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On the Validity of the Two-term Approximation in the Solution of Boltzmann's Equation for Electron Motion

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Abstract

Monte Carlo techniques have been used to study the validity of the two-term spherical harmonics expansion for the distribution function for electrons moving through a gas under the influence of a constant electric field and undergoing elastic collisions with the gas particles. The validity of the expansion was studied by comparing simulated values of the electron drift velocity, lateral diffusion coefficient and mean energy with the values predicted by the conventional theory. From the results of the simulations and from general considerations it is argued that, if the momentum transfer cross section is related to the electron energy by a power-law dependence, then the two-term approximation is equally valid at all E/N. It is shown that the presence of a minimum in the cross section can render the two-term approximation invalid. However, the conditions under which the approximation is invalid do not correspond to any known electron–atom combination and it is concluded that, if only elastic scattering occurs, the two-term approximation is valid for electron motion in helium, neon and argon.

Introduction

We consider the theoretical description of a group of electrons of mass m moving through a gas under the influence of a spatially uniform and time-independent electric field $\boldsymbol{E}$. It is assumed that only elastic collisions take place between the electrons and the gas atoms. The electron number density $n(\boldsymbol{r}, t)$ is everywhere sufficiently small that electron–electron collisions can be neglected. In addition the gas number density N is small enough to ensure that only two-body collisions occur. Under these conditions the electron distribution function $f \equiv f(\boldsymbol{r}, \boldsymbol{v}, t)$ is described by the Boltzmann equation

$$\frac{\partial f}{\partial t} + \boldsymbol{v} \cdot \frac{\partial f}{\partial \boldsymbol{r}} - \frac{e\boldsymbol{E}}{m} \cdot \frac{\partial f}{\partial \boldsymbol{v}} = C(f), \tag{1}$$

where $C(f)$ is the collision integral and e is the electronic charge. To solve Boltzmann's equation the assumption is usually made that the electron velocity distribution function is almost spherically symmetric and that the expansion of $f(\boldsymbol{r}, \boldsymbol{v}, t)$ in spherical harmonics in velocity space, namely

$$f(\boldsymbol{r}, \boldsymbol{v}, t) = \sum_{l=0}^{\infty} f_l(\boldsymbol{r}, v, t) \, \mathrm{P}_l(\cos\theta), \tag{2}$$

where

$$\cos\theta = (\boldsymbol{E} \cdot \boldsymbol{v})/Ev, \tag{3}$$

can be truncated after two terms without appreciable error. The assumption of near

spherical symmetry of the velocity distribution is based on the following considerations. Since the electronic mass m is very much less than the atomic mass M, the electrons suffer large directional changes but lose only a small fraction of their energy ($\sim 2m/M$) in collisions with the neutral atoms. It follows that under steady state conditions the mean fractional gain in energy and change in direction in a free path is small. Although these considerations combine to argue strongly for the validity of the approximation it is necessary to discuss the approximation in detail since the accuracy of the collision cross sections derived from the analysis of transport coefficient measurements depends ultimately on it. For some model cross sections the validity of the approximation has already been discussed. Robson and Kumar (1971) used a matrix solution of the Boltzmann equation to study the case of an energy-independent momentum transfer cross section. In this way it was shown that the two-term approximation leads to an accurate description of electron motion in a helium-like gas at 77 K in the range of E/N from 10^{-3} to 4×10^{-2} Td. Due to the very large matrices required at higher E/N it was not possible to calculate the transport coefficients exactly, but from the structure of the formulae it was inferred that the two-term expansion is an adequate approximation at all E/N. The case of constant collision frequency for momentum transfer has been investigated by including three terms in the expansion for $f(\boldsymbol{r}, \boldsymbol{v}, t)$ and comparing the computed transport properties of an electron swarm with the predictions based on the two-term expansion (Francey and Stewart 1972). It was concluded that the two-term expansion is adequate even at high E/N. These analytical approaches suffer from the serious disadvantage that they cannot easily be applied to analyse transport data for real gases. To overcome this disadvantage, and also to incorporate the advantages of simplicity and directness, the present Monte Carlo investigation was undertaken. Simulated values of the drift velocity W, lateral diffusion coefficient D_T and mean energy $\bar{\varepsilon}$ of an electron in a gas have been compared with the corresponding results derived from the solution of the Boltzmann equation based on the two-term approximation (see e.g. Huxley and Crompton 1974),

