

## Two-component particle transport and superionic conductors

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The rapid motion of distinguishable species of charged particles in superionic conductors allows one to perform a variety of possible transport experiments. The general theory of transport for the case of two species of mobile charge carriers is presented, and several applications of the formalism are discussed.

### I. INTRODUCTION

Superionic conductors exhibit large ionic conductivities typical of liquid electrolytes even though they are solids.<sup>1,2</sup> The rigid structure and high conductivity coexist because one can generally divide the particles in superionic conductors into "mobile" and "immobile" classes; the mobile ions produce the large ionic conductivity and the immobile particles provide the rigidity. Interstitial sites in the immobile lattice are occupied by the mobile ions, and the rapid motion of the mobile ions appears to be closely related to an excess number of available sites compared with the number of mobile ions. The details of the ionic motion are not well understood.

The transport properties of superionic conductors are important probes of the ionic motion. Because superionic conductors allow the motion of distinguishable particles, transport experiments yield a richer variety of data than for the case of single component transport. Not only can the motion of different isotopes of the mobile ions be monitored,<sup>3</sup> but in mixed conductors<sup>4</sup> both electrons and ions carry current, and some superionic conductors such as  $\beta$ -alumina allow the simultaneous transport of chemically different mobile ions.

An example of the utility of transport experiments is the comparison of the isotope diffusion constant with the ionic conductivity.<sup>3</sup> This comparison has yielded parameters which have been correlated with the hopping theory of ion motion. A number of other transport properties besides the total conductivity and the diffusion constant can be measured. The relative amount of current carried by the various charges (transport numbers) can be obtained. By using electrodes which allow the passage of only one type of charge carrier, one can measure a separate conductivity characterizing that charge.<sup>5</sup> Thermoelectric effects can also be obtained.

A system with two types of charge carriers is the simplest example of multicomponent transport. The two types of carriers are assumed to move through the immobile ion structure which

for brevity is called the "lattice." Since this lattice serves to define the coordinate system, it must be assumed that the lattice itself does not participate in the charge transport. Although the motion of the lattice through defect motion or any other mechanism must be ignored, this lattice need not be perfect, static, thermally insulating, or undistorted.

The two types of mobile charges, denoted  $A$  and  $B$ , may be different isotopes of the same mobile ion, electrons, and mobile ions in a mixed conductor, or chemically different mobile ions. Transport experiments on superionic conductors involve temperature gradients and gradients in the densities of the  $A$  and  $B$  charges. These gradients can distort the lattice. Despite this distortion, the most convenient coordinate system is a lattice-based coordinate system. This means that the particle densities  $n_A$  and  $n_B$  are proportional to the number of particles per unit cell. Components of the current densities  $\vec{J}_A$  and  $\vec{J}_B$  are proportional to the number of particles crossing unit cell boundaries per unit time. Despite the peculiar coordinate system, the continuity equation is obeyed. Because of the lattice-based coordinates the condition that the system be electrically neutral is simply

$$q_A \vec{\nabla} n_A + q_B \vec{\nabla} n_B = 0. \quad (1)$$

General transport theory relates "forces" and "fluxes."<sup>6-8</sup> The obvious choice of the fluxes for the two component superionic conductors are the current densities of the  $A$  and  $B$  charges ( $\vec{J}_A$  and  $\vec{J}_B$ ) and the heat current ( $\vec{J}_Q$ ). The corresponding forces can be chosen to be the electrochemical potential gradients for the two charges ( $\vec{\epsilon}_A$  and  $\vec{\epsilon}_B$ ) and the temperature gradient ( $-\vec{\nabla}T/T$ ). The vectors  $\vec{\epsilon}_A$  and  $\vec{\epsilon}_B$  are related to the electric field and the chemical potentials by

$$\vec{\epsilon}_A = \vec{E} - (1/q_A)\vec{\nabla}u_A, \quad \vec{\epsilon}_B = \vec{E} - (1/q_B)\vec{\nabla}u_B, \quad (2)$$

where  $u_A$  and  $u_B$  are the chemical potentials for the  $A$  and  $B$  ions. The condition of charge neutrality [Eq. (1)] means that at a given temperature  $u_A$  and  $u_B$  depend on only one parameter which is

chosen to be  $n_A$ . Hence

$$\tilde{\epsilon}_A = \tilde{E} - \gamma_A q_A \nabla n_A, \quad \tilde{\epsilon}_B = \tilde{E} + \gamma_B q_B \nabla n_A, \quad (3)$$

where

$$\gamma_A = \frac{1}{q_A^2} \frac{du_A}{dn_A}, \quad \gamma_B = \frac{-1}{q_A q_B} \frac{du_B}{dn_A}. \quad (4)$$

