Diffusion corrections in electron conductance transients

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The effect of diffusion upon drift-velocity measurements in electron-conductance-transient experiments is analyzed analytically, and the correction procedure employed by Wada and Freeman is argued to be inappropriate.

Electron mobilities have been determined from electron conductance transients resulting from x-ray radiation of gas filling a region between two plane-parallel electrodes by Wada and Freeman.[1,2] These authors conclude that low-energy momentum-transfer cross sections for electron scattering from H_2 and N_2 exhibit a Ramsauer minimum, contradicting the traditional viewpoint.[3] Cassidy[4,5] argues that the Wada-Freeman diffusion correction factor of $1+\sqrt{2D_L t_d}/l$ is incorrect and is possibly responsible for the discrepancy in their derived cross sections. (Here D_L is the longitudinal diffusion coefficient, and $t_d = l/W$ is the time of flight for electrons drifting with velocity W over a distance l.) Cassidy obtains a correction factor numerically close to $1+2D_L t_d/l^2$ from approximate solution of the diffusion equation, but this required an involved iterative process with three successive numerical integrations. The purposes of this paper are (i) to show that under certain conditions transients must indeed be corrected in the manner suggested by Cassidy, but by following an exact analytic treatment, with any approximations left until the end, (ii) to give the general formulas for a quantitative description of the transients under all conditions, and (iii) to point out that the Wada-Freeman and Cassidy correction factors have apparently been applied under quite different circumstances, with the validity of the former subject to some doubt.

The experimental situation may be idealized by plane-parallel geometry. Ionizing radiation creates electrons in the gap, which then drift and diffuse under the influence of the constant electric field $E = V/l$, where V is the voltage applied to the electrodes and l is their separation distance. The density n of electrons is assumed sufficiently low so that no space-charge distortions occur, and is governed by the diffusion equation

$$\partial_t n + W\partial_z n - D_L \partial_z^2 n = 0 \ , \tag{1}$$

where W and D_L are the usual (constant) transport coefficients, and z is a coordinate measured normal to the electrodes. Equation (1) is to be solved subject to the boundary conditions that $n=0$ at $z=0$ (cathode) and $z=l$ (anode). The solution obtained by separation of variables for the initial condition that electrons are produced at time $t=t_0$ by ionizing radiation uniformly in the plane $z=z_0$, i.e., for

$$n(z,t_0) = n_0 \delta(z-z_0) \tag{2}$$

is

$$n(z,t) = \frac{2n_0}{l}\sum_{j=1}^{\infty} \exp[\lambda(z-z_0) - \omega_j(t-t_0)]\sin(k_j z)\sin(k_j z_0) \tag{3a}$$

$$= \frac{n_0}{l}\sum_{j=1}^{\infty} \exp[\lambda(z-z_0) - \omega_j(t-t_0]\{\cos[k_j(z-z_0)] - \cos[k_j(z+z_0)]\} \ . \tag{3b}$$

Symbols appearing in (3a) and (3b) are defined as follows:

$$\omega_j = D_L(\lambda^2 + k_j^2), \quad \lambda = \frac{W}{2D_L}, \quad k_j = \frac{j\pi}{l} \ . \tag{4}$$

An alternative form to (3b) can be found by employing the well-known Poisson summation theorem

$$\delta \sum_{j=-\infty}^{\infty} f(j\delta) = \sum_{j=-\infty}^{\infty} F(j/\delta) \ , \tag{5}$$

where δ is an arbitrary parameter, and

$$F(k) \equiv \int_{-\infty}^{\infty} e^{-2\pi ikx} f(x)\, dx \tag{6}$$

is the Fourier transform of $f(x)$. Thus, it can be shown that (3b) transforms to

$$n(z,t) = \frac{n_0}{\sqrt{4\pi D_L(t-t_0)}} \exp\{\lambda[z-z_0-\tfrac{1}{2}W(t-t_0)]\} \sum_{j=-\infty}^{\infty} \{\exp[-(z-z_0-2jl)^2/4D_L(t-t_0)] - \exp[-(z+z_0-2jl)^2/4D_L(t-t_0]\} \ . \tag{7}$$

