CORRELATION EFFECTS IN IONIC CONDUCTIVITY

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I. INTRODUCTION

Correlation effects in atomic transport in solids refer to those effects which enhance or depress the value of the transport quantity in question compared with that for a random walk. In general, correlation effects are manifested as a memory between successive jump vectors of the diffusing entity. As is shown herein, the diffusing entity can be an ion, a group of ions of the same type, or even the entire system.

Historically, the study of correlation effects in diffusion has mainly been directed to tracer correlation effects. As a prelude to our detailed discussion here of correlation effects in ionic conductivity, it is worthwhile to review briefly tracer correlation effects. Bardeen and Herring[1] discovered the tracer correlation effect in diffusion some 30 years ago. Since that time, the effect has been the subject of extensive continued study.

Tracer correlation effects are conventionally embodied in the so-called tracer correlation factor f, which appears as a correction factor in the random walk expression for the tracer diffusion coefficient D*. For isotropic cubic solids D* is expressed as[1,2]

$$D^* = \Gamma a^{*2} f/6 \tag{1}$$

where Γ is the atomic jump frequency and a* is the jump distance. The tracer correlation factor itself is conventionally expressed via the Einstein equation as[2]

$$f = \lim_{n \to \infty} \langle \Delta R^2 \rangle / n a^{*2} \tag{2}$$

where ΔR is the displacement of a particle after n jumps in time t and the Dirac brackets indicate a large number of ions for averaging purposes.

Equation 2 is conventionally expanded to

$$f = 1 + \lim_{n \to \infty} \left(2 \sum_{i=1}^{n} \sum_{j=1}^{\infty} \langle r_i r_{i+j} \rangle / \sum_{i=1}^{n} \langle r_i^2 \rangle \right) \tag{3}$$

where $r_1, r_2, \ldots, r_n$ are the individual displacements of a particle. The correlation between directions of jump vectors is a natural consequence of the proximity of the defect (which makes the jump possible) to a given tracer atom after the atom has just jumped with the defect, see Figure 1. In this figure, which uses the vacancy as the defect for diffusion, we assume that the tracer atom (hatched) has just exchanged places with the vacancy. Since the vacancy is still adjacent to the tracer atom, the tracer may reverse its last jump with a probability greater than a jump elsewhere. This is a rudimentary description of the correlation
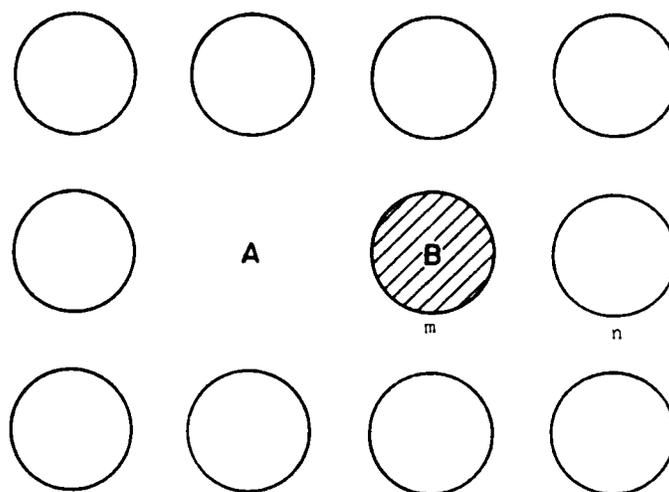
FIGURE 1.   Illustration of the vacancy mechanism in the square planar lattice (see text for a description of the correlation factors f and g associated with the mechanism).

process, but it suffices well enough for our purposes. Other reasons for tracer correlation include a tracer atom (now formally an impurity) which has an exchange frequency with the vacancy different from the host,[3] and the so-called physical correlation effect,[4] e.g., in ordered alloys, where an atom which takes a jump from its lattice to the lattice of the other component, i.e., from a "right" site to a "wrong" site, tends to reverse that jump on the next jump in order to maintain order.

Much of the earlier work on tracer correlation was concerned with the calculation of f for the common diffusion mechanisms in the common lattices. This kind of work has continued up to the present day, partly to obtain f to a higher level of accuracy,[5] sometimes exactly,[6] and partly for more specialized mechanisms in specialized lattices.[7] Other early work concentrated on the calculation of f for impurity diffusion. The large literature on the subject was reviewed in 1970 at length in an authoritative review by Le Claire.[2] More recent calculations in the area have not been reviewed.

Starting about the time of Le Claire's review, calculations were made of f for models which required master equation approaches for their solution. Sato and Kikuchi[4,8-15] and co-workers are the pioneers in this area. They developed their Path Probability Method (PPM) to cope with problems in alloys which exhibit order (previous to this, only random alloys had been examined), superionic conductors, and nonstoichiometric compounds. A little later, numerical calculations based on Monte Carlo computer simulation were also performed on similar models and, in fact, also for many of the more familiar diffusion mechanisms in the common lattices.[16]

The substantial interest in the rather innocuous quantity f comes about not because f is a particularly important quantity numerically in the expression for the tracer diffusion coefficient. For example, in the f.c.c. lattice and the vacancy mechanism, f equals 0.7815 and therefore reduces the value of D* only some 22% from the random walk value. This is really not much greater than the reproducibility in measuring D* by standard serial sectioning.[17] There are occasions, of course, when f is sufficiently small (e.g., an ordered alloy), where the inclusion of f is in fact important. The real significance of f comes about because it is possible, in principle, to measure experimentally f or a quantity closely related to it. Since f is dependent upon mechanism, among other things, then a measurement of f can sometimes throw considerable light on the diffusion mechanism operating. The experimental methods used to determine f include the isotope effect[18] and the Haven Ratio.[2,19]

The former relies on a special means of accurately measuring the small difference in the values of the tracer diffusion coefficient of two tracers which have been permitted to diffuse (usually simultaneously, though not always). The latter relies on the measurement of the ionic conductivity of the sample as well as the tracer diffusion coefficient and can be used only when the sample is principally an ionic conductor. The Haven Ratio affords a convenient introduction to correlation effects in ionic conductivity.

The Haven Ratio and its connection to f *originally* depended on the ionic conductivity σ being expressed in the following form:

$$\sigma = Cq^2\Gamma a^2/6kT \tag{4}$$

where C is the concentration of charge carriers, q is the ionic charge, and k and T are the Boltzmann constant and temperature, respectively, and a is the distance moved by the charge. This distance is not necessarily the same distance as the distance an ion moves, e.g., with the interstitialcy mechanism. The ionic conductivity can be converted to a dimensionally correct diffusion coefficient D_σ by way of the relation

$$\sigma/D_\sigma = Cq^2/kT \tag{5}$$

Equation 5 is sometimes called the Nernst-Einstein relation. This title is not, in fact, strictly correct. The exact Nernst-Einstein relation refers to a relation between a *chemical* diffusion coefficient and the ionic conductivity.[20] In addition, the exact relation contains a thermodynamic factor. The exact relation reduces to Equation 5 at low concentrations of charge carriers or under thermodynamically ideal conditions. When Equation 5 is used indiscriminately, it should be seen only as a way of converting an ionic conductivity to a dimensionally correct diffusion coefficient, D_σ. Such a diffusion coefficient normally has no meaning in the Fickian sense. That is to say, it is not necessarily a proportionality factor between a flux and a concentration gradient.

When Equations 1, 4, and 5 are combined, one has for the Haven Ratio, H_R:

$$H_R \equiv D^*/D_\sigma = f(a^*/a)^2 \tag{6}$$

Thus a measurment of D* and σ gives direct access to f: with assumptions about the tracer jump distance a* and the charge jump distance a, it is possible to infer a value of f from a measurement of H_R and, from this, to infer the mechanism of diffusion.