Physically,  $\gamma_A$  and  $\gamma_B$  are measures of the change in chemical potentials produced by a change in the density of  $A$  ions in the electrically neutral system. In Secs. II and III it will be shown that for most experimental measurements, the important parameter is  $(\gamma_A + \gamma_B)$ . If the  $A$  and  $B$  charges were free and noninteracting particles obeying Boltzmann statistics, then

$$\gamma_A \approx 1/\beta n_A q_A^2$$

and

$$\gamma_B \approx 1/\beta n_B q_B^2, \quad (5)$$

where  $\beta = 1/k_B T$ . In practice,  $\gamma_A$  and  $\gamma_B$  will have this form only in the limit that the particle density becomes very small. In this case,  $(\gamma_A + \gamma_B)$  will be dominated by the dilute charge term. If, for example, there are only a few  $B$  charges, and many  $A$  charges,

$$(\gamma_A + \gamma_B) \approx 1/\beta n_B q_B^2.$$

If  $(\gamma_A + \gamma_B)$  is negative, the system is unstable and a phase separation will take place. Qualitatively, this can be seen from Eq. (3). If an electric field is applied so that the  $B$  charges experience no net field ( $\tilde{\epsilon}_B = 0$ ), then the effective force on the  $A$  charges is

$$\tilde{F}_A = q_A \tilde{\epsilon}_A = -(\gamma_A + \gamma_B) q_A^2 \nabla n_A.$$

If  $(\gamma_A + \gamma_B)$  is negative, the  $A$  charges will move toward the region of larger  $n_A$ . A more convincing demonstration that the vanishing of  $(\gamma_A + \gamma_B)$  leads to a phase separation will be seen when diffusion is discussed in Sec. II.

The most-general linear relations between the fluxes and forces are

$$\begin{aligned} \tilde{J}_A &= \sigma_{AA} \tilde{\epsilon}_A + \sigma_{AB} \tilde{\epsilon}_B + X_{AQ} (-\nabla \tilde{T}/T), \\ \tilde{J}_B &= \sigma_{BA} \tilde{\epsilon}_A + \sigma_{BB} \tilde{\epsilon}_B + X_{BQ} (-\nabla \tilde{T}/T), \\ \tilde{J}_Q &+ X_{QA} \tilde{\epsilon} + X_{QB} \tilde{\epsilon}_B + L_{QQ} (-\nabla \tilde{T}/T). \end{aligned} \quad (6)$$

For simplicity, the coefficients which appear in the above relations are taken to be scalars rather than tensors. The Onsager reciprocal relations<sup>6</sup> imply that

$$\sigma_{AB} = \sigma_{BA}, \quad X_{AQ} = X_{QA}, \quad X_{BQ} = X_{QB}. \quad (7)$$

The coefficients  $\sigma, X, L$  cannot be calculated exactly in realistic systems. The quantities  $\sigma_{ij}$  are ordinary conductivities since a fictitious electric

field  $\tilde{E}_A$  which exerts a force on only the  $A$  charges would produce charge currents  $\tilde{J}_A = \sigma_{AA} \tilde{E}_A$  and  $\tilde{J}_B = \sigma_{AB} \tilde{E}_A$ . Note that the conductivity  $\sigma_{AA}$  is not the conductivity of the system with only  $A$  charges present. Rather it is a measure of the current of  $A$  charges produced by a field which acts only on the  $A$  charges. If the  $A$  and  $B$  charges were totally independent,  $\sigma_{AB}$  would be zero. In general,  $\sigma_{AB}$  is nonzero because the motion of the  $B$  charges produced by  $\tilde{\epsilon}_B$  will tend to move the  $A$  charges. There is no *a priori* reason to expect  $\sigma_{AB}$  to be very small. If the  $A$  and  $B$  charges are different mobile ion isotopes in a material with one-dimensional or tunnel-like structures,  $\sigma_{AB}$  should approach  $(\sigma_{AA} \sigma_{BB})^{1/2}$ .

