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Electrical response of materials with recombining space charge†

J Ross Macdonald‡, Donald R Franceschetti‡§ and R Meaudre‖

‡ Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27514, USA

‖ Laboratoire de Physique Electronique, Université Claude-Bernard, Lyon, France

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Abstract. The small-signal transient and sinusoidal steady-state responses of a material with generation and recombination (G/R) of charge are considered. Immobile positive charge and mobile negative charge arise from the dissociation of intrinsic or donor centres and recombine bimolecularly. The mobile charge may react at electrodes. An exact solution for the steady-state admittance of the system is presented, along with exact and approximate equivalent circuits. The simple approximate circuits, made up entirely of frequency-independent elements, whose relations to basic material properties are given in cases of interest, are found to approximate the exact admittance to better than 1% for all frequencies and for realistic G/R conditions in the completely blocking situation. Similar accuracy is obtained for partly blocking conditions provided G/R and electrode reaction time constants are well separated. The approximate equivalent circuits, which represent a more accurate and simpler solution of the system than available heretofore and are thus appropriate for data analysis, lead to a transient response made up of the sum of two exponential decays. Finally, conditions are considered for the appearance of appreciable G/R effects in either admittance or in transient current decay after a small step function of voltage is applied to the system. It is concluded that for ionic conductors and for many electronic semiconducting materials recombination times will be sufficiently short that only minor G/R effects will be apparent.

1. Introduction

Considerable discussion of the electrical response of solids with recombining space charge has appeared recently. Meaudre and Mesnard (1974) (to be referred to as MM) have given approximate results for the small-signal transient and AC steady-state response of a solid containing fixed positive ionized centres and mobile negative charge carriers which may recombine bimolecularly with the positive centres. It is assumed that the negative charges may also react at the plane-parallel electrodes present. As usual (Macdonald 1973, 1975b), only one-dimensional current flow is considered. Macdonald (1974a, 1975a) showed how some of the MM work could be simplified and related to earlier results. Some differences between some of the MM AC results and more accurate expressions have also been discussed in detail (Macdonald 1974a, 1975a, Meaudre 1976).

Here, it seems worthwhile to present the complete solution of the small-signal AC response problem (available since 1974 but heretofore unpublished) and exhibit some

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useful approximations for AC and transient response. These approximations are far simpler and more accurate, under most conditions of interest, than the MM and Meaudre (1976) results and are also generally far easier to use in analysing experimental results than the exact solution.

2. Material and derived parameters

Meaudre and Mesnard (1974) consider only uni-univalent material with mobile negative charge and immobile positive charge carriers. This restriction will be accepted here, but one of us (JRM) hopes to present at a later time simplified results like those of the present work for arbitrary mobilities and intrinsic/extrinsic material. Some brief discussion of these matters has already been given (Macdonald 1976a, b).

The above MM situation corresponds to either an intrinsically conducting material or to a donor-type extrinsic material with such high doping that mobile positive charges arising from intrinsic-centre dissociation can be entirely neglected. To avoid such approximation or the greater complexity of the full extrinsic solution (to be published elsewhere), we shall primarily consider the intrinsic situation hereafter. Let the concentration of neutral intrinsic centres before any dissociation be N_i and that of the negative carriers be $n \equiv n_i \equiv c_i$, with a valence number of unity assumed for the carriers. Then the intrinsic dissociation ratio is $\mathscr{D}_i \equiv c_i/N_i$ and the useful related quantity Λ_i is given by $\mathscr{D}_i/(1 - \mathscr{D}_i)$. In terms of the generation or dissociation constant k_g and bimolecular recombination constant k_r (termed k and β, respectively, by MM), one has $\Lambda_i \equiv k_g/k_r c_i$. Another related parameter is $R_i \equiv (\mathscr{D}_i \Lambda_i)^{-1} \equiv k_r N_i/k_g$ (Macdonald 1958, 1962). Then, $\Lambda_i^{-1} = [R_i + \frac{1}{4}]^{1/2} - \frac{1}{2}$ and $\mathscr{D}_i = [R_i^{-1} + (2R_i)^{-2}]^{1/2} - (2R_i)^{-1}$.

We denote the mobility of the negative carriers by μ_n and the dielectric constant of the material by ϵ. If l is the electrode separation length and e the protonic charge, then for unit electrode area the geometric capacitance of the system is $C_g \equiv \epsilon/4\pi l$ and the high-frequency limiting resistance is $R_\infty \equiv l/e\mu_n c_i$. The dielectric relaxation time τ_D is then given by $R_\infty C_g = \epsilon/4\pi e\mu_n c_i$. It will often be convenient to normalize resistances and impedances with R_∞ and capacitances with C_g, denoting normalized quantities with a subscript 'N' (Macdonald 1973). Further, we define the normalized frequency $\Omega \equiv \omega\tau_D$.

