Are Correlations Important in Diffusion?*

Graeme E. Murch¹, Nagraj Kulkarni² and Irina V. Belova¹

¹Center for Mass and Thermal Transport in Engineering Materials, School of Engineering
The University of Newcastle, Callaghan, NSW 2308, Australia

²Microelectronic Systems Research Group
Measurement Science and Systems Engineering Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831-6006, USA.

*This paper is dedicated to the memories of the late John Manning and Alan Le Claire.
Outline:

- **Tracer correlations**
  - Self and solute diffusion in metals
  - Self-diffusion in disordered alloys
  - Self-diffusion in intermetallics

- **Collective correlations**
  - Chemical diffusion in disordered alloys
  - Chemical diffusion in intermetallics

- **Haven Ratios and Vacancy-Wind factors**
  - Disordered alloys
  - Intermetallics

- **Final comments**
Tracer correlation factors
Random walk of a atom on a lattice

Einstein (also Einstein-Smoluchowski) relation:

\[ \langle R^2 \rangle = 6Dt \]

relates the mean square displacement to the diffusion coefficient \( D \) and time \( t \)
The tracer correlation factor

\[
\langle R^2 \rangle = \left( \sum_{i=1}^{n} r_i \right) \left( \sum_{k=1}^{n} r_k \right) = (r_1 + r_2 + \ldots + r_n)(r_1 + r_2 + \ldots + r_n)
\]

\[
\langle R^2 \rangle = \sum_{i=1}^{n} r_i^2 \left[ 1 + 2 \frac{\sum_{i=1}^{n-1} \sum_{k=1}^{n-i} \langle r_i r_k \rangle}{\sum_{i=1}^{n} r_i^2} \right]
\]

\[f = \left[ 1 + 2 \frac{\sum_{i=1}^{n-1} \sum_{k=1}^{n-i} \langle r_i r_k \rangle}{\sum_{i=1}^{n} r_i^2} \right] = 1 + 2 \sum_{m=1}^{\infty} \langle \cos \theta^{(m)} \rangle
\]

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).

\[0 \leq f \leq 1\]
Do these correlations converge?

\[ f = 1 + 2 \sum_{m=1}^{\infty} < \cos \theta^{(m)} > \]

Example of the convergence of the cosine between the first tracer A jump and the \( m^{th} \) tracer A jump.
Tracer correlation factors depend on:

- the type of lattice.
- the diffusion mechanism.
- the type of diffusing atom in the matrix.
- the degree of local order of the atomic components.
Direct interstitial mechanism – for small solutes

Small solutes such as H, C, N, and O in bcc and fcc metals are dissolved in octahedral and/or tetrahedral sites. They diffuse via direct interstitial jumps.

At low concentrations all jump directions are equally probable → no correlation

\[ \langle r_i r_k \rangle = 0 \]

\[ f = 1 \]

NOTE: \( f = 1 \) means no correlation
**Vacancy mechanism** -- dominates self- and solute diffusion in metals, most disordered alloys and ionic crystals.

After a vacancy-tracer exchange a reverse tracer jump is more likely, simply because the vacancy is still available on the neighbour site.

For **self-diffusion** in cubic lattices, the correlation factors for vacancy-assisted diffusion are just numbers, often called geometric correlation factors $f_0$:

- **fcc**: $f_0 = 0.781$
- **bcc**: $f_0 = 0.727$
- **sc**: $f_0 = 0.653$
- **diamond**: $f_0 = 0.5$
**Divacancy mechanism** — contributes to self- and solute diffusion in metals at high temperatures. In correlation terms, it is closely related to the triple-defect mechanism in intermetallics.

\[ \langle r_1 r_2 \rangle < 0 \]
\[ f < 1 \]

Correlation factors for divacancy-assisted diffusion are usually much smaller than those for vacancy-assisted diffusion, e.g.:

\[ f(\text{divacancy in fcc}) = 0.456 \]
\[ f(\text{vacancy in fcc}) = 0.781 \]
Tracer correlation factors for self-diffusion in various lattices and for various diffusion mechanisms:

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Mechanism</th>
<th>Correlation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1d chain</td>
<td>vacancy</td>
<td>0</td>
</tr>
<tr>
<td>honeycomb</td>
<td>vacancy</td>
<td>1/3</td>
</tr>
<tr>
<td>2d-square</td>
<td>vacancy</td>
<td>0.467</td>
</tr>
<tr>
<td>2d hexagonal</td>
<td>vacancy</td>
<td>0.56006</td>
</tr>
<tr>
<td>diamond</td>
<td>vacancy</td>
<td>1/2</td>
</tr>
<tr>
<td>simple cubic</td>
<td>vacancy</td>
<td>0.6531</td>
</tr>
<tr>
<td>bcc cubic</td>
<td>vacancy</td>
<td>0.7272, (0.72149)</td>
</tr>
<tr>
<td>fcc cubic</td>
<td>vacancy</td>
<td>0.7815</td>
</tr>
<tr>
<td>fcc cubic</td>
<td>divacancy</td>
<td>0.4579</td>
</tr>
<tr>
<td>bcc cubic</td>
<td>divacancy</td>
<td>0.335 to 0.469</td>
</tr>
<tr>
<td>fcc cubic</td>
<td>⟨100⟩ dumb-bell interstitial</td>
<td>0.4395</td>
</tr>
<tr>
<td>any lattice</td>
<td>direct interstitial</td>
<td>1</td>
</tr>
<tr>
<td>diamond</td>
<td>colinear interstitialcy</td>
<td>0.727</td>
</tr>
<tr>
<td>CaF₂(F)</td>
<td>non-collinear interstitialcy</td>
<td>0.9855</td>
</tr>
<tr>
<td>CaF₂(Ca)</td>
<td>colinear interstitialcy</td>
<td>4/5</td>
</tr>
<tr>
<td>CaF₂(Ca)</td>
<td>non-collinear interstitialcy</td>
<td>1</td>
</tr>
</tbody>
</table>
For the hopping model (discrete jumps) the diffusion coefficient can be seen as the product of correlated and uncorrelated parts:

\[ D_j^* = \frac{<R^2>}{6t} \]

\[ = f_j (Z c_v w_j a^2) \]

- \( f_j \): exchange frequency of an atom of type \( j \) with a vacancy
- \( Z \): coordination number
- \( c_v \): vacancy concentration
- \( w_j \): jump distance

\( Z \) and \( c_v \) are correlated with each other.
Normal solute-diffusion in metals

Solute diffusivity: \[ D = f_{\text{solute}} a^2 \omega_c C_V \exp\left(\frac{H_B}{kT}\right) \]

\[ \propto f_{\text{solute}} a^2 \exp \left[ -\left( H_F - H_B + H_{\text{solute}}^M \right)/kT \right] \]

- \( H_F \): Formation enthalpy of vacancy
- \( H_B \): Binding enthalpy vacancy-solute pair
- \( H_{\text{solute}}^M \): Migration enthalpy vacancy-solute exchange
- \( f_{\text{solute}} \): Correlation factor for solute diffusion

Activation enthalpy for solute diffusion:

\[ Q_2 = H_F - H_B + H_{\text{solute}}^M - C \]

- \( H_B < 0 \) repulsion or \( H_B > 0 \) attraction
- \( H_{\text{solute}}^M \) barrier for exchange between solute and vacancy
- \( C \) contribution to the activation energy from the correlation factor
Where does the temperature dependence of the solute correlation factor come from?

Example: the five-frequency model (Le Claire and Lidiard 1956, Manning 1964)

\[
f_{\text{solute}} = \frac{w_1 + 7Fw_3/2}{w_2 + w_1 + 7Fw_3/2}
\]

where

\[
7F = \frac{7 (10b^4 + 180.5b^3 + 927b^2 + 1341b)}{(2b^4 + 40.2b^3 + 254b^2 + 597b + 436)}
\]

and

\[
b = \frac{w_4}{w_0}
\]

Over a surprisingly wide temperature interval, \( f_{\text{solute}} \) can be approximated by an Arrhenius expression:

\[
f_{\text{solute}} \approx f_{\text{solute}}^0 \exp \left( -\frac{C}{kT} \right)
\]

\( w_4 \) is the reverse of a \( w_3 \) type jump
\( w_0 \) is the frequency of a host jump far from the solute
How big is this contribution of C to the overall activation energy for diffusion?

