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A GENERALIZATION OF THE NERNST-EINSTEIN EQUATION FOR SELF-DIFFUSION IN HIGH-DEFECT-CONCENTRATION SOLIDS*

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We show that the Nernst-Einstein equation can be generalized for a high defect concentration solid to relate the mobility or conductivity to the self-diffusion coefficient in the standard form:

$$\frac{\lambda_a}{D_a} = \frac{q_a}{k_B T}$$

where λ_a is the mobility of the charge carriers, q_a is their charge, and D_a is the self-diffusion coefficient; k_B and T are Boltzmann's constant and the temperature. We derive this relationship assuming that the diffusing particles interact strongly and that the mobility is concentration-dependent. We derive this relationship for interstitial disordered structures, but it is perfectly general to any mechanism of self diffusion as long as diffusion in a pure system is considered.

1. INTRODUCTION

In an ionic solid, a classic method for developing interpretations of defect structures is to compare conductivity measurements with diffusion measurements. The electrical conductivity of the solid, σ , is related to the mobility of the charge carriers, λ_a , by

$$\sigma = N_a q_a \lambda_a \quad (1)$$

with N_a and q_a the number of carriers and their charge. The mobility is related to the diffusion coefficient of the charge carrier by the familiar Nernst-Einstein equation

$$\frac{\lambda_a}{D_a} = \frac{q_a}{k_B T} \quad (2)$$

k_B and T are Boltzmann's constant and the temperature.

The usefulness of Eqs. (1) and (2) has centered around a correct interpretation of the diffusion coefficient in Eq. (2) and the question of the general applicability of the Nernst-Einstein equation as expressed in Eq. (2).

When diffusion occurs by the motion of isolated point defects in a pure system, (i.e., NaCl, AgCl, ...), D_a is just the self-diffusion coefficient and is related to the tracer diffusion coefficient, D_a^* , by

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$$D_a = \frac{D_a^*}{f_a} \quad (3)$$

with f_a the correlation factor. However, if the defects are not isolated noninteracting defects, then it is not clear that Eq. (2) is generally applicable, and evaluations of conductivity and tracer diffusion coefficient comparisons have had to be done in other than quantitative terms because of defect interactions.

In this paper, we examine the assumptions that were used in the derivation of a Nernst-Einstein relationship and see that as long as diffusion in a pure system (whether stoichiometric or not) is considered, the expression as presented in Eq. (2) is perfectly general and that the diffusion coefficient, D_a , is always the self-diffusion coefficient of the charge carriers.

The derivation is done for an interstitial disordered system, and although a phenomenological development is used, a specific kinetic model calculation is given to illustrate the detailed physical justification of Eq. (2).

2. NERNST-EINSTEIN RELATION BETWEEN DIFFUSION AND CONDUCTIVITY

A derivation of the Nernst-Einstein equation as written in Eq. (2) was done by Mott and Gurney¹ for a solid in which it was assumed that the mobile charge carriers were independent and non-interacting. Mott and Gurney derived Eq. (?) proceeding from a simple statement of a no-current condition for a solid electrolyte with a uniform electric field externally applied. The system is "blocked" at the electrodes, the

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particles accumulate in regions of lower electrical potential energy, and a concentration gradient is established. As a result of the forced motion from the electrical field, an equal and opposite diffusional flow down the concentration gradient is set up to maintain the particles in equilibrium with a no-current condition on the crystal. A statement of this no-current condition in terms of the intrinsic diffusion coefficient of the particles, D_a^I , and the mobility of the particles, λ_a , is

$$J_e = 0 = q_a J_a = q_a \left\{ -N D_a^I \frac{dC_a}{dx} + N C_a \lambda_a E \right\}; \quad (4)$$

N is the total number of sites in the crystal, C_a is the fraction of sites occupied by the particles, and E is the negative gradient of the electrical potential ϕ .

Mott and Gurney integrated Eq. (4) assuming that D_a^I and λ_a were constants, thus implying that $D_a^I = D_a$ (the self diffusion coefficient of the particles). Therefore, the particles distribute themselves in the electrical field according to

$$N C_a = \text{constant} \cdot \exp \left(-\frac{\lambda_a \phi}{D_a} \right). \quad (5)$$

Mott and Gurney then combined this result with the well known prediction from the Maxwell-Boltzmann distribution,

$$N C_a = \text{constant} \cdot \exp \left(-\frac{q_a \phi}{k_B T} \right), \quad (6)$$

to obtain

$$\frac{\lambda_a}{D_a} = \frac{q_a}{k_B T}. \quad (7)$$

Equation (7) is the commonly accepted expression for the Nernst-Einstein equation.

What we will do in the following is to remove the restriction that D_a^I and λ_a remain constant and rederive Eq. (7). However, since the more general case for particles interacting will be treated, we cannot use the convenience of the Maxwell-Boltzmann distribution, but an equation similar to Eq. (6) can be derived from flux equations obtained using irreversible thermodynamics.