The one-mobile Debye length is given by $L_{D1} = [\epsilon kT/4\pi e^2 c_i]^{1/2}$ and that for both positive and negative uni-univalent charges mobile by $L_{D2} = L_{D1}/\sqrt{2}$. Here k is Boltzmann's constant and T is the absolute temperature. We define the dimensionless quantities $M_1 \equiv l/2L_{D1}$ and $M_2 \equiv l/2L_{D2}$. Usually M_1 and M_2 are much greater than unity in cases of practical interest. We denote the internal recombination time by $\tau_r \equiv (k_r c_i)^{-1} = (\Lambda_i/k_g)$ and the normalized recombination time by $\xi_r \equiv \tau_r/\tau_D$. Since $\mu_p = 0$ in the present situation, it leads to $\pi_m = \infty$, where the mobility ratio $\pi_m \equiv \mu_n/\mu_p$ is a natural variable used in earlier work (Macdonald 1973, 1974b, 1976a, b). If k_n is the heterogeneous reaction rate constant of negative charges at the electrodes, a related dimensionless boundary parameter variable is $r_n \equiv (l/D_n)k_n$, where $D_n = (kT/e)\mu_n$ is the diffusion coefficient for negative charges. When $r_n = 0$ the electrode is completely blocking and when $r_n = \infty$ it is completely non-blocking. Finally let $g_n \equiv 1 + (r_n/2)$.

3. Exact AC solution

The exact solution of the present problem, following from a slight generalization of

earlier work (Macdonald 1973) leads to the equivalent circuit of figure 1. In terms of normalized quantities, its elements are given by

$$R_{DN} \equiv G_{DN}^{-1} = 2g_n/r_n, \tag{1}$$

$$R_{EN} \equiv G_{EN}^{-1} = g_n, \tag{2}$$

$$Z_{iN} \equiv R_{iN} + (i\Omega C_{iN})^{-1} = g_n^2[1 + (i\Omega)^{-1}]t_2^{-1}, \tag{3}$$

where

$$t_2 \equiv \gamma_2 - 1, \tag{4}$$

$$\gamma_2 \equiv (M_2\theta_2)\coth(M_2\theta_2), \tag{5}$$

$$\theta_2^2 \equiv (1 + i\Omega)F_2, \tag{6}$$

and

$$F_2 \equiv (\tfrac{1}{2})\left[\frac{2 + \Lambda_i + i\Omega\xi_r}{1 + \Lambda_i + i\Omega\xi_r}\right]. \tag{7}$$

Note that $G_{EN} + G_{DN} \equiv 1$. The total normalized input admittance of the circuit. $Y_{TN} \equiv Y_T/G_\infty \equiv Z_{TN}^{-1} \equiv G_{PN} + i\Omega C_{PN}$ may then be written as

$$Y_{TN} = \frac{(1 + i\Omega)[G_{DN} + i\Omega\{g_n^{-1}t_2 + 1\}]}{1 + i\Omega\{g_n^{-1}t_2 + 1\}}. \tag{8}$$

Some simplified and $\Omega \to 0$ results following from these expressions have already been discussed (Macdonald 1974a, 1975a). Because of the complexity of equation (8), exact inverse Laplace transformation to yield the current response to a small-signal voltage step V_0 applied at $t = 0$ is impractical. Here and in the work of MM the small signal restriction $|V_0| \ll (kT/e)$ is required to maintain linear response behaviour.

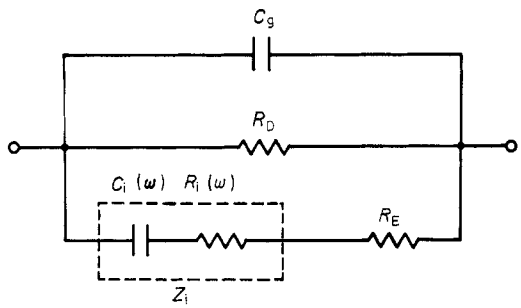

Figure 1. Equivalent circuit appropriate for exact solution.

The complicated nature of the relations yielding Y_{TN}, and the non-linear dependence of Y_{TN} on material parameters such as Λ_i, M_2, and ξ_r makes it somewhat difficult to compare theory and experiment and, for example, to obtain parameter estimates by least-squares fitting of data. Therefore, it is convenient to approximate equation (8) by a simpler result. The method of approximation to be used is quite different from that of MM, who derived an approximate transient response function and then obtained the approximate AC response by Laplace transformation.

4. Approximate equivalent circuits

It is well known that the Voigt circuit model of figure 2(*a*) and the Maxwell model of 2(*b*) may be made to have the same Z_T at all frequencies by proper selection of circuit elements. Although neither representation corresponds exactly to the circuit of figure 1, except when $C_i(\omega)$ and $R_i(\omega)$ are frequency independent, it has been found (Macdonald 1974b, 1976a, b) that a Voigt circuit made up of frequency-independent elements, such as that in figure 2(*a*), can very well approximate exact results under many conditions of interest.

