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SYMMETRY PROPERTIES OF THE TRANSPORT COEFFICIENTS OF CHARGED PARTICLES IN DISORDERED MATERIALS*

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Abstract

The transport coefficients of a charged particle in an isotropic material are shown to be even functions of the applied electric field. We discuss the limitation which this result and its consequences place upon formulae used to represent these coefficients.

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I. Introduction

The mobility of charged particles in gases and liquids must be an even function of the applied electric field. This important theorem may occasionally be found cited in the literature.[1] The proof upon which it is based, however, is almost never given, and its implications for experiment are sometimes misunderstood or ignored. In this paper we review the proof, which follows from general considerations of symmetry, and apply the theorem to problems of charged particle transport in disordered materials. In the case of electron transport in liquids, for example, there is no completely rigorous theory for the electric field dependence of the mobility. In the absence of theory, empirical formulae have special significance. As we shall see, the theorem and its consequences place limitations upon the kinds of functions which may be used in these formulae.

In Section II, we shall show that for any isotropic material, the invariance of the conduction law upon transformation from a right-handed to left-handed coordinate system (parity transformation) requires the mobility to be an even function of the electric field. This result also follows from the invariance of the law upon replacement of every particle by its antiparticle (charge conjugation). In Section III, we apply invariance under parity and charge conjugation to show that the components of the diffusion tensor must also be even functions of the applied electric field. In Section IV, we discuss the implications of these results for experiment.

II. The Mobility

A. Parity Invariance

In a general material, the drift velocity $\underset{\sim}{w} = (w_1, w_2, w_3)$ is related to the electric field $\underset{\sim}{E} = (E_1, E_2, E_3)$ by multiplication of the latter by a tensor of rank two, called the mobility. We have

$$\begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix} = \pm \begin{bmatrix} \mu_{11} & \mu_{12} & \mu_{13} \\ \mu_{21} & \mu_{22} & \mu_{23} \\ \mu_{31} & \mu_{32} & \mu_{33} \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}, \tag{1}$$

where the upper sign applies to a positive particle and the lower to a negative particle. We presume that Eq. (1) is given in terms of a Cartesian coordinate frame (x_1, x_2, x_3) with origin at some point in the material. We now perform a rotation of this frame about an arbitrary direction through an angle of any amount. If the material is isotropic, then its properties will not appear any different from the rotated coordinate system than they did from the original. This requirement places a limitation on the form taken by the mobility tensor. Specifically, the only tensor of rank two which is invariant under this type of rotation is a scalar times the unit tensor.[2] Hence, Eq. (1) reduces to

$$\begin{bmatrix} w_1 \\ w_2 \\ w_3 \end{bmatrix} = \pm\mu \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix} \tag{2}$$

If further we rotate our coordinate system so that it points along the E_1 direction, then $E_2 = 0 = E_3$, $w_2 = 0 = w_3$, and Eq. (2) may be written in scalar form

$$w_1 = \pm\mu E_1 \ . \tag{3}$$

Although the material is isotropic, the drift velocity may not be a linear function of the electric field. This has been observed experimentally in both gases[3] and liquids.[4] In Fig. 1, we show qualitatively the situations encountered with electron drift in liquids. To take this into account, we must consider the mobility to be an explicit function of the electric field. Equation (3) then becomes

$$w = \pm\mu(E)E \ , \tag{4}$$

where for simplicity we have dropped the subscripts.

