ is half the pulse width at $1/e$ of its maximum value, is more than eight times greater than $D_0$. The time for the maximum collector current ($d = 1$) decreases roughly linearly with $n_{(0,0)}$. For the illustrative example, the resulting apparent percentage increase in mobility is about $1.5 \times 10^{-8}$ $n_{(0,0)}$ percent. This is illustrated in figure 4 for various initial pulse sizes. The resulting field distortion for the example of figure 3 is shown in figure 5. The initial densities that can be used are limited since the computer is programmed to halt calculations if negative fields are calculated.

* The contrary increase of time between current peaks, noted in the introduction for calculations including ionization, results from the steep, unidirectional concentration gradient of electrons present after the first gap traversal.
Figure 2. Transport of an electron pulse in fictitious gas across a gap. Points indicate computer results, while solid lines are plotted from equation (5), using equation (15) to determine $D_0$. Space charge effect is negligible. The times in nanoseconds are indicated on each curve.
Figure 3. Effect of space charge upon transport in fictitious gas. Conditions are identical with those of figure 2 except injected pulse is 1000 times larger. Parameter is time in nanoseconds.
Figure 4. Collection current as a function of time for various initial pulse sizes. The parameter for the various curves is the value of \( N_0 \).
Figure 5. Field distortion across the gap for the example of figure 3. The parameter is again time in nanoseconds.
The fractional apparent change of diffusion coefficient, $(D^*-D)/D$, seems to be a function of the fractional field distortion for those calculations made so far. The functional relationship appears to be approximately

$$(D^*-D)/D_0 = A(D, \mu) \left(\Delta E/E_0\right)^{1.25}$$

where $A(D, \mu)$ has varied from about 2 to 20 for each fraction expressed in percentage. Two examples illustrating this variation are shown in figure 6.

Runs made with $n(0,0) = n_{(0,0)}$ at $n_{(0,0)}$ values used above show considerably different field distortions but the changes of the apparent diffusion coefficients are generally reduced only about 10 percent at most.

4. ELECTRON-ATTACHING GASES

Under certain experimental conditions, the effect of diffusion and/or space charge may be important in determining attachment coefficients, $\alpha$, in electron-attaching gases. Normally, these conditions are avoided as far as possible (ref 4).

A number of calculations have been made to compare with unpublished measurements of A. V. Phelps of the Westinghouse Research Laboratories. The experimental method has been published (ref 4). A pulse of electrons forms an initial distribution of negative ions that drift across a gap under a constant applied field and are collected to give a temporal current pulse. The gas used was 3 percent O$_2$ in He. The experimental conditions chosen for comparison with calculations were such that both space charge and diffusion effects were noticeable and are not typical of conditions used to obtain published attachment coefficients. They include $V = 1.84$ v, $p = 72.4$ torr (measured with gas at 195°K), $d = 2.54$ cm (i.e., $E/p = 0.01$ v/cm-torr), estimated area = 5 cm$^2$, and a temperature = 195°K, which yields $D/\mu = 0.0168$ ev. The width of the initiating electron pulse was 3 msec and a collector duty cycle of 6 percent was used. From data taken with more favorable conditions, tentative values of $v_- = 74$ cm/sec and $\alpha = 0.61$ cm$^{-1}$ were selected. A tentative initial distribution was chosen and calculations were made with $M = 28$ and $F = 0.49$. On the basis of these results, a better initial distribution was chosen$^*$ and new calculations made with adjusted $\alpha$ values. The fit to the experimental data with $\alpha = 0.66$ and $v_- = 74$ cm/sec, and the initial distribution as given in figure 8, is shown in figure 7. The diffusion of the pulse as it drifts across the gap is also shown in figure 8. The initial field distortion for the distribution used is $\sim 5$ percent as shown in figure 9, which also shows the field distributions at subsequent times.