In the present $\pi_m = \infty$ situation, one expects no Warburg effects, and no adsorption of an intermediate species at electrodes (Macdonald 1976b) has been included in the present model. One might then hope that a circuit such as that of figure 2(*a*), which

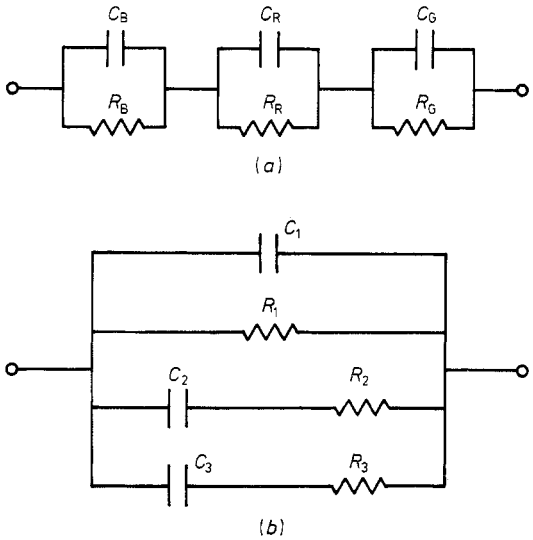

Figure 2. Approximate equivalent circuits: (*a*) Voigt form; (*b*) Maxwell form.

incorporates elements representing bulk, reaction, and generation–recombination (G/R) effects might indeed be appropriate and useful. It has already been mentioned, however, (Macdonald 1976b) that partition of separate effects into subcircuits which represent each effect essentially separately is a good approximation only when the time constants of the subcircuits are well separated (i.e., differ from each other by a factor of 100 or more). It has been found, nevertheless, that for a considerable range of conditions where this requirement is not satisfied a circuit such as that of figure 2(*a*) may approximate $Z_T(\omega)$ adequately even though individual circuit elements may not then be identified with individual effects (Macdonald 1976b).

When $r_n = 0$ and the electrodes are completely blocking, it turns out that the reaction resistance R_R is infinite, since there is no electrode reaction present, and the R_D of figure 1 must also be infinite. There is then no problem associated with $R_{\bar{G}}$, the effective G/R resistance. But it is clear that recombination, while it can effectively mobilize immobile (positive) charge at non-zero frequencies, cannot actually lead to any resistive contribution at zero frequency (thus in the exact solution R_{DN} is independent of Λ_i and ξ_r). Therefore, when $r_n > 0$, in principle the figure 2(*a*) circuit partition into separate

subcircuits for separate effects cannot be entirely applicable even when time constants are well separated. For $r_n > 0$, only the well-separated case will be considered here (the exact solution may be used for other cases). Then, it is found that the circuit is indeed useful and an effective R_G exists, but it cannot be entirely identified with G/R and, as always, it is necessary that $R_{BN} + R_{RN} + R_{GN} = R_{1N} \equiv R_{DN}$, where R_1 occurs in the circuit of figure 2(*b*).

For most solids, the usual case of interest is that of small dissociation ($\Lambda_i \ll 1$). But for strong liquid or solid electrolytes, dissociation may be nearly complete and Λ_i large. Therefore, there is some interest in not restricting the situation to $\Lambda_i \ll 1$. The basic procedure for developing the figure 2(*a*) circuit approximation to the exact results has been to fit over a wide Ω range by non-linear least-squares the formal expression for the Z_{TN} of the 2(*a*) circuit to $Z_{TN}(\Omega)$ results obtained from the exact solution and thus obtain estimates of the normalized circuit elements. By means of a sequence of such fitting, the dependences of these elements on input parameters such as r_n, M, and ξ_r is then obtained either directly or by further least-square fitting of appropriate functional dependences.

If the circuit of figure 2(*a*) represented the exact solution without error and were thus completely equivalent to the figure 1 circuit, it would be pertinent to carry out least-squares fitting using either exact $\mathrm{Re}(Z_{TN})$ or $\mathrm{Im}(Z_{TN})$ results. Since these quantities are related by Kronig–Kramers transforms, either fit should then yield the same set of parameters. In the present case, however, the figure 2(*a*) circuit generally provides only a good approximation to the exact results, and separate fitting of real or imaginary parts of exact Z_{TN} values yield slightly different sets of estimates of parameter values. Since the aim of the fitting is to obtain those values of the figure 2(*a*) circuit parameters which best allow the circuit to approximate the exact Z_{TN} as a whole, it is clear that the determination of the parameters should be carried out by a method which ensures a best fit to $\mathrm{Re}(Z_{TN})$ and $\mathrm{Im}(Z_{TN})$ values simultaneously.

It has been found that a simple modification of the generalized non-linear least-squares programs of Britt and Luecke (1973) or Powell and Macdonald (1972) (see also Macdonald 1975d) allows such fitting of complex data to be readily carried out in both an easier and possibly more accurate fashion than the least-squares approach of Sheppard (1973), the only other fitting method for complex data thus far reported in the literature. All the numerical results discussed subsequently in this paper were obtained by such generalized non-linear least-squares fitting using equal weighting of real and imaginary squared residuals.

