Vacancy mediated substitutional diffusion in binary crystalline solids

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\textbf{Abstract}

We describe a formalism to predict diffusion coefficients of substitutional alloys from first principles. The focus is restricted to vacancy mediated diffusion in binary substitutional alloys. The approach relies on the evaluation of Kubo-Green expressions of kinetic-transport coefficients and fluctuation expressions of thermodynamic factors for a perfect crystal using Monte Carlo simulations applied to a cluster expansion of the configurational energy. We make a clear distinction between diffusion in a perfect crystal (i.e. no climbing dislocations and grain boundaries that can act as vacancy sources) and diffusion in a solid containing a continuous distribution of vacancy sources that regulate an equilibrium vacancy concentration throughout. A variety of useful metrics to characterize intermixing processes and net vacancy fluxes that can result in the Kirkendall effect are described and are analyzed in the context of thermodynamically ideal but kinetically non-ideal model alloys as well as a realistic thermodynamically non-ideal alloy. Based on continuum simulations of diffusion couples using self-consistent perfect-crystal diffusion coefficients, we show that the rate and mechanism of intermixing in kinetically non-ideal alloys is very sensitive to the density of discrete vacancy sources.

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\textbf{Contents}

1. Introduction ................................................................. 62
2. Substitutional solids: perfect crystals ................................ 65
1. Introduction

Substitutional diffusion in multi-component alloys is a kinetic phenomenon that plays an important role in solid-state phase transformations [1–11]. It also determines degradation rates of multilayer structures characterized by large concentration gradients.

Theoretical and computational methods in materials research can provide essential guidance in the interpretation of solid state phenomena and are increasingly capable of predicting materials properties before experiments are ever performed. First-principles electronic structure methods [12], for example, have reached a point where thermodynamic and kinetic properties of perfect crystals can be predicted with reasonable accuracy. Phase diagrams of crystalline solids are now routinely calculated by combining first-principles-parameterized lattice models with Monte Carlo simulations or meanfield approximations such as the cluster variation method [13–36]. The statistical mechanical techniques used to calculate phase diagrams from first principles have also been implemented to predict diffusion coefficients in multi-component solids [37–39]. However, these methods describe properties of perfect crystals, whereas kinetic phenomena such as substitutional diffusion can be sensitive to the presence of dislocations and grain boundaries.

This paper focuses on substitutional diffusion mediated by vacancies and seeks to (i) describe a formalism that connects phenomenological transport coefficients in a binary alloy to well-defined quantities that can be calculated from first principles for a perfect crystal and (ii) to clarify the link between substitutional diffusion in a perfect crystal (i.e., without dislocations and grain boundaries) with diffusion in a real solid containing vacancy sources and sinks. We exclude in our analysis fast diffusion along grain boundaries and dislocation cores, which can be considered separately.
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>A</td>
<td>slow diffuser</td>
</tr>
<tr>
<td>a</td>
<td>atomic hop distance</td>
</tr>
<tr>
<td>B</td>
<td>fast diffuser</td>
</tr>
<tr>
<td>(C_i)</td>
<td>concentration of the (i)th diffusing species ((i = A, B \text{ or } V)) defined as the number of atoms per unit volume</td>
</tr>
<tr>
<td>(\bar{C}_B)</td>
<td>fast diffuser concentration normalized by the lattice density</td>
</tr>
<tr>
<td>(C_{BC}^\ast)</td>
<td>non-dimensionalized fast diffuser concentration calculated in a perfect-crystal model</td>
</tr>
<tr>
<td>(C_{BC}^\ast)</td>
<td>non-dimensionalized fast diffuser concentration calculated in a continuous-vacancy-source approximation</td>
</tr>
<tr>
<td>(D_i)</td>
<td>self-diffusion coefficient of the (i)th diffusing species</td>
</tr>
<tr>
<td>(D_i^T)</td>
<td>tracer diffusion coefficient of the (i)th diffusing species</td>
</tr>
<tr>
<td>(D_{ij})</td>
<td>diffusion coefficient relating the (i)th flux to the (j)th concentration gradient in a perfect crystal</td>
</tr>
<tr>
<td>(D)</td>
<td>diffusion coefficient matrix of a perfect crystal</td>
</tr>
<tr>
<td>(E(\bar{\sigma}))</td>
<td>ground state energy of configuration (\bar{\sigma})</td>
</tr>
<tr>
<td>(E_s)</td>
<td>energy of microstate (s)</td>
</tr>
<tr>
<td>(f)</td>
<td>correlation factor in a single component solid</td>
</tr>
<tr>
<td>(f_i)</td>
<td>correlation factor of the (i)th diffusing species ((i = A, B \text{ or } V))</td>
</tr>
<tr>
<td>(J_i)</td>
<td>flux of the (i)th diffusing species ((i = A, B \text{ or } V)) defined as the number of atoms of species (i) crossing a unit area per unit time</td>
</tr>
<tr>
<td>(\hat{J}_i)</td>
<td>intermixing flux ((i = A \text{ or } B)) in a perfect crystal</td>
</tr>
<tr>
<td>(\tilde{J}_i)</td>
<td>interdiffusion flux ((i = A \text{ or } B)) within the continuous-vacancy-source approximation</td>
</tr>
<tr>
<td>(G)</td>
<td>Gibbs free energy of the system</td>
</tr>
<tr>
<td>(g)</td>
<td>Gibbs free energy per crystal site</td>
</tr>
<tr>
<td>(h)</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>(k_B)</td>
<td>Boltzmann's constant</td>
</tr>
<tr>
<td>(L_{ij})</td>
<td>kinetic-transport coefficient relating the (i)th flux to the (j)th driving force</td>
</tr>
<tr>
<td>(L)</td>
<td>non-dimensionalized length of the planar diffusion couple</td>
</tr>
<tr>
<td>(M)</td>
<td>total number of crystal sites of a perfect crystal</td>
</tr>
<tr>
<td>(N_i)</td>
<td>number of the (i)th diffusing species ((i = A, B \text{ or } V))</td>
</tr>
<tr>
<td>(N_g)</td>
<td>number of grains in the planar diffusion couple</td>
</tr>
<tr>
<td>(\bar{N}_{iAC})</td>
<td>norm measuring the deviation of concentration evolution of a diffusion couple containing explicit vacancy sources from that of a continuous-vacancy-source approximation</td>
</tr>
<tr>
<td>(P)</td>
<td>pressure</td>
</tr>
<tr>
<td>(p(\bar{\sigma}))</td>
<td>probability of a configuration (\bar{\sigma})</td>
</tr>
<tr>
<td>(Q)</td>
<td>(\langle (N_A^2 - \langle N_A \rangle)^2 \rangle \langle (N_B^2 - \langle N_B \rangle)^2 \rangle - (\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle)^2)</td>
</tr>
<tr>
<td>(T)</td>
<td>absolute temperature</td>
</tr>
<tr>
<td>(t)</td>
<td>time</td>
</tr>
<tr>
<td>(\hat{t})</td>
<td>non-dimensionalized time ((\hat{t} = ta^2 \Gamma_A/L^2))</td>
</tr>
<tr>
<td>(V)</td>
<td>vacancy</td>
</tr>
<tr>
<td>(V_e)</td>
<td>effective cluster interaction for the empty cluster</td>
</tr>
<tr>
<td>(V_x)</td>
<td>effective cluster interaction for a cluster of sites (x)</td>
</tr>
<tr>
<td>(v_i)</td>
<td>crystal frame velocity relative to the laboratory frame</td>
</tr>
<tr>
<td>(x_i)</td>
<td>concentration variable defined as the fraction of crystal sites occupied by the (i)th species</td>
</tr>
<tr>
<td>(\hat{y})</td>
<td>non-dimensionalized coordinate variable in a planar diffusion couple</td>
</tr>
<tr>
<td>(Z)</td>
<td>partition function</td>
</tr>
<tr>
<td>(z)</td>
<td>coordination number of each substitutional site</td>
</tr>
<tr>
<td>(\Gamma_i)</td>
<td>exchange frequency of the (i)th atomic species with an nearest neighbor vacancy ((i = A \text{ or } B))</td>
</tr>
<tr>
<td>(\Gamma_i^T - F)</td>
<td>frequency of a hop connecting configuration (\bar{\sigma}_i) to configuration (\bar{\sigma}_F)</td>
</tr>
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</table>
Connecting the characteristics of correlated atomic hops in non-dilute alloys to the diffusion coefficients appearing in macroscopic flux expressions requires a statistical mechanical theory that can accurately account for short- and long-range ordering tendencies within the solid. Several such theories have been developed relying on meanfield approximations, including the path probability method of Kikuchi and Sato [40–44] and the self-consistent mean field theory of Nastar et al. [45–47]. An alternative approach is the use of Monte Carlo simulations to sample atomic trajectories explicitly [48–55,37–39]. Such simulations rigorously capture the short- and long-range order that prevails in most multi-component solids as well as correlations between successive hops due to differences in hop frequencies among the components of the solid.