This simple picture for the makeup of H_R was accepted in the 1960s until Sato and Kikuchi[9,10] showed that things could be rather more complicated. Using the PPM, they showed, for a lattice gas model of nearest-neighbor interacting particles diffusing on a honeycomb lattice with inequivalent sites arranged alternately, that the ionic conductivity itself included a "correlation factor". They showed for the foregoing model that

$$\sigma = Cq^2\Gamma a^2 f_I/6kT \tag{7}$$

where f_I is the physical or conductivity correlation factor. The factor was found to be nontrivial, i.e., $\neq 1$ when a relatively high vacancy concentration was present. In other words, Equation 4 is not correct in general. Sato and Kikuchi's results[9] for f_I are shown in Figure 2. The existence of f_I of course changed the simplicity of Equation 6 so that in general

$$H_R = (f/f_I)(a^*/a)^2 \tag{8}$$

Sato and Kikuchi's calculation of f_I was the starting point for the development of the new
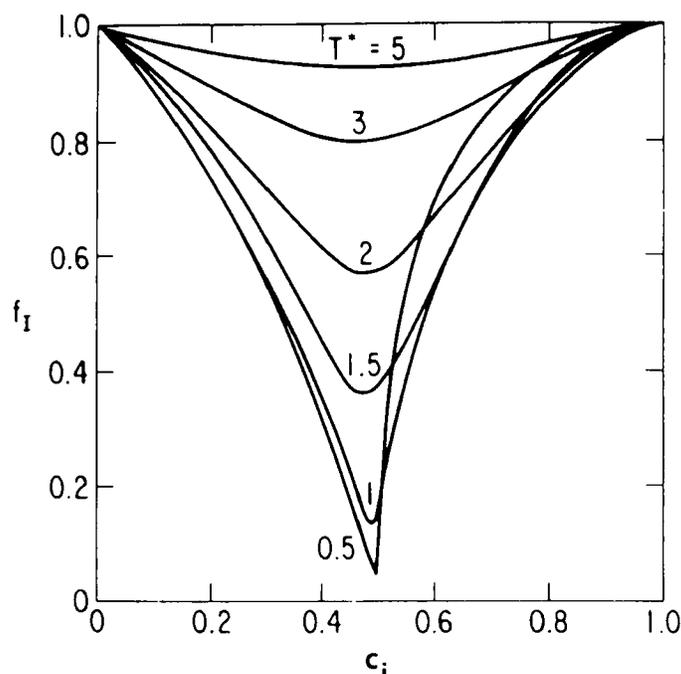
FIGURE 2.   Path Probability Method results for the dependence of f_i on ion concentration in the honeycomb lattice:[89] the effect of nearest-neighbor repulsion and alternate site inequivalence in energy. $T^* = kT/\epsilon_{nn}$ and $w/\epsilon_{nn} = 5.0$, where w is the difference in site energies and ϵ_{nn} is the interaction energy.

area of correlation in ionic conductivity, although some years earlier Manning[21] had discovered a related effect in binary systems called the vacancy-wind effect. In the case of ionic conductivity σ_i of an impurity, this effect led to the following expression for σ_i:

$$\sigma_i = C_i q_i^2 \Gamma_i a^2 f_i (1 + 2q_s \langle n_p \rangle / q_i) \tag{9}$$

where q_i and q_s are the charges on the impurity and host ions, respectively, and $\langle n_p \rangle$ is a complex kinetic quantity.

In this review, we first discuss f_i, its physical meaning in the light of recent findings, and its formal relationship to f. Then we discuss the binary analogs of f_i and make connection to the vacancy-wind effect of Manning.

II. CONDUCTIVITY CORRELATION IN THE UNARY SYSTEM

A. General Features

The original name for f_i was the "physical correlation factor". This was later found to be a somewhat unfortunate choice because the adjective "physical" was supposed to refer to those physical effects which we have already discussed in relation to tracer diffusion in an ordered alloy.[4] That is to say, interactions and/or inequivalent site potential energies can work in such a way as to reverse disordering-like jumps. Other cases have since been found where these physical effects are not so obvious. Some workers have then referred to f_i as the conductivity or charge correlation factor. Even this is not entirely satisfactory because f_i also occurs in chemical diffusion.[22] It should also be noted that in the literature sometimes the symbol f_c is used rather than f_i. We have used f_i in this review. -

In Sato and Kikuchi's original PPM calculation f_i turned up as a *deviation* from the

expected flow of ions in the static electric field. To make this clearer, let us assume that the motions of the current carriers in the assembly are uncorrelated. Then we can write the following expression for their random walk diffusion coefficient D_R:

$$D_R = \Gamma a^2/6 \tag{10}$$

Using Equation 5, with $D_\sigma = D_R$, this time to convert to the ionic conductivity, we find that the ionic conductivity would simply be Equation 4. This is to say, the *expected* conductivity derives from uncorrelated motion.

If the determination of σ is made by means of calculating the flow either by the PPM or by Monte Carlo simulation, and a deviation exists from Equation 4, then this deviation is ascribed to f_I. This is perfectly reasonable and is by way of analogy with the way f represents a deviation in random walk behavior for D^*. It does not shed much light, however, on the physical nature of f_I. As it turned out, for quite a few years after the discovery of f_I, and certainly up to 1983, the physical nature of f_I, and especially whether it had correlation factor status like f, was by no means clear. It is not going too far to say that there seemed to be a certain mystery surrounding f_I which none of the calculations really dispelled since they were all based on the calculation of a flow. It must be admitted that there were skeptics who were quite uneasy about f_I, possibly because it spoiled the simple (but incorrect) picture of H_R and possibly because f_I could not be explained in any sort of transparent physical way (such as f has in Figure 1) without resorting to a calculation of a flow.

It turns out that the Onsager equations of irreversible thermodynamics partly by themselves but mostly in conjunction with the time-correlation formulas for the phenomenological coefficients provide the necessary understanding of f_I. Let us see how this understanding comes about by starting with the flux equations for a system containing host ions A, tracer ions A^*, and vacancies V. It is assumed here and in the rest of Section II.A that the lattice is cubic and the vacancy mechanism operates. All of the considerations that follow can readily be generalized to any other diffusion mechanism, etc. The flux equations are

$$J_A = L_{AA}X_A + L_{AA^*}X_{A^*} \tag{11a}$$

$$J_{A^*} = L_{A^*A^*}X_{A^*} + L_{A^*A}X_A \tag{11b}$$

where the L_{ij} are the phenomenological coefficients, and the X_i are the driving forces, for example, $X_i = -\text{grad } \mu_i$, where μ_i is the chemical potential of species i.

Let us first show the surprising result that f itself is a conductivity correlation factor. Since the tracer diffusion coefficient D_{A^*} is defined by way of Fick's First Law for $c_{A^*} + c_A = \text{const.}$

$$J_{A^*} = -D_{A^*} \frac{\partial C_{A^*}}{\partial x} \tag{12}$$

where $\partial C_{A^*}/\partial x$ is the concentration gradient, it is straightforward to show that D_{A^*} is given by[23]

$$D_{A^*} = \frac{kTV}{N} \left(\frac{L_{A^*A^*}}{c_{A^*}} - \frac{L_{A^*A}}{c_A} \right) \quad \text{all } c_{A^*} \tag{13}$$

where V is the volume, N is the total number of entities (tracer and nontracer ions and vacancies), and c_i is the mole fraction of species i. Note that in the general case, D_{A^*} actually depends on two phenomenological coefficients, $L_{A^*A^*}$ and L_{A^*A}. For vanishingly small tracer concentrations such as are normally encountered experimentally, Equation 13 reduces to

$$D_{A^*} = kTVL_{A^*A^*}/Nc_{A^*} \qquad c_{A^*} \to 0 \tag{14}$$

The ionic conductivity of either or both components A and A* can also be conveniently expressed in terms of the L_{ij}. In order to show that f is a conductivity correlation factor, it is convenient here to consider a "thought experiment". It is not one which can be performed experimentally, although it can be simulated easily on a computer. We consider the situation where *only* tracer ions feel the static electric field whereas host ions do not. Accordingly, $X_{A^*} = q_{A^*}.E$ and $X_A = 0$, where E is the static electric field strength. The flux of A* is given by

$$J_{A^*} = q_{A^*}.EL_{A^*A^*} \tag{15}$$

and the ionic conductivity of the A* ions can easily be shown to be given by[23]

$$\sigma_{A^*} = q_{A^*}^2.L_{A^*A^*} \tag{16}$$

Accordingly, when we combine Equations 14 and 16 for the condition $c_{A^*} \to 0$, we have

$$\sigma_{A^*}/D_{A^*} = C_{A^*}q_{A^*}^2/kT \tag{17}$$

Since D_{A^*} can always be written in the correlated random walk form (Equation 1), then by virtue of Equation 17 σ_{A^*} must also contain f (cf. Equation 7):

$$\sigma_{A^*} = C_{A^*}q_{A^*}^2.\Gamma a^2 f/6kT \qquad c_{A^*} \to 0 \tag{18}$$