$$W = -\frac{eE}{3N}\left(\frac{2}{m}\right)^{\frac{1}{2}} \int_0^\infty \frac{\varepsilon}{q_m(\varepsilon)} \frac{\mathrm{d}f_0}{\mathrm{d}\varepsilon}\,\mathrm{d}\varepsilon, \tag{4}$$

$$D_T = \frac{1}{3N}\left(\frac{2}{m}\right)^{\frac{1}{2}} \int_0^\infty \frac{\varepsilon f_0(\varepsilon)}{q_m(\varepsilon)}\,\mathrm{d}\varepsilon, \tag{5}$$

and

$$\bar{\varepsilon} = \int_0^\infty \varepsilon^{3/2} f_0(\varepsilon)\,\mathrm{d}\varepsilon, \tag{6}$$

where $q_m(\varepsilon)$ is the momentum transfer cross section and $f_0(\varepsilon)$, the isotropic part of the energy distribution function, is given by

$$f_0(\varepsilon) = A\exp\left(-\int_0^\varepsilon \left(ME^2e^2/6mN^2\varepsilon\, q_m^2(\varepsilon)\right)^{-1}\mathrm{d}\varepsilon\right). \tag{7}$$

The normalizing constant A in equation (7) is obtained through the relationship

$$\int_0^\infty \varepsilon^{\frac{1}{2}} f_0(\varepsilon)\,\mathrm{d}\varepsilon = 1. \tag{8}$$

In this work particular emphasis has been given to the case of electron motion in argon, as the momentum transfer cross section for electron–argon scattering has a deep and narrow minimum (Milloy *et al.* 1977; present issue p. 61). Electrons with energies in the vicinity of the minimum have very long free paths compared with other electrons in the swarm, and thus have relatively large energy gains and direction changes in a free path. It follows that electrons with such energies may cause the velocity distribution of the entire swarm to be inadequately described by a two-term expansion in spherical harmonics. In the case of a cross section which exhibits a maximum (shallow maxima are observed in the e^-–He and e^-–Ne cross sections) there is no equivalent class of electrons which might invalidate the conventional analysis.

There have now been several simulation studies of electron motion (Englert 1971; McIntosh 1974, and references therein; Lucas and Saelee 1975) and ion motion (Skullerud 1973*a*, 1973*b*) in gases, but apart from the work of Yarnold (1945), Bell and Kostin (1968) and McIntosh (1974) most of the electron studies were aimed at a better understanding of electron swarm behaviour at near-breakdown conditions. Bell and Kostin calculated the drift velocities of electrons in helium, hydrogen and nitrogen as functions of E/N and obtained satisfactory agreement with experiment. They also commented on the validity of the two-term expansion; from an examination of the average of the cosine of the angle between $\boldsymbol{E}$ and the electron velocity just before impact it was concluded that the two-term expansion was adequate for the E/N conditions used.

The work of McIntosh (1974) was carried out to test the theories of electron motion which take account of the spatial dependence of the velocity distribution function. Stochastic simulations of the drift velocity and diffusion coefficients were made for the case of a helium-like gas ($M = 4$ a.m.u., $q_m = 7{\cdot}0$ Å^2) at $E/N = 3{\cdot}036$ Td. The simulated transport coefficients were in good agreement with the analytic values but it was concluded that the initial spread of the swarm was not accurately described by Huxley's (1972) theory. This conclusion was later justified analytically by Skullerud (1974).