Consider the parallel plate drift experiment diagrammed in Fig. 2. Between the plates there is an isotropic, nonlinear material. We suppose that there is present in the material adjacent to the anode a source of ionizing radiation capable of producing positive ions and electrons. The electrons are captured by the anode, while the positive ions drift toward the cathode. We are thus considering Eq. (4) with the upper sign only. The positive x_1-axis points from the anode toward the cathode as shown in the figure. The electric field and drift velocity are +E and +w, respectively. According to Eq. (4), the mobility is $\mu(E) = w/E$. Suppose now that we reverse the direction of the electric field by reversing the connections of the power supply. The electric field and drift velocity have the same magnitudes as before, but the signs have changed [i.e. ($+w \rightarrow -w$ and $+E \rightarrow -E$)]. We note that since w and E are measured with respect to the coordinate system (x_1, x_2, x_3), the same effect could be achieved by leaving the connections to the power supply alone and inverting the coordinate system through the origin [i.e. ($x_1 \rightarrow -x_1$, $x_2 \rightarrow -x_2$, $x_3 \rightarrow -x_3$)]. The coordinate inversion constitutes a parity transformation. It has the effect of changing a right-handed coordinate system into a left-handed one and vice versa. After either reversing the power supply or inverting the coordinate system the mobility is given by $\mu(-E) = (-w)/(-E) = w/E$. We feel, intuitively, however, that the magnitude of the mobility should not depend upon the arbitrary choice of electric field direction or equivalently the parity

of the coordinate system. Hence, we conclude that the mobility must be an even function of the field, $\mu(E) = \mu(-E)$.

It should be emphasized that the basis for this proof is our intuition that the conduction law should be the same in right- and left-handed coordinate systems. The electromagnetic force which gives rise to conduction is still regarded as conforming to this intuition. By contrast, the nuclear weak force which governs beta decay was shown long ago to be parity noninvariant.[5]

B. Charge Conjugation Invariance

To explore the effect of charge conjugation on Eq. (4), we rewrite it as

$$w = \frac{q}{|q|}\,\mu(E)E\,, \tag{5}$$

where q is the charge of the particle. Consider an electron drifting through matter contained between parallel plates as in Fig. 3. We show explicitly the particles which are the source of the uniform electric field E. These are positive ions in the metal anode and excess electrons on the surface of the cathode. Being repelled from the cathode, the electron drifts contrary to the direction of the electric field. The drift velocity and the electric field thus have opposite signs. Likewise, the charge of the electron is negative, so that $q = -|q|$. According to Eq. (5), the mobility is $\mu(E) = [|q|/(-|q|)][(-w)/E] = w/E$. Now let us replace all of the particles involved by their antiparticles. The electron becomes a positron, and the matter between the plates is replaced by antimatter. The ions in the anode are replaced by antinuclei thereby transforming the anode into a cathode. Likewise, the electrons in the cathode are replaced by positrons, transforming the cathode into an anode. The consequence, as shown in Fig. 3, is that the direction of

the electric field is reversed, but the direction of the drift velocity remains the same. We calculate for the mobility $\mu(-E) = [|q|/(+|q|)]$ $[(-w)/(-E)] = w/E$. If we require the interactions of particles to be invariant under replacement by their antiparticles, we must conclude $\mu(E) = \mu(-E)$.

As was pointed out above, the proof based upon parity invariance depends upon the correctness of our intuitions concerning the equivalence of right- and left-handed coordinate frames. By contrast, invariance of physical laws involving electromagnetic forces under charge conjugation has a deeper basis. It follows as a consequence of the Dirac equation.[6]

III. The Diffusion Coefficients

A. Parity Invariance

In general for transport of charged particles in an isotropic material, there is defined a diffusion tensor $\underset{\sim}{D}(E)$ which is a function of the field E. The tensor is diagonal with a longitudinal component $D_{\parallel}(E)$ for diffusion along the field and two transverse components equal to $D_{\perp}(E)$ for diffusion perpendicular to the field.[7] Combining both diffusion and convection, Fick's law for the current density $\underset{\sim}{J} = (J_1, J_2, J_3)$ can be written as three equations

$$J_1 = -D_{\parallel}(E)\frac{dN}{dx_2} + \frac{q}{|q|}N\mu(E)E, \tag{6a}$$

$$J_2 = -D_{\perp}(E)\frac{dN}{dx_2}, \tag{6b}$$

$$J_3 = -D_{\perp}(E)\frac{dN}{dx_3}, \tag{6c}$$

where we have taken as before E to be in the x_1- direction. We have seen previously that under a change in parity, the drift velocity and the electric field change signs. Since $\underset{\sim}{J}$ is the product of a particle density, N, and an effective velocity, $\underset{\sim}{J}$ also must change sign. The density N is a scalar and is invariant. Likewise, since in the parity transformation the coordinates change sign, so also does the gradient $(dN/dx_1, dN/dx_2, dN/dx_3)$. Summarizing, $N \to N$, $E \to -E$, $\underset{\sim}{J} \to -\underset{\sim}{J}$ and $\underset{\sim}{\nabla}N \to -\underset{\sim}{\nabla}N$. Equations (6) read in the parity reversed coordinate system