The conductivities  $\sigma_{ij}$  can be formally obtained from Kubo formulas involving current-current correlations.<sup>9</sup> If both the charge carriers are ions, the classical version of the Kubo formulas may be valid. If the ion motion proceeds as simple hops involving the motion of a small number of ions the classical Kubo formula becomes the traditional expression involving lattice constants, hopping frequencies and correlation factors.<sup>10,11</sup> The thermal and thermal-electric terms  $L_{QQ}$ ,  $X_{AQ}$ , and  $X_{BQ}$  could also be calculated for a sufficiently simple model of a superionic conductor.

The general structure of two component transport in superionic conductors is described by Eqs. (3), (6), and (7). Application of these formal results will be described in Sec. II.

## II. APPLICATIONS

The generality of Eqs. (3), (6), and (7) means that they may be applied to essentially all transport measurements involving two types of charge carriers. However, this generality means that there are a large number of transport coefficients and there has been considerable work done based on approximations which reduce the number of coefficients.<sup>1</sup> Here, simplifications will be avoided, and a number of examples will be presented to demonstrate that actual experiments often measure simple combinations of these transport coefficients.

If one is concerned only with isothermal currents in superionic conductors, Eqs. (3), (6), and (7) can be combined to give

$$\begin{aligned} \tilde{J}_A &= (\sigma_{AA} + \sigma_{AB}) \tilde{E} - q_A \nabla n_A (\gamma_A \sigma_{AA} - \gamma_B \sigma_{AB}), \\ \tilde{J}_B &= (\sigma_{AB} + \sigma_{BB}) \tilde{E} - q_A \nabla n_A (\gamma_A \sigma_{AB} - \gamma_B \sigma_{BB}). \end{aligned} \quad (8)$$

The relations between the current densities  $\tilde{J}_A$  and  $\tilde{J}_B$ , the electric field  $\tilde{E}$ , and the density gradient  $\nabla n_A$  are completely specified by the three conductivities  $\sigma_{AA}$ ,  $\sigma_{AB}$ , and  $\sigma_{BB}$  and the thermodynamic parameters  $\gamma_A$  and  $\gamma_B$ . As the four following ex-

amples of idealized experiments will show, most experimentally measurable quantities depend only on the sum  $(\gamma_A + \gamma_B)$  so the isothermal transport depends on only four independent numbers. Results (i)–(iv) can all be simply obtained from Eq. (8).

(i) The total conductivity  $\sigma_0$  is the ratio of the total current magnitude  $|\vec{J}_A + \vec{J}_B|$  divided by the electric field in a system with no density gradients. Thus

$$\sigma_0 = \sigma_{AA} + \sigma_{BB} + 2\sigma_{AB}. \quad (9)$$

(ii) The transport number for the  $A$  charges is the ratio of the current  $|\vec{J}_A|$  to the total current obtained in a conduction experiment

$$|\vec{J}_A| / |\vec{J}_A + \vec{J}_B| = (\sigma_{AA} + \sigma_{AB}) / \sigma_0. \quad (10)$$

(iii) By using electrodes which block the passage of the  $B$  charges, a conductivity for the  $A$  charges alone,  $\sigma_A$ , may be obtained as a ratio of  $|\vec{J}_A|$  to  $|\vec{\epsilon}_A|$ :

$$\sigma_A = \sigma_{AA} - \sigma_{AB}^2 / \sigma_{BB}. \quad (11)$$

The condition that  $\vec{J}_B = 0$  means that there is a gradient of the densities of the  $A$  and  $B$  charges for single-component conduction given by