The results obtained for $r_n = 0$ will be discussed first. Only the usual $M_2 \gtrsim 100$ situation will be considered. Then one finds to good approximation that $C_{BN} \simeq C_{gN} \equiv 1$ and $R_{BN} \simeq R_{\infty N} \equiv 1$. In addition, one obtains $R_{RN} = \infty$,

$$C_{RN} \simeq M_2[(2 + \Lambda_i)/(2 + 2\Lambda_i)]^{1/2} = M_1[(2 + \Lambda_i)/(1 + \Lambda_i)]^{1/2}, \tag{9}$$

$$C_{GN} \simeq [2{\cdot}4547 + 1{\cdot}4162\Lambda_i]M_2, \tag{10}$$

and

$$R_{GN} \simeq \frac{(\xi_r/M_2)}{4{\cdot}014 + 4{\cdot}953\Lambda_i + 1{\cdot}4147\Lambda_i^2}. \tag{11}$$

The C_{RN} result is exactly the low-frequency limiting normalized double-layer capacitance found long ago (Macdonald 1958) for two double layers in series, appropriate for mobile negative charge and fixed positive charge possibly mobilized by recombination. Note

that when $\Lambda_i \ll 1$, such mobilization is complete and $C_{RN} = M_2$, but for $\Lambda_i \gg 1$ $C_{RN} \simeq M_1$ since no such mobilization occurs with very strong dissociation. For example, when $\Lambda_i = 20$, $\mathscr{D}_i \simeq 0{\cdot}952$ and $C_{RN} \simeq 1{\cdot}024\, M_1$. The above results show that when either $\Lambda_i \to \infty$ or $\xi_r \to 0$, $R_{GN} \to 0$ and the parallel section made up of the R_G and C_G of figure 2(*a*) then contributes nothing to the impedance.

The above expressions for the circuit elements of the figure 2(*a*) equivalent circuit are most accurate and applicable when $\xi_r < M_2$, a condition we shall see later is often encountered. For example, the overall standard deviations of typical $Z_{TN}(\Omega)$ fits run from 10^{-6} to 10^{-7} for $\Lambda_i \to \infty$ and/or $(\xi_r/M_2) \to 0$ to 10^{-3} to 10^{-2} as $(\xi_r/M_2) \sim 10$ to 10^2 for $\Lambda_i \ll 1$. The availability of the above circuit element relations means that data analyses need involve only least-squares fitting of $Z_T(\omega)$ data to the circuit of figure 2(*a*) to obtain element estimates and then their use to obtain estimates of the basic parameters ξ_r, Λ_i, and M_2. Values of R_∞, C_g, ξ_r, Λ_i, and M_2, together with l may finally be employed to obtain estimates of the basic material parameters ϵ, c_i, μ_n, and k_r. If Λ_i is large enough to be adequately estimated, one may also estimate N_i and k_g values as well.

5. Specific complete blocking results

Meaudre (1976) has presented numerical AC and transient response results in the $r_n = 0$ case for the following conditions: $\Lambda_i \ll 1$, $\tau_D M_1 = 1$ s, and $\tau_r = 4$ s. His choice of L_{D1} or τ_D was not reported. To obtain specific results, we shall pick $\Lambda_i = 10^{-4}$ and $\tau_D = 10^{-6}$ s, yielding $M_1 = 10^6$ and $\xi_r = 4 \times 10^6$.

It is first of interest to plot the real and (negative) imaginary parts of the exact $Z_{TN}(\Omega)$ which follows from these input numbers as parametric functions of Ω in the complex plane. Such plots are shown in figure 3 for the above input values, which emphasize G/R effects, and for $\Lambda_i = \infty$, full dissociation. Note that the presence of frequency-dependent G/R effects ($\Lambda_i < \infty$) causes the normally vertical low-frequency rise associated with the reactance of C_R to be curved away from vertical to the right over a considerable region, which is larger the larger (ξ_r/M_2). The limiting asymptote at which the curve again becomes vertical occurs at $R_{BN} + R_{GN} \simeq 1 + R_{GN}$. It is common to find such deviation from verticality experimentally, although it can arise from several other causes besides that shown here (Macdonald 1974b, 1975c).

Non-linear least-squares fitting of exact $Z_{TN}(\Omega)$ results for the range $10^{-9} \leqslant \Omega \leqslant 10$ (81 points) derived for the $\Lambda_i = 10^{-4}$, $\xi_r = 4 \times 10^6$ input values led to $R_{RN} = \infty$ and to the estimates

$$R_{BN} \simeq 1{\cdot}0003848(1 \pm 1{\cdot}7 \times 10^{-4}) \tag{12}$$

$$C_{BN} \simeq 1{\cdot}0000013(1 \pm 9{\cdot}1 \times 10^{-4}) \tag{13}$$

$$C_{RN} \simeq 1{\cdot}4141777 \times 10^6(1 \pm 1{\cdot}1 \times 10^{-6}), \tag{14}$$

$$R_{GN} \simeq 0{\cdot}705529(1 \pm 4{\cdot}4 \times 10^{-4}), \tag{15}$$

and

$$C_{GN} \simeq 3{\cdot}472664 \times 10^6(1 \pm 1{\cdot}4 \times 10^{-3}). \tag{16}$$

The $\pm$ quantities in parentheses are estimates of the parameter relative standard deviations. They are only indicative here since the residuals were not normally distributed.