From Equation 18 we see that f itself clearly can have the status of a conductivity correlation factor, i.e., it reflects a deviation in the flow of the A* ions in a neutral matrix of A. Thus we have shown, not that f_I enjoys correlation factor status like f, but rather the converse, that f can have conductivity correlation factor status like f_I enjoys!

An important development in the area of solid-state diffusion is the fact that the L_{ij} can be expressed in terms of atomistic Einsteinian formulas[24]

$$L_{ij} = \lim_{V \to \infty} \lim_{t \to \infty} (6VkTt)^{-1} \langle \Delta R^{(i)}(t) \cdot \Delta R^{(j)}(t) \rangle \tag{19}$$

where $\Delta R^{(i)}$ (t) is the total displacement of species i in time t and the Dirac brackets denote a thermal average. In practical applications of Equation 19 (e.g. in computer simulations), the average is calculated with periodic boundary conditions, while the vector $\Delta R^{(i)}$ is cumulative and may extend outside the finite volume.

It is instructive at this point in our discussion to sketch a simple derivation of Equation 19, taking advantage of the fact that the flux equations are perfectly general and apply even to hypothetical situations which are not easily realized in the laboratory. Let us first consider a single particle alone in the world performing a random walk. The fundamental equation which characterizes the motion of the particle is the Einstein equation

$$\langle \Delta R^2(t) \rangle = 6Dt \qquad t \to \infty \tag{20}$$

Here, the diffusion coefficient D is linked to the mobility u by the Nernst-Einstein equation (exact in this form in the limit of a single particle)

$$u/D = q/kT \tag{21}$$

Note that the mobility is the velocity per unit field. (The ionic conductivity is simply Cqu.) By combining Equations 20 and 21, we find that

$$u = \lim_{t \to \infty} q\langle \Delta R^2(t)\rangle(6kTt)^{-1} \tag{22}$$

where the limit $t \to \infty$ is introduced because Equation 10 is only valid in the limit of large times. Equation 22 is a special case of the celebrated fluctuation-dissipation theorem.[25] The general idea is that the linear response toward an external field is determined by the size of certain fluctuations in thermal equilibrium. Thus, according to Equation 22, the mobility is proportional to $\lim_{t} \to \infty \langle \Delta P^2(t)\rangle/t$, where $P = q R$ is the dipole moment. Now, since the fluctuation-dissipation theorem is completely general, Equation 22 applies just as well for a *system* of particles. The reason for this is simply that nature does not know and cannot know just *how* the dipole movement fluctuations occur, that is, whether they are due to the motion of one or several particles.

We now apply Equation 22 to the hypothetical case where all A* particles carry a charge while the A particles do not. The particle flux in a static external field E is given by Equation 15. The flux is also given by

$$J_{A^*} = C_{A^*}u_{A^*}E \tag{23}$$

and u_{A^*} is the mobility of a single A* particle. Thus

$$L_{A^*A^*} = C_{A^*}u_{A^*}/q_{A^*} \tag{24}$$

Combining this with Equation 22, where now ΔR is the sum of the A* particle position vectors and, similarly $u = VC_{A^*}u_{A^*}$, we get

$$L_{A^*A^*} = \lim_{V \to \infty} \lim_{t \to \infty} \langle \Delta R^{(A^*)}(t) \cdot \Delta R^{(A^*)}(t)\rangle(6VkTt)^{-1} \tag{25}$$

This is the A*-A* case of Equation 19. The limit $V \to \infty$ is introduced in order to eliminate finite size effects and arrive at a true bulk result. The A-A case is derived analogously. Finally, in order to derive the cross-term case A-A*, we assume that all particles carry the same charge. Then, according to Equation 11, the *total* flux is given by

$$J = J_A + J_{A^*} = (L_{A^*A^*} + L_{AA} + 2L_{A^*A})qE \tag{26}$$

where we have applied the Onsager reciprocal condition $L_{A^*A} = L_{AA^*}$. Similar to Equation 25, we get

$$L_{A^*A^*} + L_{AA} + 2L_{A^*A} = \lim_{V \to \infty} \lim_{t \to \infty} \langle \Delta R^{(tot)}(t) \cdot \Delta R^{(tot)}(t)\rangle(6VkTt)^{-1} \tag{27}$$

where $\Delta R^{tot} = \Delta R^{(A^*)} + \Delta R^{(A)}$. By utilizing Equation 19 for the A*-A* and A-A cases, we are led immediately to the required A-A* case

$$L_{AA^*} = \lim_{V \to \infty} \lim_{t \to \infty} \langle \Delta R^{(A)}(t) \cdot \Delta R^{(A^*)}(t)\rangle(6VkTt)^{-1} \tag{28}$$

Next in our discussion, we use Equation 19 to sketch out the derivation that f and f_I are in fact related by a third, two-particle correlation factor g.[26,27] First we note that the total

displacement of species i, $\Delta R^{(i)}$ (t) in Equation 19 is of course given by the sum of the individual ion displacements, i.e.,

$$\Delta R^{(i)}(t) = \sum_m \Delta r_m^{(i)}(t) \tag{29}$$

If Equation 29 is substituted back into Equation 19, for i = j = A*, we have

$$L_{A^*A^*} = \lim_{V \to \infty} \lim_{t \to \infty} (6VkTt)^{-1} \cdot$$
$$\left[\sum_m \langle \Delta r_m^{(A^*)2}(t) \rangle + \sum_{m \neq n} \langle \Delta r_m^{(A^*)}(t) \cdot \Delta r_n^{(A^*)}(t) \rangle \right] \tag{30}$$

Now, the usual tracer correlation factor f is given by the Einstein expression in the terminology of this section

$$f = \lim_{V \to \infty} \lim_{t \to \infty} \langle \Delta r^2(t) \rangle / \Gamma t a^2 \tag{31}$$

Furthermore, we can *define* a two-particle correlation factor g by

$$g = \lim_{V \to \infty} \lim_{t \to \infty} N \langle \Delta r_m(t) \cdot \Delta r_n(t) \rangle / \Gamma t a^2 \qquad m \neq n \tag{32}$$

The factor N (the total number of entities) in Equation 32 compensates for the fact that interactions giving rise to correlations between ions m and n take place less frequently as the volume is increased. Upon substituting the definitions of f and g (Equations 31 and 32) into Equation 30, we immediately find

$$L_{A^*A^*} = \Gamma a^2 N c_{A^*} (f + c_{A^*} g)/6VkT \qquad V \to \infty \tag{33}$$

The conductivity of A* is given by Equation 16 for all c_{A^*} and certainly for $c_A = 0$, which we now focus on. When $c_A = 0$, A* is the sole source of current in the system. Accordingly, the conductivity correlation factor, f_I, which is defined for a situation where all the ions carry the charge, must in fact be given by

$$f_I = f + c_{A^*} g \qquad c_A = 0 \tag{34}$$

Equation 34 has also been illustrated by Monte Carlo simulation.[26] We might mention that f and g depend only on $c_A + c_{A^*}$ since A* and A ions move in an identical manner.