$$q_A \vec{\nabla} n_A = -q_B \vec{\nabla} n_B = -\frac{\vec{J}_A (\sigma_{BB} - \sigma_{AB})}{\text{Det}(\sigma) (\gamma_A + \gamma_B)}, \quad (12)$$

where

$$\text{Det}(\sigma) = \sigma_{AA}\sigma_{BB} - \sigma_{AB}^2. \quad (13)$$

(iv) The diffusion constant  $d$  is the ratio of the current  $\vec{J}_A$ , to the negative gradient of  $A$  charge ( $-q_A \vec{\nabla} n_A$ ) in a system where no net charge is allowed to flow ( $\vec{J}_A + \vec{J}_B = 0$ ). The result is

$$d = [\text{Det}(\sigma) / \sigma_0] (\gamma_A + \gamma_B). \quad (14)$$

At this point the choice of a lattice-based coordinate system becomes significant. In an absolute coordinate system, a gradient of  $A$  charges could distort the lattice so that  $q_A \vec{\nabla} n_A + q_B \vec{\nabla} n_B \neq 0$ . Then two slightly different diffusion constants for the  $A$  and  $B$  charges would be obtained, and each of these constants would depend on the lattice distortion.

In general, the condition that  $\vec{J}_A + \vec{J}_B = 0$  can be satisfied only if the electric field  $\vec{E}$  is nonzero. This field, which is produced by the accumulation of small amounts of charge on sample surfaces is given by

$$\vec{E} = -\frac{\vec{J}_A [\gamma_A (\sigma_{AA} + \sigma_{AB}) - \gamma_B (\sigma_{AB} + \sigma_{BB})]}{\text{Det}(\sigma) (\gamma_A + \gamma_B)}. \quad (15)$$

The quantities  $\vec{\epsilon}_A$  and  $\vec{\epsilon}_B$  in diffusion, which are more directly measurable have a simpler form.

For example,

$$\vec{\epsilon}_A = [(\sigma_{AB} + \sigma_{BB}) / \text{Det}(\sigma)] \vec{J}_A. \quad (16)$$

Although the conductivities and the quantity  $(\gamma_A + \gamma_B)$  cannot be calculated exactly, there are some bounds on their values. As was mentioned earlier,  $(\gamma_A + \gamma_B)$  must be positive if no phase separation is to take place. This can be seen in the diffusion constant [Eq. (14)], where the diffusion vanishes as  $(\gamma_A + \gamma_B)$  vanishes. The conductivity  $\sigma_0 = \sigma_{AA} + \sigma_{BB} + 2\sigma_{AB}$  must be positive, and if  $(\gamma_A + \gamma_B) > 0$ ,  $d$  must also be positive. This means that  $\text{Det}(\sigma) > 0$ . Also, since  $\sigma_A$  is positive,  $\sigma_{AA}$  and  $\sigma_{BB}$  must be positive.

It is, in principle, possible to obtain the four numbers which characterize isothermal transport ( $\sigma_{AA}$ ,  $\sigma_{BB}$ ,  $\sigma_{AB}$ , and  $\gamma_A + \gamma_B$ ) from experiments. For example, using Eqs. (10), (11), and (16),  $\sigma_{BB}$  can be written in terms of observable quantities

$$\sigma_{BB} = (\sigma_{AB} + \sigma_{BB}) \left( \frac{1}{\sigma_{AA} - \sigma_{AB}^2 / \sigma_{BB}} \right) \left( \frac{\text{Det}(\sigma)}{\sigma_{AB} + \sigma_{BB}} \right) \quad (17)$$

or

$$\sigma_{BB} = (J_B / E)_{ii} (1 / \sigma_A)_{iii} (J_A / \epsilon_A)_{iv},$$

where the subscripts ii, iii, and iv denote the particular experimental situation discussed in the numbered examples. Once  $\sigma_{BB}$  is known, all other parameters are easily obtained from experimental data.

