

## Energy Loss of Moving Electrons to Dipolar Relaxation

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The relation between energy loss of a moving charged particle and dielectric loss in an insulator is analyzed, and a formula giving the rate of energy loss to dielectric relaxation of an electron traversing a dipolar medium is deduced. For an electron having kinetic energy lower than the lowest electronic excitation potential, this interaction makes a substantial contribution to the total energy loss, one often comparable to the loss to molecular or lattice oscillations. Possible applications in physics and in radiobiology are mentioned.

**A** PURPOSE of this note is to point to a close relationship between the energy loss of a moving charged particle and dielectric loss in an insulator. This implies in particular that dielectric absorption stemming from dipolar relaxation, which in dipolar substances such as water is very important, should also give rise to a substantial energy loss of a moving charged particle—a fact which appears to have been overlooked, or at least rarely appreciated, heretofore. An understanding of this process is of considerable importance for many theoretical and practical problems in the study of the electrical behavior of solids and liquids, and in the study of chemical and biological effects of ionizing radiations.

For an electron of kinetic energy sufficiently high to excite the electronic system of a molecule, atom, or ion of the medium, that interaction always dominates, and is well understood.<sup>1</sup> If the kinetic energy is lower than the lowest electronic excitation potential, further dissipation of the kinetic energy proceeds by excitation of oscillational modes of the lattice or of individual molecules; the rate of energy loss by this interaction is also rather well understood.<sup>2</sup> It will be shown here that the aforementioned interaction of the electron with the permanent electric dipole moments of molecules in a dipolar medium may contribute significantly to the energy loss in this second energy region. An approximate expression for this contribution to the rate of energy loss will now be deduced.

We shall use a method whereby the moving particle is considered as a moving point charge, and in calculating the rate of transfer of energy to the medium shall neglect in first order the reaction on the particle, which will thus be considered to be moving along a straight path. The rate of transfer of energy can be obtained with the use of the empirically determined complex dielectric constant by developing the field of the point charge into its Fourier components. This method is similar to (and, in first approximation, gives a result identical with) that of the equivalent radiation field first developed by Fermi<sup>3</sup> (see also Williams<sup>4</sup>). It

should be noted that, in the problem under consideration, all magnetic effects can properly be neglected.<sup>4</sup> The method is limited, of course, to sufficiently fast particles, and to small energy transfer per “collision.”

The electric displacement vector  $\mathbf{D}(\mathbf{p}, t)$  at a point  $P$  due to a point charge  $e$  moving with velocity  $v$  in a path having shortest distance from  $P$  (impact parameter) equal to  $\mathbf{p}$  has components

$$D_1(\mathbf{p}, t) = e\mathbf{p}(\mathbf{p}^2 + v^2t^2)^{-\frac{3}{2}}, \quad D_2(\mathbf{p}, t) = evt(\mathbf{p}^2 + v^2t^2)^{-\frac{3}{2}}, \quad (1)$$

perpendicular and parallel to the direction of motion, respectively (with appropriate choice of the zero of time  $t$ ). Let

$$\mathbf{D}(\mathbf{p}, t) = \int_{-\infty}^{\infty} \mathbf{D}_\omega(\mathbf{p})e^{-i\omega t}d\omega, \quad \mathbf{E}(\mathbf{p}, t) = \int_{-\infty}^{\infty} \mathbf{E}_\omega(\mathbf{p})e^{-i\omega t}d\omega, \quad (2)$$

whence

$$\mathbf{D}_\omega(\mathbf{p}) = (2\pi)^{-1} \int_{-\infty}^{\infty} \mathbf{D}(\mathbf{p}, t)e^{i\omega t}dt, \quad \mathbf{E}_\omega(\mathbf{p}) = (2\pi)^{-1} \int_{-\infty}^{\infty} \mathbf{E}(\mathbf{p}, t)e^{i\omega t}dt. \quad (3)$$

Here  $\mathbf{E}(\mathbf{p}, t)$  is the electric field strength, and reality of  $\mathbf{D}(\mathbf{p}, t)$  and  $\mathbf{E}(\mathbf{p}, t)$  requires that

$$\mathbf{D}_\omega = \mathbf{D}_{-\omega}^*, \quad \mathbf{E}_\omega = \mathbf{E}_{-\omega}^*. \quad (4)$$

Hence,<sup>5</sup> if

$$\epsilon_\omega = \epsilon_1(\omega) + i\epsilon_2(\omega), \quad \epsilon_{-\omega} = \epsilon_\omega^* \quad (5)$$

is the complex dielectric constant ( $\epsilon_1$  and  $\epsilon_2$  are real),  $\omega/2\pi$  being the frequency, then

$$\mathbf{D}_\omega = \epsilon_\omega \mathbf{E}_\omega, \quad \text{or} \quad \mathbf{E}_\omega = \epsilon_\omega^* \mathbf{D}_\omega / \epsilon_\omega \epsilon_\omega^*. \quad (6)$$

The energy transfer from the particle to unit volume at  $P$ , due to the complete path of a single particle, is given (ignoring quantum effects) by<sup>5</sup>

$$L(\mathbf{p}) = (4\pi)^{-1} \int_{-\infty}^{\infty} \mathbf{E}(\mathbf{p}, t) \cdot \frac{\partial \mathbf{D}(\mathbf{p}, t)}{\partial t} dt.$$

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<sup>1</sup> N. Bohr, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. 18, No. 8 (1948).

