Phenomenological Coefficients in Solid State Diffusion
(an introduction)

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G'day!

Fick's First Law (1855):

$$J_i = -D_i \frac{dC_i}{dx}$$

Because it does not recognize all of the direct and indirect driving forces acting on species *i*, Fick's First Law is frequently insufficient as a condition for describing the flux.

The actual driving force for diffusion is not the concentration gradient but the chemical potential gradient.

The Onsager (1934) Flux Equations of irreversible processes provide the general formalism through the postulate of linear relations between the fluxes and the driving forces:

$$J_i = \sum_j L_{ij} X_j$$

$L_{ij} = L_{ji}$
(reciprocity condition)

L_{ij} : the phenomenological coefficients
(independent of driving force)

X_j : the driving forces

Consider a binary system AB. The Onsager Flux Equations are:

$$J_A = L_{AA} X_A + L_{AB} X_B$$

$$J_B = L_{BB} X_B + L_{AB} X_A$$

Consider a hypothetical situation where A is charged and B is not, and the system is placed in an electric field E.

The driving forces are then: $X_A = -q_A E$ and $X_B = 0$

The fluxes are then: $J_A = -L_{AA} q_A E$ and $J_B = -L_{AB} q_A E$

The A atoms respond only to the direct force $q_A E$. The B atoms only respond to the indirect force $q_A E$ and are then 'dragged along' by the A atoms.

What are these phenomenological coefficients?

$$L_{ij} = \frac{<R_i \cdot R_j>}{6VkTt}$$

(Allnatt 1982)

R_i: the 'collective displacement' or displacement of the center-of-mass of species **i** in time t.

E.g.

$$L_{AA} = \frac{<R_A^2>}{6VkTt}$$

$$L_{AB} = \frac{<R_A \cdot R_B>}{6VkTt}$$

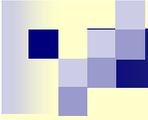If the moving **A** species does not interfere with the moving **B** species

e.g.   **A** and **B** do not compete for the same defects

or   **A** and **B** do not interact (i.e. different sublattices)

$\Rightarrow$ $<R_A \cdot R_B> = 0$ and $L_{AB} = 0.$

However, in most cases in solid-state diffusion the off-diagonal coefficients can be significant. They can be positive or negative.

$$L_{ij} = \frac{< R_i \cdot R_j >}{6VkTt}$$

Allnatt's (1982) equation for the L_{ij} is a generalization of the Einstein (1905) equation for the tracer or self-diffusion coefficient:

$$D^* = \frac{< r^2 >}{6t}$$

r = displacement of a tracer atom in time t

The Einstein Equation is frequently used in Molecular Dynamics simulations, see Poster 31: Zhao et al., Poster 37: Leroy et al., Poster 38: Leroy et al., Poster 54: Plant et al., Poster 42: Chihara et al., Poster 39: Habasaki et al.

The relationship between the Einstein Equation and the Allnatt Equation can be appreciated if we consider a binary system of A* and A in which we allow the tracer A* concentration to be very low.

Then we would have that:

$$L_{A^*A^*} = \frac{D^*}{VkT}$$

In solid-state diffusion, the motion of the atoms normally takes place by discrete jumps or hops (often called the 'hopping model').

I can hop too!

Defects such as vacancies provide the vehicles for atom motion.

The hopping model is frequently used directly or indirectly in the modelling of solid state diffusion, see Poster 18: Maas et al., Poster 28: Sholl, Poster 41: Kalnin et al., Poster 49: Radchenko et al.

In solid-state diffusion, the motion of the atoms normally takes place by discrete jumps or hops (often called the 'hopping model').

I can hop too!

It is usual then to partition diffusion coefficients such as the tracer diffusion coefficient in the following way:

$$D_j^* = f_j \; (Z \; c_v \; w_j \; a^2)$$

$\uparrow$ $\uparrow$

correlated part   uncorrelated part

Z: coordination number
c_v: vacancy concentration
w_j: **exchange frequency of an atom of type j with a vacancy**
a: jump distance

f_j: tracer correlation factor of atoms of type j. It is an expression of the correlation between the directions of the successive jumps of a given atom of type j.

The tracer correlation factor can be expressed in terms of the cosine of the angle between the 'first' jump and all subsequent jumps of a given atom (the tracer):

$$f = 1 + 2 \sum_{m=1}^{\infty} <\cos\theta^{(m)}>$$
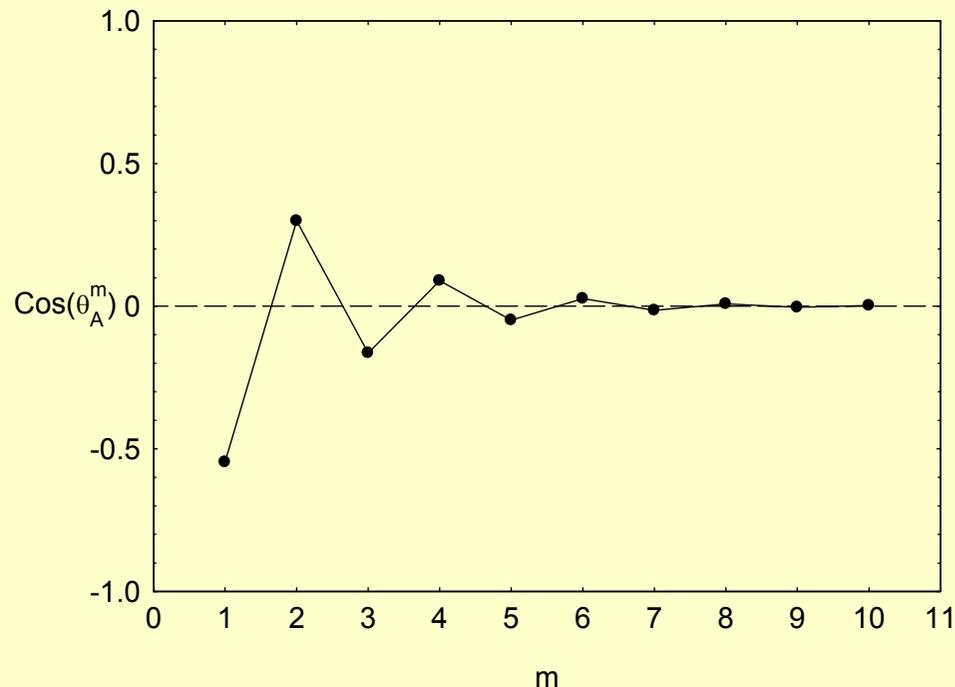
Example of the convergence of the cosine between the first tracer A jump and the m'th tracer A jump. .

