

## CORRELATION EFFECTS IN TRACER DIFFUSION AND IONIC CONDUCTIVITY. II

Jeppe C. DYRE

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

and

G.E. MURCH

*Department of Chemical and Materials Engineering, University of Newcastle, N.S.W. 2308, Australia*

Received 12 December 1985

In this paper it is shown that the physical or conductivity correlation factor can be simply and directly expressed in terms of the well-known tracer correlation factor and a new two particle correlation factor. A Monte Carlo calculation of these correlation factors was performed to illustrate the use of the expression. The physics of the two-particle correlation factor are discussed.

### 1. Introduction

In the preceding paper [1], hereafter referred to as I, it was shown that there exists a formal link between the geometrical correlation factor,  $f$ , and the physical or conductivity correlation factor  $f_I$ . The idea developed in I was to study the tracer ionic mobility as a function of the tracer concentration at a fixed total ion concentration with the restriction that the host ions carried no charge. The correlation factor contained in this tracer ionic mobility reduces to  $f$  at low tracer concentration and  $f_I$  at high tracer concentration. This was illustrated by Monte Carlo simulations of diffusion by the vacancy mechanism on a square planar lattice. In this case the link between  $f$  and  $f_I$  turned out to be a linear function of the tracer concentration. In the present paper this will be proved analytically to be generally the case. The proof relies on a reduction of the phenomenological coefficients to two correlation factors which refer directly to motion at the atomic level: the usual single-particle correlation factor  $f$ , and a new two-particle correlation factor  $g$ .

By showing that  $f_I$  can be decomposed into  $f$  and  $g$  we remove the mystery which has surrounded  $f_I$  ever since its introduction in 1971 by Sato and

Kikuchi [2]. The question of the correlation factor status of  $f_I$  is finally settled, in addition, a good deal of insight into the physics of  $f_I$  is obtained.

### 2. Reduction of the phenomenological coefficients to two atomic level correlation factors

For simplicity we assume diffusion to take place on a three dimensional simple-cubic lattice by means of the vacancy mechanism but the discussion below can be generalized to any other lattice and diffusion mechanism. The lattice has a volume  $V$  and a lattice constant  $a$ . The jump frequencies may vary, the lattice may have traps, complicated ion-ion interactions may be present, etc. The only assumption to be made is that the lattice is macroscopically isotropic and homogeneous. The numbers of tracer ions, unmarked ions and vacancies are denoted by  $N_{A^*}$ ,  $N_A$  and  $N_V$ , respectively. The total number of ions is given by  $N_a$  and  $N = N_{A^*} + N_A + N_V$  ‡. The corresponding concentrations ( $= N_{A^*}/V$  etc.) are denoted by  $n_{A^*}$ ,  $n_A$ ,  $n_V$ , and  $n_a$

‡ Note that  $N$  is here defined as the total number of entities whereas in I it was defined as the total number of entities per unit volume.

while the relative concentrations ( $= N_{A^*}/N_{\text{etc}}$ ) are given by  $c_{A^*}$  etc. Of course we have that

$$c_{A^*} + c_A + c_V = 1. \quad (1)$$

The central idea is to study the phenomenological coefficients as a function of  $N_{A^*}$  at fixed  $N_A$ . A convenient starting point for the calculation of the phenomenological coefficients is the Einsteinian formula given by Allnatt [3,4]

$$L_{ij} = \lim_{V \rightarrow \infty} \lim_{t \rightarrow \infty} (6VkTt)^{-1} \langle \overline{\Delta R}^{(i)}(t) \overline{\Delta R}^{(j)}(t) \rangle, \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\overline{\Delta R}^{(i)}(t)$  is the total displacement of species  $i$  in time  $t$ , and the Dirac brackets denote a thermal average. The average is calculated assuming a finite volume  $V$  and periodic boundary conditions. Finally the limit of infinite diffusion time and volume is taken subject to the condition of constant ion concentration.

Here we are interested in the case of only two species: tracer ( $A^*$ ) and non-tracer ( $A$ ) ions. To calculate  $L_{AA}$  we write the total displacement of non-tracer ions as the sum of the *individual* ion displacements.

$$\overline{\Delta R}^{(A)}(t) = \sum_m \overline{\Delta r}_m^{(A)}(t). \quad (3)$$

Substituting eq. (3) into eq. (2) one finds

$$L_{AA} = \lim_{V \rightarrow \infty} \lim_{t \rightarrow \infty} (6VkTt)^{-1} \times \left[ \sum_m \langle \overline{\Delta r}_m^{(A)}(t) \rangle^2 + \sum_{m \neq n} \langle \overline{\Delta r}_m^{(A)}(t) \overline{\Delta r}_n^{(A)}(t) \rangle \right]. \quad (4)$$

Now, if  $\Gamma$  denotes the average ion jump frequency, the usual geometrical correlation factor  $f$  is given by

$$f = \lim_{V \rightarrow \infty} \lim_{t \rightarrow \infty} \langle \overline{\Delta r}^2(t) \rangle / \Gamma t a^2. \quad (5)$$

This expression is independent of the ion position at time  $t = 0$  since the ion traces out the whole volume  $V$  as  $t$  goes to infinity. Therefore the first term in square brackets in eq. (4) is simply equal to  $N_A \Gamma t a^2 f$ . By a similar argument  $\lim_{t \rightarrow \infty} \langle \overline{\Delta r}_m^{(A)}(t) \overline{\Delta r}_n^{(A)}(t) \rangle / t$  for  $m \neq n$  is independent of the position of  $m$  and  $n$  at  $t = 0$ .

