

$$-\beta^{-1}\nabla_1\log g(1,2)=\nabla_1\phi(1,2)+(C/w) \times \int d(3)g(1,3)g(2,3)\nabla_1\phi(1,3). \quad (5.3)$$

Thus our result differs from the result of Born and Green only in the presence of $w(1,3)$ in the integrand instead of $\phi(1,3)$. This difference is not necessarily trivial, however; in the case of long-range forces the difference

between ϕ and w may be quite large. The connection with the other theories can be exhibited by analogous procedures.

The author speculates that the present theory will give satisfactory results for short-range forces but rather poor results for long-range forces.

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Note on Theories of Time-Varying Space-Charge Polarization

J. ROSS MACDONALD

Texas Instruments Incorporated, 6000 Lemmon Avenue, Dallas 9, Texas

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The nonlinearity of the differential equations governing space-charge buildup or decay cause the principle of superposition to be inapplicable. Thus, charging and discharging curves should differ and depend strongly on applied voltage when space-charge formation is appreciable. Two approximate theories of space-charge formation and decay are compared, and it is found that one of their main differences is that one has been partly linearized while the other has not. Finally, it is mentioned that of the several theories of the ac response of materials with space charge, only one has not been linearized; hence, it is the only one applicable for applied voltages above about kT/e .

THE partial differential equations governing space-charge polarization buildup or decay in solids and liquids are nonlinear even when some discharge of current carriers occurs at one or both electrodes.^{1,2} Because of this voltage-dependent nonlinearity, the equations have not been solved exactly. Another consequence of the nonlinearity is that the principle of superposition does not hold, and differences in the temporal variation of charging and discharging currents may be expected, as well as strong nonlinear dependence on applied voltage.

There are presently available two approximate theories of transient polarization effects. The earlier² makes the approximation that the electric field in the medium is homogeneous. This assumption is strictly valid only in the limit of small applied voltages and represents a partial linearization of the basic differential equations. Since the equations are not completely linearized, however, their solutions for the charging and discharging currents still depend nonlinearly on applied voltage. For discharge, a method is briefly discussed of correcting the first-order solution for the originally neglected field inhomogeneity. Of the infinite number of additional terms required to correct exactly for this inhomogeneity, only the first (second-order) term is treated. Further, this correction term itself is only approximated since the field inhomogeneity is once more neglected. Such neglect means that the correction term exhibits only the same type of voltage-dependent

nonlinearity as the first-order term. For these reasons, the corrected discharge solution still does not include any nonlinear voltage dependence arising from the field inhomogeneity. Unlike the theory discussed below, the earlier theory takes explicit account of a finite rate of discharge of current carriers at the electrodes.

The second approximate theory is based on somewhat different assumptions. It is possible to solve the nonlinear space-charge equations exactly for completely blocking electrodes under static conditions.^{3,4} If a material containing free charges blocked at one or both electrodes is charged (or discharged) through an external resistance much greater than the effective internal resistance of the material, determined by its dimensions and the concentrations and mobilities of the free charges, the charging rate is almost entirely limited by the external resistance. In this case, charging of the material occurs in a quasistatic fashion, and the polarization buildup at any instant may be calculated to good approximation by using the exact static solution corresponding to the actual fraction of the total applied voltage which appears across the electrodes of the material at the given instant.⁵ This theory yields both very strong voltage dependence and large differences between charging and discharging current curve shape, in contradistinction to the first theory.

Extensive measurements to test the applicability of

³ J. R. Macdonald and M. K. Brachman, *J. Chem. Phys.* **22**, 1314 (1954).

⁴ J. R. Macdonald, *J. Chem. Phys.* **22**, 1317 (1954).

⁵ J. R. Macdonald and M. K. Brachman, *Proc. Inst. Radio Engrs.* **43**, 71, 741 (1955).

¹ J. R. Macdonald, *Phys. Rev.* **92**, 4 (1953).

² G. Jaffé and C. LeMay, *J. Chem. Phys.* **21**, 920 (1953).

the earlier theory have yielded good agreement between theory and experiment.^{2,6} It should be pointed out, however, that such agreement is not a conclusive test of this theory. Curve fitting is accomplished by the adjustment of six or eight disposable constants. Several of these constants refer to the properties of slow current carriers whose presence, in addition to that of faster carriers, must be assumed to obtain agreement between theory and experiment. However, no physical reasons are given for the presence of these slow carriers. The presence of appreciable electrode discharge in these experiments prevents the appearance of very strong nonlinear voltage dependence. Such dependence as does appear is treated, however, by the trial-and-error selection of a single theoretical applied voltage for all curves, no matter what the experimentally applied voltage, and by the introduction of some dependence of the mobility and exponential decay constant of the slow carriers on applied voltage magnitude and polarity. These assumptions seem unjustifiable. In addition, the homogeneous field approximation used is only valid for applied voltages of the order of 0.02 volt or less; the voltage employed for all curve fitting is 0.2 volt, however, and the experimentally applied voltage was often as large as 380 volts.