$^*$ Following the suggestion of Dr. A. V. Phelps, an initial distribution was calculated by taking a time average of the computed density at each gap position over the 3-msec duration of the pulse.
Figure 6. Proportional change in apparent diffusion coefficient as a function of the maximum field distortion.
Figure 7. Comparison of calculated with experimental measurement of collected negative ion pulse in oxygen mixture. The experimental data (Ref 4) are shown as solid curve and calculations as individual points. The initial peak in the experimental curve is due to electrons that cross the gap without attachment.
Figure 8: Initial distribution of negative ions used for calculation of figure 7, together with calculated distributions for later times, indicated on each curve in milliseconds.
Figure 9. Field distributions which correspond to the density distributions of figure 8. Times are again given in milliseconds.
In order to separate the effect of diffusion from that of space charge upon the collected pulse, the initial distribution was reduced by a factor of 100 for an initial distribution corresponding to \( \alpha = 0.58 \). Doehring (ref 5) has calculated the effect of diffusion upon the collected pulse and gave an approximation that the apparent attachment coefficient, \( \alpha' \), is related to the true coefficient by

\[
\alpha' = \alpha(1 + \alpha D/\mu E) \tag{16}
\]

For the illustrative case one obtains \( \alpha'/\alpha = 1.013 \) from (16), using \( v = 85 \text{ cm/sec} \). For the space-charge-free run on the computer, a value of \( \alpha'/\alpha = 1.017 \) was obtained initially, a value that dropped slowly to 1.013 at about 15 msec, in substantial agreement with (16). For the corresponding run with the densities near that used experimentally, \( \alpha'/\alpha \) initially was equal to 1.04, but dropped to unity at about 10 msec. This shows that at a current density of about \( 10^{-13} \text{ amp/cm}^2 \), space charge causes a greater error in the attachment coefficient than does diffusion at \( 195^\circ \text{K} \).

The calculations bear out the statement (ref 4) that the true transit time is intermediate between the time of the ion current peak and the time at which the ion current has dropped to half its peak value.

A second experimental method was used by Morrison and Edelson (ref 6) to measure attachment coefficients in \( \text{SF}_6 \) at 10 torr. They measured the total current due to the movement of ions within a gap of 0.8 cm. Using intense illumination they obtained considerable distortion due to space charge. They also presented a calculation of the effect of space charge distortion, but omitted the diffusion of carriers. The conditions assumed in their calculations were used with the present computer program. A comparison of the present results with their calculation and with their experimental data is shown in figure 10. The agreement between the two calculations is satisfactory, but shows the effect of diffusion on the apparent mobility. Better agreement with the experimental data could be obtained with different values of the attachment coefficient and mobility of the ions. The calculations were made with \( M = 32, \ P = 0.8 \) and \( V = 150 \text{ v} \). It is noted that these values yield \( D/\mu = 0.47 \text{ ev} \), which is probably too high a value. A better value of the ion mobility would undoubtedly require a smaller diffusion energy to fit the experimental data. These calculations were made before (15) was derived.

5. SOLID-STATE TRANSPORT

The injection of minority carriers into a semiconductor and the measurement of the pulse at a collector after drift and diffusion is utilized to measure mobilities in a semiconductor. Normally
Figure 10. The ratio of the negative ion current to its maximum value, calculated neglecting space charge or diffusion, as a function of time on a similar nondimensional scale. Present computer calculation is given by the solid curve, the calculation of Morrison and Edelson (ref 6) by the dashed curve, their experimental data by individual points, and the no-space-charge approximation by the dotted line.
pulses of several sizes are used and the drift time is extrapolated to zero pulse current to account for space charge effect (ref 7).

Although the present formulation was developed for gases, it may be applied with reservation to the solid state. The present program is limited to a dielectric constant of unity; hence carrier densities must be multiplied by the dielectric constant of the solid to relate to the space charge effect. Recombination and trapping are omitted from the formulation; the former could easily be introduced while the latter is more complicated. Further, in most semiconductors, doping creates a large concentration of majority carriers, which are neutralized by fixed charges. Such fixed charges could easily be introduced in a computer program.