Not all experimentally observable isothermal transport effects are independent since they are all related to four numbers. For example, the ratio of transport numbers in simple conduction is equal to the ratio of electrochemical potential gradients in diffusion. From Eqs. (10) and (16)

$$\frac{\sigma_{AA} + \sigma_{AB}}{\sigma_{AB} + \sigma_{BB}} = \left( \frac{|\vec{J}_A|}{|\vec{J}_B|} \right)_{ii} = \left( \frac{|\vec{\epsilon}_B|}{|\vec{\epsilon}_A|} \right)_{iv}. \quad (18)$$

An important special case of two component transport occurs when one of the charge densities ( $n_B$ ) is very small. This situation is encountered in tracer isotope diffusion experiments,<sup>3</sup> and in mixed conductors when the number of electrons is very small.<sup>4</sup> In these situations, all of the previous relations remain valid except that  $(\gamma_A + \gamma_B)$  can be replaced by  $(\beta n_B q_B^2)^{-1}$  [see Eq. (5)]. For tracer isotope experiments, further simplifications can be made because  $\sigma_{AA} \gg (\sigma_{BB}, |\sigma_{AB}|)$  if  $n_A \gg n_B$ . Hence,

$$\sigma_0 \approx \sigma_{AA}, \quad (19)$$

and, except for the pathological case where mobile ions lie in channels and cannot get around each other,

$$\text{Det}(\sigma) \approx \sigma_{AA}\sigma_{BB}. \quad (20)$$

This simplifies the diffusion constant, and

$$d = \sigma_{BB}/\beta n_B q_B^2. \quad (21)$$

The simplest form of the Nernst-Einstein relation for isotope diffusion states that

$$\sigma_0 = d \beta n q^2, \quad (22)$$

where  $q_A = q_B = q$  and  $n = n_A + n_B$ . This relation is not obeyed and an experimental factor  $f$  is defined by

$$f = \beta n q^2 d / \sigma_0. \quad (23)$$

According to Eq. (21), a theoretical expression for  $f$  which depends only on the assumption that the tracer isotope ( $B$ ) is dilute is

$$f = (\sigma_{BB}/n_B)/(\sigma_{AA}/n_A). \quad (24)$$

As an example of how one can obtain hopping model results from these formal expressions, consider the motion of isotopes  $A$  and  $B$  caused by the hopping of a small number of vacancies on a lattice. Assuming the classical Kubo formula is valid gives

$$\sigma_{AA} = \frac{\beta q^2}{\Omega} \sum_{i,j \in \{A\}} \int_0^\infty \dot{X}_i(0) \dot{X}_j(t) dt,$$

where  $\dot{X}_j(t)$  is the  $x$  component of the velocity of the  $j$ th type  $A$  ion at time  $t$ . An analogous expression holds for  $\sigma_{BB}$ . The ion motion consists of hopping from one site to a nearest neighbor site and oscillations about fixed sites, but the oscillatory motion is irrelevant for dc conductivity.

In general, there are two contributions to the conductivities from hopping motion. The first contribution occurs when  $i = j$  and  $t$  is small so that the velocity correlations are nonzero due to a single hopping process. Integrating  $t$  over a hopping time gives

$$\sigma_{AA}/n_A = \frac{1}{6} \beta q^2 \bar{a}^2 \Gamma,$$

where  $\Gamma$  is the hopping frequency of an  $A$  ion,  $\bar{a}$  is the hopping distance, and the lattice is assumed to be cubic.

The second contribution to the conductivity occurs when  $\dot{X}_i(0)$  and  $\dot{X}_j(t)$  are nonzero by virtue of two distinct vacancy hops. If the  $B$  ions are dilute, there will be no significant correction to  $\sigma_{AA}$  from this effect because the vacancy motion is random in direction and it is surrounded by  $A$  ions. There will, however, be a correction to  $\sigma_{BB}$  because the isolated  $B$  ion which hops from site  $m$  to site  $m'$  is relatively likely to return to site  $m$ . Summing over all later vacancy hops yields<sup>12</sup>

$$\sigma_{BB}/n_B = \frac{1}{6} \beta q^2 \Gamma a^2 [(1+C)/(1-C)],$$

where  $C$  is the average value of the cosine of the angle between two consecutive jumps of the  $B$  ion.

Substituting the hopping expressions for  $\sigma_{AA}/n_A$  and  $\sigma_{BB}/n_B$  into Eq. (24) yield the standard hopping expression for the correlation factor  $f$ .

