Solid State Ionics 20 (1986) 203–207
North-Holland, Amsterdam

CORRELATION EFFECTS IN TRACER DIFFUSION AND IONIC CONDUCTIVITY

G.E. MURCH
Research Group, ICI Australia Operations Pty. Ltd., Newsom Street, Ascot Vale, Victoria 3032, Australia

and

Jeppe C. DYRE
Institute of Mathematics and Physics, IMFUFA, University of Roskilde, P.O. Box 260, DK-4000 Roskilde, Denmark

Received 23 October 1985

In this paper a conceptual link between the tracer correlation factor and the physical or conductivity correlation factor is explored in detail. As an aid to the discussion Monte Carlo simulation is used to calculate diagonal and cross phenomenological transport coefficients. It is shown that the tracer correlation factor can be regarded as a conductivity correlation factor and that the question of the formal correlation factor status of the conductivity correlation factor is meaningless.

1. Introduction

Correlation effects in the solid state diffusion process have attracted considerable attention ever since the discovery of the existence of such effects in tracer motion by Bardeen and Herring [1]. Much of the work up to 1970 was concerned with the calculation of the tracer correlation factor, f, for different mechanisms and models; this work has been reviewed in the excellent treatise by Le Claire [2]. Starting with the classic papers of Sato and Kikuchi [3,4], there has since been a greater concern with other types of correlation, particularly in the ionic conduction process. Sato and Kikuchi discovered that in some cases of ionic diffusion by the vacancy mechanism, when the vacancy concentration is not small, one is required to introduce a correlation factor into the expression for the dc ionic conductivity. This extra factor is called the physical or conductivity correlation factor and is symbolized by f_I (sometimes f_c). For such cases it turns out that the Haven ratio, H_R, is now given by (assuming the vacancy mechanism) f/f_I rather than f alone [‡].

The importance of conductivity correlation cannot be overstated. Recent calculations for Y_2O_3 doped CeO_2 by Murray et al. [5] using a hybrid lattice relaxation/Monte Carlo simulation scheme showed that the conductivity correlation factor can reduce the ionic conductivity by more than 1.5 orders of magnitude.

The formal correlation factor status of f_I has been a matter of difficulty. Sato and Kikuchi [3,4] originally argued that f_I is a correlation factor in the ionic conductivity in much the same way as f is a correlation factor in the tracer diffusivity. More recently, Sato and Kikuchi [8] have referred to it as a correlation factor or efficiency of motion of the assembly of atoms relative to a random walk. One implication of this could seem to be that f_I represents the correlation factor of charged atoms in an ionic conductor or, more generally, unmarked atoms. This latter interpretation was used in much of the early Monte Carlo work of Murch and Thorn [9,10]. Later Murch [6] argued against this formal description since it was based on an out-of-context use of the Nernst–Einstein equation. Nonetheless, one has an intuitive feel that f and f_I are related and have similar interpretations. It is this point which will be explored in the present paper.

In a recent review Sato [11] discussed briefly what amounts to a formal connection between f and f_I. He focused on the dependence of the correlation factor on tracer concentration for various boundary condi-

[‡] The subject of the Haven ratio has been reviewed in detail by Murch [6].

tions. That review was written from the perspective of, and in the language of, the Path Probability Method. His approach is to reduce the conductivity correlation factor to a geometrical correlation factor. In the present paper, our approach is the converse. Here we explore the link between f and f_I by means of some elementary irreversible thermodynamics and the Monte Carlo method. While the question of the correlation factor status of f_I is not answered, we will show that f itself can be regarded as a conductivity correlation factor and, by doing so, show that any argument over the formal correlation factor status of f_I is in fact meaningless.