Exploratory calculations have been made to indicate the usefulness of the present program in determining the effect of space charge and diffusion upon mobility measurements in germanium. Calculations made assuming carriers of only one charge show that under typical experimental conditions, a space charge sufficient to broaden the pulse to the observed width distorts the pulses to nearly rectangular shapes. The use of sufficient carriers of the opposite sign to neutralize the gap as a whole, but distributed uniformly across the gap, leads to quite different field distortions, and to more normally distributed pulses. Calculations were made with: \( V = 40 \text{ v}, d = 2.0 \text{ cm}, \mu_{-} = 3800 \text{ cm}^2/\text{v sec}, \mu_{+} = 1800 \text{ cm}^2/\text{v sec}, M = 100, F = 0.87, \) and the total number of initial carriers of one charge in the gap per square centimeter varied up to \( 8 \times 10^6 \). The collected pulses for several initial pulse sizes are shown in figure 11. Comparison with experimental measurements shows some disagreement. Experimental measurements show a pronounced increase in the time taken for the pulse maximum to be collected as the pulse size increases. The calculations made with carriers of only one charge show a slight decrease in this time, although the total time for pulse collection increases by the correct order of magnitude. Calculations made with initial overall charge neutrality show peaks delayed in time. By overcompensation of the injected carriers, the pulse is further delayed as shown in figure 11. This suggests that a program utilizing fixed charges would enable attainment of good agreement with experimental data. It is further suggested that temporary trapping could account for further delay because carriers may be removed from the early portion of the collected pulse and added to the later portions.

It is believed that the present model for calculations of diffusion effects in the presence of space charge can easily be adapted to make valid calculations for semiconductors. By proper selection of a spatial distribution of fixed charges, a semiconductor junction may also be simulated.

6. DISCUSSION

It has been shown that the present program is very useful in interpreting the effect of space charge upon the transport properties of charge carriers.
Figure 11. Collected pulses of holes calculated as a function of size of injected pulse of holes in Ge. Pulse size is indicated by relative, not absolute, numbers. Calculations with only holes present are shown dashed, while initially overall neutral calculations are shown as a solid curve, and those for an over-compensated electron distribution by the dot-dashed curves. The hole transit time, $t_p$, is indicated. Results for diffusion at two temperatures are shown in two cases.
It is natural to ask why the exact second-order equations (3) and (4) including diffusion directly are not used. The main difficulty is that an additional boundary condition is needed for each of the two equations. Considerable effort has been made to determine these two extra boundary conditions for steady-state, rather than time-dependent, calculations. No solution to the problem has been found that has been considered worthwhile to test on the computer. It is possible that the dynamic problem is easier, but any set of equations must be investigated to insure that the solution is exact in the limit of small differences. The present program has proved to be exact, including diffusion, in that limit.

The chief deficiency of the present program is that the positive ion temperature must be higher than the electron (or negative ion) temperature as shown by (15). Just the reverse is the usual case in gases. In many cases, large concentration gradients apply to the carriers of one sign only, in which case the diffusion of carriers of the other sign is not important anyway. However, this fundamental deficiency of the present calculations indicates that the second-order equations should be solved numerically.

It is planned to publish at a later date the results of calculations where the ionization coefficients are not set equal to zero.

7. REFERENCES

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Numerical calculations have been made that determine the effect of space charge, composed of mobile charge carriers, on the drift and diffusion of other carriers in an electric field. This calculated diffusion is shown to be exact in the absence of space charge and in the limit of infinitely small calculation intervals. Numerical results illustrating the effect of space charge upon apparent diffusion coefficients and drift velocities are given for a fictitious gas. Calculations show good agreement with experimental data taken in two other laboratories to measure attachment coefficients in gases. Exploratory calculations have indicated the usefulness of this model for calculations in solid-state transport.