One of the major differences between the work reported here and that of Bell and Kostin (1968) and of McIntosh (1974) is that it was necessary to place more emphasis on the accuracy of the simulations. This change of emphasis was required in order to determine whether the two-term approximation gives rise to errors in the expressions for W and D_T which are comparable with errors in their measurement (typically 1–2 %). The increase in accuracy was obtained primarily by simulating more collisions.

Method

In all the simulations it was assumed that the scattering was isotropic, the gas atoms were stationary and all collisions were elastic.

For each run the electron was released from the origin with velocity cosines chosen at random and with an arbitrarily chosen speed. The free time of the electron was then selected. The Monte Carlo procedure used to generate the time between collisions was similar to that described by Englert (1971). Suppose $p(t \mid v_0)$ is the probability density of the time of flight of the electron lying in the interval $(t, t+\mathrm{d}t)$, given that its initial speed was v_0. Let $P(t \mid v_0)$ be the corresponding cumulative distribution function measuring the probability that the time of flight is

less than or equal to some value t. Then it is straightforward to show (Englert 1971) that

$$p(t \mid v_0) = \nu(v(t)) \exp\left(- \int_0^t \nu(v(s))\, \mathrm{d}s \right), \tag{9}$$

where the collision frequency ν is

$$\nu(v(t)) = N v q_m(v). \tag{10}$$

The cumulative distribution function is given by

$$P(t \mid v_0) = 1 - \exp\left(- \int_0^t \nu(v(s))\, \mathrm{d}s \right). \tag{11}$$

It is shown in any text book on Monte Carlo methods (e.g. Hammersley and Handscomb 1964) that if R is a random number uniformly distributed on [0, 1] then R is related to some probability density $p(x)$ by

$$R = \int_0^x p(x)\, \mathrm{d}x, \tag{12}$$

where x is a random variable drawn from the distribution $p(x)$. Equations (11) and (12) are the basis of the method used to generate the time of flight of an electron. A uniformly distributed random variable R was generated using a pseudo-random number generator and the equation

$$R = P(t \mid v_0) \tag{13}$$

was solved for t, where $P(t \mid v_0)$ is given by equation (11). It follows from (11) that (13) can be written as

$$\int_0^t \nu(v(s))\, \mathrm{d}s = \log\{1/(1-R)\}$$

and t is found by integrating the left-hand side, using the trapezoidal rule, until the equation is satisfied. It should be noted that the velocity at any time s is given by

$$v(s) = v(0) - eEs/m, \tag{14}$$

where E is the applied field. The accuracy of the generation of the time-of-flight distribution was checked by ensuring that the results were independent of the mesh size used in the integration.

Once the time of flight had been determined the electron trajectory and direction cosines at impact were calculated. The direction cosines of the electron trajectory after impact were then randomly chosen from an isotropic distribution. The angle of scattering and the change in electron energy were then calculated in the manner described by McIntosh (1974), who also assumed that the gas atoms were stationary and all collisions were elastic.

The position coordinates (x, y, z) and energy ε of the electron were sampled at a regular time interval, corresponding approximately to a mean free time. From

these data the mean energy and energy distribution were calculated in a straightforward way. The lateral diffusion coefficient was calculated from the expression

$$D_T = \lim_{\tau \to \infty} (4\tau)^{-1} \langle \{x(t+\tau)-x(t)\}^2 + \{y(t+\tau)-y(t)\}^2 \rangle . \quad (15)$$

It was necessary to use values of τ about 100 times greater than a mean free time to ensure that there was no significant correlation between the values of $x(t+\tau)$ and $x(t)$. The electron drift velocity was calculated from the distance travelled per unit time.

The number of collisions required for convergence of the results depended, as explained below, on the atomic mass used. Typically 10^6 collisions were simulated per run but in some cases the number was as large as 10^7. The CPU time required to simulate 10^6 collisions with the Univac 1108 computer was about 40 min. A simulation was terminated when none of $\bar{\varepsilon}$, D_T and W had varied by more than 2% over the second half of the run.