These results agree within about 0·1 % or better with those following from the expressions of equations (9)–(11). For comparison purposes, more significant figures are retained above than are justified by the apparent fitting uncertainty. Examination of the residuals derived from the fit showed strong systematic behaviour, since the approximation was not perfect, but the maximum absolute value of $\mathrm{Re}(Z_{TN})$ and $\mathrm{Im}(Z_{TN})$ relative residuals (residual divided by true values of variable) was less than 0·5 % and most values were

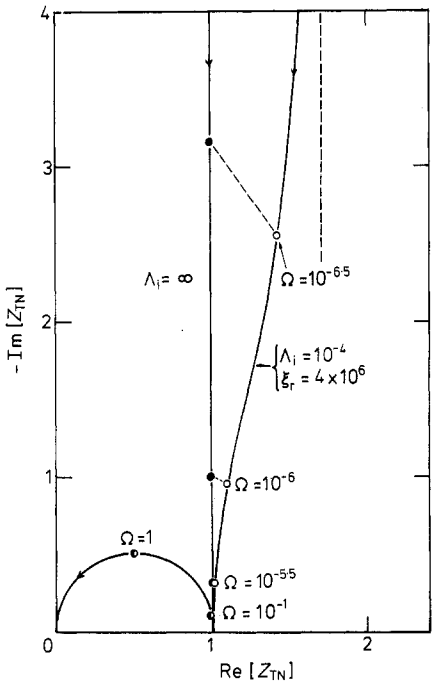

Figure 3. $-\mathrm{Im}[Z_{TN}(\Omega)]$ versus $\mathrm{Re}[Z_{TN}(\Omega)]$ in completely blocking case for no recombination ($\Lambda_i = \infty$) and for appreciable generation–recombination ($\Lambda_i = 10^{-4}$, $\xi_r = 4 \times 10^6$). $r_n = r_p = 0$, $\pi_m = \infty$, $M_1 = 10^6$.

much smaller. Thus, the degree of misfit here, and in all other $M_1 \gg 1$ fittings made, was appreciably less than one would expect from experimentally likely random measurement uncertainties in all but the most accurate experimental data. By contrast, Meaudre's (1976) approximate analytical CA response results, developed to second order in M_1/ξ_r, are slightly less accurate, yielding about a 3·4 % smaller C_{PN} in the $\Omega \to 0$ limit than the exact solution or than the present result for this quantity, C_{RN}, which is exactly equal to the $\Omega \to 0$ value of C_{PN}.

Although transient results can be calculated directly for the figure 2(*a*) circuit, it is considerably simpler to derive them from that of figure 2(*b*). Either of two methods may be used to obtain values of the circuit elements of figure 2(*b*). Exact relations exist connecting the values of elements of one of these circuits to those of the other when they represent the same impedance, but in the present three-subcircuit situation transformations from (*a*) to (*b*) are very complicated and require a quadratic equation solution, and those from (*b*) to (*a*) require a cubic solution. A convenient alternative way to find the elements of (*b*) is to fit the circuit of 2(*b*) by least-squares to exact $Y_{TN}(\Omega) \equiv [Z_{TN}(\Omega)]^{-1}$

values. The results obtained on fitting the complex $Y_{TN}(\Omega)$ data associated with the present numerical input values are $C_{1N} \equiv 1$, $R_{1N} \equiv R_{DN} = \infty$,

$$R_{2N} = 1{\cdot}224133(1 \pm 2{\cdot}7 \times 10^{-4}), \tag{17}$$

$$C_{2N} = 7{\cdot}00965 \times 10^{5}(1 \pm 5{\cdot}1 \times 10^{-4}), \tag{18}$$

$$R_{3N} = 5{\cdot}46214(1 \pm 1{\cdot}2 \times 10^{-3}), \tag{19}$$

and

$$C_{3N} = 7{\cdot}09412 \times 10^{5}(1 \pm 4{\cdot}9 \times 10^{-4}). \tag{20}$$

Note that $(G_{2N} + G_{3N})$ should equal unity here but the sum is actually 0·999983, and $C_{1N} + C_{2N} + C_{3N}$ should equal $1{\cdot}4142 \times 10^{6}$ but is actually about $1{\cdot}4104 \times 10^{6}$, both indicative of the good but not perfect fit of the equivalent circuit. Notice further that here the $C_{1N} + C_{2N} + C_{3N}$ value differs from the exact zero-frequency value by nearly three apparent standard deviations, confirming the presence of systematic errors inherent in the use of the approximate equivalent circuit.

The transient response to $V_0 u_0(t)$ follows from $i(t) = V_0 \mathscr{L}^{-1}[p^{-1} Y_T(p)]$, where $u_0(t)$ is the unit step function, $\mathscr{L}$ denotes Laplace transformation, and p is the complex Laplace variable associated with $i\omega$. Thus, the transient response for circuit 2(*b*) is

$$\mathrm{i}(t) = V_0[C_1 \delta(t) + G_2 \exp(-t/\tau_2) + G_3 \exp(-t/\tau_3)], \tag{21}$$

where $\delta(t) \equiv u_{-1}(t)$ is the Dirac delta function, $G_i \equiv R_i^{-1}$, $\tau_i \equiv R_i C_i$ $(i = 2, 3)$. On omitting further consideration of the immediate delta function response and noting that $G_2 + G_3$ must equal $G_\infty = R_\infty^{-1}$ in the present $r_n = 0$ case, one may write, in normalized terms

$$[i(t)/i(0)] = G_{2N} \exp(-t/\tau_2) + G_{3N} \exp(-t/\tau_3). \tag{22}$$

For the present numerical input, one finds $\tau_2 \simeq 0{\cdot}8581$, $\tau_3 \simeq 3{\cdot}8749$ and thus, using $G_{2N} + G_{3N} \simeq 0{\cdot}999983$