Phenomenological coefficients can be partitioned in a similar way to diffusion coefficients:

$$L_{ij} = f_{ij}^{(j)} \quad (Z\, c_v\, w_j\, a^2\, N\, c_j\, /\, 6\, V\, k\, T)$$

$\uparrow$ correlated part $\qquad \uparrow$ uncorrelated part

$f_{ij}^{(j)}$: collective correlation factor. It is an expression of the correlation between the directions of successive jumps of the centers-of-mass of the species present.
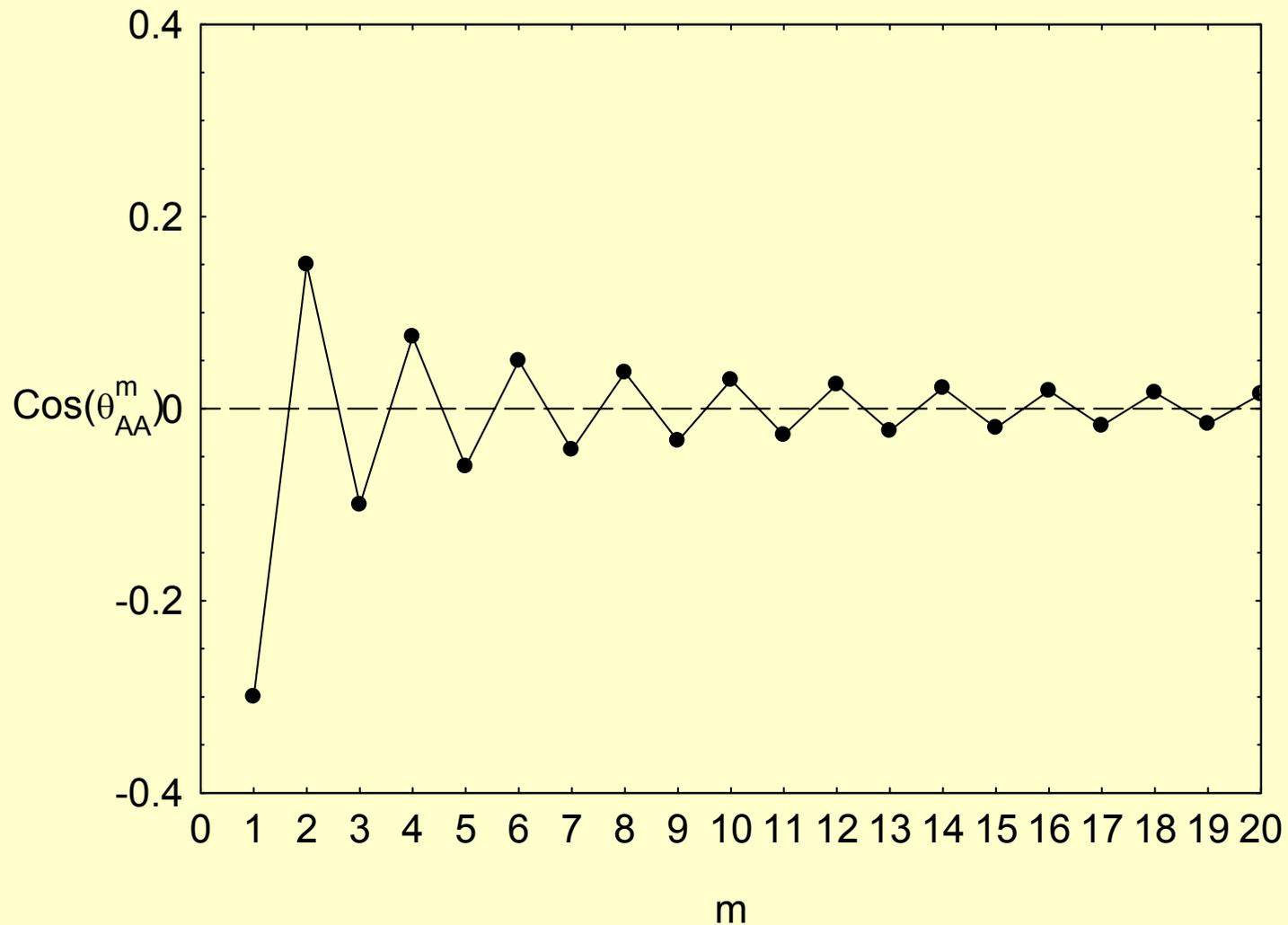
The collective correlation factors can be expressed in terms of the cosine of the angle between the 'first' jump and all subsequent jumps of the same species (diagonal factor) or another species (off-diagonal factor)

Diagonal collective correlation factor:

$$\mathbf{f_{ii}} = 1 + 2 \sum_{m=1}^{\infty} < \cos \theta_{ii}^{(m)} >$$

Off-diagonal collective correlation factor (binary case only):

$$\mathbf{f_{AB}^{(A)}} = \sum_{m=1}^{\infty} < \cos\theta_{AB}^{(m)} > + \frac{\mathbf{C_B n_B}}{\mathbf{C_A n_A}} \sum_{m=1}^{\infty} < \cos\theta_{BA}^{(m)} >$$

Example of the convergence of the cosine between the first collective jump and the m'th collective jump (of the same species A).

The phenomenological coefficients are extremely difficult to measure directly in the solid state.

If we want them, how do we proceed?