Example: Solute diffusion in silver

<table>
<thead>
<tr>
<th>Solute</th>
<th>$Q_2$ (expt.)</th>
<th>C (calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.834 eV</td>
<td>~ -0.1 eV</td>
</tr>
<tr>
<td>Sn</td>
<td>1.704 eV</td>
<td>~ -0.2 eV</td>
</tr>
</tbody>
</table>
The Random Alloy Model

This model was introduced by the late John Manning in 1968/1971 to deal with diffusion in concentrated disordered alloys.

- Random mixing of N atomic components and isolated vacancies.
- \( w_i \) – atom-vacancy exchange frequency depends on atom i and not on its surroundings.

Note that each \( w_i \) can be interpreted as an average or effective frequency that can depend on alloy composition.
Tracer diffusion in the random alloy

**Manning (1971)**

\[ f_i = \frac{H}{2w_i + H} \]

H: frequency of escape of the vacancy from a particular atom.

**Moleko, Allnatt and Allnatt (1989)**

\[ f_i = \frac{H_i}{2w_i + H_i} \]  
(Self-consistent treatment)

Seven (!) Monte Carlo studies showed that Manning’s original approach provided the best agreement.
But all seven Monte Carlo studies were wrong because the jump sequences were later found to be much too short!!

In some cases, long-time diffusion behavior is only reached after 500-1000 (!) jumps per atom (Belova and Murch PM 2000).

Cautionary Note: This finding should be noted whenever correlation factors are calculated in Kinetic Monte Carlo or Molecular Dynamics simulations.

The self-consistent treatment of Moleko, Allnatt and Allnatt is, in fact, almost exact.
Tracer correlation factor $f_B$ in the b.c.c. alloy for various values of $w_A/w_B$.
Points – Monte Carlo simulations; solid lines – Moleko, Allnatt and Allnatt 1989
Differences in the atom-vacancy exchange frequencies of a factor of 100 are common in concentrated disordered alloys.

This can lead to differences in the correlation factors of roughly a factor of 20.

The more mobile species will be more correlated: i.e. smaller correlation factors

The less mobile species will be less correlated: i.e. higher correlation factors

But correlation effects will not change the basic relationship of the exchange frequencies with the diffusivities but only weakens it:

i.e. If $w_A >> w_B$ then $D_A > D_B$

\[
c_{\text{Cu}} = 0.187, \quad c_{\text{Ni}} = 0.686, \quad c_{\text{Fe}} = 0.127
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>Correlation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.329</td>
</tr>
<tr>
<td>Fe</td>
<td>0.638</td>
</tr>
<tr>
<td>Ni</td>
<td>0.848</td>
</tr>
</tbody>
</table>

\[
c_{\text{Cu}} = 0.093, \quad c_{\text{Ni}} = 0.802, \quad c_{\text{Fe}} = 0.105
\]

<table>
<thead>
<tr>
<th>Component</th>
<th>Correlation factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.608</td>
</tr>
<tr>
<td>Fe</td>
<td>0.376</td>
</tr>
<tr>
<td>Ni</td>
<td>0.819</td>
</tr>
</tbody>
</table>
Tracer diffusion in intermetallics
Schematic representation of possible jumps in an intermetallic:

- **β sublattice**
- **α sublattice**

- B atom
- A atom
- Vacancy

Intermetallics with antistructural disorder will always have many jump reversals as atoms jump from the ‘right’ sublattice to the wrong sublattice and then immediately reverse that jump. This immediately leads to very small correlation factors for that type of intermetallic.
Tracer correlation in an intermetallic can be described by an adaptation of Manning’s diffusion kinetics formalism for the random alloy (Belova and Murch Phil Mag 1999-2003):

\[ E.g. \text{ For the B2 structure} \]

\[ f_A = \frac{H_1 H_2}{H_1 H_2 + w^\beta_\rightarrow^\alpha H_1 + w^\alpha_\rightarrow^\beta H_2}, \]

H_1 and H_2 are the positive roots of the following equations:

\[ 1 - f_0 = \frac{c^\alpha_A W^\alpha_\rightarrow^\beta}{2 w^\alpha_\rightarrow^\beta + H_1} + \frac{c^\alpha_B W^\alpha_\rightarrow^\beta}{2 w^\alpha_\rightarrow^\beta + H_1} \]

\[ 1 - f_0 = \frac{c^\beta_A W^\beta_\rightarrow^\alpha}{2 w^\beta_\rightarrow^\alpha + H_2} + \frac{c^\beta_B W^\beta_\rightarrow^\alpha}{2 w^\beta_\rightarrow^\alpha + H_1} \]