This does not work, however, for one dimension.

Next, we define a two particle correlation factor  $g$  by

$$g = \lim_{V \rightarrow \infty} \lim_{t \rightarrow \infty} N \langle \overline{\Delta r}_m^{(A)}(t) \overline{\Delta r}_n^{(A)}(t) \rangle / \Gamma t a^2, \quad (m \neq n), \quad (6)$$

where  $N = N_A + N_V$  i.e.  $N = V/a^3$ . It follows directly from eq. (4) that the limit is defined; the factor  $N$  compensates for the fact that interactions between ion  $m$  and  $n$  take place more and more seldomly when the volume is increased. Upon substituting eqs. (5) and (6) into eq. (4) we find

$$L_{AA} = \lim_{V \rightarrow \infty} (\Gamma a^2 / 6VkT) [N_A f + (N_A^2 / N) g] \quad (7a)$$

$$= (\Gamma a^2 / 6kT) n_A (f + c_A g), \quad (7b)$$

where a factor of  $N_A (N_A - 1)$  has been replaced by  $N_A^2$ .

Recognizing that the correlation factors  $f$  and  $g$  are, of course, the same for tracer and non-tracer ions, we find in a similar way from eq. (2) that

$$L_{A^*A^*} = (\Gamma a^2 / 6kT) n_{A^*} (f + c_{A^*} g) \quad (8)$$

and

$$L_{A^*A} = (L_{AA^*}) = (\Gamma a^2 / 6kT) n_A c_{A^*} g. \quad (9)$$

It is now straightforward to find the tracer concentration dependence of the phenomenological coefficients for fixed  $c_a$ . In particular we recall the tracer conductivity correlation factor introduced in I (eqs. (6) and (11))

$$s_{A^*}^0 = 6kTL_{A^*A^*} / \Gamma a^2 n_{A^*} \quad (10)$$

noting that  $\lambda^2 = a^2/3$ . It was found in I that this  $s$  factor connects  $f$  and  $f_I$ . Substituting eq. (8) of this paper we have that

$$s_{A^*}^0 = f + c_{A^*} g. \quad (11)$$

Thus  $s_{A^*}^0$  quite generally provides a link between  $f$  and  $f_I$  [1] and is a linear function of  $c_{A^*}$ .

In a similar manner, the physical or conductivity correlation factor  $f_I$  itself is given by (eqs. (4) and (10) of I) i.e.

$$f_I = (6kT/n_{A^*} a^2 \Gamma) (L_{A^*A^*} + L_{A^*A}). \quad (12)$$

Noting eqs. (8) and (9) of this paper we have that

$$f_I = f + c_{A^*} g + c_A g \quad (13a)$$

and finally that

$$f_I = f + c_a g . \quad (13b)$$

The correlation factor status and the underlying physics of  $f_I$  have been a matter of some discussion ever since it was introduced into the literature by Sato and Kikuchi [2]. From eq. (13b) we see that  $f_I$  is simply a sum of two correlation factors which refer directly to the atomic level. There are no mysterious "collective or cooperative" effects hidden in  $f_I$ . In our opinion the question of the correlation factor status of  $f_I$  is hereby finally settled.

Of course  $g$  could have been defined such that the  $c_a$  factor could have been omitted in eq. (13b). However we want  $g$  to be a direct measure of the correlation of the motion of two ions. If there had been a factor  $N_A$  instead of  $N$  in eq. (6) (thus eliminating  $c_a$  in eq. (13b)), then  $g$  could change in two ways when more atoms are added to the system: either because  $N_A$  changed, or because  $\langle \overline{\Delta r_m(t) \Delta r_n(t)} \rangle / t$ , changed. This would be unfortunate because then situations could arise, at least in principle, where  $g$  changed but that the real correlation of two atoms remained the same.

Another quantity of interest is the Haven ratio  $H_R$ . This quantity is given by [5]

$$H_R = \frac{c_A L_{A^*A^*} - c_A^* L_{A^*A}}{c_A (L_{A^*A} + L_{A^*A^*})} . \quad (14)$$

From eqs. (8) and (9) one finds that

$$H_R = f/(f + c_a g) = f/f_I , \quad (15)$$

which is valid at *any* tracer concentration.

We note of course that

$$H_R = 1 \Leftrightarrow g = 0 \Leftrightarrow L_{A^*A} = 0 . \quad (16)$$

Usually, when  $H_R$  is found to be  $\neq 1$ , it is thought that this is direct evidence of a non-trivial correlation factor  $f$ . We can now see that  $H_R \neq 1$  is in reality a unique sign of non-trivial *two*-particle correlation effects! Indeed, in principle one could, at the same time, have that  $f = 1$ .