A careful reading of the earlier theory shows that it is only applied to a thin polarization layer localized near the electrodes. The difference between the large applied voltage and the 0.2 volt assumed across the polarization layer must, therefore, appear across the ohmic bulk resistance of the material, exclusive of the polarization layer. These conclusions thus indicate that the earlier theory does not differ greatly from the second theory in some of its basic assumptions since both theories tacitly or explicitly include the effect of an ohmic resistance in series with a polarization layer, or polarization capacitance.

Although both theories are approximate, the second theory may be expected to describe nonlinear voltage dependence better than the earlier theory and with fewer *ad hoc* assumptions. On modifying the nonlinear theory to include discharge at the electrodes by putting an ohmic resistance R_p in parallel with the nonlinear capacitor, it is found that the previous results and curves⁹ hold with the following modifications. First, the final voltage across the capacitor is reduced by the voltage reduction ratio $\gamma = R_p / (R_p + R_s)$, where R_s is the original series resistance. Second, the normalized time unit is changed from $\tau = t / R_s C_\infty$ to $t / \gamma R_s C_\infty$. Since γ will usually be much less than unity, this result shows that charging and discharge occur essentially γ^{-1} times as rapidly as before⁷ and that the actual maximum potential across the nonlinear capacitor will usually be much smaller than the applied potential.

The above conclusions are in general qualitative

agreement with the data of references 2 and 6. In particular, the large observed ratios between charging and discharging times are consistent with the small values of the final voltage appearing across the polarization layer capacitance which may be inferred by comparing experimental and theoretical charging curve shapes as a function of time and externally applied voltage. An especially satisfying feature of the theory which is observed experimentally is a progressively more rapid current decay in the initial portions of the charging curves as the applied voltage is increased.

The second theory predicts a ratio between initial and final charging currents of $(1-\gamma)^{-1}$. When γ is much less than unity, as expected in the present case, this ratio is itself near unity, in disagreement with experiment. When it is remembered that the second theory was originally developed for a system including an external ohmic resistor in series with the material showing space-charge formation, while it is here applied to such a material alone, the reason for the discrepancy is obvious. The liquid materials used in the experiments were almost insulators. Initially, they may be expected to contain an appreciable concentration of charge-carrying impurities. When an external voltage is first applied, these impurities contribute strongly to the initial current. However, as the impurities are drawn to the electrodes, their influence progressively diminishes and the final current is determined by the large bulk resistance of the intrinsic material in series with the much smaller parallel resistance R_p . Note that the charged impurities may perhaps be identified with the faster ions of the earlier theory and the slower "ions" with the intrinsic conductivity of the material.

Rather wide claims for the applicability of the Jaffé theories of ac polarization effects in electrical conduction have been made.^{2,6,8,9}

These theories represented important advances in understanding at the time of their appearance. It is desirable to point out now that (a) they have since been improved by less approximate theories for blocking electrodes¹ and for electrodes with discharge,¹⁰ and that (b) all these theories apply only in the small signal range where the applied ac voltage is less than about 25 millivolts at room temperature. No theory is available of the large signal ac response because of the difficulty of solving the governing equations when their nonlinearity is not neglected. A theory of the differential capacitance of materials exhibiting space-charge polarization in the presence of dc voltages as large as a few volts, has, however, been recently given.¹¹ This theory is exact and shows strong voltage nonlinearity. It includes the effect of an insulating layer between the electrodes and the bulk material; in electrolytes, the insulating layer may be an ionic hydration layer.

⁸ G. Jaffé, *Phys. Rev.* **85**, 354 (1952).

⁹ H. C. Chang and G. Jaffé, *J. Chem. Phys.* **20**, 1071 (1952).

¹⁰ R. J. Friauf, *J. Chem. Phys.* **22**, 1329 (1954).

¹¹ J. R. Macdonald, *J. Chem. Phys.* **22**, 1857 (1954).

⁶ J. A. Rider, *J. Chem. Phys.* **23**, 61 (1955).

⁷ See reference 5 for details of the time variation of charge and discharge currents.