Results and Discussion

In many of the simulations an atomic mass of 1 or less was used to increase the fractional energy loss per collision. This had two advantages. First, it ensured that any breakdown of the two-term approximation would be more readily observed and, second, by increasing the energy range through which an electron could move in a given number of collisions, a good approximation to the true energy distribution was more quickly obtained.

The results plotted in Figs 1*a* and 1*b* illustrate a somewhat extreme example of the effect of varying m/M on the convergence of the results. In both figures the distance travelled by one electron in the field direction during a simulation of 4×10^6 collisions is plotted as a function of time. The momentum transfer cross section for electrons in argon derived by Golden (1966) was used in each run. The atomic masses were taken to be (*a*) 40 proton masses and (*b*) 1 proton mass. In each run E/N (0·005 Td in Fig. 1*a* and 0·04 Td in 1*b*) was chosen so that the mean electron energy was approximately equal to the energy of the cross section minimum (0·23 eV). The straight dashed line plotted in each figure represents the average motion, as calculated from the conventional Boltzmann approach outlined in the Introduction. It can be seen that the deviation of the electron at time t from the mean position Wt is typically much larger for the heavy atom case. In fact the deviation observed in Fig. 1*a* in the time interval from 32 to 54 μs is so large that it can be regarded as a good example of a 'runaway' electron. This runaway effect is partly due to the small energy transfer per collision and partly due to the form of the minimum in the cross section. If the electron energy is in a region of the cross section which corresponds to a collision frequency that is lower than average, then the mean velocity of the electron in the field direction can be greater than W. The smaller the energy loss per collision the longer the electron spends in a given energy range and hence the larger the deviations on a distance versus time plot from the average behaviour. In the example shown in Fig. 1*a* the average energy of the electron in the time interval 32–54 μs was 230 meV (i.e. about four times the true mean energy), which corresponds to an energy near the cross section minimum.

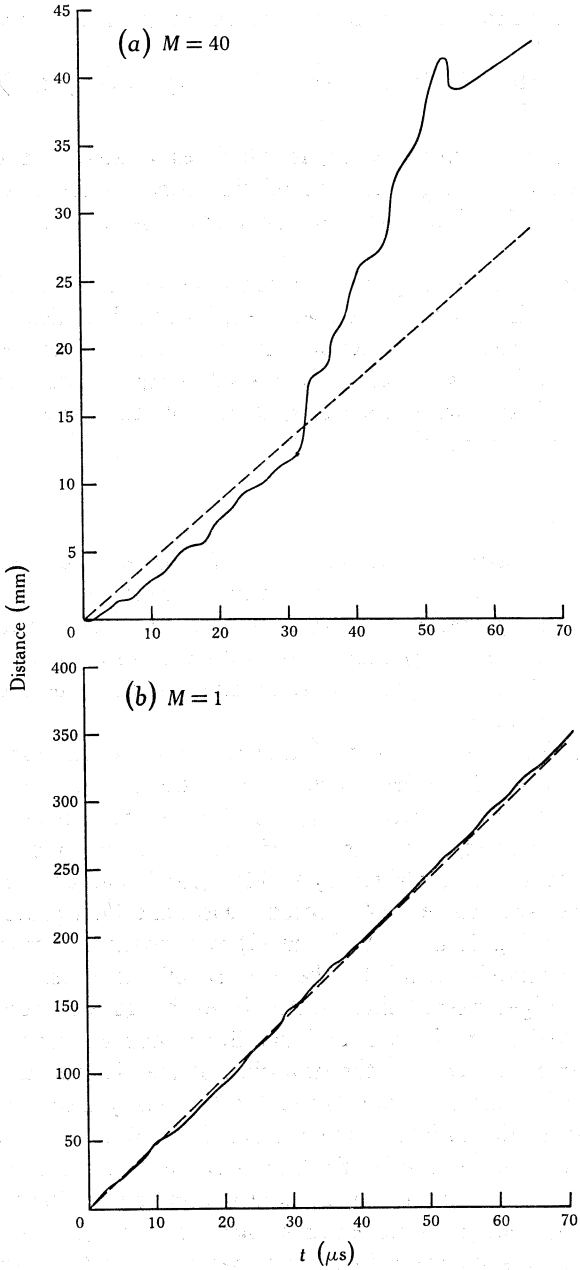

Fig. 1. Simulated motion of an electron in the field direction plotted as a function of the drift time t. The straight dashed lines correspond to the average motion, as calculated from the conventional solution to Boltzmann's equation. In the simulations it was assumed that the atomic masses M were (*a*) 40 and (*b*) 1 a.m.u. Golden's (1966) momentum transfer cross section for electron–argon collisions was used in each case.