2. Correlation effects in tracer diffusion and ionic conductivity

Ionic diffusion in solids is normally described within the framework of irreversible thermodynamics [1,6,12,13]. Consider a system containing host ions A, tracer ions A* and vacancies V. The fluxes of these components are given by [6]

$$J_A = L_{AA}X_A + L_{AA^*}X_{A^*} , \tag{1a}$$

$$J_{A^*} = L_{A^*A}X_A + L_{A^*A^*}X_{A^*} \tag{1b}$$

and

$$J_V = -(J_A + J_{A^*}) , \tag{1c}$$

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

From these equations one can easily derive explicit expressions for such quantities as the tracer diffusion coefficient D_{A^*}, the dc ionic conductivity and the chemical diffusion coefficients [6,14,15] as well as relations among these quantities such as the Haven Ratio and the exact Nernst–Einstein equation [16].

Of interest to us in the present context is the tracer diffusion coefficient

$$D_{A^*} = \frac{kT}{N}\left(\frac{L_{A^*A^*}}{c_{A^*}} - \frac{L_{A^*A}}{c_A}\right) , \tag{2}$$

where c_i is the mole fraction of species i and N is the total number of entities of all species per unit volume. Eq. (2) is valid for any value of c_{A^*} except, of course, $c_{A^*} = 0$ and $c_{A^*} = 1 - c_V$ (i.e., $c_A = 0$). Since in an actual tracer diffusion experiment the tracer concentration is very low, it is usual to let $c_{A^*} \to 0$ in eq. (2) with the result that

$$D_{A^*} = \frac{kT}{N}\left(\frac{L_{A^*A^*}}{c_{A^*}}\right) , \quad c_{A^*} \to 0 . \tag{3}$$

Also of interest to us is the expression for the dc ionic mobility

$$u_{A^*} = \frac{q_{A^*}}{N}\left(\frac{L_{A^*A^*} + L_{A^*A}}{c_{A^*}}\right) , \quad q_A = q_{A^*} . \tag{4}$$

Eq. (4) was derived with the condition that both A and A* carry the same charge, i.e., $q_A = q_{A^*}$. Because of this condition u_{A^*} cannot depend on c_{A^*}. In passing we note that we can, of course, let $c_{A^*} = 1 - c_V$, i.e., $c_A = 0$. Then $L_{A^*A} = 0$ and we simply have that

$$u_{A^*} = \frac{q_{A^*}L_{A^*A^*}}{Nc_{A^*}} , \quad c_A = 0 . \tag{5}$$

Now let us consider a "thought experiment" in which one measures the dc ionic mobility of A* with the condition that *only* the tracer ions carry a charge, i.e., $q_A = 0$. Following the same procedure as described in [14] we find that this mobility, which we will call $u^0_{A^*}$, is given by

$$u^0_{A^*} = \frac{q_{A^*}L_{A^*A^*}}{Nc_{A^*}} , \quad q_A = 0 . \tag{6}$$

Comparing eq. (6) with eq. (3) and eliminating $L_{A^*A^*}$ which is, of course, independent of force, we find that

$$\frac{u^0_{A^*}}{D_{A^*}} = \frac{q_{A^*}}{kT} , \quad c_{A^*} \to 0, q_A = 0 . \tag{7}$$

Eq. (7) is seen to be a version of the Nernst–Einstein equation, see ref. [16]. It is not new, however, since it can be easily found, with the appropriate substitutions, from eq. 4.73 in ref. [7] which relates the impurity ionic mobility to the impurity diffusion coefficient, with the impurity representing the tracer.

The existence of eq. (7) implies a rather interesting result. Since D_{A^*} always has the form

$$D_{A^*} = \Gamma\lambda^2 f/2 , \tag{8}$$

where Γ is the tracer jump frequency, λ is the average component of the jump distance in the diffusion direction and f is the tracer correlation factor, then, according to eq. (7), $u^0_{A^*}$ must have the following form ***in the limit*** $c_{A^*} \to 0$

$$u^0_{A^*} = q_{A^*}\Gamma\lambda^2 f^0/2kT, \quad c_{A^*} \to 0, q_A = 0. \tag{9}$$