<sup>2</sup> H. Fröhlich, Proc. Roy. Soc. (London) A160, 230 (1937).

<sup>3</sup> E. Fermi, Z. Physik 29, 315 (1924).

<sup>4</sup> E. J. Williams, Kgl. Danske Videnskab. Selskab, Math.-fys. Medd. 13, No. 4 (1935).

<sup>5</sup> H. Fröhlich, *Theory of Dielectrics* (Oxford University Press, Oxford, 1949).

By use of Eqs. (2) and (4) to (6) we find

$$L(p) = -i(4\pi)^{-1} \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty} d\omega \int_{-\infty}^{\infty} d\mu (\mathbf{D}_\omega \cdot \mathbf{E}_\mu) \omega e^{-i(\omega+\mu)t}$$

$$= \int_0^{\infty} \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} \mathbf{D}_\omega \cdot \mathbf{D}_\omega^* \omega d\omega. \quad (7)$$

Now from Eqs. (1) and (3),

$$\mathbf{D}_\omega(p) \cdot \mathbf{D}_\omega^*(p) = |D_{1\omega}(p)|^2 + |D_{2\omega}(p)|^2$$

$$= (e^2 \alpha^2 / \pi^2 p^2 v^2) [K_0^2(\alpha) + K_1^2(\alpha)], \quad (8)$$

where we have introduced a new parameter

$$\alpha = \omega p / v \quad (9)$$

and  $K_0$  and  $K_1$  are the modified Bessel functions of the second kind, of order 0 and 1, respectively. If  $W$  is the kinetic energy of the particle, its average rate of loss of energy then follows, with application of Eqs. (7) to (9):

$$-\frac{dW}{dt} = v \int_{p_{\min}}^{\infty} L(p) 2\pi p dp$$

$$= \frac{2e^2}{\pi v} \int_0^{\infty} d\omega \left\{ \frac{\omega \epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} \right.$$

$$\left. \times \int_x^{\infty} [K_0^2(\alpha) + K_1^2(\alpha)] \alpha d\alpha \right\}$$

$$= \frac{2e^2}{\pi v} \int_0^{\infty} \frac{\omega \epsilon_2(\omega)}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} x K_0(x) K_1(x) d\omega, \quad (10)$$

where  $x$  is defined by

$$x = \omega p_{\min} / v,$$

$p_{\min}$  being the minimum value of  $p$ . This value will be taken to be of the order of magnitude of the intermolecular distance  $d$ . If the de Broglie wavelength  $\lambda$  of the particle were greater than  $d$ , then  $p_{\min} = \lambda$  should be chosen, but in this case it will be shown that the results become inaccurate for another reason, and we therefore restrict our treatment to velocities which satisfy

$$v > \hbar / md, \quad (11)$$

where  $m$  is the mass of the particle.

It has already been mentioned that a condition for the validity of the method used here requires that, in general, the transfer of energy in a single "collision" be small compared to  $W$ . The individual energy-transfer events can in this context be assumed to occur in quanta of energy  $\hbar\omega$ . Hence the final integral (10) may not be extended beyond

$$\omega_{\max} = W / \hbar,$$

and the main contributions to the integral should arise from frequencies small compared to  $\omega_{\max}$ . If this is the case, then the value of the integral will be altered only insignificantly if it is extended to infinity instead of to

$\omega_{\max}$ . Now the maximum effective frequency in the Fourier development occurs at about  $\omega \sim v / p_{\min}$ . The aforementioned condition thus requires that

$$\omega_{\max} = W / \hbar \gg v / d, \quad \text{or,} \quad x_{\max} = \omega_{\max} d / v \gg 1. \quad (12)$$

Since  $W = mv^2/2$ , this condition is essentially the same as condition (11).