The calculation of kinetic-transport coefficients for diffusion is greatly simplified with the fluctuation–dissipation theorem of statistical mechanics, which lets us link macroscopic diffusion coefficients to ensemble averages of the trajectories of diffusing atoms in a solid at equilibrium [56]. Mathematical techniques that connect phenomenological kinetic coefficients to fluctuations at equilibrium are commonly referred to as Kubo-Green methods [57–69], and enable the calculation of diffusion coefficients using kinetic Monte Carlo simulations [70,71] to sample representative atomic trajectories in a crystal at equilibrium [52–54,37,38,55,39]. These calculated diffusion coefficients can then be implemented in continuum simulations to study the evolution of diffusion couples or to predict the rates of diffusional phase transformations [72–74].

The standard treatment of substitutional diffusion relies on the assumption that there are sufficient crystalline defects (i.e. dislocations and grain boundaries) uniformly distributed to regulate an equilibrium vacancy concentration throughout the solid [2,75,69,76]. Theoretical treatments of substitutional diffusion, however, are often only tractable for perfect crystals. Furthermore, as materials are increasingly synthesized with precisely controlled microstructures, gross assumptions about a continuous and dense distribution of vacancy sources and sinks become questionable. Most materials in modern technologies are likely somewhere in between the two extremes, with the continuous
source/sink treatment approximating diffusion at high temperatures and the perfect crystal description approximating diffusion at low temperatures.

We can distinguish between two modes of diffusion in substitutional binary alloys. One corresponds to the process of intermixing between the two components of the alloy while the other corresponds to the emergence of unbalanced vacancy fluxes. The intermixing diffusion mode is responsible for the homogenization of any non-uniform distribution of the components of the alloy. An unbalanced vacancy flux can arise from a concentration gradient among the components of the alloy if one component has a higher exchange frequency with vacancies than the other. Vacancy fluxes in the presence of active vacancy sources cause the crystal to drift relative to a laboratory frame of reference, as was first observed by Kirkendall [78,77], often leading to swelling and void formation. The presence of vacancy sources and sinks can also play an important role in mediating intermixing. The mechanisms of intermixing in a perfect crystal therefore differ significantly from that in a solid containing many vacancy sources and sinks, especially in solids exhibiting a strong tendency for the Kirkendall effect. (While in the strictest sense, the term ‘Kirkendall effect’ refers specifically to the drift of markers in a diffusion couple, here we will use the term more broadly to refer to any phenomena caused by vacancy fluxes that arise from differences in vacancy exchange frequencies among the various components of a substitutional alloy.)