$$[i(t)/i(0)] \simeq 0{\cdot}8169\mathrm{e}^{-1{\cdot}1654t} + 0{\cdot}1831\mathrm{e}^{-0{\cdot}2581t}, \tag{23}$$

where t is in seconds. Meaudre's (1976) more complicated and somewhat less accurate result for the same situation is

$$[i(t)/i(0)] \simeq 0{\cdot}8125\mathrm{e}^{-1{\cdot}1640t} + 0{\cdot}1250\mathrm{e}^{-0{\cdot}2344t} + (0{\cdot}09375\phi - 0{\cdot}03095)\mathrm{e}^{-0{\cdot}25t}, \tag{24}$$

considerably different. For example at $t = 0$; 2; 4; 8; and 12 s, equations (23) and (24) yield, respectively, 1, 1·0003; 0·1887, 0·1892; 0·0729, 0·0729; 0·0233, 0·0236; and 0·00827, 0·00870. At $t = 12$ s, the difference is about 5%. Here $\phi \equiv \phi(-0{\cdot}5, 2, -t/\tau_r)$ is a degenerate hypergeometric function (Meaudre 1976). Although equation (24) shows three different time constants, plus a small amount of non-exponential behaviour associated with ϕ, the above numerical results show, nevertheless, that the actual difference from two-time-constant response is essentially negligible for the main part of the transient response. Even though the exact transient response involves an infinite number of time constants, to the degree to which the circuits of figure 2 approximate the exact result, generally considerably better than 1% for all frequencies in the present example and in most cases of interest, one can conclude that the transient response will also be well approximated for all times by just two exponential decays as in equation (23). General

expressions for the G_2, G_3, τ_2, and τ_3 parameters of equation (21) may be obtained by writing expressions for the elements of the circuit of figure 2(*b*) in terms of those of 2(*a*) and then using the approximate general expressions already given for these quantities.

Meaudre plotted his approximate $C_p(\omega)$ and $G_p(\omega)$ for the present situation and found results quite close to single-time-constant Debye behaviour, whereas his transient response clearly showed two major time constants, as was found more approximately long ago from AC analysis in the $r_n = 0$ situation (Macdonald 1953). On this basis, he concluded that when space charge and G/R phenomena are not well separated, their study is easier with transient response results than with steady-state AC results. Consideration of figure 3, which shows appreciable difference between steady-state AC situations with and without recombination effects, suggests a different conclusion. Even in the presence of appreciable experimental errors, such as those currently encountered in very low frequency measurements, discrimination between the two cases, either on a graphical basis (impedance plane plotting) or by least-squares fitting to the circuit of figure 2(*a*), should be practical but possibly difficult. For the present linear situation, the same basic information is contained in figure 2(*a*) as in 2(*b*) and in either transient or AC response. The time constants of the system may be obtained in principle equally well from either transient or AC response. In practice, however, it may be possible to measure one or the other of these more accurately. For example, in cases where classical capacitance bridges may be used, one should be able to derive more accurate and resolved results from steady-state AC measurements than from transient measurements.

6. Partly blocking results

When $r_n \geqslant 0$, $R_{DN} = 1 + (2/r_n)$ in the present $\pi_m = \infty$ situation. In addition, when $M_2 \gtrsim 100$ and $r_n \ll M_2$, $\tau_{BN} \simeq 1$ and $\tau_{RN} \gg 1$, ensuring that the bulk and reaction regions are well separated in time or frequency. Only this loosely coupled case will be considered here. Then $R_{BN} \simeq C_{BN} \simeq 1$, and the relation $R_{DN} \equiv R_{BN} + R_{RN} + R_{GN}$ yields

$$R_{RN} \simeq (2/r_n) - R_{GN}, \tag{25}$$

which holds down to $r_n = 0$. Notice that when $r_n > 0$, equation (25) exhibits the necessary mixing of reaction and recombination effects mentioned earlier.

By fitting the impedance of the figure 2(*a*) circuit to that obtained from the exact solution in the present $r_n > 0$ situation, one can again derive useful approximations for the 2(*a*) circuit elements. Let us now denote the $r_n = 0$ approximations of equations (9)–(11) by means of a superscript zero. Then one finds for any Λ_i and for r_n small compared with unity

$$C_{RN} \simeq C^0_{RN} + r_n, \tag{26}$$

$$C_{GN} \simeq C^0_{GN} - 1{\cdot}5\xi_r r_n, \tag{27}$$

and

$$R_{GN} \simeq R^0_{GN}[1 + 2r_n R^0_{GN}] \tag{28}$$

To first order, one then has, for $\Lambda_i \ll 1$, $\tau_{RN} \simeq 2M_2/r_n$ and $\tau_{GN} \simeq 0{\cdot}61\xi_r$. It is found that the above circuit element results apply very well when $\tau_{RN} \gg \tau_{GN}$ but not when $\tau_{GN} \sim \tau_{RN}$ or $\tau_{GN} \gg \tau_{RN}$. No adequate expressions for circuit elements have been discovered in the