Evaluation of the final integral (10) requires knowledge of  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$ . In general  $\epsilon_2(\omega)$  has contributions due to the various absorption mechanisms of the medium. [Empirical values of  $\epsilon_1(\omega)$  and  $\epsilon_2(\omega)$  could, in principle, be used in (10).] For dipolar substances which, like water, show Debye absorption (single relaxation time),<sup>5</sup>

$$\epsilon_1(\omega) = \epsilon'(\omega) + \frac{\epsilon_s - \epsilon_{ir}}{1 + \omega^2 \tau^2} \quad (13)$$

and

$$\epsilon_2(\omega) = \epsilon''(\omega) + \frac{(\epsilon_s - \epsilon_{ir}) \omega \tau}{1 + \omega^2 \tau^2}, \quad (14)$$

where  $\tau$  is the relaxation time,  $\epsilon_s = \epsilon_0 = \epsilon_1(0)$  the static dielectric constant, and  $\epsilon_{ir}$  the dielectric constant at frequencies sufficiently lower than the lowest main infrared absorption frequency  $\omega_{ir}$ . The quantity  $\epsilon''(\omega)$  describes the absorption due to ionic oscillations in the infrared, and in the regions of still greater frequency;  $\epsilon'(\omega)$  describes the corresponding dispersion. In particular,

$$\epsilon'(\omega) \approx \epsilon_{ir} \quad \text{if} \quad \omega < \omega_{ir}, \quad \epsilon'(\omega) \approx n^2 \quad \text{if} \quad \omega > \omega_{ir}, \quad (15)$$

where  $n$  is a suitable average of the optical refractive index.

To find the contribution to  $dW/dt$  due to Debye absorption alone, we substitute, in the final integral (10),  $[\epsilon_2(\omega) - \epsilon''(\omega)]$  for  $\epsilon_2(\omega)$ . It will be seen from (14) that the quantity  $\omega[\epsilon_2(\omega) - \epsilon''(\omega)]$  increases proportionally to  $\omega^2$  for small  $\omega$ , but becomes  $(\epsilon_s - \epsilon_{ir})/\tau$ , independent of  $\omega$ , if  $\omega \gg 1/\tau$ . Now Eq. (15) shows that the denominator ( $\epsilon_1^2 + \epsilon_2^2$ ) is smallest for  $\omega > \omega_{ir}$ , where it is  $\epsilon_1^2 + \epsilon_2^2 \approx n^4$ . Thus

$$\frac{\omega[\epsilon_2(\omega) - \epsilon''(\omega)]}{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} \approx \frac{\epsilon_s - \epsilon_{ir}}{\tau n^4} \quad \text{if} \quad \omega > \omega_{ir}. \quad (16)$$

For  $\omega < \omega_{ir}$ , the left-hand expression has a considerably smaller value. Therefore the  $\omega$  integration in (10) can, with sufficient accuracy for our purposes, be restricted to values  $\omega > \omega_{ir}$ , provided that

$$x_{ir} = \omega_{ir} d / v \ll 1, \quad (17)$$

because relatively little energy is then transferred in the region  $\omega < \omega_{ir}$ , owing to the effective "screening" manifested as a relatively great value of  $(\epsilon_1^2 + \epsilon_2^2)$ . In water, for example,

$$\omega_{ir} \approx 3 \times 10^{13} \text{ sec}^{-1}, \quad d \approx 3 \times 10^{-8} \text{ cm},$$

so that, in view of (11), condition (17) is always fulfilled for electrons. (This value of  $\omega_{ir}$  is obtained from an examination of the available data on the frequency-

dependent refractive index of water,<sup>6</sup> and is that value of  $\omega$  above which  $n$  has essentially the optical magnitude.)

The average rate of energy loss is now found by inserting (16) in (10), and restricting the integration as indicated in the preceding paragraphs:

$$-\frac{dW}{dt} \approx \frac{2e^2 \epsilon_s - \epsilon_{ir}}{\pi d \tau n^4} \int_{z_{ir}}^{z_{\max}} x K_0(x) K_1(x) dx. \quad (18)$$

In view of (17) and (12), the limits of integration can with adequate accuracy now be extended from 0 to infinity. The integral is then equal to  $\pi^2/8$ . Thus, finally,

$$-\frac{dW}{dt} \approx \frac{\pi e^2 \epsilon_s - \epsilon_{ir}}{4d \tau n^4}. \quad (19)$$

It should be noted that  $-(dW/dt)/v$  gives the energy loss per unit of actual path length, but that, because (chiefly) of elastic scattering, there is frequent angular deflection, and the actual path is usually tortuous. Therefore Eq. (19) cannot be used to ascertain a measurable range.