H_1 and H_2 are the so-called ‘vacancy escape’ frequencies for the vacancy to be able to ‘escape’ from an atom on the \( \alpha \) and \( \beta \) sublattices.
Predicted tracer correlation factors in CuZn from experimental knowledge of the ratio of the tracer diffusion coefficients, the long range order parameter and $T_c$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$\frac{D_{Zn}}{D_{Cu}}$ (expt. (Chipman and Warren))</th>
<th>$f_{Zn}$ (predicted)</th>
<th>$f_{Cu}$ (predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>523</td>
<td>1.54</td>
<td>0.07</td>
<td>0.61</td>
</tr>
<tr>
<td>573</td>
<td>1.58</td>
<td>0.10</td>
<td>0.64</td>
</tr>
<tr>
<td>618</td>
<td>1.61</td>
<td>0.19</td>
<td>0.67</td>
</tr>
<tr>
<td>653</td>
<td>1.63</td>
<td>0.31</td>
<td>0.695</td>
</tr>
<tr>
<td>683</td>
<td>1.64</td>
<td>0.41</td>
<td>0.70</td>
</tr>
</tbody>
</table>

$f_{Zn}$ contributes 29% of the observed activation energy for tracer Zn diffusion. $f_{Cu}$ contributes 18% of the observed activation energy for tracer Cu diffusion.
Typical comparison of calculated tracer correlation factors using Manning type arguments with Monte Carlo simulation:

Note the loss of agreement at high levels of order: this is a result of concatenated mechanisms (six-jump-cycle)
Another approach to tracer correlation in intermetallics

A theory based on the six-jump-cycle as the ‘diffusion unit’. (the approach from the ordered state)

The six-jump-cycle (6JC) is a minimum energy penalty cycle that provides for effective diffusion in a stoichiometric intermetallic with perfect order.

The 6JC is then taken as the basic diffusion ‘unit’. Extrinsic antistructural atoms (from nonstoichiometry) and intrinsic antistructural atoms (from thermal activation) can participate directly and indirectly (via interactions) in the 6JC. Belova and Murch (2002-2004).
The five-frequency model for describing the interaction of a vacancy with a solute inspired the 6JC diffusion unit’s interaction with an antistructural atom.
Application of the 6JC-unit theory to interdiffusion and tracer diffusion data in $\beta$-AgMg.

Fit to the interdiffusion coefficient data (Iijima, et al. 1995) provides values for the ordering energy $E = 7.19$ kJ mol$^{-1}$ ($T_C=1129^\circ$C) and $E_{\text{MgMg}} - E_{\text{AgAg}} = +0.7E$. 
Corresponding tracer correlation factors in $\beta$-AgMg predicted from the 6JC-unit theory (Belova and Murch J Phys C 2005):

$$f_{\text{Ag}}$$ contributes 19% of the observed activation energy for tracer Ag diffusion. 

$$f_{\text{Mg}}$$ contributes 28% of the observed activation energy for tracer Mg diffusion.
Collective correlation factors appear in ‘collective’ mass transport quantities such as:

- Ionic conductivity
- Intrinsic diffusion coefficients
- Interdiffusion coefficients
Fick’s First Law (1855):

\[ J_i = - D_i \frac{dC_i}{dx} \]

Because it does not recognize all of the driving forces, direct and indirect, acting on species \( i \), Fick’s First Law is frequently insufficient as a condition for describing fluxes.
The Onsager (1934) Flux Equations of irreversible processes provide a more general formalism through the postulate of linear relations between the fluxes and the driving forces:

\[ J_i = \sum_j L_{ij} X_j \]

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

\( X_j \): the driving forces
Consider a binary alloy $AB$.
The Onsager Flux Equations are written as:

\[
J_A = L_{AA} X_A + L_{AB} X_B \\
J_B = L_{BB} X_B + L_{AB} X_A
\]

What is the meaning of the off-diagonal or cross terms?