The structure of this paper can be summarized as follows. We start with the development of a formalism to calculate diffusion coefficients from first principles in a defect-free, binary substitutional solid containing a dilute concentration of vacancies. This requires a precise description of the thermodynamics of a binary substitutional alloy containing vacancies along with the kinetics using Kubo-Green expressions, first derived by Allnatt for substitutional solids [67,68], to connect phenomenological kinetic-transport coefficients to density fluctuations at the atomic scale. Next we describe convenient metrics, derived from the matrix of diffusion coefficients, that characterize intermixing and net vacancy fluxes in a perfect-crystal substitutional solid. Here, we build on earlier work of Kehr et al. [51], and analyze the behavior of thermodynamically ideal model systems as well as a thermodynamically non-ideal system. In this context, the analysis of the characteristics of substitutional diffusion in thermodynamically ideal but kinetically non-ideal alloys is greatly facilitated by the derivations of Moleko et al. [79] of analytical expressions for phenomenological transport coefficients. After a comprehensive analysis of substitutional diffusion in a perfect crystal, we consider substitutional diffusion under the assumption that there is a sufficiently high and uniform density of vacancy sources and sinks to regulate an equilibrium vacancy concentration throughout the solid. Within this approximation, invoked in most textbook treatments of substitutional diffusion, we link the various diffusion coefficients, including self-diffusion coefficients and the interdiffusion coefficient, to well-defined quantities that can be calculated from first principles for perfect crystals. We conclude with an analysis of diffusion in a solid containing discrete vacancy sources and sinks, showing that the unbalanced vacancy fluxes responsible for the Kirkendall effect can play an important role in the process of intermixing as the density of vacancy sources and sinks increases.

2. Substitutional solids: perfect crystals

2.1. Phenomenological description

Diffusion in the solid state is a kinetic process that proceeds not too far from thermodynamic equilibrium but rather evolves between states that are in local equilibrium. A solid removed from equilibrium is in local equilibrium if thermodynamic quantities such as temperature and chemical potentials are well-defined and constant within any macroscopically small subregion of the solid even when they vary from subregion to subregion. The theory of irreversible thermodynamics, which describes kinetic processes within the local equilibrium approximation, then stipulates that the flux of diffusing atoms at constant temperature is driven by a gradient in the chemical potentials of the diffusing species [80]. Before formulating the relevant flux equations for substitutional diffusion, it is useful to first consider aspects of the thermodynamics of a substitutional alloy containing a dilute concentration of diffusion-mediating vacancies. In this section, we will restrict ourselves to what will be referred to throughout
as a perfect crystal, defined as a multi-component crystal containing vacancies but no extended defects such as dislocations and grain boundaries that can serve as vacancy sources and sinks.

2.1.1. Thermodynamics of a substitutional solid with vacancies

A binary substitutional alloy with vacancies has three components that include A, B and vacancies V. The number of vacancies is conserved in the absence of vacancy sources and sinks. The sum of the number of atoms and vacancies $N_A + N_B + N_V$ then equals the total number of crystal sites $M$ of the substitutional alloy. In terms of concentration variables $x_i = N_i/M$, the conservation of lattice sites is expressed as $x_A + x_B + x_V = 1$. The substitutional alloy has a free energy $G(N_A, N_B, N_V)$ from which the chemical potentials of each component can be calculated according to

$$\mu_i = \frac{\partial G}{\partial N_i}$$

where $i$ refers to A, B or V. The partial derivatives are taken at constant temperature, $T$, pressure, $P$, and $N_j$ with $j \neq i$. The chemical potential $\mu_i$ corresponds to the change in free energy of the solid as component $i$ is added to the solid. Since the other components $j \neq i$ are held fixed, adding more of $i$ to a substitutional can only be achieved by extending the crystalline network of the solid; that is, by increasing $M$ [81–83].

Normalizing $G$ by the number of crystal sites $M$ yields a free energy per crystal site $g(x_A, x_B)$. In terms of this quantity, the chemical potentials $\mu_i$ can be written as [84]

$$\mu_i = g(x_A, x_B) + (\delta_{iA} - x_A) \frac{\partial g}{\partial x_A} + (\delta_{iB} - x_B) \frac{\partial g}{\partial x_B},$$

where $\delta_{ij}$ is the Kronecker delta. The chemical potentials $\mu_i$ have a convenient graphical interpretation in a $g(x_A, x_B)$ versus $x_A$ and $x_B$ plot: the $\mu_i$ are equal to the intercepts with the axes $x_i = 1$ of the plane tangent to $g$ at the overall concentration $x_A, x_B$. This is illustrated in Fig. 1a. Free energies of a perfect multi-component crystal can be calculated from first principles. The approach relies on a cluster expansion of the configurational energy combined with for example the cluster variation method or Monte Carlo simulations to calculate thermodynamic properties [13,20,29,36,85]. More details on the first-principles computation of the free energy of a substitutional alloy are provided in Section 2.2.1.

Real solids contain dislocations and grain boundaries that act as vacancy sources and sinks. In thermodynamic equilibrium, the chemical potential of vacancies is then equal to zero as vacancies are no
longer a conserved species [83]. The equilibrium vacancy concentration \( x_V \) is determined by the condition that 
\[
\lambda_V(x_A, x_B) = 0.
\]
Graphically, this constraint manifests itself as the projection in composition space \((x_A, x_B)\) of the line formed by the contact of the envelope of planes passing through \( \lambda_V = 0 \) at \( x_V = 1 \) and simultaneously tangent to the \( g(x_A, x_B) \) surface. This is schematically illustrated in Fig. 1b, where the dashed line on the \( g(x_A, x_B) \) surface corresponds to the free energy of the alloy with an equilibrated vacancy concentration. The trajectory in composition space of the alloy having an equilibrium vacancy concentration must satisfy the constraint that \( d\lambda_V = 0 \). Written explicitly in terms of the independent variables \( x_A \) and \( x_B \),
\[
\frac{\partial \lambda_V}{\partial x_A} dx_A + \frac{\partial \lambda_V}{\partial x_B} dx_B = 0, \tag{3}
\]
and substituting expression (2) for \( \lambda_V \) into (3) yields
\[
\frac{dx_A}{dx_B} = -\frac{x_B \left( \frac{\partial^2 g}{\partial x_B \partial x_A} \right) + x_A \left( \frac{\partial^2 g}{\partial x_A \partial x_B} \right)}{x_A \left( \frac{\partial^2 g}{\partial x_A^2} \right) + x_B \left( \frac{\partial^2 g}{\partial x_B^2} \right)}. \tag{4}
\]
This differential equation in terms of second derivatives of the free energy \( g(x_A, x_B) \) determines a functional relationship between \( x_A \) and \( x_B \) for an alloy having a constant vacancy chemical potential, including alloys having an equilibrium vacancy concentration for which \( \lambda_V = 0 \). This functional relationship will be denoted by \( x_A(x_B)_{\lambda_V=0} \). In using free energies for a perfect crystal to determine the equilibrium vacancy concentration, contributions from grain-boundary free energies and dislocation-line free energies are neglected.