For simplicity, we will develop the expressions for a crystal with interstitial disorder, but for generality, we will include the results of an analysis that will apply to vacancy disorder. Consider a crystal containing tracer and nontracer interstitial ions of charge q_a . Then the fluxes of tracer ions, A^* , and nontracer ions, A , are

$$J_{A^*} = L_{A^*A^*} X_{A^*} + L_{A^*A} X_A, \quad (8)$$

and

$$J_A = L_{AA^*} X_{A^*} + L_{AA} X_A. \quad (9)$$

The L_{ij} are phenomenological coefficients, and the X_j are thermodynamic forces

$$X_j = -(\nabla \bar{\mu}_j)_T, \quad (10)$$

where $\bar{\mu}_j$, the electrochemical potential of j , is the sum of the chemical potential, μ_j , and the potential energy of a charged particle in an electrical potential ϕ ,

$$\bar{\mu}_j = \mu_j + q_a \phi; \quad (j = A, A^*), \quad (11)$$

q_a is the charge.

Substituting $\bar{\mu}_j$ into Eqs. (8), (9) and (10) gives

$$J_{A^*} = -L_{A^*A^*} \nabla \mu_{A^*} - L_{A^*A} \nabla \mu_A + q_a (L_{A^*A^*} + L_{A^*A}) E, \quad (12)$$

and

$$J_A = -L_{AA^*} \nabla \mu_{A^*} - L_{AA} \nabla \mu_A + q_a (L_{AA^*} + L_{AA}) E; \quad (13)$$

E is the electric field, $E = -\nabla \phi$. With Eqs. (12) and (13), we get the electrical current as

$$\begin{aligned} J_e &= q_a J_a = q_a (J_{A^*} + J_A) \\ &= q_a \{ -(L_{A^*A^*} + L_{AA^*}) \nabla \mu_{A^*} \\ &\quad - (L_{A^*A} + L_{AA}) \nabla \mu_A + q_a (L_{A^*A^*} + L_{A^*A} + L_{AA^*} + L_{AA}) E \}. \end{aligned} \quad (14)$$

When we first apply the electrical field to our crystal, the interstitial particle distribution is homogenous with $C_A/C_{A^*} = \text{constant}$, and as it evolves into a nonhomogeneous crystal, the force from the electrical field acts equally on A and A^* interstitials; C_A/C_{A^*} remains constant. Therefore, for all time

$$\nabla \mu_{A^*} = \frac{k_B T}{C_{A^*}} \nabla C_{A^*} \alpha = \frac{k_B TVC_a}{C_a} \alpha, \quad (15)$$

$$\nabla \mu_A = \frac{k_B T}{C_A} \nabla C_A \alpha = \frac{k_B TVC_a}{C_a} \alpha, \quad (16)$$

so that

$$\nabla \mu_{A^*} = \nabla \mu_A = \frac{k_B TVC_a}{C_a} \alpha. \quad (17)$$

In Eqs. (15-17) $C_a = C_{A^*} + C_A$ and α is the non-configurational contribution to the chemical potential gradient,

$$\alpha = 1 + \frac{\partial \ln \gamma}{\partial \ln C_a}; \quad (18)$$

γ is the activity coefficient and accounts for particle interaction effects. Substituting Eqs. (15) and (16) into Eq. (14) we get

$$J_e = q_a J_a = q_a \{ - (L_{A^*A^*} + L_{A^*A} + L_{AA^*} + L_{AA}) \left(\frac{k_B T V C_a}{C} \alpha - q_a E \right) \}. \quad (19)$$

Now the no-current condition gives

$$\frac{N k_B T V C_a}{N C} \alpha = q_a E. \quad (20)$$

This expression can be integrated to give the particle distribution in the electric field as

$$N C_a = \exp \left[- \int \frac{q_a}{k_B T \alpha} \frac{d\phi(x)}{dx} dx \right], \quad (21)$$

and while the result is similar to the one given by the Maxwell-Boltzmann distribution, it cannot be integrated generally since α is a function of x ; α accounts for particle interactions and depends upon the particle concentration. Now to complete the analysis, we simply integrate Eq. (4) in its general form not assuming D_a^I and λ_a to be constant

$$N C_a = \text{constant} \cdot \exp \left[- \int \frac{\lambda_a}{D_a^I} \frac{d\phi(x)}{dx} dx \right]. \quad (22)$$

Although the result is dependent upon integral expressions, the arguments of the integrals in Eqs. (21) and (22) can be equated and give

$$\frac{\lambda_a}{D_a^I} = \frac{q_a}{k_B T \alpha}. \quad (23)$$

Equation (23) is now the generalized form of the Nernst-Einstein relationship that we seek, and it differs from the apparently less general case that Mott and Gurney derived assuming no particle interaction. However, we shall see that there is no difference in the basic result obtained by both methods.

The results obtained by Mott and Gurney apply when Eq. (4) can be integrated assuming D_a^I and λ_a to be constants (i.e., not functions of C_a). The results obtained when D_a^I and λ_a are not constant are given in Eq. (23) and appear to be

different from Mott and Gurney's formulation of the Nernst-Einstein relation. However, they are in fact the same.