Thus, f_I is simply a sum of two correlation factors which refer to the atomic level. There is no mystery about the nature of f_I, and there are no collective or cooperative effects contained in it. The physics of f are of course well known as we have already discussed in conjunction with Figure 1. The physics of g are new and are worth discussing here in a little detail. Consider, for example, a specific example such as that indicated in Figure 1. When the vacancy concentration is very low, f_I is in fact trivially equal to unity, so that g = 1 − f > 0. Suppose that ion m (the hatched one) has just exchanged sites with the vacancy. If the subsequent jump of the vacancy is perpendicular to that jump, then there is no contribution to either f or g. If the vacancy jumps back again (with m), this of course contributes to make f less than unity, as is well known. However, there is an additional probability that the vacancy jumps in the same direction as the initial jump by exchanging with a new atom n. It is this jump which will give a positive contribution to g for ions m and n. This contribution to g is the most important one and results in g ending up positive.

A qualitative comment on the sign of g is appropriate here. When one part of a solid is pulled, the rest follows in the same direction. From the fluctuation-dissipation theorem, this fact should be reflected by a correlation of the form $g > 0$. These are situations where $g > 0$ can be regarded perhaps as "solid-like". In liquids, we have just the opposite. When a particle of the liquid is pulled, the rest tends to flow the other way locally to fill the vacuum left behind the pulled particle. Thus, such a situation could be regarded as being "liquid-like", with $g < 0$. As it turns out, f is <1 in solids, in agreement with $g > 0$, while f can be >1 in liquids,[61] thereby in agreement with $g < 0$.

The form of Equation 34 has significant ramifications on the interpretation of the Haven Ratio, which, for the vacancy mechanism, now becomes

$$H_R = f/(f + c_A \cdot g) \qquad c_A = 0 \tag{35}$$

In the "pre-f_I" era when $H_R \neq 1$, this was considered to be direct evidence of a nonunity, that is, a nontrivial value of the tracer correlation factor f. However, from the form of H_R in Equation 35, it is seen that $H_R \neq 1$ is in reality a unique indication of a nontrivial two-particle correlation effect. In principle, although we admit it is not very likely, it could be possible for $f = 1$ at the same time.

Next, in this section on the nature of f_I, we wish to draw specific attention to the fact that f_I can in fact be expressed in a simple Einsteinian form quite reminiscent of the form that f itself takes.[28] Starting again with Equation 19, we write for $L_{A^*A^*}$:

$$L_{A^*A^*} = \lim_{V\to\infty} \lim_{t\to\infty} (6VkTt)^{-1} \langle \Delta R^{(A^*)}(t) \cdot \Delta R^{(A^*)}(t) \rangle \tag{36}$$

Let us assume that A* ions are the only type of ions in the system, i.e., $c_A = 0$. Accordingly, if A* ions are the only source of current in the system, then from Equations 7 and 16

$$f_I = 6kTL_{A^*A^*}/C_A \cdot \Gamma a^2 \tag{37}$$

and from Equation 36

$$f_I = \lim_{t\to\infty} \langle \Delta R^{(A^*)2} \rangle / Nc_A \cdot \Gamma a^2 \tag{38}$$

The total number of A* ions is Nc_{A^*}, so the jump frequency of the vector $\Delta R^{(A^*)}$ is $Nc_{A^*} \cdot \Gamma$. Therefore, whereas f encompasses correlation effects of a single particle in a system, f_I encompasses correlation effects of the entire system in a manner as if the system acts like a (hypothetical) particle. This is made clear in Figure 3, which shows a Gaussian spread of the displacement of a *system* (observed 10,976 times) compared with the displacements of 10,976 individual particles.

Finally, in this section on the general features of f_I, we wish to show that f_I can be expressed as the ratio between low- and high-frequency conductivity, i.e.,

$$f_I = \sigma(0)/\sigma(\infty) \tag{39}$$

Let us consider the case of a single particle alone in the world. (Equation 21 is the expression for the DC ionic mobility u(o)). Combining this equation with Equation 20 led to Equation 22 as we have seen. The mean square displacement of the particle in time t is given by

$$\langle \Delta R^2(t) \rangle = f\Gamma ta^2 \qquad t\to\infty \tag{40}$$
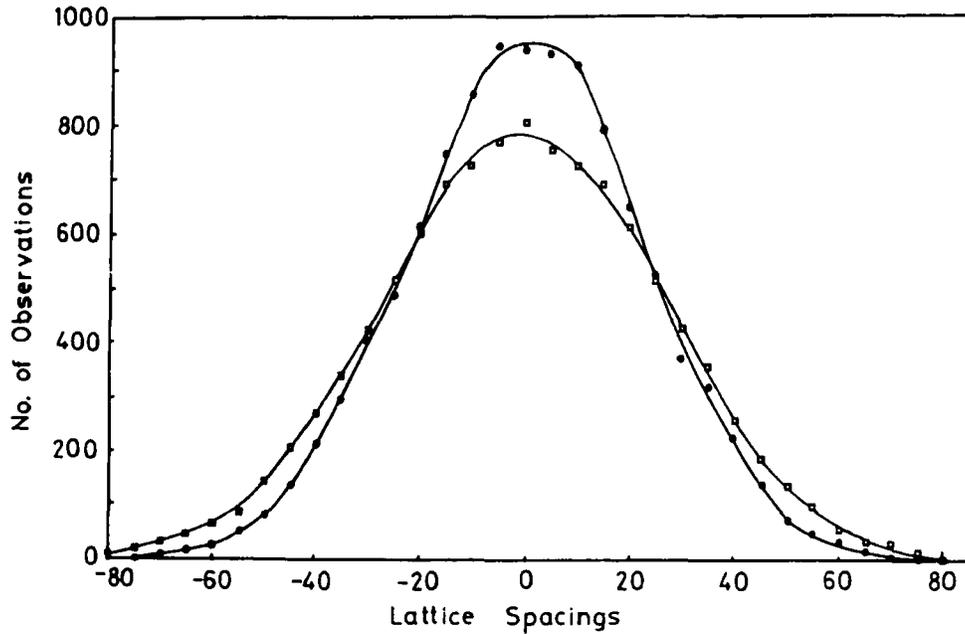
FIGURE 3.   (●) Monte Carlo results[28] of the calculation of the x-displacements of 10,976 ions in a 21,952-site simple cubic lattice with 10,976 random traps, exp ($-w/kT$) = 0.1 and 2500 jumps per ion. This results in f = 0.6328. (□) Monte Carlo results of 10,976 observations of the x-displacement of the entire system of 500 ions in a 1000-site simple cubic lattice with 500 traps, same conditions as above. This results in f_i = 0.8626.

where the walk is assumed, for convenience, to take place on a simple cubic lattice with jump distance a. Equations 22 and 40 imply that

$$u(0) = fqa^2\Gamma/6kT \qquad (41)$$

i.e., the analog of Equation 18 for one particle.

Now the high-frequency mobility $u(\infty)$ is given by the same expression, but without the f.[29] Why? Because on a short time scale, there occurs maximally one single jump, and therefore correlations or memories between the directions of consecutive jumps can play no role. We thus find that the geometrical correlation factor is simply given by

$$f = u(0)/u(\infty) \qquad (42a)$$

$$= \sigma(0)/\sigma(\infty) \qquad (42b)$$

when expressed in terms of the mobilities or conductivities for the single particle. A special case of the equation was derived by Dyre.[30] In order to arrive at Equation 39, we now note, just as previously, that the behavior of a many-particle system is completely analogous to that of a single particle if just ΔR in Equations 40, etc. is thought of as being the *sum* of the displacements of the individual particles composing the system. We have already shown that f_i is actually the geometric correlation factor of the total displacement vector. Thus, we get the required Equation 39 directly from Equation 42a. It is worth noting that because $f_i = f + c_A \cdot g$, then Equation 42b now becomes a special case of Equation 39. This comes about because a system of completely noninteracting particles (more than one particle per site) is equivalent in its behavior to one single particle in the system. For that situation, $g = 0$.