The equivalent forms, (3) and (7), are exact solutions of (1) satisfying the required boundary conditions, but we find it more convenient to work with (3) when carrying out subsequent integrations. On the other hand, Cassidy[4,5] starts with an approximate, truncated form of (7) (only $j=0,1$ terms are retained) making it impossible to satisfy the boundary condition at $z=0$. The loss of accuracy resulting from this truncation is, however, believed to be small. The main use of (7) as far as we are concerned is that it facilitates certain limiting processes, e.g., for small D_L

$$n(z,t) \approx \frac{n_0}{\sqrt{4\pi D_L(t-t_0)}} \exp\left[-\frac{[z-z_0-W(t-t_0)]^2}{4D_L(t-t_0)}\right] \rightarrow n_0\delta(z-z_0-W(t-t_0)) \text{ as } D_L \rightarrow 0 \ . \tag{8}$$

Equation (8) represents a pulse starting at $z=z_0$ at time $t=t_0$ and traveling with velocity W, as would be expected in the absence of diffusion.

As explained in Ref. 4, it is the total number of electrons within the gap at any time t which is effectively determined in experiment. If electrons are produced uniformly across the gap by an instantaneous pulse of ionizing radiation at time t_0, then at a later time t the number is

$$\begin{aligned} N(t-t_0) &= \int_0^l dz \int_0^l dz_0 n(z,t) \\ &= \frac{4n_0}{l} \sum_{j=1}^{\infty} e^{-\omega_j(t-t_0)} \frac{k_j^2}{(\lambda^2+k_j^2)^2} [1+(-1)^{j+1}\cosh(\lambda l)] \ . \end{aligned} \tag{9}$$

If, on the other hand, the radiation pulse is of finite length τ, the number of electrons in the gap at time t is given by

$$\begin{aligned} N_\tau(t) &= \int_0^t N(t-t_0)\, dt_0 \\ &= \frac{4n_0}{lD_L} \sum_{j=1}^{\infty} \frac{k_j^2}{(\lambda^2+k_j^2)^3} [1+(-1)^{j+1}\cosh(\lambda l)](1-e^{-\omega_j t}), \quad t \leq \tau \ , \end{aligned} \tag{10a}$$

or

$$N_\tau(t) = \int_0^\tau N(t-t_0)\, dt_0 = \frac{4n_0}{lD_L} \sum_{j=1}^{\infty} \frac{k_j^2}{(\lambda^2+k_j^2)^3} [1+(-1)^{j+1}\cosh(\lambda l)](e^{-\omega_j(t-\tau)} - e^{-\omega_j t}), \quad t > \tau \ . \tag{10b}$$

These expressions are exact, and in a form suitable for numerical computation. The current in the circuit external to the electrodes is proportional to $N_\tau(t)$ [see Ref. 4, Eq. (4), but note that this is in error by a factor equal to the inverse of the electrode spacing]. Thus we have theoretical expressions which can be compared with experimental data to furnish W and D_L, at least in principle. For practical purposes, however, we do not use the full expressions above, but rather approximations to them valid for a certain time regime, viz., the linear decay region. To see that $N_\tau(t)$ does in fact exhibit linearity in t under certain conditions, it is sufficient to show that $N(t)$ of Eq. (9) also has this property, and then integrate as in (10b).