● **First Strategy: Find relations between the phenomenological coefficients and the (measurable) tracer diffusion coefficients:**

Example 1: The Darken Relations (1948) :

$$L_{ii} = C_i D_i^* / kT$$

$$L_{ij} = 0$$

## *Example 2*: The Manning Relations (1971) for the random alloy:

$$L_{ii} = \frac{C_i D_i^*}{kT}\left(1 + \frac{2C_i D_i^*}{M_0 \sum\limits_k C_k D_k^*}\right)$$

$$L_{ij} = \frac{2C_i D_i^* C_j D_j^*}{kT(M_0 \sum\limits_k C_k D_k^*)}$$

The Manning Relations can also be derived on the basis of two 'intuitive' assumptions without recourse to the random alloy model (Lidiard 1986). They have also been derived for binary ordered structures (Belova and Murch 1997)

● **Second Strategy: Find relations between the phenomenological coefficients themselves in order to reduce their number.**

$$\Rightarrow \text{ 'Sum-Rules'}$$
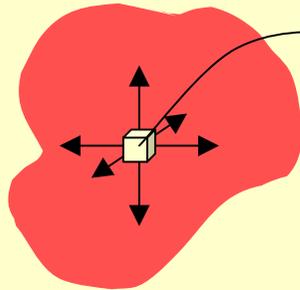
Possible vacancy jumps after time t
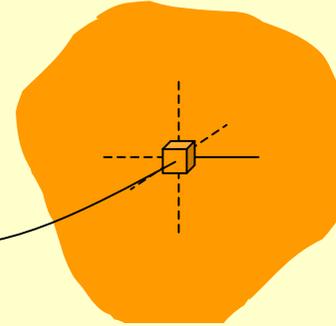
Initial vacancy-atom jump

Vector summation of $\nwarrow\!\!\uparrow\!\!\nearrow\!\!\leftarrow\!\!\rightarrow\!\!\swarrow\!\!\downarrow\!\!\searrow$ = 0
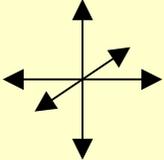
Schematic illustration for the origin of the 'Sum-Rule'.

The 'Sum-Rule' for the phenomenological coefficients in a multicomponent random system is (Moleko and Allnatt 1986):

$$\sum_{i=1}^{M} L_{ij} w_j / w_i = A w_j c_j c_V$$
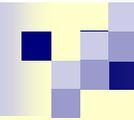
For the binary system, the 'Sum-Rule' is:

$$L_{AA} = \frac{N c_V c_A w_A a^2}{kT} - \frac{w_A}{w_B} L_{AB}, \quad L_{BB} = \frac{N c_V c_B w_B a^2}{kT} - \frac{w_B}{w_A} L_{AB}$$

➡ **In the binary system there is then only one independent phenomenological coefficient, not three.**
(In the ternary random system there are three independent phenomenological coefficients, not six.)

Analogous 'Sum-Rule' expressions have since been derived for:

- **Diffusion via divacancies in the random alloy (Belova and Murch 2005).**

- **Diffusion via dumb-bell interstitials in the random alloy (Sharma, Chaturvedi, Belova and Murch 2000).**

- **Diffusion via vacancy-pairs in strongly ionic compounds (Belova and Murch 2004).**

- **Diffusion via vacancies in substitutional intermetallics (Belova and Murch 2001, Allnatt, Belova and Murch 2005).**

- **Diffusion via vacancies in the five-frequency impurity diffusion model (Belova and Murch 2005).**

Application of the Onsager flux equations and the Sum-Rule (binary alloy):

The Onsager flux equations are:

$$J_A = L_{AA} X_A + L_{AB} X_B$$

$$J_B = L_{BB} X_B + L_{AB} X_A$$

$$X_i = -\frac{\partial \mu_i}{\partial x} = -\frac{kT}{C_i} \frac{\partial C_i}{\partial x} \left(1 + \frac{\partial \ln \gamma}{\partial \ln c} \right)$$

The intrinsic diffusion coefficients (found from the Kirkendall shift and the interdiffusion coefficient) are:

$$D_A^I = kT \left(\frac{L_{AA}}{C_A} - \frac{L_{AB}}{C_B} \right) \phi$$

$$D_B^I = kT \left(\frac{L_{BB}}{C_B} - \frac{L_{AB}}{C_A} \right) \phi$$

Local lattice reference frame

$$J_i = -D_i^I \frac{\partial C_i}{\partial x}$$

ϕ is the 'thermodynamic factor':

$$\phi = \left(1 + \frac{\partial \ln \gamma}{\partial \ln c_B} \right)$$

The ratio of the intrinsic diffusion coefficients is:

$$\frac{D_A^I}{D_B^I} \equiv \frac{c_B L_{AA} - c_A L_{AB}}{c_A L_{BB} - c_B L_{AB}}$$

Application of the Sum-Rule then gives (Belova and Murch 1997):

$$\boxed{\frac{D_A^I}{D_B^I} = \frac{W_A}{W_B}}$$

Measurement of the ratio of the intrinsic diffusivities directly thus gives the ratio of the exchange frequencies. There are no complicating correlation factors.

If we had simply used the Darken relations (where all off-diagonal phenomenological coefficients are put equal to zero) we would then have obtained:

$$\frac{D_A^I}{D_B^I} = \frac{D_A^*}{D_B^*}$$

(This is a very rough approximation)

The interdiffusion coefficient:

$$\tilde{D} = c_B D_A^I + c_A D_B^I$$

$$J_A^0 = -\tilde{D}\frac{\partial C_A}{\partial x} = -J_B^0$$ Lab. reference frame

After application of the Allnatt Equation for the L_{ij} :

$$L_{ij} = \frac{< R_i \cdot R_j >}{6VkTt}$$

$$\Rightarrow \boxed{\tilde{D} = \frac{< (c_B R_A - c_A R_B)^2 >}{6Ntc_A c_B}\phi}$$ Belova and Murch 1998

This general equation for the interdiffusion coefficient in a binary alloy is, in effect, an extension of the Einstein Equation (1905).