Equations 39 and 42 hold quite generally for hopping conduction and a general proof has been given[62] as well as a model-specific one in the context of the PPM.[63]

Kimball and Adams[29] showed that σ (0) $\leq$ σ (∞) in *any* stochastic model. This means that $f_I \leq 1$ always. This condition limits the variation of f and g:

$$f + c_A \cdot g \leq 1 \qquad c_A = 0 \tag{43}$$

In particular, whenever $f > 1$, g must be negative.

B. Calculations of f_I

As already mentioned, the first calculation of f_I was made by Sato and Kikuchi using the PPM.[9,10] Their model consisted of a honeycomb lattice gas in which particles were distributed over the sites subject to nearest-neighbor interactions and a site energy difference between alternate sites. This particular model was conceived for β-alumina. The result (Figure 2) showed the characteristic minimum at about 50% occupation, which was to be found again and again in other lattice gas systems (see later). The minimum was interpreted as a percolation difficulty since the efficiency of motion of the ions was reduced (relative to a random walk) because of the ordering between the ions. In this lattice gas, the maximum ordering occurs at 50% occupation.

The PPM calculation was followed sometime later by a series of Monte Carlo simulations.[31,32] These calculations have been reviewed in detail elsewhere.[16] The Monte Carlo calculations verified Figure 2 and also demonstrated that similar behavior to that shown in this figure can in fact be obtained with interactions between the particles alone, i.e., without the site energy difference. This was not found by Sato and Kikuchi, who originally found that f_I equals unity in that situation. Subsequent improvements to the PPM calculation have now given essential agreement with all the Monte Carlo results.

It should be noted that in the PPM the overall transition probability is defined by the maximization process of the PPM function and includes the distribution of atoms and vacancies. In principle, the meaning is the same in the procedure of Monte Carlo simulation once reaching "thermal equilibrium". A problem with the original PPM was that the distribution in the overall transition probability was given as an *average* of the state and not as the *instantaneous* value when an atom is ready to jump. The Monte Carlo calculation naturally uses the instantaneous value.

Although we have said that the minimum in f_I is due to the inefficiency of motion of the ions which is associated with ordering, it should not be concluded that ordering alone is the actual cause of the minimum. The basic transition probability for a single ion to jump to a vacant neighboring site used in these lattice gas calculations is of the form

$$\omega = \exp(-U_o/kT)\exp(z\epsilon_{nn}/kT) \tag{44}$$

where ϵ_{nn} is the nearest-neighbor interaction energy, z is the number of nearest neighbors around a given ion chosen to attempt to jump, and U_o is the activation energy for an isolated ion. From the form of this equation, it is clear that the ion does not "know" beforehand the energy of the site to which it is jumping. This is in contrast with many transition probabilities used in the literature, especially in Monte Carlo work, where one often uses such probabilities as the Metropolis one:[33]

$$\omega = \exp(-\Delta E/kT) \qquad \Delta E \geq 0 \tag{45a}$$

$$= 1 \qquad \Delta E < 0 \tag{45b}$$

where ΔE is the change in energy of the system.

All of these transition probabilities satisfy detailed balance of course, that is, they maintain the same degree of "equilibrium" or order. The transition probability used in Equation 44, however, while reasonably "realistic", somewhat exaggerates the effects of order on the dynamics. Thus, an ion which jumps from a low-energy to a high-energy site ("right" site to a "wrong" site) does not "know" until it gets to the new site that is is in fact a "wrong" site. There will then be a high probability of returning again to the low-energy site. Obviously this leads to a preponderance of jump reversals and a resultant inefficiency in motion or a "percolation difficulty". With Equation 45, the ion in a low-energy site neighboring a high-energy site "knows" about this high-energy site and would probably not even jump in the first place! It would be interesting to compare the effects of the choice of transition probability on the behavior of f_I.

A rather large number of other Monte Carlo calculations have been made of f_I in various lattice gases. They include the simple cubic lattice gas with nearest-neighbor repulsion/attraction,[34] the simple cubic lattice gas with nearest-neighbor blocking,[35] the square planar lattice gas with next-nearest-neighbor and/or nearest-neighbor blocking,[36] the square planar lattice gas with nearest-neighbor blocking,[36] the square planar lattice gas with nearest-neighbor repulsion and next-nearest-neighbor attraction,[37] the square planar lattice gas with nearest-neighbor repulsion at 50% occupation,[38] the simple cubic lattice gas with alternate[39] or random sites inequivalent,[40] the ordered honeycomb lattice gas[41,42] and a variety of one-dimensional models.[43] We make mention also of a calculation making use of the hybrid (Monte Carlo + Relaxation) computer simulation method.[44] In this new type of calculation, which was applied to Y_2O_3-doped CeO_2, the activation energies for motion were first calculated for 30 unique environments of Y^{3+} ions in the CeO_2 matrix using the CASCADE program. These were fed into a subsequent Monte Carlo lattice gas program that sampled the energies as jump frequencies. In this simulation, perhaps the first realistic simulation of diffusion in a complex oxide, f_I was found to change from unity at low Y^{3+} content to the extremely low value of 0.05 at high Y^{3+} content as a result of trapping. The importance of f_I in the description of ionic conductivity in such materials obviously cannot be overstated.

Other nonsimulation calculations of f_I include the 1D lattice gas with alternate sites inequivalent[45] and the 1D lattice gas with nearest-neighbor interactions.[46] Calculations for binary systems will be presented in Section III.B.

As a result of this very large body of information regarding the behavior of f_I, for specific models, it is reasonable to ask: what is the *minimum* requirement for a nontrivial, that is, nonunity, value of f_I? It is clear that in the absence of interactions apart from self-blocking — only one particle to a site — f_I is definitely only equal to unity in a homogeneous solid. However, by the simple artifice of making some sites inaccessible (i.e., by introducing obstacles), then this simple model *alone* is sufficient to make $f_I < 1$.[47] At high concentrations, that is, at and above the percolation threshold (e.g., at a site concentration of the [random] obstacles of 80.2% in f.c.c.), then $f_I = 0$ and percolation through the forest of obstacles is impossible. Also, f_I may differ from unity in models of *completely* noninteracting particles moving in inhomogeneous solids.[30]

When site inequivalence in energy is introduced, by either random traps or low-energy sites in some ordered arrangement, this also is sufficient to result in $f_I < 1$.[39,40] In such models, the transition probability takes two values: at a regular site

$$\omega = 1 \tag{46a}$$

and at a trapping site

$$\omega = \exp(-w/kT) \tag{46b}$$

where w is the trap energy. The trapping case is probably more common than the obstacle case mentioned previously. The role of the vacancy concentration is rather important here.

At very low vacancy concentrations, $f_I \rightarrow 1$ no matter how many ion jump frequencies there are in the lattice. (This remark does not apply to the case of completely noninteracting particles.[30]) For practical considerations, as distinct from purely theoretical ones, conductivity correlation effects tend to be amplified by increasing the vacancy concentration in such models, and this could explain why conductivity correlation effects were not noticed for so long since the study (either experimental or theoretical) of diffusion in systems with high defect concentrations did not really begin until the discovery of fast-ion transport in the late 1960s.

We can briefly summarize the situation by saying first that the appearance of a nontrivial ($\neq 1$) value for f_I is connected to the deviation of the hopping process from a random walk by the inequality of lattice sites due to such processes as crystallographic differences, mutual interactions among the hopping ions, differences in accessibilities of sites, etc. We can also say that, whereas f encompasses the correlation effects of a *single* particle in a system, f_I encompasses correlation effects of the *entire system* as if the system itself acted like a single hypothetical particle. Sato and co-workers prefer to say, equivalently, that f is the *percolation efficiency* of a single particle, whereas f_I is the *percolation efficiency* of the *entire system*. It is now clear that f_I is certainly as important as f and in some respects could be regarded as a more general quantity than f.