The subsequent discussion is aided by employing dimensionless quantities

$$l^* = \lambda l, \quad t^* = t/t_d, \quad N^* = N/n_0 l, \delta = \pi/l^*, \quad \alpha = \tfrac{1}{2} l^* t^* \ , \tag{11}$$

and then we have from (9) that

$$N^*(t^*) = \frac{4e^{-\alpha}}{\pi l^*} [S_1(t^*) + \cosh l^* S_2(t^*)] \ , \tag{12}$$

where

$$S_1 = \delta \sum_{j=1}^{\infty} f(j\delta) \ , \tag{13a}$$

$$S_2 = -\delta \sum_{j=1}^{\infty} (-1)^j f(j\delta) \ , \tag{13b}$$

and

$$f(x) \equiv \frac{x^2}{(1+x^2)^2} e^{-\alpha x^2} \ . \tag{14}$$

These summations can be evaluated using the Poisson summation formula (5) and the corollary

$$\begin{aligned} \delta \sum^{\infty} (-1)^j f(j\delta) &= -\tfrac{1}{2}\delta f(0) + F(1/2\delta) + F(3/2\delta + \cdots \\ &= F(l^*/2\pi) + F(3l^*/2\pi) + \cdots \ , \end{aligned} \tag{5'}$$

where F is found by substituting (14) into (6).

For large l^* (typically $l^* \gtrsim 10$), it can be shown that $S_1(t^*)$ is significant only for times such that $\alpha < 1$, i.e., $t^* < 2/l^*$, and decays rapidly at later times. Thus for times $t^* > 2/l^*$, we have from (12) that

$$N^*(t^*) = \frac{2e^{l^*-\alpha}}{\pi l^*} S_2(t^*) \ , \tag{15}$$

to a good approximation. Further restricting the discussion to times

$$\frac{2}{l^*} < t^* \lesssim 1 - \left[\frac{2}{l^*}\right]^{1/2} \ , \tag{16}$$

it can be shown that

$$F\left[\frac{l^*}{2\pi}\right] \approx \frac{\pi}{2} e^{\alpha - l^*}(1 + l^* t^* - l^*) - \frac{4\pi\alpha^{3/2}}{(l^*)^2} e^{-(l^*)^2/4\alpha} \ . \tag{17}$$

The last term is negligible for $l^* >> 1$.

Thus from (13b), (5′), (15), and (17), it follows that

$$N^*(t^*) = 1 - \frac{1}{l^*} - t^* + O(e^{-2l^*}) \ , \tag{18}$$

i.e., a linear time dependence.

For no diffusion (or for an infinite gap) $l^* \rightarrow \infty$ and

$$N^*(t^*) \rightarrow 1 - t^* \ , \tag{18'}$$

precisely the result which one would obtain starting from

(8) and carrying out the integrations (9).

For times $t^* > 1-\sqrt{2/l^*}$, $S_2(t^*)$ decays exponentially with time and $N^*(t^*)$ deviates from the linear behavior (18).

To find the expression for the quantity corresponding to radiation of finite duration $\tau^* = \tau / t_d$, we integrate (18) as in (10b):

$$N^*_{\tau^*}(t^*) \equiv \frac{N_\tau(t)}{n_0 l t_d}$$
$$= \int_0^{\tau^*} \left[1 - \frac{1}{l^*} - (t^* - t_0^*)\right] dt_0^*$$
$$= \tau^* \left[1 - \frac{1}{l^*} + \tfrac{1}{2}\tau^* - t^*\right] . \quad (19)$$

This expression indicates a linear transient, and is valid in the time interval

$$\tau^* + \frac{2}{l^*} < t^* < 1 - \sqrt{2/l^*} . \quad (20)$$

Figure 1 shows a transient calculated for $l^* = 10$, $\tau^* = 0.2$ from Eqs. (10a) and (10b). The linear segment is evident, and the extrapolation of this to the time axis gives an intercept of $t_0^* = 1$, in agreement with (19), which indicates, in general, that

$$t_0^* = 1 - \frac{1}{l^*} + \tfrac{1}{2}\tau^* ,$$

or, equivalently,

$$t_0 = t_d \left[1 - \frac{1}{l^*}\right] + \tfrac{1}{2}\tau , \quad (21)$$

as the intercept on the base axis for arbitrary τ and l^*. Also shown in Fig. 1 is the transient for the case where $1/l^* \to 0$, i.e., no diffusion effects. Diffusion, then, clearly has the effect of *reducing* the value of intercept on the time axis obtained by extrapolation of a transient with a linear portion. We might think of the quantity

$$t_d' \equiv t_0 - \tfrac{1}{2}\tau = \left[1 - \frac{1}{l^*}\right] t_d \quad (22)$$