In eq. (9) we have introduced $f^0 = \lim_{c_{A^*}\to 0} f$ for reasons which will become apparent later. The formal appearance of f in an expression for an ionic mobility is unusual and implies that f can be considered a conductivity correlation factor in the same sense that f_I is in the following accepted expression for u_{A^*} [6]

$$u_{A^*} = q_{A^*}\Gamma\lambda^2 f_I/2kT, \quad q_A = q_{A^*}. \tag{10}$$

The formal similarity between these expressions now suggests a useful conceptual link between f and f_I. Thus f represents the correlation in the tracer ionic mobility $u^0_{A^*}$ when $c_{A^*} \to 0$ and $q_A = 0$, while f_I represents the correlation in the tracer ionic mobility u_{A^*} when $q_A = q_{A^*}$. Now, since u_{A^*} is in fact independent of c_{A^*}, for definiteness let us consider u_{A^*} when there is no A present, i.e., $c_A = 0$ and $c_{A^*} = 1 - c_V$. Starting with such a lattice and progressively replacing A^* atoms with A atoms (*with however the restriction* $q_A = 0$) one can traverse the concentration range of c_{A^*} and reach the domain where $c_{A^*} \to 0$ and $u^0_{A^*}$ is relevant. Since all that is changing in this "thought experiment" is the concentration of charged A^* ions, it is natural to ask two questions. What is the behavior of the usual tracer correlation factor $f(c_{A^*})$ in this range $0 < c_{A^*} \leqslant 1 - c_V$? What is the behavior of the conductivity correlation factor of the A^* ions in the same range?

These questions can be answered by resorting to a particular model and using Monte Carlo simulation. But first a few general comments are in order. Comparing eqs. (2) and (6) and noting that Γ and λ cannot depend on c_{A^*}, we see that $f(c_{A^*})$ must in general depend on $L_{A^*A^*}$ and L_{A^*A}. In addition, by the same argument, the conductivity correlation factor contained in $u^0_{A^*}$, depends only on $L_{A^*A^*}$. For definiteness we will refer to this latter conductivity correlation factor as $s^0_{A^*}(c_{A^*})$, i.e.

$$u^0_{A^*} = q_{A^*}\Gamma\lambda^2 s^0_{A^*}/2kT, \quad q_A = 0. \tag{11}$$

We note of course that

$$s^0_{A^*} = f^0, \quad c_{A^*} \to 0 \tag{12}$$

and

$$s^0_{A^*} = f_I, \quad c_A = 0, \tag{13}$$

where in the latter case $u^0_{A^*} = u_{A^*}$.

Finally, it is worth noting that in the one dimensional case with self-blocking between the ions it is known that $f = 0$ (for $c_{A^*} \to 0$) [17,18]. The existence of eq. (7) implies that the tracer mobility, $u^0_{A^*}$, is also zero under the same conditions.

3. Monte Carlo simulation of conductivity correlation factors

Our goal is to calculate $f(c_{A^*})$ and $s^0_{A^*}(c_{A^*})$. The calculation centers on the determination of $L_{A^*A^*}$ and L_{A^*A}. We already have an expression relating $u^0_{A^*}$ (and therefore $s^0_{A^*}$) to $L_{A^*A^*}$, see eq. (6). In a similar "thought experiment" leading to eq. (6) let us calculate the flux of A^* when only the A atoms carry a charge. This is a tracer flux arising from an indirect force and contains the very essence of the meaning of the cross phenomenological coefficient L_{A^*A}. Following the same procedure as described in ref. [14] we find that the corresponding dc tracer mobility, which we will call u'_{A^*}, is given by

$$u'_{A^*} = \frac{q_A L_{A^*A}}{N c_{A^*}}, \quad q_{A^*} = 0. \tag{14}$$

The conductivity correlation factor contained in u'_{A^*} will be symbolized by s'_{A^*}.

For convenience, we can simulate both "thought experiments" simultaneously by calculating $u^0_{A^*}$ and u'_A, i.e., calculate the fluxes of A^* *and* A with $q_A = 0$ and, in the case of u'_A change the symbol A to A^* to obtain u'_{A^*} noting, of course, that $L_{A^*A} = L_{AA^*}$.