With direct access to the ratio of the atom-vacancy exchange frequencies, one can also use a diffusion kinetics theory to gain access to the tracer correlation factors:

The Ag-Cd system:
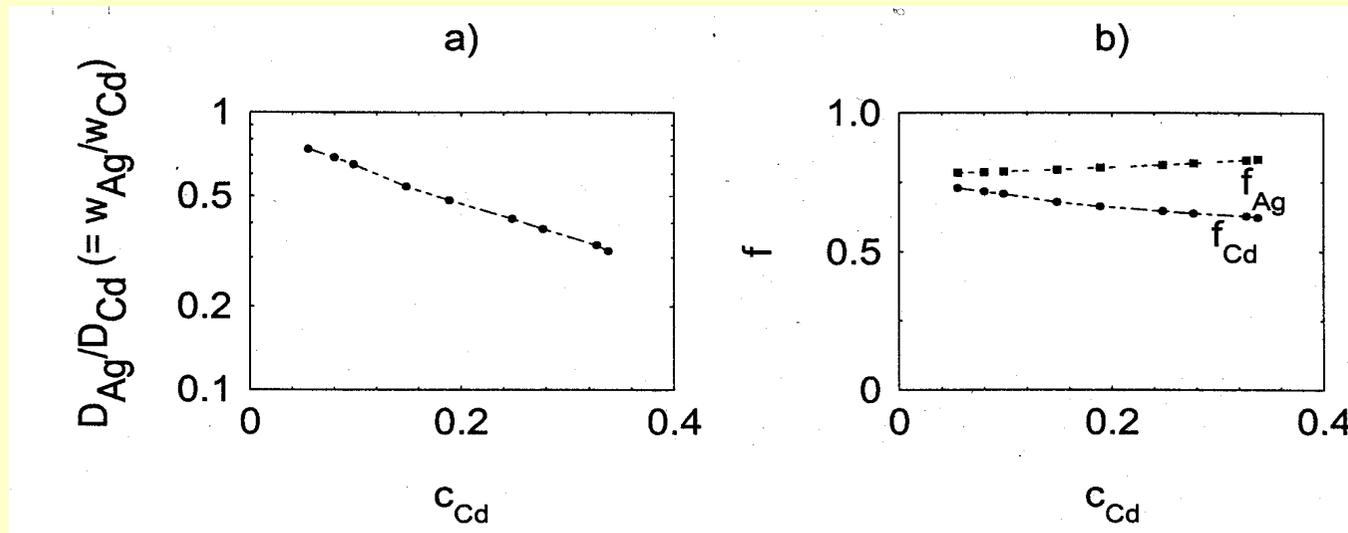
a) The ratio D^I_{Ag}/D^I_{Cd} $(= w_{Ag}/w_{Cd})$ as a function of c_{Cd} at **873K**. (Iorio *et al.* **1973**);

b) Corresponding tracer correlation factors using the Moleko *et al.* (1986) Self consistent diffusion kinetics formalism.

$\Rightarrow$ **Cd is more correlated (more jump reversals) in its motion than Ag.**

Demixing of A and B cations in (A,B)O in an oxygen potential gradient (gives a gradient of cation vacancies):
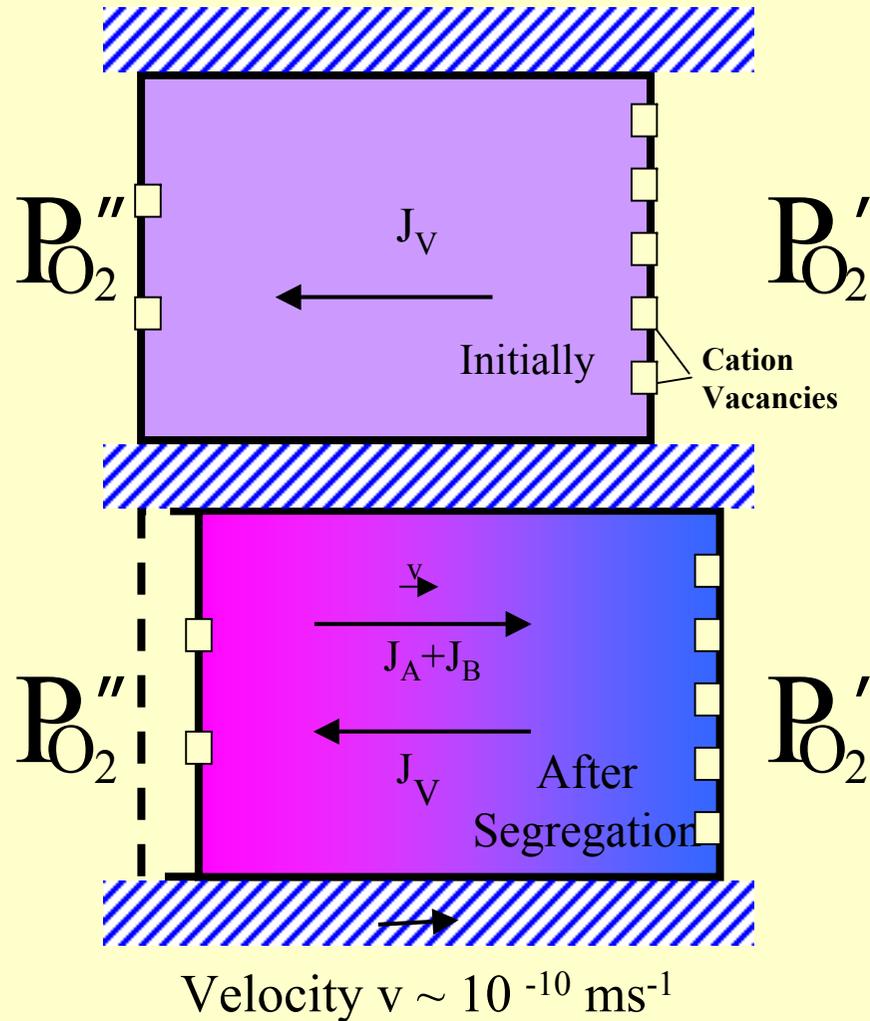
$$P''_{O_2} \;<\; P'_{O_2}$$

$$w_A \;>\; w_B$$

(A is blue and B is pink)

Demixing of A and B cations in (A,B)O in an electric field.