Let us now briefly discuss the physics of  $g$ . Consider, for example, diffusion by the vacancy mechanism for a small vacancy concentration in a simple cubic lattice. In this case  $f_I = 1$ , so that  $g = 1 - f > 0$ . The physics involved is straightforward. Suppose ion  $m$  has just exchanged sites with a vacancy. If the next

vacancy jump is perpendicular to the first, there will be no contribution to either  $f$  or  $g$ . If the vacancy jumps back again (with  $m$ ) this contributes to make  $f$  smaller than unity for ion  $m$  as is well-known. Finally there is the possibility that the vacancy jumps in the same direction as the first jump by exchanging sites with a new ion  $n$ . This will give a positive contribution to  $g$  for ions  $m$  and  $n$ . This contribution to  $g$  is the most important one, so it is not surprising that the total  $g$  ends up being positive.

A negative value for  $g$  corresponds to  $H_R$  being greater than unity. This has been observed, for instance, in Monte Carlo simulations of a high density lattice gas with nearest neighbor exclusion [6]. In this case one may speculate that the negative sign of  $g$  is due to a backflow effect similar to that discussed by Feynman and Cohen [7] for liquid helium. This effect results from the hydrodynamic equation of continuity, so it may be that  $g < 0$  corresponds to liquid-like situations. This alleged liquid-like situation is actually what was previously called solid-like.

### 3. Monte Carlo simulation of $f_I$ and $g$

In this section we make use of some of the equations derived in previous section in order to illustrate how  $f$  (eq. (5)),  $f_I$  (eq. (13b)) and  $g$  (eq. (6)) can be calculated in a Monte Carlo calculation. We focus on two models. First we examine the square planar lattice of 50176 ( $224 \times 224$ ) sites with a single vacancy. In the usual way [8] the walk of the vacancy was directed through the use of machine-generated random numbers. An average of 10 jumps per atom was specified. The run was repeated 400 times to obtain adequate statistics for  $g$  (and  $f_I$ ). Results are shown in table 1. As expected  $f_I$  is very close to unity,  $f$  is close to the exact value of  $1/(\pi - 1)$  [9] and  $g$  is given by  $1 - f$ .

Next, we examined a model where  $f_I \neq 1$ . We chose a model where much Monte Carlo data had already been collected for  $f_I$  using the external field method [8,10]. In addition, much data on  $f$  was also available. The model chosen was the simple cubic lattice of 27000 ( $30 \times 30 \times 30$ ) sites with random (single-site) traps where the number of vacancies equals the total number of traps. We selected a concentration where half of the lattice contains traps

Table 1  
Comparison of calculated values of correlation factors.

Method	$f$	$g$	$f_I$
Square planar lattice present study	0.4671	0.5325	0.9996
Square planar lattice exact results	0.46694...	0.53305...	1.0
Simple cubic lattice with traps present study	0.6579	0.3572	0.8365
Simple cubic lattice with traps ref. [10]	0.655	—	0.852

and a temperature such that  $\exp(-w/kT) = 0.1$  where  $w$  is the trapping energy. An average of 10 jumps per atom was specified. Again we averaged over 400 observations in order to obtain good statistics. The results are shown in table 1 along with previous determinations of  $f$  and  $f_I$  (the latter obtained using the external field method). The agreement is quite reasonable. The only difficulty with this method is the very much greater demand put on computer time than that required by the external field method [8]. Allnatt and Allnatt [4] found a similar behaviour when they calculated the binary equivalent of  $f_I$  in the case of the f.c.c. random alloy.

#### 4. Conclusions

It is well-known that all observable diffusion phenomena pertaining to the linear response regime can be calculated from the phenomenological coefficients. From the treatment in this paper we see that these coefficients depend essentially on the two correlation factors,  $f$  and  $g$  which together contain the basic phys-

ics of the diffusion process. While the tracer correlation factor is as old as the subject itself, the discovery of  $g$  is surprisingly recent: it is implicitly in the paper by Allnatt [3]. We might surmise that  $g$  may well be as important as  $f$  in future works in solid state diffusion theory.

#### References

- [1] G.E. Murch and J.C. Dyre, *Solid State Ionics* 20 (1986) 203.
- [2] H. Sato and R. Kikuchi, *J. Chem. Phys.* 55 (1971) 677.
- [3] A.R. Allnatt, *J. Phys.* C15 (1982) 5605.
- [4] A.R. Allnatt and E.L. Allnatt, *Phil. Mag.* A49 (1984) 625.
- [5] G.E. Murch, *Solid State Ionics* 7 (1982) 177.
- [6] G.E. Murch, *Phil. Mag.* A41 (1980) 701.
- [7] R.P. Feynman and M. Cohen, *Phys. Rev.* 102 (1956) 1189.
- [8] G.E. Murch, in: *Diffusion in crystalline solids*, eds. G.E. Murch and A.S. Nowick (Academic Press, New York, 1984) p. 379.
- [9] D.D. Pruthi, *Diffusion Defect Data* 42 (1985) 1.
- [12] G.E. Murch, *J. Phys. Chem. Solids* 46 (1985) 53.