III. CONDUCTIVITY CORRELATION IN BINARY SYSTEMS

A. General Features

Although the system we focused on in Section II, namely, A and A*, was ostensibly a "binary" one, the jump frequency of A and A* was implicitly assumed to be identical. Of course, real tracers in materials do have different frequencies from the host, but these differences are very small and do not affect the physics and mathematics contained in Section II. The small differences in jump frequency between tracer and host or, more correctly, between types of tracer can be put to good use in the experimental measurement of the isotope effect and related to f, but that is altogether another subject which has been reviewed elsewhere.[18] In this section, we are interested in binaries where the jump frequencies are sufficiently different that this difference significantly affects the diffusion behavior of either component.

Let us write expressions for the fluxes using the Onsager equations of irreversible thermodynamics. Again, let us assume that this lattice is cubic and the vacancy mechanism operates. All of the considerations can be readily generalized to other diffusion mechanisms. The flux equations are

$$J_A = L_{AA}X_A + L_{AB}X_B \tag{47a}$$

$$J_B = L_{BB}X_B + L_{BA}X_A \tag{47b}$$

where the L_{ij} are the phenomenological coefficients and the X_i's are the driving forces. Although the L_{ij}'s are treated as being "phenomenological", they can in fact be derived analytically using methods such as the PPM.

Let the charges on A and B ions be q_A and q_B, respectively. It is convenient to decompose q_A and q_B to Z_Ae and Z_Be, respectively, where Z is the number of charges and e is the electronic charge. If a static electric field E is applied, the driving forces on A and B ions are Z_AeE and Z_BeE, respectively. The fluxes are

$$J_A = eE(Z_AL_{AA} + Z_BL_{AB}) \tag{48a}$$

and

$$J_B = eE(Z_B L_{BB} + Z_A L_{BA}) \qquad (48b)$$

It is convenient at this point to split up the L_{ij}'s into correlated and uncorrelated parts.[48] The "uncorrelated" part contains jump frequency and concentration information, and from our point of view in this discussion, the uncorrelated part contains spectator quantities. The "correlated" part of the L_{ij} contains, of course, information on correlation effects. For the diagonal phenomenological coefficients, we write

$$L_{ii} = L_{ii}^{(o)} f_{ii} \qquad i = A,B \qquad (49)$$

where $L_{ii}^{(o)}$ is the uncorrelated part of L_{ii}, i.e.,

$$L_{ii}^{(o)} = C_i \Gamma_i a^2 / 6kT \qquad i = A,B \qquad (50)$$

For the off-diagonal terms, we note the Onsager condition $L_{AB} = L_{BA}$. We can write L_{AB} in two forms:

$$L_{AB} = L_{AA}^{(o)} f_{AB}^{(A)} = L_{BB}^{(o)} f_{AB}^{(B)} \qquad (51)$$

because we have a choice given by the different jump frequencies of A and B. The f_{ij}'s are called correlation functions, for want of a better name! To make contact with the work of Sato et al.,[49] at this point we note that they give the f_{ij} the symbol ℓ_{ij} and use the terminology $\ell_{AB} = f_{AB}^{(A)}$ and $\ell_{BA} = f_{AB}^{(B)}$. It should be noted that $f_{AB}^{(A)} \neq f_{AB}^{(B)}$ because the jump frequencies differ. This is made clearer in the following discussion.

The expressions for σ_A and σ_B now become

$$\sigma_A = \frac{e^2 Z_A^2 C_A \Gamma_A a^2}{6kT} \left[f_{AA} + \frac{Z_B}{Z_A} f_{AB}^{(A)} \right] \qquad (52a)$$

and

$$\sigma_B = \frac{e^2 Z_B^2 C_B \Gamma_B a^2}{6kT} \left[f_{BB} + \frac{Z_A}{Z_B} f_{AB}^{(B)} \right] \qquad (52b)$$

A comment on the general nature of the f_{ij} is useful here. The Einsteinian form for the f_{ij}, while convenient for their calculation by Monte Carlo, does not on this occasion provide very much insight into their physical meaning. Thus, we have

$$f_{ii} = \langle (\Delta R_i)^2 \rangle / N c_i \Gamma_i a^2 \qquad i = A,B \qquad (53)$$

where ΔR_i is the displacement of the system of atoms of type i.
Similarly, we have (from Equation 19)

$$f_{AB}^{(i)} = \langle \Delta R_A \cdot \Delta R_B \rangle / N c_i \Gamma_i a^2 \qquad i = A,B \qquad (54)$$

From the denominator in this equation, it is clear why $f_{AB}^{(A)}$ differs from $f_{AB}^{(B)}$. One can make the usual observation that the off-diagonal correlation functions, derived as they are from the L_{ij} (i $\neq$ j), reflect the interference of the flux of the i-th species on the flux of the j-th and vice versa. The diagonal coefficients, derived from the L_{ii}, reflect the effect of the flux of the i-th species upon themselves *in the presence* of the flux of the j-th species.[50]

Sato groups the terms in square brackets in the expressions for σ_A and σ_B (Equation 52) to give

A   B
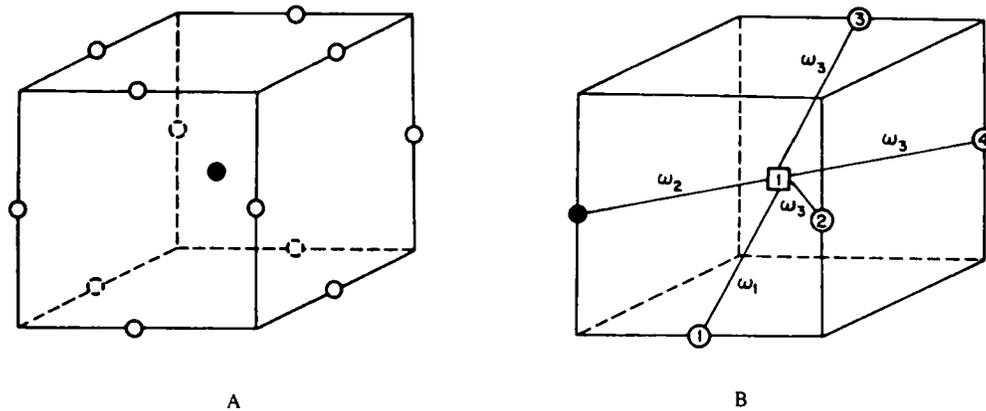
FIGURE 4.   (A) The location of the 12 nearest neighbors of an impurity in the f.c.c. lattice. (B) Illustration of the jump frequencies w_1, w_2, and w_3. The digit 1 at two sites indicates the *first* nearest-neighbor site, similarly for the other digits. w_4 (not shown) is the reverse of w_3, and w_0 (not shown) is the jump frequency for any other jump.

$$\sigma_A = e^2 Z_A^2 C_A \Gamma_A a^2 f_{IA}/6kT \tag{55a}$$

$$\sigma_B = e^2 Z_B^2 C_B \Gamma_B a^2 f_{IB}/6kT \tag{55b}$$

The correlation factors f_{IA} and f_{IB} are seen to be the binary analogs of f_I in the unary system (see Equation 7).