The second derivatives of \( g(x_A, x_B) \) appearing in Eq. (4) play a central role in the formalism of substitutional diffusion and are elements of the Hessian of the free energy
\[
k_B T \bar{\Theta} = \begin{pmatrix}
\frac{\partial^2 g}{\partial x_A^2} & \frac{\partial^2 g}{\partial x_B \partial x_A} \\
\frac{\partial^2 g}{\partial x_A \partial x_B} & \frac{\partial^2 g}{\partial x_B^2}
\end{pmatrix}. \tag{5}
\]
The matrix \( \bar{\Theta} \) will be referred to as the thermodynamic factor for perfect-crystal diffusion.

### 2.1.2. Atomic transport in a substitutional solid

In writing flux expressions for a substitutional solid, we start with a perfect crystal. The vacancy concentration in a perfect crystalline network, in which the number of sites is conserved, can locally deviate from its equilibrium value, leading to a vacancy chemical potential that is locally not zero. This also occurs in crystalline solids with a low density of defects in regions away from vacancy sources and sinks. Such gradients in vacancy chemical potential drive fluxes in vacancies as well as \( A \) and \( B \) atoms. For a conserved crystalline network, the flux equations for substitutional diffusion mediated by vacancies become [75,51]
\[
J_A = -L_{AA} \nabla \mu_A - L_{AB} \nabla \mu_B - L_{AV} \nabla \mu_V \\
J_B = -L_{BA} \nabla \mu_A - L_{BB} \nabla \mu_B - L_{BV} \nabla \mu_V \\
J_V = -L_{VA} \nabla \mu_A - L_{VB} \nabla \mu_B - L_{VV} \nabla \mu_V, \tag{6}
\]
where the fluxes are here defined as the number of atoms (as opposed to mole of atoms) crossing a unit area per unit time. The chemical potentials in Eq. (6) are defined according to Eqs. (1) and (2). Due to Onsager’s reciprocity theorem [57,58,80], the kinetic-transport coefficients form a symmetric matrix
\[
L_{AB} = L_{BA}, \quad L_{AV} = L_{VA}, \quad L_{VB} = L_{BV}. \tag{7}
\]
The flux equation (6) can be simplified further by exploiting properties resulting from the conservation of crystal sites in a perfect crystal

\[ J_A + J_B + J_V = 0. \]  
(8)

Substituting Eq. (6) into Eq. (8) and invoking the Onsager reciprocity relations, Eq. (7), leads to linear relations between the different kinetic coefficients of the form

\[ \begin{align*}
L_{AV} &= L_{VA} = -(L_{AA} + L_{AB}) \\
L_{BV} &= L_{VB} = -(L_{BA} + L_{BB}),
\end{align*} \]  
(9)

which can be used to simplify the flux Eq. (6) to yield

\[ \begin{align*}
J_A &= -L_{AA} \nabla \tilde{\mu}_A - L_{AB} \nabla \tilde{\mu}_B \\
J_B &= -L_{BA} \nabla \tilde{\mu}_A - L_{BB} \nabla \tilde{\mu}_B,
\end{align*} \]  
(10)

where the driving forces are now the gradients of differences in the chemical potentials of \( i \) and the vacancies

\[ \tilde{\mu}_i = \mu_i - \mu_V, \]  
(11)

with \( i = A \) or \( B \). This form of the diffusion potential is specific for substitutional diffusion and arises from the constraints of a crystalline network [81, 82]. (In the formalism of Andersson and Ågren [72], these driving forces emerge within the volume-fixed frame if vacancies are taken as the reference element and assigned a volume equal to that of \( A \) and \( B \)). The substitution of Eq. (2) into Eq. (11) shows that the diffusion potentials are equal to the derivatives of the free energy \( g(x_A, x_B) \) with respect to the concentration of the \( i \)-th component

\[ \tilde{\mu}_i = \frac{\partial g}{\partial x_i}. \]  
(12)

The emergence of \( \tilde{\mu}_i \) as the driving force for substitutional diffusion in a binary system can be understood on physical grounds. To this end, it is useful to view diffusion as the redistribution of atoms between different subregions of the solid. As a result of the conservation of sites in a perfect crystal, the accommodation of excess atoms diffusing to a region from neighboring subregions can only occur through an exchange with vacancies. Thus, one subregion gains vacancies while the other loses them. The change in free energy in each subregion due to diffusion occurs by adding or removing atoms at the expense of vacancies. Hence, the \( \tilde{\mu}_i = \mu_i - \mu_V \) instead of the \( \mu_i \) are the relevant driving force for atomic transport.

2.2. Atomistic description

2.2.1. Thermodynamics from first principles

The formal link between thermodynamic properties of a binary crystalline alloy, as encapsulated in the Gibbs free energy \( G \), and the electronic structure of the solid resides with the partition function \( Z \) according to

\[ G = -k_B T \ln Z \]  
(13)

where at constant temperature \( T \), pressure \( P \) (which we effectively take to be equal to zero) and compositions, the partition function becomes

\[ Z = \sum_s \exp \left( \frac{-E_s}{k_B T} \right). \]  
(14)

The sum in Eq. (14) extends over all microstates \( s \) having energy \( E_s \) that are accessible to the alloy through thermal fluctuations under the externally imposed thermodynamic boundary conditions. The energies \( E_s \) correspond to the eigenvalues of the Schrödinger equation of the solid. In a binary substitutional alloy, the most important microstates contributing to the partition function arise from
electronic excitations, vibrational excitations and configurational degrees of freedom associated with all possible ways of distributing A, B and V over the M sites of the crystal.