On combining eqs. (2), (6) and (11) and thereby eliminating $L_{A^*A^*}$ and L_{A^*A} we have that

$$D_{A^*} = kT\left(\frac{u^0_{A^*}}{q_{A^*}} - \frac{c_{A^*}}{c_A}\frac{u'_{A^*}}{q_A}\right). \tag{15}$$

In passing we note that eq. (15) could be considered another Nernst–Einstein-like equation.

The conductivity correlation factors $s^0_{A^*}$ and s'_{A^*} are related to the corresponding tracer drift distances in the field by the following definitions

$$s^0_{A^*} = 2kT\langle X^0_{A^*}\rangle/q_{A^*}E_x n_{x,A^*}\lambda^2, \quad q_A = 0, \tag{16a}$$

$$s'_{A^*} = 2kT\langle X'_{A^*}\rangle/q_A E_x n_{x,A^*}\lambda^2, \quad q_{A^*} = 0, \tag{16b}$$

where the $\langle X\rangle$ are the tracer drift distances in the field

E_x in time t and n_{x,A^*} is the number of jumps that would occur in the absence of the field. The drifts are related to the respective tracer mobilities by

$$u^0_{A^*} = \langle X^0_{A^*} \rangle / E_x t \,, \tag{17a}$$

$$u'_{A^*} = \langle X'_{A^*} \rangle / E_x t \,. \tag{17b}$$

Combining eqs. (8), (15), (16a,b) and (17a,b) we have that

$$f = s^0_{A^*} - \frac{c_{A^*}}{c_A} s'_{A^*} \,. \tag{18}$$

This is a general relation, valid for $0 < c_{A^*} \leqslant 1 - c_V$, between the tracer correlation factor and the conductivity correlation factors $s^0_{A^*}$ and s'_{A^*}. Calculation of $s^0_{A^*}$ and s'_{A^*} as functions of c_{A^*} permits the calculation of $f(c_{A^*})$.

In our calculations we examined (1) the square planar lattice (100 X 100) with a single vacancy and a random distribution of A* and A, and (2) the same lattice but with 50% occupation by vacancies again with a random distribution of A* and A. In both cases f_I is equal to unity [6]: we have chosen this case for convenience in the present discussion. The procedure to simulate ionic conductivity in an electric field has been documented in detail [19] and need not be repeated here.

4. Results and discussion

In fig. 1 we give results for the calculation of $s^0_{A^*}$ and s'_{A^*} as functions of c_{A^*} in the square planar lattice with a single vacancy. It is clear that in this model both quantities exhibit simple linear dependence on c_{A^*}. In the case of s'_{A^*} the results extrapolate to $1 - f^0$ when $c_{A^*} \to 0$. Upon forming the tracer correlation factor [eq. (18)] we find that f does *not* in fact depend on c_{A^*}.

In fig. 2 we give similar results for $s^0_{A^*}$ and s'_{A^*} this time in the square planar lattice with 50% vacancies. Again in the case of $s^0_{A^*}$ the results extrapolate to f^0 (~0.712 Tahir-Kheli and El-Meshad [20]) when $c_{A^*} \to 0$ while results for s'_{A^*} extrapolate to $1 - f^0$. Again upon forming f with eq. (18) we find that f does *not* depend on c_{A^*}.

Depending on one's intuition this independence of c_{A^*} by f is perhaps a somewhat surprising result. Sato [11] claims that this behaviour is a result of the application of the Gibbs–Duhem relation. He maintains that this relation does not necessarily hold rigorously under the nonequilibrium condition pertaining to diffusion processes. In particular, the relation imposes a very strong restriction on the driving forces which is manifested by the fact that the motion of A* atoms is always compensated by the motion of A atoms (see