strong coupling $\tau_{GN} \sim \tau_{RN}$ case. Then the circuits of figure 2 are poor approximations and the exact solution should be used. On the other hand, when $\tau_{GN} \ll \tau_{RN}$ recombination is so slow in the frequency region of interest that it is a good approximation to neglect it even when $\Lambda_i \ll 1$. Then the following expressions for the normalized elements are appropriate: $R_{BN} \simeq C_{BN} \simeq 1$, $R_{RN} \simeq 2/r_n$, $C_{RN} \simeq (C^0_{RN})_{\Lambda_i=\infty} = M_1$, $R_{GN} \simeq (R^0_{GN})_{\Lambda_i=\infty} = 0$, and $C_{GN} \simeq (C^0_{GN})_{\Lambda_i=\infty} = \infty$. There is no contribution to the equivalent circuit from recombination in this case.

Let us demonstrate the degree of accuracy of the above approximations by comparing them to a few results obtained by direct fitting of exact 'data'. For $M_2 = 10^6$ and $\Lambda_i = 10^{-4}$ and on fixing R_{BN} and C_{BN} at unity, one finds the results shown in table 1. Here the numbers arising from least-squares fitting of exact data appear just above the corresponding predictions of the above circuit element approximations. The quantity σ_f is the

Table 1. Comparison of normalized circuit element values for $M_2 = 10^6$ and $\Lambda_i = 10^{-4}$. Least-squares estimates appear above, formula results below.

r_n	ξ_r	σ_f	R_{RN}	$10^{-6} C_{RN}$	R_{GN}	$10^{-6} C_{GN}$
0	4×10^6	$1{\cdot}54 \times 10^{-3}$	—	0·999975	0·9992	2·4529
		—	—	0·999975	0·9964	2·4548
0·01	4×10^6	$1{\cdot}48 \times 10^{-3}$	198·983	1·01015	1·0167	2·3932
		—	198·986	1·00998	1·0140	2·3948
0·04	4×10^6	$1{\cdot}40 \times 10^{-3}$	48·926	1·04322	1·0740	2·2240
		—	48·929	1·03998	1·0709	2·2148
0·02	10^{10}	$6{\cdot}4 \times 10^{-2}$	99·787	0·70729	—	—
		—	100	0·70711	—	—
2	10^8	$7{\cdot}8 \times 10^{-4}$	0·99834	0·70730	—	—
		—	1	0·70711	—	—

estimated standard deviation of the least-squares fitting. The first three r_n values result in $\tau_{RN} \gg \tau_{GN}$ and the last two in $\tau_{GN} \gg \tau_{RN}$. Note, however, that by $r_n = 0{\cdot}04$ τ_{RN} is only $\sim 21\tau_{GN}$, not, in fact, a very loosely coupled situation, as shown by the increased differences between fitted and predicted normalized parameter values.

The impedance of the circuit of figure 2(*a*), when plotted parametrically in the complex plane, can in principle lead to three distinct semicircles of differing sizes (Macdonald 1976a, b). In the present $r_n > 0$ situation, one might expect one of them to be associated with bulk effects, as in figure 3, one mostly with G/R effects, and one mostly with electrode reaction effects. But actually, three separate semicircles are never found for any value of τ_{GN}/τ_{RN}. Instead, one finds the bulk semicircle, and, at lower frequencies a second arc which may vary from a good semicircle to a somewhat distorted one. Because τ_{GN}/τ_{RN} and R_{GN}/R_{RN} are both nearly proportional to $\xi_r r_n/M_2$, the condition $\tau_{GN} \ll \tau_{RN}$ ensures that $R_{GN} \ll R_{RN}$ as well; thus the diameter of the G/R semicircle, R_{GN}, will be much smaller than that of the reaction one, R_{RN}, and they will always overlap sufficiently that their sum leads to at most a distorted semicircle. Even for

$\tau_{GN}/\tau_{RN} \gtrsim 1$, no visible separation occurs, and as $\tau_{GN}/\tau_{RN} \to \infty$ one finds, as discussed above, that only the reaction semicircle occurs with $C_{RN} = M_1$.

7. Generation-recombination mechanisms and the ξ_r ratio

Meaudre and Mesnard (1974) considered that their treatment applied to extrinsic semiconductors and dielectric materials. For donor-type semiconductors, they neglected mobile holes. For insulators, they considered that the negative mobile charge could be electrons, ions, vacancies, or interstitials arising from neutral centres (intrinsic) or donor atoms. One must now ask to what degree the simple bimolecular recombination law used by MM applies to these situations and what range of ξ_r is physically plausible for them.

These matters have been considered recently by one of us (Franceschetti 1977). He finds that for non-degenerate semiconductors, direct recombination of holes and electrons (photon or phonon assisted) may be represented by the ordinary intrinsic-conduction bimolecular generation–recombination expression, $G - R = k_g n_c - k_r np$ (where n, p and n_c are, respectively, the local instantaneous concentrations of negative charge carriers, positive charge carriers and undissociated neutral centres) when n and $p \ll n_c \approx N_i$, i.e. $\mathscr{D}_i$ and $\Lambda_i \ll 1$. The same G/R result is found to be a good approximation, for small deviations from equilibrium, for Auger recombination and for Shockley–Read sequential trapping in the limit of low trap concentration. Of course, the above bimolecular G/R terms are applicable as well (for any Λ_i) for electron–donor recombination in semiconductors and to Schottky or Frenkel defect recombination in such materials as single crystal NaCl or AgBr. Thus, the G/R expressions used by Macdonald (1953, 1958, 1962, 1974a, 1975a,b, 1976a,b) and Meaudre (1976) and Meaudre and Mesnard (1974) have a wide range of applicability.