Constant Cross Section and Constant Collision Frequency

The computer codes were first used with the model cases of an energy-independent cross section and a cross section which was proportional to $\varepsilon^{-\frac{1}{2}}$ (constant collision frequency).

Using an energy-independent cross section of 1 Å^2 and an atomic mass of 0·2 proton masses, simulations were carried out in an E/N range covering two orders of magnitude (0·5–50 Td). The values of W, D_T and $\bar{\varepsilon}$ were always within $\pm 2\%$ of the values calculated from the conventional analysis based on the two-term expansion for the velocity distribution. Similar agreement was obtained when with the same atomic mass the cross section $q_m = (0{\cdot}1)^{\frac{1}{2}}\varepsilon^{-\frac{1}{2}}$ (q_m in Å^2 and ε in eV) was used with $E/N = 1{\cdot}0$ Td.

The results obtained for the case of constant cross section show no evidence of breakdown of the validity of the two-term approximation; that is, there is no evidence that the velocity distribution becomes increasingly anisotropic with increasing E/N. The following two approaches helped us understand in physical terms why, if the cross section has a uniform energy dependence, the two-term approximation is equally valid at all E/N. (We can safely ignore the trivial case of finite gas temperature and low E/N.)

We first argue that a 'necessary' condition for the validity of the approximation is that the mean fractional energy gain per free path is small. Since, when scattering is isotropic, the mean fractional energy loss per collision depends only on the mass ratio and not on the field strength it follows that the mean fractional energy gain per free path does not depend on E/N.

A second argument can be based on the assumed criterion that the average distance $\langle\Delta\lambda\rangle$ travelled by the electron in a free path due to the action of the field must be very much less than the mean free path $\bar{\lambda}$. If the cross section is related to the electron energy by a power-law dependence then the dependence of $\langle\Delta\lambda\rangle/\bar{\lambda}$ on E/N can be easily calculated. For example we consider the case of constant collision frequency. Here

$$\langle\Delta\lambda\rangle = (\tfrac{1}{2}eE/m)\langle t^2\rangle \propto \tfrac{1}{2}eE/mv^2,$$

where t is the free time between collisions and the collision frequency $\nu = \langle t\rangle^{-1}$ = const. It follows that

$$\langle\Delta\lambda\rangle/\bar{\lambda} \propto E/\nu^2\bar{\lambda} = E/\nu\langle v\rangle \propto E/\bar{\varepsilon}^{\frac{1}{2}},$$

but for this case $\bar{\varepsilon} \propto (E/N)^2$ (Huxley and Crompton 1974) and hence $\langle\Delta\lambda\rangle/\bar{\lambda}$ is independent of the field. The same result applies for all cross sections with a power-law dependence on electron energy, but is not generally true.

Breakdown of Two-term Approximation

Simulations were carried out using a cross section with a very deep minimum to investigate whether the presence of a significant number of electrons with much longer free paths than average would lead to a breakdown of the two-term approximation. In the first runs an atomic mass of 1 was used together with the cross section derived by Golden (1966). The results for these calculations are shown in Fig. 2, where the differences between the simulated and analytic values of D_T, W and $\bar{\varepsilon}$ are plotted as functions of the mean electron energy. Golden's cross section was chosen because it is considerably deeper and broader than the most recent

determination, and it was assumed that this would make any breakdown of the validity of the two-term approximation easier to observe. It can be seen from Fig. 2 that there is excellent agreement between the analytic and simulated values of W and $\bar{\varepsilon}$ but that the D_T values disagree by up to 40%. It is concluded from the data in this figure that the two-term approximation is invalid under these conditions. The fact that the breakdown is only observed by comparing the D_T values, and not the W or $\bar{\varepsilon}$ values, is consistent with the fact that D_T is many times more sensitive than W or $\bar{\varepsilon}$ to the presence of the minimum (Milloy *et al.* 1977).