Consider a hypothetical situation where $A$ feels a force $X_A$ but $B$ does not feel a corresponding force $X_B$. ($X_B=0$)

The fluxes are then: $J_A = L_{AA} X_A$ and $J_B = L_{AB} X_A$

The $A$ atoms are responding only to the direct force $X_A$. The $B$ atoms only respond to the indirect force $X_A$ and are in effect ‘dragged’ along by the $A$ atoms.
The strength of this drag is dictated by the size of $L_{AB}$. 
Do the phenomenological coefficients have an atomistic meaning?

\[ L_{ij} = \frac{< \mathbf{\mathcal{R}}_i \cdot \mathbf{\mathcal{R}}_j >}{6VkTt} \]  
(Allnatt 1982)

\( \mathbf{\mathcal{R}}_i \): the ‘collective displacement’ or displacement of the ‘center-of-mass’ of species \( i \) in time \( t \).

e.g.

\[ L_{AA} = \frac{< \mathbf{\mathcal{R}}_A^2 >}{6VkTt} \]

\[ L_{AB} = \frac{< \mathbf{\mathcal{R}}_A \cdot \mathbf{\mathcal{R}}_B >}{6VkTt} \]

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)

\[ < \mathbf{\mathcal{R}}_A \cdot \mathbf{\mathcal{R}}_B > = 0 \quad \text{and} \quad L_{AB} = 0. \]

However, in most cases of solid-state diffusion, the off-diagonal coefficients can be quite significant and should never be casually discarded.
The phenomenological coefficients can be expanded out in much the same way as tracer diffusion coefficients:

For example, for a binary alloy:

\[ L_{AA} = \frac{a^2 w_A c_V c_A N f_{AA}}{kT} \]

\[ L_{BB} = \frac{a^2 w_B c_V c_B N f_{BB}}{kT} \]

\[ L_{AB} = L_{BA} = \frac{a^2 w_A c_V c_A N f_{AB}^{(A)}}{kT} = \frac{a^2 w_B c_V c_B N f_{AB}^{(B)}}{kT} \]

N: number of lattice sites per unit volume

\( f_{ii}, f_{ij}^{(i)} \): collective correlation factors (the correlated parts of the phenomenological coefficients)
Expressions for collective correlation factors can also be developed in much the same way as tracer correlation factors.

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 factors:

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

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

\[
 f_{AB}^{(A)} = \sum_{m=1}^{\infty} < \cos \theta_{AB}^{(m)} > + \frac{C_B n_B}{C_A n_A} \sum_{m=1}^{\infty} < \cos \theta_{BA}^{(m)} > 
\]
Example of the convergence of the cosine between the first collective jump and the $m'$th collective jump (of the same species A) in a binary alloy.
Collective correlation factors depend on:

- the type of lattice.
- the diffusion mechanism.
- the types of diffusing species in the matrix.
- the degree of local order of the atomic components.
Collective correlation factors in disordered alloys

Collective correlation factors for the fcc random alloy with $w_A/w_B=0.1$
Typical comparison of collective correlation factors calculated using Manning-type arguments with Monte Carlo simulation:

Collective correlation factors for ordered and disordered alloys

Note the loss of agreement at high levels of order: this is a result of concatenated diffusion mechanisms (six-jump-cycle)
Haven Ratios and Vacancy-Wind factors in diffusion
One mobile component.

Ionic conductivity and tracer diffusion (the Haven Ratio)

The Haven Ratio $H_R$ is the ratio of the tracer diffusion coefficient $D^*_A$ of a single mobile species (A) to a dimensionally correct diffusion coefficient $D_\sigma$ obtained from the d.c. ionic conductivity $\sigma_A$. G.E. Murch: Solid State Ionics Vol. 7 (1982), p.177.

$$H_R = \frac{C_A q_A^2 D^*_A}{kT \sigma_A} = \frac{D^*_A}{D_\sigma} = \frac{f_A}{f_{AA}}$$

$C_A$ is the concentration of charge carriers, $q_A$ is the charge on a mobile ion, $f_A$ is the tracer correlation factor, $f_{AA}$ is the collective correlation factor, sometimes also called the conductivity or physical correlation factor.
Interpretation of the Haven Ratio

If we neglect collective correlations, the interpretation of the Haven Ratio is straightforward in ionic conductors for diffusion mechanisms such as the vacancy mechanism where $H_R$ then simply equals $f_0$ the geometric correlation factor.