Recently it has been shown² that when the interstitial content is high enough and interstitial-interstitial interactions occur, interstitial diffusion is nonrandom so that the intrinsic diffusion coefficient, D_a^I , is related to the tracer diffusion, D_a^* , and the correlation factor, f_a , according to

$$D_a^I = \frac{D_a^*}{f_a} \alpha, \quad (24)$$

α is the thermodynamic factor given in Eq. (18). Putting Eq. (24) into Eq. (23) we find

$$\frac{\lambda_a}{D_a^* / f_a} = \frac{q_a}{k_B T}, \quad (25)$$

which is precisely the Mott and Gurney result since the self-diffusion coefficient for the interstitial defects equals D_a^* / f_a . Therefore, even when defect interaction occur, the interpretation of the diffusion coefficient in the Nernst-Einstein equation remains the same, namely, the mobility is proportional to the self-diffusion coefficient for a randomly moving particle. This result leaves an evaluation of the mobility or conductivity in a nonstoichiometric crystal dependent on only an understanding of how the average jump frequency of the charge carriers depends on concentration.

We can illustrate this with a specific example that applies to site exclusion effects in interstitial disordered structures. The tracer diffusion coefficient and the self diffusion coefficient are related according to Eq. (3), and we can also write the tracer diffusion coefficient as

$$D_a^* = \frac{\lambda^2}{6} f_a \Omega_a, \quad (26)$$

where Ω_a is the average jump frequency and λ is the jump distance. Using Eqs. (26) and (3) we find that

$$D_a = \frac{D_a^*}{f_a} = \frac{\lambda^2}{6} \Omega_a. \quad (27)$$

By using a simple model of interstitial pairing in octahedral sites of the fcc lattice (see Fig. 1), we can write down an expression for Ω_a . This interstitial-pairing model has been used to explain the concentration dependence of carbon diffusion in fcc iron;² we can use it here to illustrate how Ω_a depends on the combined effects of site exclusion and altered jump rates in defect complexes.

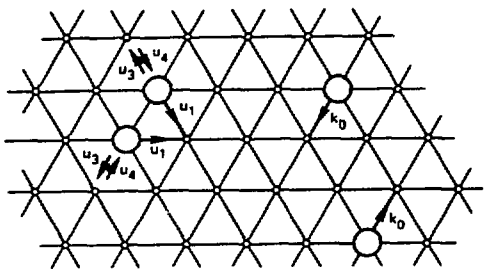


Fig. 1. Schematic diagram of a (111) plane of the fcc interstitial lattice showing available interstitial positions o , isolated interstitials O , and an interstitial-interstitial pair $O-O$. The various jump types and frequencies are indicated.

The interstitial defects in our model move as isolated interstitials at rate k_0 , and the basic jump rate k_0 is perturbed in or near a pair to rates u_1 , u_3 , and u_4 . The average interstitial jump rate, Ω_a , is simply a sum relationship for contributions made by k_0 -, u_1 -, u_3 -, and u_4 -type jumps:

$$\Omega_a = \Omega_{k_0} + \Omega_{u_1} + \Omega_{u_3} + \Omega_{u_4} . \quad (28)$$

Either by a simple mass action approach³ or by a more sophisticated statistical mechanics approach,² we find that Ω_a can be written to first order as

$$\begin{aligned} \Omega_a = & 12k_0 + 12\left(\frac{u_4}{u_3}\right)\{4u_1 + 7u_1 - 12k_0 \\ & + 7(u_4 - k_0)\left(\frac{u_3}{u_4}\right)\}C ; \end{aligned} \quad (29)$$

C is the fraction of occupied interstitial sites in the crystal.

There are many facets of this general problem that we could examine with this simple model, but let us consider its utility in discussing site exclusion. If we ask this question, and it often

arises, "how does the simple problem of site exclusion manifest itself in high defect concentration solids?" we can answer it quantitatively with Eq. (29). Equation (29) gives us an expression for how the average jump frequency for the charge carrying interstitial ions varies with concentration. If we set all jump frequencies to the value for the isolated interstitial k_0 -type jump, Ω_a illustrates only the site exclusion effect and becomes

$$\Omega_a = 12k_0(1 - C) . \quad (30)$$

This result tells us, in a quantitative form, that the probability for an interstitial ion jump decreases as the total interstitial concentration, C , increases. It is a necessary extension of this result to analyze more complicated structures with higher defect concentrations, and such techniques as Monte Carlo methods are being applied (for examples see the excellent work by Murch⁴).

III. CONCLUSION

Space does not make its presentation possible here, but Eq. (25) is perfectly general and works for any mechanism of self-diffusion; it can be derived for vacancy diffusion with the exact same result.⁵ Therefore, for diffusion-conductivity experiments in a pure crystal (whether stoichiometric or not), the diffusion coefficient in a Nernst-Einstein equation is always the self-diffusion coefficient when the Nernst-Einstein equation is written as Mott and Gurney presented it, and we have derived it more generally here.

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