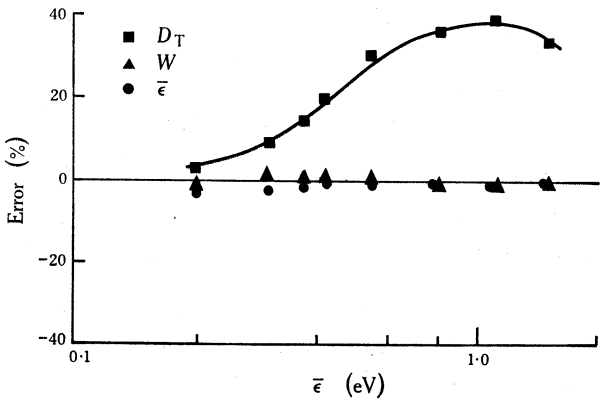

Fig. 2. Percentage errors in the theoretical values of D_T, W and $\bar{\varepsilon}$ plotted as functions of the theoretical $\bar{\varepsilon}$. In the simulations the atomic mass was taken as 1 a.m.u. and the momentum transfer cross section for electron–argon collisions derived by Golden (1966) was used. The theoretical values of D_T were greater than the simulated values. The E/N range was from 0·04 to 2·4 Td.

The position of the maximum in the D_T curve in Fig. 2 is controlled by two competing effects. On one hand the fraction of the electrons in the vicinity of the minimum decreases with increasing mean energy, but on the other hand an increase in E/N leads to an increase in the fractional energy gain per free path for the electrons near the minimum.

The large discrepancies between the simulated and analytic values of D_T are not due simply to differences in the energy distributions. This can be deduced by comparing the simulated and analytic energy distributions plotted in Fig. 3. It is seen that there are only small differences between the distributions although the values of D_T differed by 40%. Moreover according to equation (5) the differences in the distributions that do exist would give rise to an error in D_T of apposite sign to that observed, since in the region of the cross section minimum (0·23 eV) the simulated values of $f_0(\varepsilon)$ are greater than the analytic values. It is therefore concluded that the expression (5) for D_T is inaccurate under these conditions.

The discrepancies between the simulated and analytic values of D_T were found to be reduced by increasing the mass of the neutral particle. When the neutral mass was changed, E/N was adjusted to give the same energy distribution. The required scaling factor for E/N can be readily deduced from an examination of the expression for the energy distribution for elastic scattering in a zero temperature gas (equation 7). The dependence of the error on mass was not studied in detail but an increase in atomic mass from 1 to 9 reduced the error by a factor of two. The errors were also reduced when the depth of the cross section was reduced; an increase in the value of the cross section at the minimum from 0·03 to 0·1 Å^2 reduced the error by a factor of two in simulations using unit atomic mass. If the cross section at the minimum was set at 0·26 Å^2 there was $<2\%$ disagreement between simulation and theory. The simulations with different values of the cross section at the minimum

illustrate an important point. In each run the mean fractional energy loss per collision and gain per free path is unchanged and therefore it follows that the criterion $\langle \Delta\varepsilon \rangle / \bar{\varepsilon} \ll 1$ is not a sufficient condition for the validity of the two-term approximation.