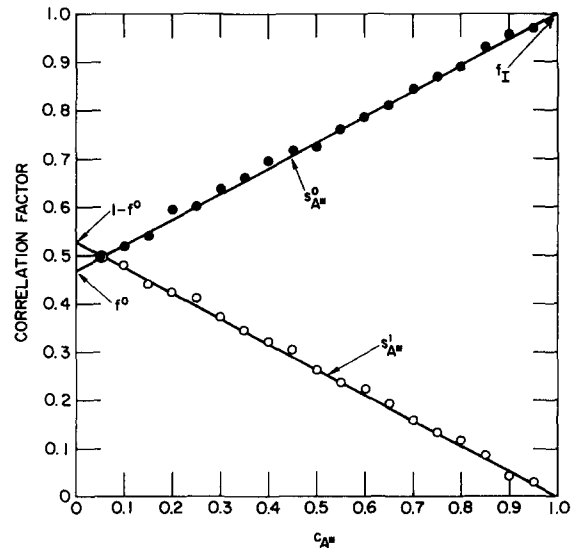

Fig. 1. The correlation factors $s^0_{A^*}$ and s'_{A^*} plotted as functions of c_{A^*} for the square planar lattice (100 X 100) with a single vacancy.

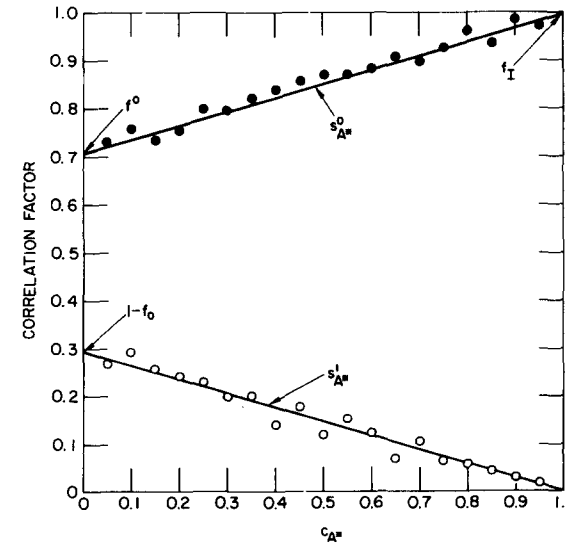

Fig. 2. The correlation factors $s^0_{A^*}$ and s'_{A^*} as functions of c_{A^*} for the square planar lattice (100 X 100) with 50% vacancies.

also ref. [23]). Because of this, the condition actually leads to the evaluation only of the diffusive behaviour of a single atom. Since the above problem apparently could be associated with eq. (2), one would like to calculate D_{A^*}, i.e. f, from a purely Fickian definition of D_{A^*}. In a different context from the present one this was in fact done by Murch and Thorn [21], and in such a way that the tracer concentration was quite high. No deviation from f^0 was observed so we must conclude that for this model f does not depend on c_{A^*} whether or not the Gibbs–Duhem relation is rigorously enforced.

Sato [11] also discusses a tracer correlation factor which evidently is the same as our $s^0_{A^*}$. In effect, Sato converts $u^0_{A^*}$ to a new tracer diffusion coefficient $D^0_{A^*}$ by means of a quasi Nernst–Einstein equation

$$u^0_{A^*}/D^0_{A^*} = q_{A^*}/kT\,, \quad q_A = 0\,, \tag{19}$$

which he assumes to be valid for all c_{A^*}. As we have seen, it *is* valid for $c_{A^*} \to 0$ [eq. (7)]. Accordingly, $s^0_{A^*}$ now appears as