Diffusion at the atomic scale results from configurational rearrangements of the various components of the solid. Hence any atomic scale description of diffusion in an alloy requires an explicit treatment of configurational degrees of freedom. Therefore, it is useful to assign occupation variables, \( \sigma_i \), to each substitutional site \( i \) of the solid, which is for example +1 if an A atom resides there, −1 if a B atom resides there and 0 if the site is vacant. The collection of all occupation variables, \( \vec{\sigma} = (\sigma_1, \ldots, \sigma_i, \ldots, \sigma_M) \) then uniquely characterizes the arrangement of A, B and V components over the M sites of the substitutional solid. Between successive diffusive hops leading to configurational rearrangements, the solid will sample a large number of vibrational and electronic excitations. Recognizing the large difference in characteristic time scales of the “fast” vibrational and electronic transitions versus the “slow” configurational rearrangements, it is convenient to introduce a constrained free energy by summing over the vibrational and electronic excitations at fixed configuration \( \vec{\sigma} \) according to [17,85]

\[
G(\vec{\sigma}, T) = -k_B T \ln \left[ \sum_{s_v\neq s_{\text{elec}}} \exp \left( \frac{-E_s(\vec{\sigma})}{k_B T} \right) \right].
\]  

In terms of this coarse grained free energy, the partition function can be reduced to that of a lattice model according to [85]

\[
Z = \sum_{\vec{\sigma}} \exp \left( \frac{-G(\vec{\sigma}, T)}{k_B T} \right),
\]

where now the summation extends over the configurational degrees of freedom only. The probability that the solid has a particular configuration \( \vec{\sigma} \) then becomes

\[
p(\vec{\sigma}) = \frac{\exp \left( \frac{-G(\vec{\sigma}, T)}{k_B T} \right)}{Z}.
\]

We point out that the introduction of coarse grained free energies \( G(\vec{\sigma}, T) \) is only meaningful as long as every configuration of A, B and V over the substitutional sublattice is mechanically stable (i.e., it corresponds to a local minimum with respect to vibrational degrees of freedom). While many high temperature phases observed in nature have been shown to be mechanically unstable at zero Kelvin [86–88], forming at finite temperature through anharmonic vibrational degrees of freedom [89–91], here we will restrict the treatment to the large class of substitutional alloy phases that are mechanically stable at zero Kelvin.

The prediction of thermodynamic properties of binary alloys becomes straightforward with the above coarse graining procedure using standard statistical mechanical tools such as cluster expansions [13,20] and Monte Carlo simulations [92]. The Metropolis Monte Carlo algorithm [93] samples configurational microstates with a frequency given by Eq. (17), thereby enabling an explicit calculation of thermodynamic averages of extensive quantities such as the internal energy and number of atoms when controlling chemical potentials in grand canonical Monte Carlo simulations. With free energy integration techniques, it is then possible to calculate the free energy of the alloy as a function of temperature and composition [29,36]. An essential input for these simulations, however, is knowledge of the functional dependence of the coarse grained free energies \( G(\vec{\sigma}, T) \) on configuration \( \vec{\sigma} \).

The coarse grained free energies \( G(\vec{\sigma}, T) \) can be calculated within the (quasi) harmonic approximation by integrating over the phonon densities of state at fixed configuration \( \vec{\sigma} \) determined with first-principles electronic structure methods based on density functional theory (DFT) [94–97] as described for example in Ref. [98]. The electronic contribution to \( G(\vec{\sigma}, T) \) can also be determined by integrating over the electronic densities of state calculated with DFT; however, this approach provides at best only qualitative predictions as there is no formal justification that DFT should be able to predict excited electronic states. A direct first-principles calculation of \( G(\vec{\sigma}, T) \) for all configurations \( \vec{\sigma} \) sampled in Monte Carlo simulations is intractable. Therefore, cluster expansion techniques [13,20] are needed.
to extrapolate the values of \( G(\bar{\sigma}, T) \) calculated from first principles for a small number of configurations to all other configurations accessible in Monte Carlo simulations.

The cluster expansion formalism provides a set of basis functions to support any property of the crystal that uniquely depends on how the various components of the solid are arranged [13]. For a binary \( A-B \) alloy, for example, these basis functions \( \phi_x \) are simply the products of occupation variables \( \sigma_i \) of each site of a cluster \( x \) of the crystal, where \( x \) corresponds to a pair cluster, triplet cluster, quadruplet cluster, etc.:

\[
\phi_x(\bar{\sigma}) = \prod_{i \in x} \sigma_i. \tag{18}
\]

Defining a scalar product over configuration space \( \bar{\sigma} \) between two functions of configuration, \( f(\bar{\sigma}) \) and \( g(\bar{\sigma}) \), according to

\[
\langle f \cdot g \rangle = \frac{1}{2^N} \sum_{\bar{\sigma}} f(\bar{\sigma})g(\bar{\sigma}), \tag{19}
\]

it can be shown that the collection of cluster functions \( \phi_x(\bar{\sigma}) \) then form a complete and orthonormal basis [13]. Hence any property that depends on configuration \( \bar{\sigma} \), including the coarse grained free energy \( G(\bar{\sigma}, T) \), can be expanded in terms of the polynomial basis functions \( \phi_x(\sigma) \) according to

\[
G(\bar{\sigma}, T) = V_o + \sum_x V_x \phi_x(\bar{\sigma}) \tag{20}
\]

where the expansion coefficients, \( V_o \) and \( V_x \), that depend only on temperature are formally related to \( G(\bar{\sigma}, T) \) through the scalar product [13,20]

\[
V_x = \langle G(\bar{\sigma}, T) \cdot \phi_x(\bar{\sigma}) \rangle. \tag{21}
\]

While the expansion extends over all possible \( 2^M \) clusters, Eq. (20) can usually be truncated above a maximal sized cluster, while symmetry considerations drastically reduces the number of independent effective cluster interaction (ECI) coefficients \( V_x \). The truncated expansion is then a convenient tool to rapidly and accurately calculate values of \( G(\bar{\sigma}, T) \) for arbitrary configurations \( \bar{\sigma} \) sampled in Monte Carlo simulations.