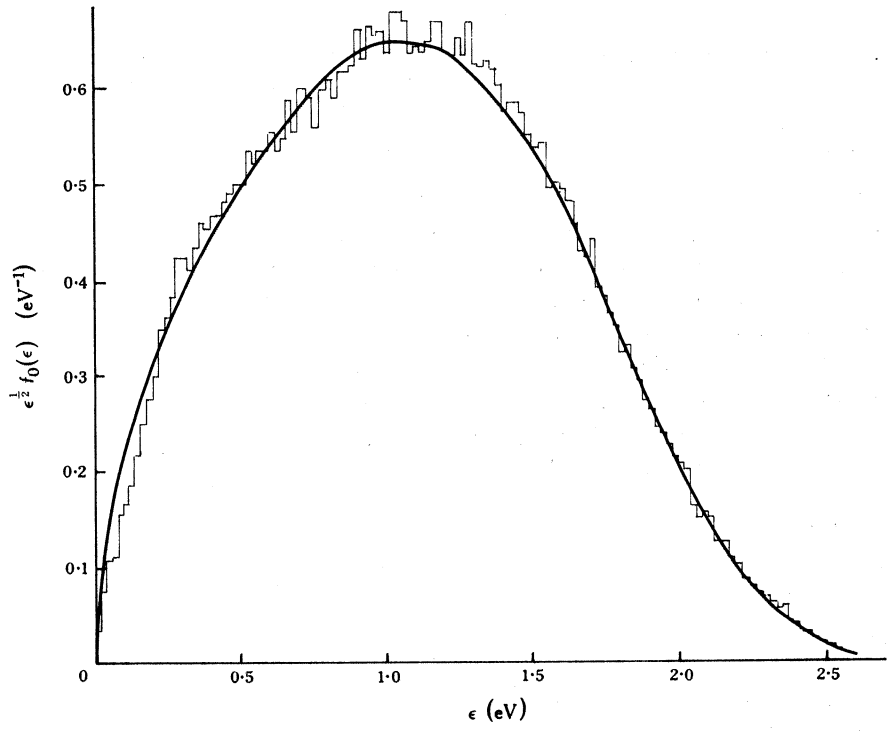

Fig. 3. Comparison of the simulated and analytic energy distributions for the point in Fig. 2 where there is a maximum difference (40%) between the corresponding values of D_T. The minimum in Golden's (1966) electron–argon momentum transfer cross section occurs at 0·23 eV.

Electron Motion in Argon

Milloy *et al.* (1977) have recently derived the momentum transfer cross section from an analysis of the W and D_T/W data of Robertson (1977) and Milloy and Crompton (1977) (present issue pp. 39 and 51 respectively). To determine whether the cross section is in error due to the use of the two-term approximation in the analysis, two simulations were carried out with the derived cross section and an atomic mass of 40. The values of E/N (0·05 and 0·20 Td) were chosen so that the mean electron energies (0·56 and 1·09 eV) lay within the range at which there were large errors in the D_T data plotted in Fig. 2. The simulated values of D_T, W and $\bar{\varepsilon}$ were all within $\pm 3\%$ of the analytic values. It was therefore concluded that the cross section of Milloy *et al.* is not significantly in error due to the use of the conventional analysis.

Longitudinal Diffusion

The theory of longitudinal diffusion of electrons is the subject of controversy at the present time. In the case of constant cross section, for example, the Francey and

Jones (1975, 1976) value of D_L/D_T (0·58) does not agree either with the result (0·69) obtained by Lucas (1970) or with the result (0·495) obtained independently by Skullerud (1969), Parker and Lowke (1969) and Huxley (1972). In each of these analytic treatments the validity of the two-term approximation was asssumed. It follows that simulated values of D_L cannot be used to test the validity of the two-term approximation until the theory of longitudinal diffusion is better understood. However, it seems likely that simulation techniques could be used to help explain the discrepancies between the theories, and work on this topic is continuing.

Conclusions

We draw the following conclusions from this work:

(1) For elastic scattering the two-term approximation is equally valid at all E/N if the cross section for momentum transfer is related to the electron energy by a power-law dependence.

(2) The presence of a minimum in the cross section can lead to a breakdown of the validity of the two-term approximation.

(3) The two-term approximation is valid for the description of the drift and lateral diffusion of electrons in argon at all E/N values where inelastic scattering can be neglected.

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