For cooperative diffusion mechanisms e.g. the interstitialcy mechanism, the displacement of the charge in an electric field is different from the displacement of a tracer atom:

$$H_R = \frac{(r*)^2 f_A}{(r_q)^2 f_{AA}}$$

Nonetheless, the interpretation of $H_R$ still remains straightforward.

When the defect concentration is high, perhaps above several percent, then the collective correlation factor $f_{AA}$ must be included in the interpretation of the Haven Ratio.

Unfortunately, after a promising start with lattice gas models, little progress has been achieved recently in the analysis of $H_R$ for realistic models of ionic materials, especially glasses.
The Haven Ratio also appears for interstitial diffusion in metals:

$$H_R = \frac{D_A^*\varphi}{\tilde{D}} = \frac{f_A}{f_{AA}}$$

where $\varphi$ is the thermodynamic factor.
Haven Ratio $H_R = f_A/f_{AA}$ for carbon diffusion in Fe as a function of carbon composition at 1000 °C.

This behaviour is consistent with recent molecular dynamics results that show carbon interstitials diffuse partly as lone interstitials and partly as paired interstitials. Evteev et al. Acta Mat 2009.

Chemical diffusion and activity data: R.P. Smith, Acta Metall., 1, 578 (1953);
The vacancy-wind factor $S$ appears in the relation between the interdiffusivity and the component tracer diffusivities in a binary alloy:

\[
\tilde{D} = S \left( c_B D_A^* + c_A D_B^* \right) \phi
\]

where

\[
S = kT \frac{c_B L_{AA} / c_A + c_A L_{BB} / c_B - 2L_{AB}}{C_B D_A^* + C_A D_B^*}
\]

Note: when $L_{AB} = 0$, $S = 1$ (the Darken approximation)

and in terms of collective and tracer correlation factors:

\[
S = \left( \frac{c_B f_{AA} + c_A g f_{BB} - c_B g f_{AB} - c_A f_{AB}}{c_B f_A + c_A g f_B} \right)
\]

where $g = n_B / n_A$, $n_A$ and $n_B$ are the numbers of jumps of an $A$ or a $B$ atom in time $t$. 
The vacancy-wind factor $S$ as calculated numerically from the accurate MAA theory.

Disordered alloys rarely show $w_A/w_B$ smaller than $10^{-2}$, so $S$ will normally be greater than 1 but less than about 2.
The Darken-Manning Equation was re-derived for diffusion in B1 and B2 intermetallics (Belova and Murch 1997-1998).

The limits for the vacancy-wind factor are now quite different from the disordered alloy:

Disordered alloys:

1.0 ≤ S ≤ f_{0}^{-1} (Manning)

1.0 ≤ S ≤ ∞ (percolation limit) (MAA).
Intrinsic diffusion coefficients

Other vacancy-wind factors appear in relations between the intrinsic diffusivities and the tracer diffusivities:

(Intrinsic diffusivities are obtained by way of measurement of inert marker shifts in the interdiffusion experiment.)

\[
D^I_A = D_A^* r_A \phi \\
D^I_B = D_B^* r_B \phi
\]

where

\[
r_A = kT \frac{L_{AA} / c_A - L_{AB} / c_B}{C_A C_B D^*_A} \quad r_B = kT \frac{L_{BB} / c_B - L_{AB} / c_A}{C_A C_B D^*_B}
\]

and in terms of collective and tracer correlation factors:

\[
r_A = \left( \frac{f_{AA} - c_A f^{(A)} f^{-1}}{f_A} \right) \quad r_B = \left( \frac{f_{BB} - c_B f^{(B)} f^{-1}}{f_B} \right)
\]

When \( L_{AB} = 0 \),
\( r_A = r_B = 1 \)
A comment about the Darken approximation

**The Darken approximation**

All off-diagonal phenomenological coefficients are put equal to zero.

\[ L_{ij} = 0 \quad \text{for} \quad i \neq j. \]

All atoms must follow uncorrelated random walks, i.e. the tracer and the diagonal collective correlation factors are simply given by:

\[ f_i = 1 \quad f_{ii} = 1 \]

and the off-diagonal correlation factors are equal to zero:

\[ f_{ij} = 0 \quad \text{for} \quad i \neq j. \]

Very simple relations then exist between the diagonal phenomenological coefficients and the tracer diffusion coefficients:

\[ L_{ii} = c_i D^*_i / kT, \]

By enforcing this relation, the diagonal phenomenological coefficients are then corrupted in their meaning because they now ‘carry’ any off-diagonal information (Manning, Acta Met. 1967).
Physically, what is the vacancy-wind effect itself?
The normalized probability of finding a vacancy in the region around an average A atom and an average B atom with $D_A = 10 \, D_B$.