$$-J_1 = D_{\parallel}(-E)\frac{dN}{dx_1} - \frac{q}{|q|} N\mu(-E)E \ , \tag{7a}$$

$$-J_2 = D_{\perp}(-E)\frac{dN}{dx_2}, \tag{7b}$$

$$-J_3 = D_{\perp}(-E)\frac{dN}{dx_3} \ . \tag{7c}$$

If Eqs. (6) and (7) are to describe the same physics, we must have perforce

$$D_{\parallel}(E) = D_{\parallel}(-E) \ , \tag{8a}$$

$$D_{\perp}(E) = D_{\perp}(-E) \ . \tag{8b}$$

We see that like the mobility, the components of the diffusion tensor are also even functions of the electric field.

B. Charge Conjugation Invariance

Under charge conjugation, $\underset{\sim}{J}$, N and $\underset{\sim}{\nabla}N$ are invariant, while $q \to -q$ and $E \to -E$. The net effect is that E changes sign wherever it appears as an argument in the coefficients in Eqs. (6). The final conclusions are the same as expressed by Eq. (8).

IV. Discussion

In Section II, we showed that the mobility must be an even function of the applied electric field. This limits the kinds of functions which may be used as empirical representations of $\mu(E)$. Specifically, if $f(E)$ is a function of indefinite parity, we must have

$$\mu(E) = (1/2)[f(E) + f(-E)] . \tag{9}$$

Moreover, $f(E)$ must take on real values for negative values of its argument. Hence, multivalued functions such as $\sqrt{E}$ and $\log E$ are ruled out.

As an example, we discuss the semiempirical formula[8]

$$\mu(E) = \mu(0)(e\lambda E/kT)^{-1} \sinh (e\lambda E/kT), \tag{10}$$

which has been used to represent the mobility of electrons which proceed through a material by the process of thermally activated hopping from one potential well to another. Here, e is the magnitude of the electron charge, k is Boltzmann's constant, T is the absolute temperature, λ is an empirically determined jump distance, E is the electric field, and $\mu(0)$ is the empirically determined zero field mobility. Equation (10) corresponds to the behavior of the drift velocity shown in part (a) of Fig. 1. This equation has been used to represent the mobility of conduction electrons in amorphous solids[8] and in liquid normal alkanes.[9] Although Eq. (10) may be derived from transition state theory,[10] it can also be obtained from empirical notions on the basis of Eq. (9) by letting $f(E) = \mu(0)(e\lambda E/kT)^{-1}\exp(e\lambda E/kT)$.

In the case of the drift of He^+, Ne^+ and Ar^+ ions in their parent gases, the mobility goes over smoothly from the value $\mu(0)$ at zero fields to $\mu(E) \sim E^{-\frac{1}{2}}$ at high field.[11] This is an example of the sublinear dependence of drift velocity on electric field diagrammed in part (b) in Fig. 1. To represent this behavior, Frost suggested the empirical formula

$$\mu(E) = \mu(0)[1 + a(E/p)]^{-\frac{1}{2}}, \tag{11}$$

where p is the neutral gas pressure and a is a parameter whose value is adjusted to fit the data.[11] Equation (11) is not an even function of E as such is not acceptable. A formula with the proper symmetry which gives the same limiting behavior is

$$\mu(E) = \mu(0)\,[1 + a(E/p)^2]^{-\frac{1}{4}}. \qquad (12)$$

It should be pointed out that it is not in contradiction with the invariance principles for the mobility to be approximately proportional to $E^{-\frac{1}{2}}$ at high fields. Under the assumption that Eq. (12) applies to the data, this means that the term $a(E/p)^2$ is so much larger than unity that we have to a good degree of approximation $\mu(E) = \mu(0)a^{-\frac{1}{4}}\,(E/p)^{-\frac{1}{2}}$ at high fields. This latter formula cannot be exact, of course. Rather, an experiment with sufficient accuracy carried out at high field would indicate the presence of the term unity in the denominator of Eq. (12).