B. Calculations of the Binary Conductivity Correlation Factors

In this section, we are concerned with the various calculations that have been performed on f_{AA}, f_{AB}, and $f_{AB}^{(i)}$. There have been many calculations for dilute systems, especially with the five-frequency model (see Figure 4) for impurity transport. This area has been reviewed exhaustively recently, and it would be superfluous to go into much detail here.[51] The first calculation of the L_{ij} was made by Howard and Lidiard[52,53] for the five-frequency model in the f.c.c. lattice with a very small concentration of vacancies. For convenience, we focus here on that model. Howard and Lidiard assumed that the vacancy concentrations were at equilibrium on all sites on the second coordination sphere centered on the impurity. This assumption was shown by Manning[54] to be equivalent to assuming that vacancies which jump to the second or more distant neighbors are lost in the sense that any future return to the first-neighbor shell is considered random. Manning essentially removed this assumption by introducing a quantity F, the fraction of dissociating vacancies that are permanently lost from a site and are uncompensated for by returning vacancies. (F = 1 in the Howard and Lidiard treatment.) Manning studied the case that the trajectories of vacancies are followed which can possibly lead to their return to second, third, or fourth nearest neighbors of the impurity. This leads to

$$7F = 7 - \left[\frac{10\alpha^4 + 180.5\alpha^3 + 927\alpha^2 + 1341\alpha}{2\alpha^4 + 40.2\alpha^3 + 254\alpha^2 + 597\alpha + 436} \right] \tag{56}$$

(where $\alpha = w_4/w_0$) in the expression for f_{IA} (A is the impurity)

$$f_{IA} = f_A \left[Z_A + 2Z_B \left(\frac{w_3[3 - 7(1 - F)(w_4 - w_0)w_4^{-1}] - 2w_1}{2w_1 + 7Fw_3} \right) \right] \tag{57}$$

where f_A is the impurity correlation factor of A. More recent calculations[51] have slightly refined the coefficients of the last three terms in the numerator and the last four terms in the denominator of Equation 56. These later calculations and a Monte Carlo calculation have indicated the essential correctness of Manning's initial treatment.

What is not so obvious from the preceding expression for f_{IA} is that it can even be greater than unity and, more surprisingly, even be negative. Correlation in the conductivity of an impurity is sometimes loosely called the "vacancy-wind effect". The general physical process here is that the driving force alters the local disposition of vacancies with respect to an impurity in such a way that there is an increased tendency for the impurity to jump in a direction opposite to the vacancy flux. Accordingly, each impurity has an additional drift velocity which it would not have if the vacancy flux were absent. It can be helpful to imagine the effect is analogous to a rock (say, a slow-moving impurity) in a stream which distorts the flow of water (vacancies) in its vicinity.[55]

Now let us move onto concentrated systems. Such systems have long been a source of special difficulty in diffusion theory because there is no easy way of extending, say, the five-frequency impurity model into the concentrated regime without rapidly increasing the number of jump frequencies to an unworkable number. As a result, models have been introduced which limit the number of jump frequencies but only as a result of some loss of realism. The first of these is the "random alloy" model introduced by Manning;[3] another is the binary alloy analog of the Ising magnet, which has been developed extensively by Sato and Kikuchi[4,8,14,56] and co-workers with the PPM. We might mention that the original problem of coping with a very large number of jump frequencies in the alloy can be handled by computer simulation along the lines of the hybrid (Monte Carlo + Lattice Statics) simulation exemplified by the calculation of ionic conductivity in yttria-doped ceria.[44] This scheme makes use of pattern recognition of environments during the progress of the simulation.

The random alloy is of considerable interest because, despite its simplicity, it seems to describe fairly well the diffusion behavior of a large number of alloys. The atomic components are assumed to be (ideally) mixed randomly. The atom/vacancy exchange frequencies w_A and w_B are explicitly specified. Neither w_A or w_B change with composition/environment. Manning[3] worked out the following expressions for f_{AA}, f_{BB}, and $f_{AB}^{(i)}$ for the case of a very small concentration of vacancies

$$f_{ii} = f_i\left(1 + 2c_iw_if_i\left[M_o \sum_{k=A,B} c_kw_kf_k\right]\right) \qquad i=A,B \tag{58}$$

and

$$f_{AB}^{(i)} = 2c_Ac_Bw_Aw_Bf_Af_B\left[c_iw_iM_o \sum_{k=A,B} c_kw_kf_k\right]^{-1} \qquad i = A,B \tag{59}$$

where

$$M_o = 2f_o(1 - f_o)^{-1} \tag{60}$$

where f_o is the tracer correlation factor (for self-diffusion) in the lattice of interest. (Computer simulations[48] have shown these expressions to be rather accurate.) More important, perhaps, is the fact that Equations 58 and 59 actually come from expressions involving tracer diffusion coefficients, i.e.,

$$f_{ii} = f_i(1 + 2D_i^*[M_o(c_AD_A^* + c_BD_B^*)]) \qquad i = A,B \tag{61}$$

and

$$f_{AB}^{(i)} = c_Ac_BD_A^*D_B^*[c_iw_iM_o(c_AD_A^* + c_BD_B^*)]^{-1} \cdot \tag{62}$$

These expressions can be derived with assumptions[57] which do not involve the random alloy model, and they appear to have general significance. For example, they are valid to a good approximation for the interacting alloy model.[58]

From equations 52 and 55 we can obtain an expression for the binary physical correlation factors f_{Ii} in the random alloy model. We have

$$f_{Ii} = f_i \left(1 + 2c_i w_i f_i \left[M_o \sum_{k=A,B} c_k w_k f_k \right] + 2\frac{Z_B}{Z_A} c_A c_B w_A w_B f_A f_B \right) \cdot$$

$$\left[c_i w_i M_o \sum_{k=A,B} c_k w_k f_k \right]^{-1} \qquad i = A,B \tag{63}$$

The deviation of f_{Ii}/f_i from unity is evidence for a vacancy-wind effect. Conversely, f_i/f_{Ii} corresponds to the binary analog of the Haven Ratio.

Using their PPM, Sato and Kikuchi and co-workers made pioneering calculations for f_{Ii} in the case of the interacting alloy model.[14,49,56] In this model, one introduces interactions ϵ_{AA}, ϵ_{BB}, and ϵ_{AB} between nearest-neighbor components of the type A-A, B-B, and A-B, respectively. The exchange frequencies w_A and w_B are no longer explicitly specified as in the random alloy model, but are expressed in terms of the interaction energies which effectively modify a specified saddle-point energy U. For example, for w_A we have

$$w_A = \nu_A \exp(-U_A/kT)\exp[(z_A\epsilon_{AA} + z_B\epsilon_{AB})/kT)] \tag{64}$$

where ν_A is the lattice vibration frequency, the z_i's are the numbers of atoms of type i neighboring to the A atoms chosen to jump and the ϵ's are assumed to be negative. Sato and co-workers studied the honeycomb lattice, which also was given a site energy difference between alternate sites and a variable vacancy concentration. The interactions with the components and the vacancy, and between vacancies, were set equal to zero.

The PPM calculation showed sharp minima in f_{Ii} at about 50% occupation when there was attraction, i.e., ordering between the components (for example, see Figure 5). The minimum was said to be due to a "percolation difficulty" created by such ordered arrangements. The percolation difficulty results from the fact that the efficiency of motion of the assembly of ions is reduced relative to that of a random walk. Physically, this means that many jumps are reversed as a result of disordering jumps tending to be followed by reordering jumps (i.e., the physical correlation effect).

The appearance of the minima in f_{IA} and f_{IB} is strongest as the dimensionality is lowered and appears to be a major contributor to the so-called mixed alkali effect. This effect is characterized by a substantial decrease in the ionic conductivity at intermediate mixed compositions, for instance, in a Na,K silicate glass or Na,K β-alumina, without any obvious physical cause. Although attractive interactions alone can, through the maintenance of local order, make the jump frequencies decrease at intermediate compositions and cause the conductivity to decrease, the existence of minima in f_{IA} and f_{IB} represents an additional source of the decrease. As noted in Section II, at very high field frequencies the physical correlation factor increases to unity. This behavior also extends to f_{IA} and f_{IB} as well.[49] Indeed, the f_{Ii} can be defined by analogy with Equation 39

$$f_{Ii} = \sigma_i(0)/\sigma_i(\infty) \tag{65}$$

Since there is a substantial frequency dependence of the mixed alkali effect,[59] then this is good evidence that the f_{Ii}'s do in fact play an important role in this effect.