The vacancy-wind effect here is simply an apparent deviation from the local equilibrium vacancy concentrations as seen by moving atoms. For interdiffusion in this alloy, both A and B are slowed down by the vacancy-wind effect.
Chemical diffusion in ternary disordered alloys

The ‘Darken-Manning’ type expression for the ternary alloy is (Belova and Murch Acta Mat. 2009):

\[
\begin{bmatrix}
\tilde{D}_{AA}^C & \tilde{D}_{AB}^C \\
\tilde{D}_{BA}^C & \tilde{D}_{BB}^C
\end{bmatrix}
= \begin{bmatrix}
S_{AA}\tilde{D}_{AA}^{\text{Darken}} & S_{AB}\tilde{D}_{AB}^{\text{Darken}} \\
S_{BA}\tilde{D}_{BA}^{\text{Darken}} & S_{BB}\tilde{D}_{BB}^{\text{Darken}}
\end{bmatrix}
\begin{bmatrix}
\phi_{11} & \phi_{21} \\
\phi_{12} & \phi_{22}
\end{bmatrix}
\]

The vacancy-wind is now represented as a 2x2 matrix.

The above expression can be compared with the Darken-Manning expression for the binary alloy:

\[
\tilde{D} = S\tilde{D}^{\text{Darken}} \quad \phi = S(c_B D_A^* + c_A D_B^*)\phi
\]
Ternary disordered alloys

Manning’s ideas for the binary alloy can be extended to give approximations for the 2x2 matrix of vacancy-wind factors in the ternary alloy. (Belova and Murch, Acta Mat. 2009):

\[
S_{AA} = 1 + \frac{2c_A (c_B (D_A^* - D_B^*) + c_C (D_A^* - D_C^*)) (D_A^* - D_C^*)}{M_0 ((1 - c_C)D_A^* + c_A D_C^*) (c_A D_A^* + c_B D_B^* + c_C D_C^*)}
\]

\[
S_{BB} = 1 + \frac{2c_B (c_A (D_B^* - D_A^*) + c_C (D_B^* - D_C^*)) (D_B^* - D_C^*)}{M_0 ((1 - c_C)D_B^* + c_B D_C^*) (c_A D_A^* + c_B D_B^* + c_C D_C^*)}
\]

\[
S_{BA} = 1 + \frac{2}{M_0} \left( 1 - \frac{D_B^*}{c_A D_A^* + c_B D_B^* + c_C D_C^*} \right)
\]

\[
S_{AB} = 1 + \frac{2}{M_0} \left( 1 - \frac{D_A^*}{c_A D_A^* + c_B D_B^* + c_C D_C^*} \right)
\]

(At compositions close to the percolation threshold, the actual vacancy-wind factors could in principle, behave quite differently from these predictions)

Note the formal similarity of their mathematical structures with Manning’s original expression for \(S\) in the binary alloy:

\[
S = 1 + \frac{2c_A c_B (D_A^* - D_B^*)^2}{M_0 (c_B D_A^* + c_A D_B^*) (c_A D_A^* + c_B D_B^*)}
\]
Vacancy-wind factors in the disordered Cu-Fe-Ni fcc alloy

<table>
<thead>
<tr>
<th>$c_{\text{Fe}}$</th>
<th>$c_{\text{Ni}}$</th>
<th>$c_{\text{Cu}}$</th>
<th>$S_{\text{CuCu}}$</th>
<th>$S_{\text{FeFe}}$</th>
<th>$S_{\text{CuFe}}$</th>
<th>$S_{\text{FeCu}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.127</td>
<td>0.686</td>
<td>0.187</td>
<td>1.09</td>
<td>1.01</td>
<td>0.52</td>
<td>0.91</td>
</tr>
<tr>
<td>0.265</td>
<td>0.503</td>
<td>0.232</td>
<td>1.12</td>
<td>0.99</td>
<td>0.52</td>
<td>1.06</td>
</tr>
<tr>
<td>0.108</td>
<td>0.464</td>
<td>0.428</td>
<td>1.19</td>
<td>0.99</td>
<td>0.71</td>
<td>1.12</td>
</tr>
<tr>
<td>0.298</td>
<td>0.375</td>
<td>0.327</td>
<td>1.06</td>
<td>1.02</td>
<td>0.83</td>
<td>0.93</td>
</tr>
<tr>
<td>0.105</td>
<td>0.802</td>
<td>0.093</td>
<td>1.01</td>
<td>1.04</td>
<td>0.82</td>
<td>0.53</td>
</tr>
</tbody>
</table>