It is not acceptable to attempt to salvage Eq. (11) by writing it as

$$\mu(E) = \mu(0)\,[1 + a(|E|/p)]^{-\frac{1}{2}}. \qquad (13)$$

Although Eq. (13) is parity invariant, it is not differentiable at $E = 0$.[12] In general if $\mu(E) = f(|E|)$, then

$$\lim_{E \to 0} \frac{d\mu(E)}{dE} = \lim_{E \to 0} \frac{df}{d|E|}\,\frac{d|E|}{dE} = \begin{cases} \left(\frac{df}{d|E|}\right)_0 (-1), & E \to 0^- \\ \left(\frac{df}{d|E|}\right)_0 (+1), & E \to 0^+ \end{cases}. \qquad (14)$$

The slope of $\mu(E)$ is indeterminate at $E = 0$. This would seem impossible to occur experimentally. The behavior which would follow at low fields on the basis of Eq. (13) is shown schematically in Fig. 4.

In general if $\mu(E)$ is represented by an even, differentiable function, it will have a Taylor series expansion about $E = 0$ of the form

$$\mu(E) = \mu(0) + \frac{1}{2!}\left(\frac{d^2\mu}{dE^2}\right)_0 E^2 + \frac{1}{4!}\left(\frac{d^4\mu}{dE^4}\right)_0 E^4 + \ldots \tag{15}$$

According to Eq. (15), the slope of $\mu(E)$ at $E = 0$ is zero. Experimental data confirm this. As an example, Fig. 5 shows a plot of the mobility of electrons in gaseous 2,2,4,4-tetramethylpentane.[13]

From recent theoretical work, we know that in isotropic materials the components of the diffusion tensor are related to the mobility by[7,14]

$$D_{\parallel}(E) = (kT_{\parallel}/e)[\mu(E) + E\partial\mu(E)/\partial E], \tag{16a}$$

$$D_{\perp}(E) = (kT_{\perp}/e)\mu(E). \tag{16b}$$

Because the ions are not necessarily in equilibrium with the drift medium, the effective ion temperatures $T_{\parallel}$ and $T_{\perp}$ are not necessarily the same nor need they be equal to the ambient temperature T. Equations (16) have a basis in nonequilibrium thermodynamics.[7] On the basis of thermodynamics alone, nothing can be said about $T_{\parallel}$ and $T_{\perp}$, however. Rather, formulae satisfied by the effective temperatures must come from an analysis based upon the Boltzmann transport equation. This analysis shows that the temperatures depend in a complicated implicit fashion upon E and ∇N.[15] Because approximations are necessary, the complete dependence upon E and ∇N has not been unraveled. We have shown above, however, that if Fick's law is to be maintained, then the mobility and the components of the diffusion tensor need to be even functions of any variables which have odd parity. From this and Eqs. (16), we may conclude that $T_{\parallel}$ and $T_{\perp}$ must be even functions of these same variables. This result should prove a useful guide in any future theoretical investigations of the form assumed by the effective temperatures.

Figure Captions

1. Plot of drift velocity w as a function of electric field E. The dashed curve gives the ideal situation that occurs when the mobility is independent of the electric field. Curve (a) is for the case when the mobility decreases with increasing field, while curve (b) is for the case when the mobility increases with increasing field.

2. Schematic arrangement of apparatus for mobility measurements. (a) The electric field points in the $+x_1$-direction. (b) The electric field is reversed.

3. Schematic of apparatus for thought experiment involving the drift of (a) an electron through matter and (b) drift of a positron through antimatter.

4. Schematic of the low field dependence of the mobility under the conditions that Eq. (14) applies and $(df/d|E|)_o < 0$.

5. Electric field dependence of the electron mobility in gaseous 2,2,4,4-tetramethylpentane. ∇, 272 K; O, 240 K; □, 436 K; ◇, 480 K; Δ, 598 K; and ●, 556 K (critical temperature).

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