Other calculations of the f_{Ii} and $f_{AB}^{(i)}$ have been made by computer simulation for the interacting alloy system.[52,60] These calculations have been confined to the limit of a very
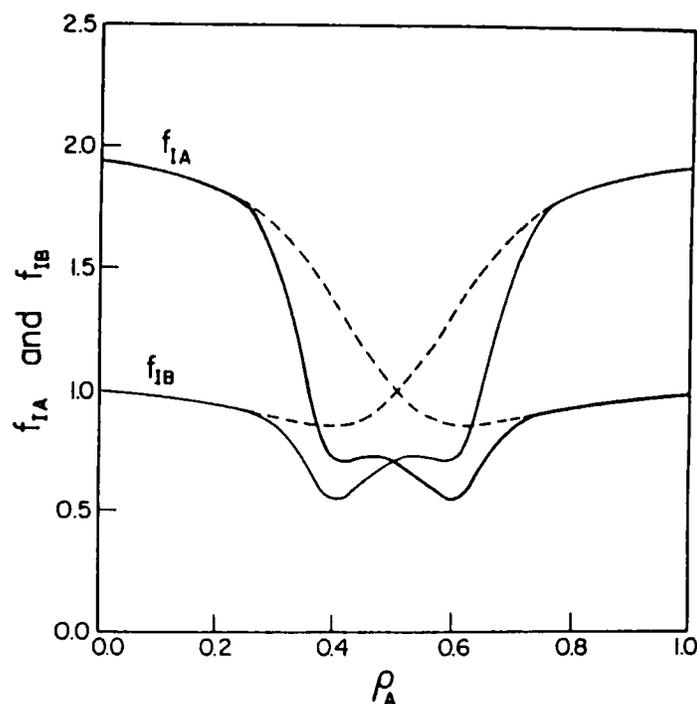
FIGURE 5. Path Probability Method results[56] for the physical correlation factors f_{IA} and f_{IB} in the two-component honeycomb lattice with $c_v = 0.2$ and $T/T_c = 0.5$, where T_c is the order/disorder temperature. The dashed line shows the case where the development of the long-range order is artificially suppressed in order to show the effect of ordering.

low vacancy concentration and also to the simple cubic lattice. The first of these simulations used an electric field which could be selectively switched on and off for various components. For example, if B atoms "feel" the field and A atoms do not ($q_A = 0$), then the drift of the B atoms in time t can be related directly to L_{BB} without the inclusion of L_{BA}. Conversely, the *indirect* drift of the A atoms in time t can be related to L_{AB} without the inclusion of L_{AA}. These drifts were expressed in terms of drift factors[59] which are related to the quantities used here by $f_{AA} = s_A^0$ and $f_{AB}^{(A)} = s_A^1 - s_A^0$. More recent calculations have used the entirely equivalent time-correlation formulas (Equations 53 and 54).[48,60]

Some results for the f_{AA} and $f_{AB}^{(A)}$ are shown in Figures 6 and 7. A brief discussion of the behavior of these quantities is appropriate here. First, with respect to f_{AA}, as $c_A \rightarrow 0$, the A atoms behave like impurities in the B matrix, and f_A reduces to the tracer or, here, the impurity correlation factor. The results here extrapolate precisely to results for f_A for the four-frequency model in the simple cubic lattice. At $c_A \approx 0.5$, the minima found are a manifestation of the percolation difficulty as described previously. As $c_A \rightarrow 1$, all curves converge on unity. This should be expected since, for a lattice containing essentially only A, correlation effects due to preservation of order must disappear. The "particle", consisting collectively of the system of A atoms, now moves on a complete random walk.

Next, let us briefly discuss $f_{AB}^{(A)}$. As $c_A \rightarrow 0$, again we have impurity conditions for A, and the results extrapolate precisely to those from the four-frequency model of impurity conduction in the simple cubic lattice. Similar to f_{AA}, minima develop at $c_A \approx 0.5$ as a result of a percolation difficulty. As $c_A \rightarrow 1$, all curves converge on zero. This is to be expected for a correlation function derived from the cross-term L_{AB} in this limit.
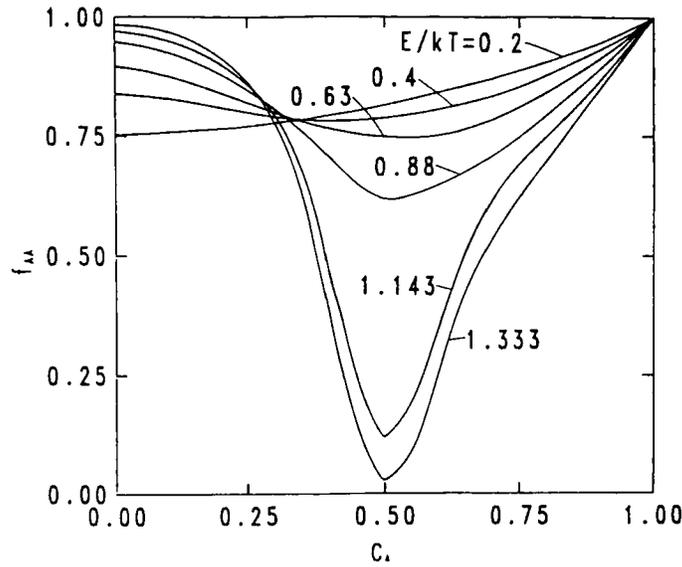
FIGURE 6.   Monte Carlo results[58] for f_{AA} in the two-component simple cubic lattice at various values of E/kT, where E is the ordering energy given by $E = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$, here $\epsilon_{AA} = \epsilon_{BB}$. $E/kT_c \approx 0.887$.
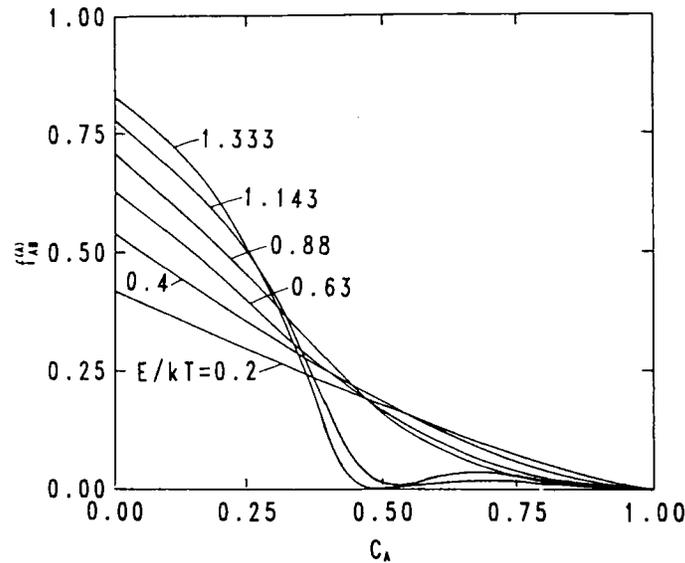
FIGURE 7.   Monte Carlo results[58] for $f_{AB}^{(A)}$ in the two-component simple cubic lattice at various values of E/kT, where E is the ordering energy given by $E = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$; here $\epsilon_{AA} = \epsilon_{BB}$. $E/kT_c \approx 0.887$.

IV. CONCLUSIONS

From the foregoing, it is clear that the area of correlation effects in ionic conductivity has expanded rapidly since its discovery almost 20 years ago. It is now no longer satisfactory to dismiss such correlation effects as being unimportant. They cannot be dismissed any more than tracer correlation effects can be ignored in tracer diffusion. In some respects, the presence of f_I in the expression for the ionic conductivity is even more important than the

presence of f in the expression for the tracer diffusion coefficient. This is because many materials with high defect contents show low coordination lattices where correlation effects tend to be largest. In addition, many defective materials are doped, thereby introducing trapping centers. These account for considerable correlation because of inefficient motion, such as rotation around the trapping site.

ACKNOWLEDGMENTS

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