(+) (−) (Applied Electric Field)

P_{O_2} Initially Cation Vacancies P_{O_2}

$w_A > w_B$

(A is blue and B is pink)

(+) J_A J_B (−)

J_V After Segregation

P_{O_2} P_{O_2}

Velocity v
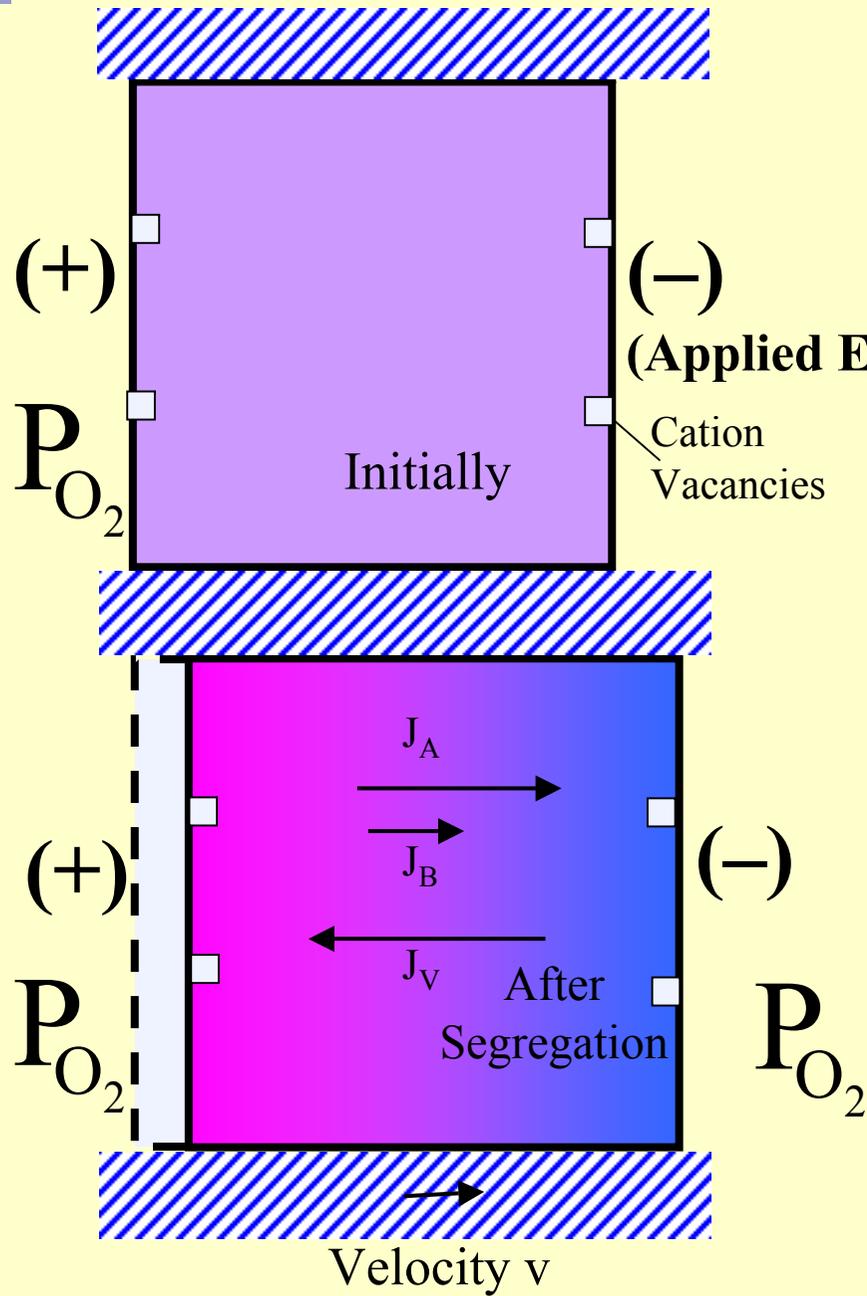
Analysis of demixing of A and B cations in a mixed oxide (A,B)O in an oxygen potential gradient and electric field:

Onsager Flux Equations:

$$\mathbf{J_A} = -L_{AA}(\nabla\mu_A - \nabla\mu_V - q_A E) - L_{AB}(\nabla\mu_B - \nabla\mu_V - q_B E),$$

$$\mathbf{J_B} = -L_{BB}(\nabla\mu_B - \nabla\mu_V - q_B E) - L_{AB}(\nabla\mu_A - \nabla\mu_V - q_A E),$$

μ_i: chemical potential of component i (A, B or V (vacancies)

E: Electric field

q_i: charge on component i

Steady-State Condition: $\mathbf{J_i} - vc_i N = 0,\quad i = A,B$

$$\Rightarrow \begin{bmatrix} \nabla(\mu_A - \mu_V - q_A E) \\ \nabla(\mu_B - \mu_V - q_B E) \end{bmatrix} = \begin{bmatrix} L_{AA} & L_{AB} \\ L_{AB} & L_{BB} \end{bmatrix}^{-1} \begin{bmatrix} -c_A vN \\ -c_B vN \end{bmatrix}$$

Application of the Sum-Rule gives simply that:

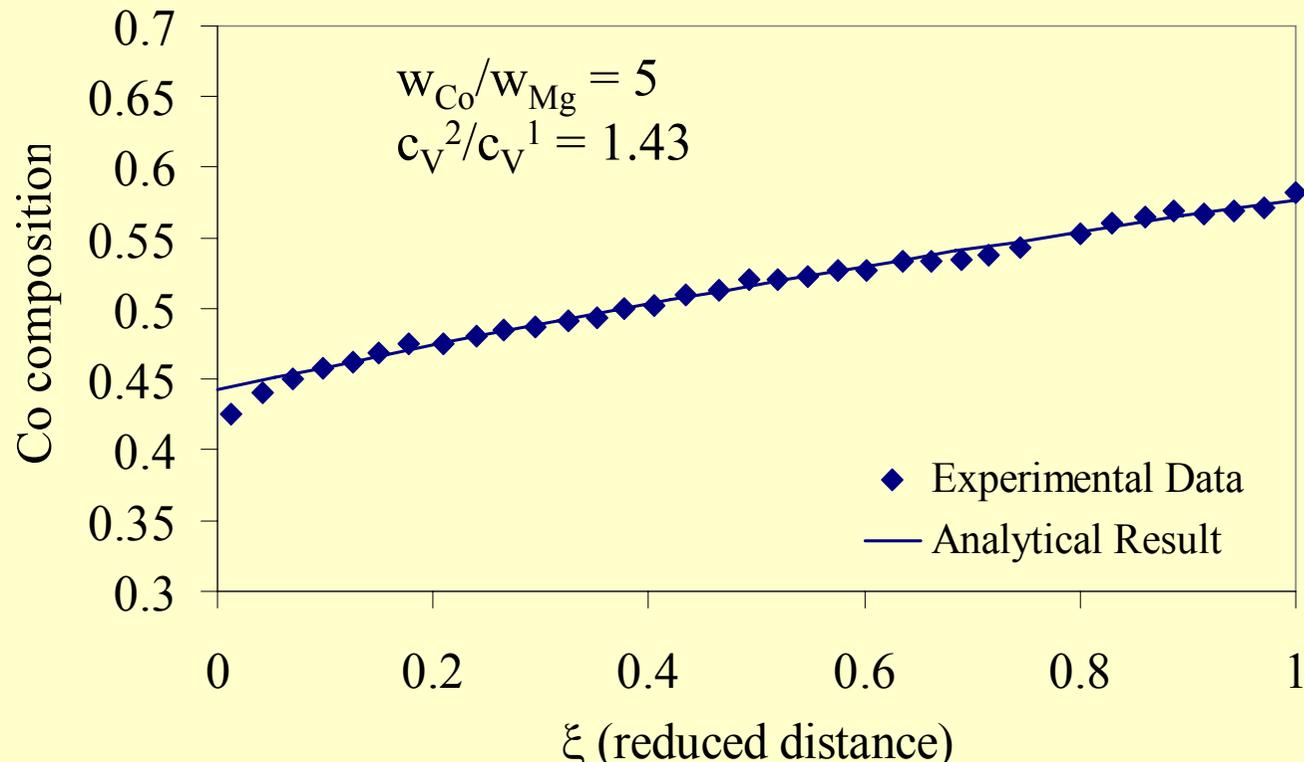$$\nabla(\mu_A - \mu_V) = -\frac{\nu NkT}{w_A c_V a^2} + q_A E$$

$$\nabla(\mu_B - \mu_V) = -\frac{\nu NkT}{w_B c_V a^2} + q_B E$$

**We now assume random mixing of the two cations.
The demixed steady-state composition profile of, say, A, is given by:**

$$\Rightarrow \qquad \frac{dc_A}{d\xi} = \frac{c_A \nu N}{c_V a^2}\left(\frac{c_A - 1}{w_A} + \frac{c_B}{w_B}\right) + \frac{c_A c_B (q_A - q_B)E}{kT}$$

Steady-state demixed profile of Co in (Co,Mg)O in an oxygen potential gradient (Experimental data: Schmalzried et al. 1979).

$w_{Co}/w_{Mg} = 5$

$c_V^2/c_V^1 = 1.43$

◆ Experimental Data

— Analytical Result

Co composition (y-axis)

ξ (reduced distance) (x-axis)

Initial composition: $c_{Co} = 0.51$

The fitting parameter is w_{Co}/w_{Mg}.

Steady-state demixed profile of Co in (Co,Ni)O in an electric field (Experimental data: Martin 2000).

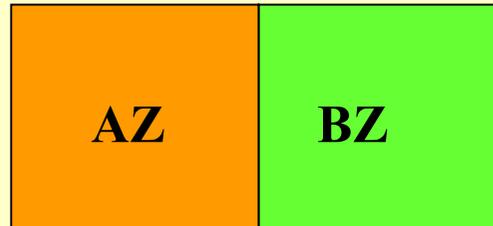$qEa/kT=0.676$ $w_{Co}/w_{Ni}= 5.0$
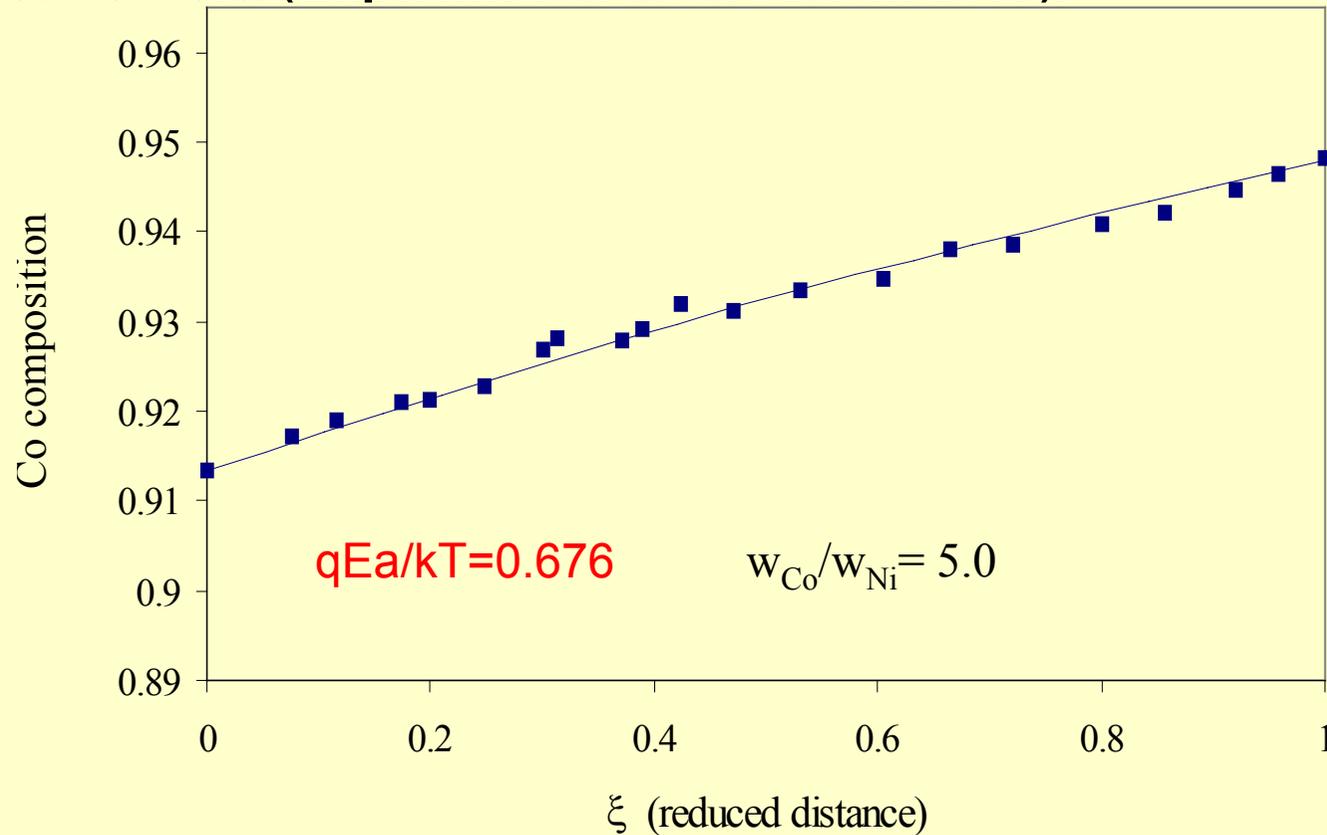
Initial composition: c_{Co} = 0.93   **The fitting parameter is w_{Co}/w_{Ni}.**