A common practice is to neglect vibrational and electronic excitations in first-principles predictions of thermodynamic properties of binary alloys. Within this approximation, the coarse grained free energies \( G(\bar{\sigma}, T) \) then reduce to the ground state energies, \( E(\bar{\sigma}) \), for each configuration \( \bar{\sigma} \) (i.e., the fully relaxed energy of configuration \( \bar{\sigma} \)). Furthermore, the ECI, \( V_x \), of the cluster expansion, Eq. (20), are rarely calculated using the scalar product, (21), but rather with a least-square fitting procedure, whereby the coefficients of a truncated cluster expansion are fit to reproduce first-principles energies of a subset of configurations \( \bar{\sigma} \). Several fitting schemes based on the minimization of a cross-validation score and the use of genetic algorithms to determine the optimal truncation have been proposed and are in common use [28,33].

A treatment of diffusion in a binary substitutional alloy needs to explicitly account for the presence of vacancies, which renders the solid a ternary mixture. An accurate description of the interactions among \( A, B \) and \( V \) would in principle require a ternary cluster expansion. However, since vacancies in binary substitutional alloys are often very dilute, it is possible to neglect interactions between vacancies and use a local cluster expansion in combination with a standard binary cluster expansion for \( A-B \) disorder to describe interactions between an isolated vacancy and \( A \) and \( B \) atoms. This is described in detail in ref. [31,36].

While cluster expansion and Monte Carlo techniques are required to predict thermodynamic properties from first principles for real binary alloys, for an ideal solution the partition function can be evaluated in closed form, and an analytical expression for the Gibbs free energy can then be derived using Eq. (13). The underlying assumption that defines an ideal solution, also commonly referred to as a random alloy, is the absence of an energetic preference for any arrangement of atoms: each arrangement of atoms in the solid has the same energy and is therefore equally likely to occur as the solid fluctuates from one configurational microstate to the next. (The cluster expansion of an ideal solution
consists of only point cluster terms with all ECI coefficients for multi-site clusters (i.e., clusters with two or more sites) being equal to zero). With this assumption, the partition function, Eq. (16), reduces to a sum of \( M!/(N_A!N_B!N_V!) \) identical terms and the free energy of the alloy becomes
\[
g(x_A, x_B) = x_V \Delta g_{V} + k_B T [x_A \ln x_A + x_B \ln x_B + x_V \ln x_V] \tag{22}
\]
where \( x_V = 1 - x_A - x_B \) and the free energies of the pure elements are taken as reference states. The vacancy formation energy, \( \Delta g_V \), is independent of composition and configuration in a random alloy. Using Eq. (2) to derive an expression for the chemical potentials yields
\[
\mu_A = k_B T \ln x_A; \quad \mu_B = k_B T \ln x_B; \quad \mu_V = \Delta g_V + k_B T \ln x_V. \tag{23}
\]
An ideal solution serves as a useful reference alloy with which to compare thermodynamically non-ideal alloys.

As noted in Section 2.1.1, the Hessian of the free energy, \( g(x_A, x_B) \), plays a central role in substitutional diffusion. Although the elements of the Hessian can be calculated from the free energy by taking the second derivative of \( g(x_A, x_B) \) with respect to the concentration variables \( x_A \) and \( x_B \), it is in general more convenient to evaluate them directly in Monte Carlo simulations by tracking fluctuations in the number of \( A \) and \( B \) atoms at constant chemical potentials \( \mu_A \) and \( \mu_B \). Indeed, it can be shown that (see Appendix A) the thermodynamic factor matrix \( \tilde{\Theta} \), defined by Eq. (5), is related to the variances of \( N_A \) and \( N_B \) in the grand canonical ensemble within a crystal with fixed number of crystal sites \( M \) according to
\[
\tilde{\Theta} = \frac{M}{Q} \begin{pmatrix} \langle \Delta_{BB}^2 \rangle & -\langle \Delta_{AB}^2 \rangle \\ -\langle \Delta_{AB}^2 \rangle & \langle \Delta_{AA}^2 \rangle \end{pmatrix}
\tag{24}
\]
where
\[
\langle \Delta_{ij}^2 \rangle = \langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle, \quad i, j = A, B;
\]
and
\[
Q = (\langle N_A^2 \rangle - \langle N_A \rangle^2)(\langle N_B^2 \rangle - \langle N_B \rangle^2) - (\langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle)^2.
\]
The angular brackets \( \langle \rangle \) denote ensemble averages in the usual statistical mechanical sense [56,99].

For an ideal solution, Monte Carlo simulations are not necessary to obtain the thermodynamic factor matrix. Direct differentiation of the ideal solution free energy expression, Eq. (22), yields
\[
\tilde{\Theta} = \begin{pmatrix} \frac{1}{x_A x_V} & \frac{1}{x_V} \\ \frac{1}{x_V} & \frac{1}{x_B x_V} \end{pmatrix}.
\tag{25}
\]
For non-ideal binary alloys, \( \tilde{\Theta} \) will deviate from this expression, but will nevertheless be dominated by the \( 1/x_V \) factor as \( x_V \to 0 \).