$$D^0_{A^*} = \Gamma\lambda^2 s^0_{A^*}/2\,, \tag{20}$$

and is an apparent tracer correlation factor. At the limits of $c_{A^*} \to 0$ and $c_{A^*} = 1 - c_V$, $s^0_{A^*}$ connects (linearly in our model as it turns out) f to f_I as a function of c_{A^*}. It should be noted that $D^0_{A^*}$ does not have a Fickian meaning nor does eq. (19) have a proof except as we have seen, for $c_{A^*} \to 0$. In a general sense, eq. (19) should be classified as a definition which provides a means for converting a mobility to a dimensionally correct diffusion coefficient. Thus $D^0_{A^*}$ is, in a Fickian sense, a hypothetical tracer diffusion coefficient: its tracer correlation factor $s^0_{A^*}$ happens also to be the conductivity correlation factor of an assembly of charged tracer ions drifting in a neutral host. Interestingly, D_{A^*}, because of its association *only* with $L_{A^*A^*}$ (eqs. (11) and (14)) can also be related in the usual way to the self-correlation function obtainable from quasi-elastic neutron scattering etc. (see ref. [22]). The Monte Carlo calculation of $s^0_{A^*}$ (and f_I) from the self correlation function and related matters will be studied in a later paper.

5. Conclusions

We have explored the link between f and f_I by means of c_{A^*}. We have shown that f, as usually interpreted, does not depend on c_{A^*} and does not itself provide a useful link. On the other hand, one can *define* a hypothetical tracer correlation factor which depends on $L_{A^*A^*}$ only (eq. (11)) and which provides a linear link (for our model) between f and f_I. This tracer correlation factor is also the conductivity correlation factor of an assembly of charged tracer ions moving in a neutral host.

Acknowledgement

We are indebted to Professor Hiroshi Sato for many useful discussions on this subject.

[1] J. Bardeen and C. Herring, in: Imperfections in nearly perfect crystals, ed. W. Shockley (Wiley, New York, 1952) p. 261.
[2] A.D. Le Claire, in: Physical chemistry – an advanced treatise, Vol. 10, ed. H. Eyring, D. Henderson and W. Jost (Academic, New York, 1970) p. 261.
[3] H. Sato and R. Kikuchi, J. Chem. Phys. 55 (1971) 677.
[4] R. Kikuchi and H. Sato, J. Chem. Phys. 55 (1971) 701.
[5] A.D. Murray, G.E. Murch and C.R.A. Catlow, Solid State Ionics 18/19 (1986) 196.
[6] G.E. Murch, Solid State Ionics 7 (1982) 177.
[7] J.R. Manning, Diffusion kinetics for atoms in crystals (Van Nostrand, Princeton, 1968).
[8] H. Sato and R. Kikuchi, Phys. Rev. B28 (1983) 648.
[9] G.E. Murch and R.J. Thorn, Philos. Mag. 36 (1977) 329.
[10] G.E. Murch and R.J. Thorn, Philos. Mag. A37 (1978) 85.
[11] H. Sato, in: Nontraditional methods in diffusion, eds. G.E. Murch, H.K. Birnbaum and J.R. Cost (TMS: AIME, Warrendale, 1984) p. 203.
[12] R.E. Howard and A.B. Lidiard, Rep. Prog. Phys. 27 (1964) 161.
[13] A.D. Le Claire, in: Treatise on solid state chemistry, Vol. 4, ed. N.B. Hannay (Plenum, New York, 1975) p. 1.
[14] G.E. Murch and R.J. Thorn, Philos. Mag. A40 (1979) 477.
[15] G.E. Murch, Solid State Ionics 6 (1982) 295.
[16] G.E. Murch, Philos. Mag. A45 (1982) 685.
[17] R.M. Richards, Phys. Rev. B16 (1977) 1393.
[18] R.A. Tahir-Kheli, Phys. Rev. B27 (1983) 6072.
[19] G.E. Murch, in: Diffusion in crystalline solids, eds. G.E. Murch and A.S. Nowick (Academic, New York, 1984) p. 379.
[20] R.A. Tahir-Kheli and N. El-Meshad, Phys. Rev. B, to be published.
[21] G.E. Murch and R.J. Thorn, Philos. Mag. A39 (1979) 673.
[22] G.E. Murch, H.K. Birnbaum and J.R. Cost, eds., in: Nontraditional methods in diffusion (TMS: AIME, Warrendale, 1984).
[23] H. Sato, T. Ishikawa and R. Kikuchi, J. Phys. Chem. Solids 46 (1985) 1361.