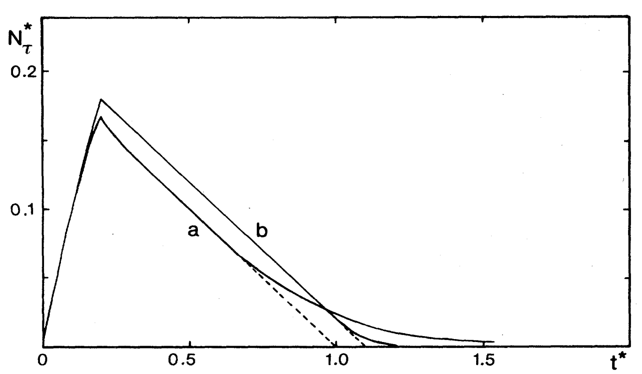

FIG. 1. Transients corresponding to $\tau^* = 0.2$ with $l^* = 10$ (curve *a*) as calculated from (10b) and $l = \infty$ (no diffusion, curve *b*). Extrapolations of the linear segments to the time axis are shown by the dashed lines. Whereas curve *b* has a sharp cutoff at time $t^*_{\text{end}} = 1 + \tau^* = 1.2$, the diffusion-affected transient curve *a* decays exponentially at long times.

as defining an apparent time of flight [cf. Ref. 1, Eq. (2)], with a corresponding apparent drift velocity

$$W' \equiv l / t_d' = \frac{W}{1 - (1/l^*)} ,$$

where the last step follows from (22) and the definition $t_d = l / W$. Hence, the true drift velocity W may be found from the empirical quantity W' through the formula

$$W = \left[1 - \frac{1}{l^*}\right] W' \approx \frac{W'}{1 + (1/l^*)} , \quad (23)$$

i.e., by *dividing* the empirical drift velocity by the correct factor

$$1 + \frac{1}{l^*} = 1 + 2D_L / Wl = 1 + 2D_L t_d / l^2 . \quad (24)$$

The present calculation is therefore consistent with Cassidy's numerical calculations,[4,5] and is what might have been anticipated on the basis of earlier work in connection with other experiments.[6]

It is important to note that the correction factor (24) is to be applied only when the transient has a linear segment, and is not to be directly compared with the Wada-Freeman factor of $1 + \sqrt{2D_L t_d} / l = 1 + 1/\sqrt{l^*}$, as a reading of Cassidy's work might suggest. Although the intended manner of application of this correction factor is not clear, even after close examination of Refs. 1 and 2, the situation is, apparently, that Wada and Freeman have found drift velocities from an examination of the *tail* of the tansient through

$$t_d' = t_{\text{end}} - \tau , \quad (25)$$

where "t_{end}" is what Wada and Freeman regard as the "end" of the transient, and we have written t_d' (instead of just t_d as in Refs. 1 and 2) to emphasize an apparent drift time. On the basis of some qualitative discussion, Wada and Freeman then effectively conclude that the true time of flight, corrected for diffusion, is

$$t_d = \frac{t_d'}{1 + 1/\sqrt{l^*}} , \quad (26)$$

and that the drift velocity is therefore [cf. Ref. 2, Eq. (2)]

$$W = l / t_d = W'(1 + 1/\sqrt{l^*}) , \quad (27)$$

the correction factor having the effect of increasing the drift velocity. The above interpretation is based upon information supplied by a collaborator[7] of Wada and Freeman, who indicates that such a correction factor was found necessary only at very low fields when the transient is curved.