(Voltage = 50 mV, sample thickness = 600 μm) $\Leftrightarrow$ (qEa/kT = 0.676)

Analysis of interdiffusion in a strongly ionic diffusion couple AZ-BZ:

- The cations A and B diffuse via vacancies on the cation sublattice.
- The anions Z diffuse via vacancies on the anion sublattice.

The Onsager Flux Equations are (we assume that qA = qB = -qZ):

$$J_A = L_{AA}X_A + L_{AB}X_B$$
$$J_B = L_{BB}X_B + L_{AB}X_A$$
$$J_Z = L_{ZZ}X_Z.$$

where for the internal forces we have:

$$X_A = -\nabla\mu_A + q_A E$$
$$X_B = -\nabla\mu_B + q_B E$$
$$X_Z = -q_Z E$$

Application of the electro-neutrality conditions and the Gibbs-Duhem relation gives for the intrinsic diffusion coefficients (e.g. Belova and Murch 2004):

$$\mathbf{J}_A = -\mathbf{D}_A^I N \nabla c_A \qquad \mathbf{J}_B = -\mathbf{D}_B^I N \nabla c_B$$

where

$$\mathbf{D}_A^I = \frac{\phi kTc_Z}{Nc_A c_B}\left(\frac{L_{AA}L_{BB} - L_{AB}^2 + L_{ZZ}(L_{AA}c_B - L_{AB}c_A)/c_Z)}{L_{AA} + L_{BB} + 2L_{AB} + L_{ZZ}}\right) \quad \text{and}$$

$$\mathbf{D}_B^I = \frac{\phi kTc_Z}{Nc_A c_B}\left(\frac{L_{AA}L_{BB} - L_{AB}^2 + L_{ZZ}(L_{BB}c_A - L_{AB}c_B)/c_Z)}{L_{AA} + L_{BB} + 2L_{AB} + L_{ZZ}}\right)$$

ϕ: **thermodynamic factor**

Application of the Sum-Rule to the ratio of the intrinsic diffusion coefficients gives:

$$\frac{D^I_A}{D^I_B} = \frac{w_A(w_B + w_Z)}{w_B(w_A + w_Z)}$$

where w_Z is the anion vacancy exchange frequency.

1. For the limiting case $w_Z \gg w_A\ (w_B)$, (anion mobility is relatively high):

$$D^I_A/D^I_B = w_A/w_B.$$

(this is the same result as for the binary alloy)

$\Rightarrow$ **The mobility on the anion sublattice no longer determines the rate of cation interdiffusion).**

2. For the limiting case $w_Z \ll w_A\ (w_B)$, (anion mobility is relatively low):

$$D^I_A = D^I_B.$$

The almost immobile anion sublattice requires that the fluxes of the cations A and B are equal and opposite.

$\Rightarrow$ **no net cation vacancy flux and no marker shift in interdiffusion.**

The interdiffusion coefficient:

The general expression for $\tilde{D}$ in a strongly ionic interdiffusion couple (AZ-BZ):

$$\tilde{D} = -\frac{(q_A + q_B)q_Z kT\phi N}{2c_A c_B}\frac{\left(c_Z^2(L_{AA}L_{BB} - L_{AB}^2) + c_A c_B L_{ZZ}(c_B d_A^I + c_A d_B^I)\right)}{c_Z \kappa}$$

where

$$d_A^I = \frac{L_{AA}}{c_A} - \frac{L_{AB}}{c_B} \qquad d_B^I = \frac{L_{BB}}{c_B} - \frac{L_{AB}}{c_A}$$

$$\kappa = q_A^2 L_{AA} + q_B^2 L_{BB} + 2q_A q_B L_{AB} + q_Z^2 L_{ZZ}$$

Using Allnatt's (1982) equation for the phenomenological coefficients:

$$L_{ij} = \frac{< R_i \cdot R_j >}{6VkTt}$$

$$\Rightarrow \quad \tilde{D} = \frac{kT\phi L_{ZZ}}{c_A c_B c_Z} \frac{< (c_B R_A - c_A R_B)(c_B R_A - p_A R_B) >}{< (R_A + R_B)^2 > + < R_Z^2 >}$$

$$p_i = \frac{c_Z^2 L_{ii}^{(0)}}{c_i L_{ZZ}} + c_i$$

There are two limiting cases to consider:

I. When the anions are much more mobile than the cations (Belova and Murch 2005) :

$$\tilde{D} = \frac{< \left(c_B R_A - c_A R_B \right)^2 >}{6 N t c_A c_B c_Z} \phi$$

II. When the cations are much more mobile than the anions (Belova and Murch 2005) :

$$\tilde{D} = \frac{\phi N c_Z a^2 c_{Va} < \left(c_B R_A - c_A R_B \right)\left(c_B w_B R_A - c_A w_A R_B \right) >}{t c_A c_B < \left(R_A + R_B \right)^2 >}$$

These equations for the interdiffusion coefficients in a strongly ionic compound are, in effect, extensions of the Einstein Equation (1905).