Now it has already been mentioned (Macdonald 1976a) that when the Langevin diffusion theory of ion-pair formation is used for k_r, one finds

$$\xi_r \equiv (k_r c_i \tau_D)^{-1} = 1 \tag{29}$$

for the intrinsic-conduction situation (or the limiting case of large donor concentration). Franceschetti (1977) points out for ionic conduction that taking into account screening, pair formation at a finite distance, field effects, and ionic discreteness effects may be expected not to change the above value very greatly, probably less than an order of magnitude. In this case, ξ_r/M_2 will generally be very much smaller than unity and R_{GN} negligible. The only remaining effect of G/R will then occur in the Λ_i dependence of C_{RN}.

The situation is somewhat different for electronic semiconductors (Lax 1960, Franceschetti 1977) where one may find both $\xi_r \ll 1$ (relaxation semiconductor) and $\xi_r \gg 1$ (lifetime semiconductor). The $\xi_r \ll 1$ situation, like that discussed above for $\xi_r \sim 1$, here leads to G/R effects only in the Λ_i dependence of C_{RN}. We have already seen that the only interesting frequency-dependent effects in Z_T associated with ξ_r appear when $\xi_r/M_2 \gtrsim 1$ and $\Lambda_i \ll 1$. For G/R between conduction band electrons and immobile traps, one has $\xi_r = 4\pi e\mu_n/\epsilon v\sigma$, where v is the electron thermal velocity and σ is the cross section for electron trapping. Lax (1960) has shown that σ for positively charged traps may be a factor of 10^4 or more smaller than that given by the Langevin theory. Representative parameters (Frederikse 1972, Lax 1960) for lifetime semiconductors are $\mu_n \sim 10^3\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$, $\sigma \sim 1{\cdot}6 \times 10^{-15}\ \mathrm{cm^2}$, $v \sim 10^7\ \mathrm{cm\ s^{-1}}$, and $\epsilon \sim 10$, yielding $\xi_r \sim 10^4$. Taking a minimum value for M_2 of 10 to allow separation of the two electrode space-charge regions, we obtain $\xi_r/M_2 = 10^3$, so that for extrinsic materials with small

dissociation G/R effects might be observable. This is not true when extrinsic centres dissociate strongly, causing Λ_i to be large and $R_{GN} \ll 1$.

Although the direct recombination of electrons and holes may occur extremely slowly in intrinsic materials, there is usually present a sufficient concentration of impurities or defects that sequential trapping is the dominant recombination mechanism, even in highly purified materials. For such samples of Si and Ge at 300 K and of InSb at 250 K, lifetimes τ_r of 2×10^{-2}, 2×10^{-2} and 10^{-7} s, respectively, have been reported (Bemski 1958). These lifetimes, together with known values of mobilities and intrinsic concentrations, lead to the values $7{\cdot}6 \times 10^4$, $4{\cdot}5 \times 10^8$ and $1{\cdot}4 \times 10^7$ for ξ_r. Since the bimolecular G/R expression provides a good approximation to the G/R of electrons and holes in semiconductors by the Schockly–Read sequential trapping mechanism when the concentration of traps is small, and since $\Lambda_i \ll 1$ in such materials (Franceschetti 1977), G/R effects should be observable in sufficiently thin samples of such materials. (Note, however, that the Debye lengths L_{D_2} of Ge and InSb under the conditions described are of the order of 10^{-5} cm.) Incidentally, the value of $t_r = 4$ s used by Meaudre (1976) was selected for illustrative purposes only.

The above results suggest that except for very pure or carefully prepared materials $R_{GN} \ll 1$, and G/R will affect only C_{RN} in the present $\pi_m = \infty$ situation. The maximum effect here is only a factor of $\sqrt{2}$, but it is worth noting that for $\pi_m \lesssim 1$, very much larger changes in C_{RN} (and the $\Omega \to 0$ value of C_p) may arise from recombination effects (Macdonald 1976a).

When $R_{GN} \ll 1$, only one time constant will appear in the transient response since the R_3, C_3 branch of the circuit of figure 2(*b*) will be missing. Since this is the expected situation for ionic conductors and some semiconductor samples, one must ask why, in fact, measured transient response of materials to which the present analysis should apply usually exhibits two or more time constants. One possibility, when indeed $R_{GN} \ll 1$, is that adsorption of an intermediate species at the electrode is also present as well as an electrode reaction. Such adsorption may or may not lead to complete blocking (even in the presence of an electrode reaction), but in either case, one finds that the figure 2 circuits are good approximations (Macdonald 1976a, b), again leading to transient response showing two time constants. When significant two-time-constant response actually appears, it thus seems, for ionic materials and in some cases involving semiconductors, that causes other than G/R are most likely involved.

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