If one considers temperature gradients as well as particle gradients, there is a confusing variety of conceivable thermoelectric experiments, and a lot of transport coefficients contained in Eq. (6). For simplicity, we consider those experimental situations with  $\vec{J}_B = 0$ . For example, one might be performing thermoelectric experiments on a mixed conductor in which no ionic currents are allowed. By setting  $\vec{J}_B = 0$ , and eliminating  $\epsilon_B$ , one obtains the standard equations characterizing single-component thermoelectric effects.

$$\begin{aligned} \vec{J}_A &= \sigma_A \vec{\epsilon}_A + X_A (-\vec{\nabla}T/T), \\ \vec{J}_Q &= X_A \vec{\epsilon}_A + L_A (-\vec{\nabla}T/T). \end{aligned} \quad (25)$$

The important point is that the coefficients in this equation are renormalized, and

$$\begin{aligned} \sigma_A &= \sigma_{AA} - \sigma_{AB}^2/\sigma_{BB}, \\ X_A &= X_{AQ} - \sigma_{AB} X_{BQ}/\sigma_{BB}, \\ L_Q &= L_{QQ} - X_{BQ}^2/\sigma_{BB}. \end{aligned} \quad (26)$$

The Kelvin relations remain valid with the renormalized coefficients. When experimental coefficients are written in terms of the original transport coefficients of Eq. (6), the resulting expressions become fairly complicated. For example, the thermal conductivity is

$$K = (1/T)(L_Q - X_A^2/\sigma_A) \quad (27)$$

or

$$K = \frac{1}{T} \left( L_{QQ} - \frac{(X_{AQ}^2 \sigma_{BB} + X_{BQ}^2 \sigma_{AA} - 2X_{AQ} X_{BQ} \sigma_{AB})}{\text{Det}(\sigma)} \right).$$

A gradient in  $n_A$  and  $n_B$  can be produced by a temperature gradient (Soret effect),<sup>8</sup> and if one imposes the condition that no current flow in the sample, the density gradient is given by

$$\frac{q_A |\vec{\nabla} n_A|}{|\vec{\nabla} T|} = \frac{|X_{BQ}(\sigma_{AA} + \sigma_{AB}) - X_{AQ}(\sigma_{AB} + \sigma_{BB})|}{(\gamma_A + \gamma_B) T \text{Det}(\sigma)}. \quad (28)$$

### III. DISCUSSION

An important conclusion one can draw from the discussion of two-component transport is that there is a generally applicable formalism which allows one to relate theoretical transport coefficients to experimental data. Little has been said about the calculation of these coefficients since they cannot be obtained exactly and will depend on the theoretical model considered. Similar formal relations apply to transport cases when there are more than two types of mobile charge carriers,

but the number of theoretical coefficients becomes so large that fewer practical results are obtained.

In some special cases, however, the results obtained here can be generalized. For example, a mixed conductor with two isotopic species of mobile ions is an example of a three component system. More than one type of diffusion can take place in such a system, but if one of the isotopes of the mobile ion is very dilute, a simple well-defined expression for isotope diffusion can be obtained which is essentially identical to Eq. (21). Two examples of this type of three component system are the mixed conductors  $\alpha$ -Ag<sub>2</sub>S and  $\alpha$ -Ag<sub>2</sub>Se with small amounts of <sup>110m</sup>Ag added. Okazaki<sup>13</sup> has compared the diffusion of the rare silver isotope with ionic conductivity measured with blocking

electrodes which eliminate the electronic current. He found that the diffusion was unusually small as compared with the ionic conductivity. One is tempted to suggest that the mixed conductor nature of these materials may lead to these anomalous results, but in fact the converse is true. Denoting the abundant and rare Ag isotopes by A and B, and the electrons by C, Okazaki actually measured

$$f = \frac{\sigma_{BB}/n_B}{(\sigma_{AA} - \sigma_{AC}^2/\sigma_{CC})/n_A},$$

and this quantity is larger, not smaller, than one would expect if coupling between the ions and the electrons were ignored and the anomalous value of  $f$  cannot be explained by mixed conductor effects.

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