A further limitation of Eq. (19) must be mentioned. According to Sack,<sup>7</sup> the Debye equations (13), (14) become inapplicable at frequencies greater than

$$\omega_c \sim kT\tau/I, \quad (20)$$

where  $I$  is an average moment of inertia of the dipolar molecule. Thus expression (19) is not valid when the maximum effective frequency  $v/d$  is of order of magnitude greater than  $\omega_c$ . Together with condition (12), this would limit the applicability of Eq. (19) to particle energies  $W$  within the limits given by

$$2\hbar^2/md^2 < W < md^2\omega_c^2/2. \quad (21)$$

For water ( $I \approx 10^{-40}$  g cm<sup>2</sup>),  $\omega_c \sim 5 \times 10^{15}$  sec<sup>-1</sup>, and Eq. (19) therefore applies in this case to electrons having kinetic energies in the range between about 1 ev and 10 ev. This restriction does not imply, of course, that energy loss to dipolar relaxation does not occur without the specified range, but rather that Eq. (19) there requires modification. However, the upper limit to  $W$  given by (21) does not appreciably diminish the usefulness of (19), because it is usually as high as or higher than the lowest electronic excitation potential, and loss by electronic excitation or ionization,<sup>1</sup> when it is energetically possible, is always very great compared to the dipolar relaxation loss. In this connection it may be noted that dipolar relaxation loss could not possibly account for the allegedly anomalously great stopping power of liquid water for alpha particles,<sup>8</sup> for (19) will always yield too great a value of  $-dW/dt$  when  $v/d > \omega_c$ , and even so it gives, for high-energy charged particles, a contribution negligible compared to the electronic loss.

<sup>6</sup> N. E. Dorsey, *Properties of Ordinary Water-Substance* (Rheinhold Publishing Corporation, New York, 1940), p. 285.

<sup>7</sup> R. A. Sack (private communication, to be published).

<sup>8</sup> R. L. Platzman, in *Symposium on Radiobiology* (John Wiley and Sons, Inc., New York, 1952), Chap. 9.

To judge the magnitude of the rate of energy loss, we consider first the case of electrons penetrating liquid water. Here, recent data<sup>9</sup> give, at 20°C,  $\epsilon_s = 80.4$ ,  $\epsilon_{ir} = 4.9$ ,  $\tau = 1.01 \times 10^{-11}$  sec; furthermore,  $n \approx 1.3$ . Then

$$-dW/dt \approx 10^{13} \text{ ev/sec (H}_2\text{O}_{\text{liquid}}, 20^\circ\text{C}).$$

Equation (19) shows that this rate of energy loss is independent of the electron energy, in the range from 1 ev to 10 ev. Its magnitude is indeed comparable to that of the energy loss<sup>10</sup> by transfer of vibrational quanta (for example, for electrons with an energy of several electron volts, emission of a quantum of 0.1 ev every  $10^{-14}$  second). Moreover, it is temperature dependent, chiefly because of the temperature dependence of  $\tau$ : in water at 75°C it is about four times<sup>9</sup> as great as at 0°C.

For the case of ice slightly below the melting point, we note that<sup>10</sup> at  $-0.1^\circ\text{C}$  only  $\tau (2 \times 10^{-5} \text{ sec})$  is markedly different from the corresponding quantity for the liquid. Thus

$$-dW/dt \approx 10^7 \text{ ev/sec (H}_2\text{O}_{\text{solid}}, -0.1^\circ\text{C}).$$

This result should be valid for all electrons with kinetic energy greater than about 1 ev (the great value of the relaxation time effectively removes the restriction imposed by  $v/d < \omega_c$ ). This will usually be an insignificant magnitude; indeed, the striking difference between liquid and solid water near the melting point could provide the basis for an experimental measurement of the dipolar-relaxation energy loss. As the temperature drops, the reciprocal relaxation time, and therefore the energy loss, declines extremely rapidly.<sup>11</sup>

Our results show that in problems dealing with the motion of electrons of low velocity (below the lowest electronic excitation potential) in dipolar solids or liquids, neglect of the dipolar relaxation excited by the moving charge must introduce an error which may be a great one. This conclusion has an obvious bearing on experiments, with dipolar materials, involving such phenomena as photoconductivity, dielectric breakdown, etc., and in interpretations in radiation chemistry of aqueous systems and radiobiology. In the latter, especially, consideration of the interaction of the many secondary, tertiary (etc.) electrons produced by ionizing radiation, with the medium, which is almost always aqueous in nature, must be essential for a realistic appraisal of fundamental mechanisms. The general role of the dielectric dispersion in radiobiology has already been emphasized.<sup>12</sup>

<sup>9</sup> Collie, Hasted, and Ritson, *Proc. Phys. Soc. (London)* **60**, 145 (1948); J. A. Lane and J. A. Saxton, *Proc. Roy. Soc. (London)* **A213**, 400 (1952).

<sup>10</sup> The energy loss due to other types of absorption can, of course, be calculated from the general expression (10), provided that the appropriate dielectric constants and dielectric loss are known as a function of frequency.

<sup>11</sup> R. P. Auty and R. H. Cole, *J. Chem. Phys.* **20**, 1309 (1952).  
<sup>12</sup> J. Franck and R. Platzman, *Radiation Biology* (McGraw-Hill Book Company, Inc., New York, 1954), Vol. 1, Chap. 3.