Before commenting on this, it is instructive to reexamine the equations developed in the present paper. Firstly, it is clear from (20) that a transient can have a linear segment if and only if

$$\tau^* < 1 - \sqrt{(2/l^*)} - (2/l^*) . \quad (28)$$

This imposes an upper limit on τ^* for given l^*. (In fact it also restricts l^* to above a critical value of $l_c^* \gtrsim 5$ for a linear transient to be possible under any circumstances.)

Thus, we can generate nonlinear transients from (10a) and (10b) for $l^* = 10$ by taking $\tau^* \gtrsim 0.4$; these have an appearance similar to the "tail" of curve *a* in Fig. 1, but of course they occupy the entire region $t^* > \tau^*$. Similarly, in the absence of diffusion $l^* \to \infty$, and the transient is nonlinear for $\tau^* > 1$, being described by the quadratic

$$N_\tau^* = \tfrac{1}{2}(1+\tau^* - t^*)^2 \ . \tag{29}$$

Whereas this has a definite cutoff at a time $t_{\text{end}} = \tau + t_d$, the finite l^* transient has no such sharp termination. The tails of curves b and a, respectively, in Fig. 1 exhibit this behavior. It is therefore not physically meaningful to designate a t_{end} for a diffusion-affected transient. One might say for practical purposes that the transient has ended when its value falls to (say) 1% of peak value, but Wada and Freeman have given no such quantitative criterion, and it is difficult to reconcile their use of a qualitative diffusion correction factor in connenction with such an ill-defined concept as t_{end}.

A more satisfactory procedure for analysis of electron conductance transients (ECT's) would therefore seem to be as follows.

(i) For ECT's with distinct linear portions, extrapolate to the base line and use (22) and (23) to estimate drift velocity.

(ii) In all other cases, use (10a) and (10b) and adjust the transport parameters until the experimental and theoretical curves agree. As a first step in the procedure, the time constant of the exponentially decaying "tail" could be determined and equated to the asymptotic time constant $(\omega_1)^{-1}$ of Eq. (10b), thereby furnishing W directly if D_L can be estimated.

It may well turn out that these corrections for diffusion do not play a crucial role in generating the discrepancies in cross sections referred to earlier, and that the suggestion of Crompton and Morrison,[3] relating to experimental procedure, is more indicative of the source of error. Nevertheless, it would seem appropriate for Wada and Freeman to reinterpret their experimental data in the light of the theoretical implications described above.

Finally, a note of warning should be sounded regarding computation of the correction factor from the Nernst-Einstein relation. It is known[8] that to a good approximation, in many cases,

$$\frac{D_L}{\mu} = \frac{kT_e}{e}\left[1 + \frac{d\ln\mu}{d\ln E/N}\right] \ , \tag{30}$$

and that the electron temperature T_e is well represented through the relation[9]

$$\tfrac{3}{2}kT_e = \tfrac{3}{2}kT + \tfrac{1}{2}MW^2 \ , \tag{31}$$

where T is the neutral gas temperature and M the mass of a gas molecule. The strongest variation with field usually comes through T_e and, hence, ignoring the term in large parentheses, we have

$$l^* = \lambda l = \frac{lW}{2D_L} = \frac{elE}{2kT_e} = \frac{\frac{1}{2}elE}{kT + \frac{1}{3}MW^2} \ . \tag{32}$$

At low fields $(MW^2 \ll 3kT)$, $l^* \approx elE/2kT$, and l^* initially increases with applied voltage $V = El$. However, at very high fields $(MW^2 \gg 3kT)$ $l^* \approx \frac{3}{2}elE/MW^2$ can actually *decrease* with increasing voltage if W increases faster than $E^{1/2}$. At intermediate fields, l^* attains a maximum.

The third suggestion is, therefore, the following.

(iii) The generalized Einstein relation (30) should be employed in all but very weak field situations in computation of diffusion corrections.

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