2.2.2. Diffusion from first principles

Diffusion in crystalline solids can be treated at the atomic scale as arising from a sequence of elementary stochastic hop events. Atoms of a solid spend most of their time in the vicinity of crystallographically well-defined positions, undergoing only small excursions due to thermal vibrations. Very occasionally, however, atoms adjacent to a vacant site follow a trajectory that takes them from their original site to a neighboring vacant site. This is referred to as a diffusive hop, and is a rare event on the time scale of typical atomic vibrations. The hop results in a change of the atomic configuration within the crystal and can be represented by a reaction equation \( \tilde{\sigma}_i \to \tilde{\sigma}_f \), where \( \tilde{\sigma}_i \) corresponds to the configuration in the initial state before the hop and \( \tilde{\sigma}_f \) is the configuration in the final state after the hop. The frequency, \( t^{i \to f} \), with which the solid in configuration \( \tilde{\sigma}_i \) transforms into configuration \( \tilde{\sigma}_f \) as a result of an elementary hop can be estimated in a statistical mechanical sense using transition state theory [100,101].
\[ I^R \to F = \frac{k_B T}{h} \exp \left( -\frac{\tilde{G}(\vec{\sigma}_1 : \vec{\sigma}_F, T) - G(\vec{\sigma}_1, T)}{k_B T} \right) \]  

(26)

where \( h \) is Planck’s constant and \( \tilde{G}(\vec{\sigma}_1 : \vec{\sigma}_F, T) \) is a constrained free energy of the solid obtained by summing over vibrational and electronic degrees of freedom in a hypersurface of phase space that passes through the saddle point separating \( \vec{\sigma}_1 \) from \( \vec{\sigma}_F \). As before, the free energy \( G(\vec{\sigma}_1, T) \) of Eq. (26) corresponds to the coarse grained free energy of configuration \( \vec{\sigma}_1 \) defined by Eq. (15). While there remains some ambiguity as to an exact definition of the free energy, \( \tilde{G}(\vec{\sigma}_1 : \vec{\sigma}_F, T) \), in the activated state \([102]\), a more precise expression for the hop frequency in which all terms are accessible from first principles emerges within the harmonic approximation in the high temperature limit (i.e., above the Debye temperature). In this limit, Eq. (26) reduces to the familiar form derived by Vineyard \([103]\).

\[ I^R \to F = v^* \exp \left( -\frac{\Delta E_b}{k_B T} \right) \]

(27)

where \( \Delta E_b \) is an activation barrier for a diffusive hop and corresponds to the difference in energy between the saddle point of the transition from \( \vec{\sigma}_1 \) to \( \vec{\sigma}_F \) and the fully relaxed energy in configuration \( \vec{\sigma}_1 \). The vibrational prefactor is equal to

\[ v^* = \frac{\prod_{l=1}^{3N-3} \nu_l}{\prod_{l=1}^{3N-4} \tilde{\nu}_l} \]

(28)

where \( N = N_A + N_B \) corresponds to the total number of \( A \) and \( B \) atoms in the crystal. The frequencies \( \nu_l \) are the \( 3N - 3 \) normal-mode vibrational frequencies of configuration \( \vec{\sigma}_1 \) while the \( \tilde{\nu}_l \) are the \( 3N - 4 \) non-imaginary normal-mode vibrational frequencies at the saddle point between \( \vec{\sigma}_1 \) and \( \vec{\sigma}_F \). In non-dilute alloys, both the activation barriers \( \Delta E_b \) and the vibrational prefactors \( v^* \) will be a function of the local configuration surrounding the migrating atom. Here again, cluster expansions can be used for example to parameterize the dependence of the activation barrier on local order/disorder \([37–39]\).

Macroscopic diffusion arises from a succession of many atomic hops over time scales that are significantly larger than those characterizing elementary hops. In a substitutional alloy, the atoms of the crystal are usually redistributed through thermally activated exchanges with a dilute concentration of vacancies wandering stochastically throughout the solid. The various components of the alloy will typically have different exchange frequencies with vacancies, leading to complex correlations between successive hops \([104, 105]\) that are further complicated by any thermodynamic tendency for short- or long-range order \([38]\).

The time evolution of local concentration inhomogeneities and variations in short- or long-range order is conveniently encapsulated in the time-dependent probability distribution, \( p(\vec{\sigma}, t) \), defined as the probability of observing a configuration \( \vec{\sigma} \) at time \( t \). The time dependence of this probability distribution is determined by a master equation

\[ \frac{dp(\vec{\sigma}_i, t)}{dt} = \sum_{\vec{\sigma}_F \neq \vec{\sigma}_i} I^R - F \cdot p(\vec{\sigma}_F, t) - \sum_{\vec{\sigma}_F \neq \vec{\sigma}_i} I^F - R \cdot p(\vec{\sigma}_i, t) \]

(29)

which states that the rate of change of \( p(\vec{\sigma}, t) \) depends on the fraction of equivalent systems transitioning from configuration \( \vec{\sigma}_F \) into configuration \( \vec{\sigma}_i \) minus the fraction of equivalent systems leaving configuration \( \vec{\sigma}_i \). Once the solid reaches thermodynamic equilibrium, the probability distribution \( p(\vec{\sigma}, t) \) becomes time invariant and reduces to Eq. (17) predicted by equilibrium statistical mechanics \([69]\). While the right hand side of the master equation Eq. (29) is equal to zero in thermodynamic equilibrium, the principle of detailed balance is even more stringent, imposing a constraint on individual transitions according to

\[ I^F \to R \cdot p(\vec{\sigma}_i) = I^R - F \cdot p(\vec{\sigma}_F) \]

(30)

which states that the rate of transitions from \( \vec{\sigma}_i \) to \( \vec{\sigma}_F \) is equal to the rate of the reverse transition. Inspection of Eqs. (17) and (26) shows that detailed balance is satisfied when using transition state theory to estimate hop frequencies \( I \).
Ultimately we are interested in linking macroscopic metrics of atomic mobility, such as the kinetic-transport coefficients $L_{ij}$, to hop characteristics as well as short- and long-range order tendencies at the atomic scale. An important property of kinetic processes linking states that are in local equilibrium is that the kinetic parameters describing non-equilibrium phenomena can be determined by considering fluctuations at equilibrium [57,58,80]. The master equation (29) and the principle of detailed balance (30) shows that even though the average short- or long-range order is invariant with time in thermodynamic equilibrium, the instantaneous arrangements of the atoms in a solid are constantly evolving as a result of diffusive hops. With what are often referred to as Kubo-Green linear response methods, it is possible to link phenomenological kinetic-transport coefficients with fluctuations in atomic arrangements that occur at equilibrium [57,58,61–66]. In the context of diffusion in crystalline solids, Allnatt [67–69] derived expressions for the kinetic coefficients $L_{ij}$, showing that

$$L_{ij} = \frac{1}{\Omega k_B T} \tilde{L}_{ij},$$

where $\Omega$ is the volume per substitutional site and

$$\tilde{L}_{ij} = \left\langle \left( \sum_i \Delta \tilde{R}_i(t) \right) \left( \sum_j \Delta \tilde{R}_j(t) \right) \right\rangle_{(2d)tM}.$$  