Vacancy-wind factor matrix elements ($S_{ij}$) calculated using the Manning-type approach from the measured *tracer diffusion coefficients* in the Cu-Fe-Ni system.
Two mobile ionic species $A$ and $B$ share the same sublattice (and therefore compete for the same defects).

The rest of the structure is essentially immobile at the temperatures of interest.

For chemical interdiffusion between $AX$ and $BX$, there is no Kirkendall effect (i.e. no marker shift) because there can be no separation of charge and therefore no net vacancy flow.

The correct equation to use under these circumstances is the Nernst-Planck Equation not the Darken–Manning equation. The Nernst-Planck Equation is also fully consistent with the Manning diffusion kinetics theory developed originally for the disordered alloy (i.e. no vacancy-wind term):

$$
\tilde{D} = \frac{D_A^* D_B^*}{c_A D_A^* + c_B D_B^*} \varphi
$$

The Nernst-Planck Equation
However, the near-exact MAA diffusion kinetics theory does give a new vacancy-wind like correction term to the Nernst-Planck Equation (I V Belova, A R Allnatt and G E Murch Acta Mat, 2009):

\[
\tilde{D} = \frac{D_A^* D_B^*}{c_A D_A^* + c_B D_B^*} S^{NP} \varphi
\]

where \( S^{NP} \) is the vacancy-wind term:

\[
S^{NP} = \frac{M_0}{2} \left( \frac{f^{(A)}_{AB}}{f_A} + \frac{f^{(B)}_{AB}}{f_B} \right)
\]
The vacancy-wind factor $S^{NP}$ as calculated by the MAA theory as a function of composition $c_A$ with $w_A/w_B = 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}$ and $10^{-5}$.

In most cases, it is unlikely that $w_A/w_B$ is smaller than $10^{-2}$, which means that at most, there is a 25% correction to the Nernst-Planck Equation.
So. Are correlations important in diffusion?

It depends......

- At the very best, a tracer diffusion coefficient can be measured with a precision of 5%. A precision of 30% is still considered very good. Thus for **self-diffusion in pure metals**, tracer correlations that typically produce a 30-50% reduction in the diffusion coefficient could be considered borderline in numerical importance.

- For typical **solute diffusion in metals**, the correlation factor can however make a sizable contribution (probably up to 10%) to the activation energy and, for a fast diffuser, perhaps reduce $D_0$ by an order of magnitude.

- For **self-diffusion in disordered alloys**, tracer correlation effects can reduce $D_0$ (of the fast diffuser) by roughly an order of magnitude in typical disordered alloys. Again there will be a contribution to the total activation energy of up to 10%.

- For **self-diffusion in intermetallics** with antisite disorder, tracer correlation effects are now greatly magnified because of jump reversals. $D_0$ can be reduced by up to 3 or 4 orders of magnitude and contributions to the activation energy may be as high as $\sim 30\%$, perhaps more.
- **Collective** transport quantities such as interdiffusion and intrinsic diffusion coefficients are affected by collective correlation effects. By and large, these effects will produce quite similar behaviour as for tracer correlation effects. For example, chemical diffusion in an intermetallic will be greatly affected.

- In quantities such as **Haven ratios and vacancy-wind factors**, most of the correlation effects that would lead to large changes in the individual diffusion coefficients, **now largely cancel out**.

  - For typical **disordered alloys**, putting in the vacancy-wind factor would give a deviation of up to a factor of two (higher) than the Darken equation.
  - For **intermetallics**, the deviation would be up to a factor of two (lower) than the Darken equation.
  - For **ionic compounds**, the deviation would be less than 25% from the Nernst-Planck equation.
Thank you for your attention!