We consider further the case where the anions are much slower than the cations, e.g. in silicates, glasses, transition metal oxides.

We apply the Sum-Rule and make use of the accurate self consistent diffusion kinetics theory of Moleko *et al.* (1989):

$$\tilde{D} = \frac{kT\phi(c_A + c_B)}{Nc_A c_B} \frac{f_0 L_{AB}}{(1 - f_0)}$$

Belova and Murch 2004:

f_0 : the geometric tracer correlation factor (depends on lattice only)

If L$_{AB}$ were to be neglected (this is the Darken approximation) it would be equivalent to implying that interdiffusion is impossible.

Direct access is now possible to L_{AB} in transition metal oxides, oxides, in silicates, in glasses etc, i.e. whenever the anion mobility is low compared with the cations.

Example: Extraction of L_{AB} from the interdiffusion coefficient in (CoO-NiO).

CoO-NiO, 1573K $(Co_{1-x}Ni_x)O$
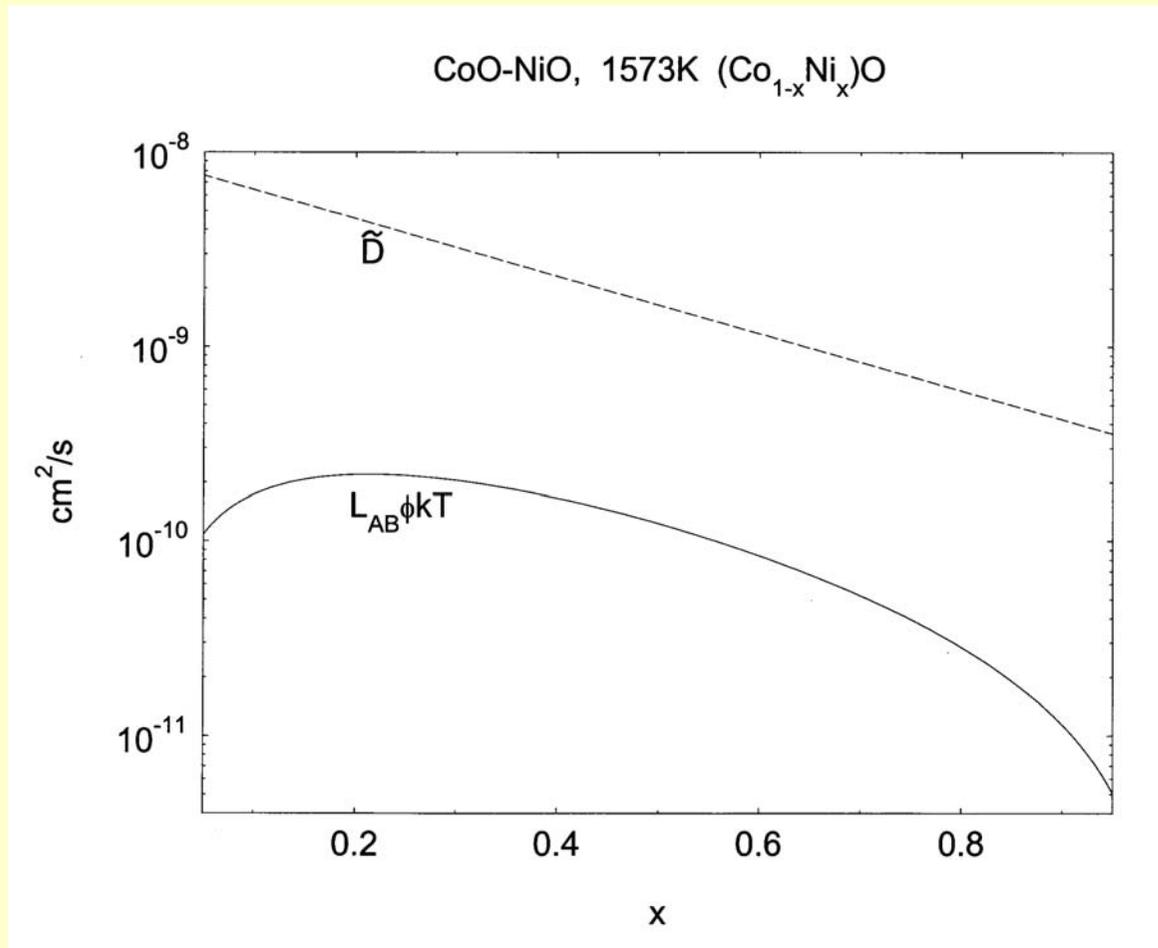
Expt. : J.J. Stiglich, Jr. *et al.* (1973).

Some other results that can be obtained at the same approximation level for strongly ionic compounds when the cations are much more mobile than the anions:

$$\widetilde{D} = \frac{D_{A^*} D_{B^*}}{c_A D_{A^*} + c_B D_{B^*}} \phi$$

(This is the Nernst-Planck Equation)

and

$$\widetilde{D} = \frac{D_{A^*} D_{B^*} q^2 C_{ion}}{f_0 \sigma_{dc} kT} \phi$$

The testing of these equations in, say, a silicate, would require measurements of the tracer diffusion coefficients, the interdiffusion coefficient, the ionic conductivity and the thermodynamic factor.

Conclusions:

- **The Onsager flux expressions and Allnatt's equation for the phenomenological coefficients can rightly be considered generalizations of Fick's First Law and the Einstein Equation**

- **The Onsager flux expressions and Allnatt's equation, together with the Sum-rule, bring substantial simplifications to many chemical diffusion problems.**

Vielen Dank!