Here, $\Delta \tilde{R}$ is the vector linking the end points of the trajectory of atom $\zeta$ of atomic species $i$ ($i = A$ or $B$) after time $t$. The parameter $d$ denotes the dimension of the substitutional network (e.g., for a three-dimensional substitutional network, $d = 3$), and $M$ is equal to the number of substitutional sites in the crystal. The brackets indicate an ensemble average performed at equilibrium. The kinetic coefficients $L_{ij}$ have the units of a diffusion coefficient (e.g., cm$^2$/s).

As with thermodynamic properties, it is useful to consider the behavior of the kinetic-transport coefficients for a thermodynamically ideal alloy. Fig. 2 illustrates the variation of the different kinetic-transport coefficients for three thermodynamically ideal fcc alloys where $A$ and $B$ atoms have different exchange frequencies with a vacancy, $\Gamma_i$. Analytical expressions for $\tilde{L}_{ij}$ have been derived for binary random alloys [75,51,79]. For an alloy that is both thermodynamically and kinetically ideal, i.e., $\Gamma_A = \Gamma_B = \Gamma$, the analytical expressions for the kinetic coefficients can be expressed as [75,51]:

$$\tilde{L}_{AA} = x_v x_A \rho a^2 \Gamma \left( 1 - \frac{x_B}{1 - x_v} (1 - f) \right)$$

$$\tilde{L}_{BB} = x_v x_B \rho a^2 \Gamma \left( 1 - \frac{x_A}{1 - x_v} (1 - f) \right)$$

$$\tilde{L}_{AB} = \frac{x_v x_A x_B}{1 - x_v} \rho a^2 \Gamma (1 - f).$$  

(33)

Here, $a$ is the hop distance and $\rho$ is a geometric factor determined by the crystal structure of the solid (for a crystal that is also a Bravais lattice, $\rho = z/2d$, where $z$ is the coordination number of each site and $d$ is the dimensionality of the crystal). The parameter $f$ is the correlation factor for tracer diffusion. In a multi-component solid, each component $i$ can be assigned a correlation factor defined as

$$f_i = \frac{\langle (\Delta \tilde{R})^2 \rangle_{i}^{n}}{n a^2},$$

(34)

where $\Delta \tilde{R}$ connects the endpoints of the trajectory of a particle of species $i$ after $n$ hops. The brackets again denote an ensemble average in thermodynamic equilibrium. In an ideal alloy in which $\Gamma_A = \Gamma_B$, the kinetic behavior of $A$ and $B$ are identical and $f_A = f_B = f$. It is this correlation factor, $f$, that appears in Eq. (33).

For random alloys where $\Gamma_A \neq \Gamma_B$, the analytical expressions for $\tilde{L}_{ij}$ derived by Moleko et al. [79] become more complicated (see Appendix B). In the most general case, the kinetic coefficients $\tilde{L}_{ij}$ can also be calculated by numerically evaluating the Kubo-Green expressions, Eq. (32), with kinetic Monte Carlo simulations to sample representative trajectories of migrating atoms at equilibrium. In a kinetic Monte Carlo simulation [70,71], atoms exchange sites with adjacent vacant sites with frequencies $\Gamma_i$ and the vectors connecting the end points of their trajectory are calculated as a function
of time to enable the numerical evaluation of $\bar{L}_{ij}$ according to Eq. (32). As an example, Fig. 2a illustrates the variation of $\bar{L}_{AA}$, $\bar{L}_{BB}$ and $\bar{L}_{AB}$ for a random fcc alloy where $\Gamma_B = \Gamma_A$, comparing the analytical

Fig. 2. Kinetic-transport coefficients $\bar{L}_{ij}$ for a random fcc alloy at 600 K with a vacancy concentration of 0.002, a cubic lattice parameter of 4.0 Å, a vibrational prefactor $\nu = 4 \times 10^{13}$ Hz and an activation barrier of 600 meV for an A hop into a vacancy for (a) $\Gamma_B = \Gamma_A$, (b) $\Gamma_B = 10 \times \Gamma_A$, (c) $\Gamma_B = 100 \times \Gamma_A$. The solid line corresponds to the analytical kinetic transport coefficients derived by Moleko et al. [79] and the circles correspond to values calculated with kinetic Monte Carlo simulations.
expressions, Eq. (33), with values obtained with kinetic Monte Carlo simulations. Fig. 2b and c show the kinetic coefficients $L_{ij}$ for a random fcc alloy in the dilute vacancy limit evaluated with the analytical expressions derived by Moleko et al. [79] and approximated with kinetic Monte Carlo simulations. Fig. 2b is for a random alloy with $\Gamma_A = 10_2 \Gamma_A$, and Fig. 2c is for a random alloy with $\Gamma_B = 100_2 \Gamma_A$. In these plots, the cubic fcc lattice parameter is equal to 4.0 Å, the activation barrier, $D_{Eb}$, for component $A$ is equal to 600 meV while its vibrational prefactor, $v^*$, is equal to $4 \times 10^{13}$ Hz. These values are typical for a metal such as Al [38]. The kinetic coefficients are evaluated at 600 K assuming a vacancy concentration of 0.002, which is relatively large for typical metallic alloys. The $L_{ij}$ coefficients scale linearly with the vacancy concentration in the dilute vacancy concentration limit in the absence of strong interactions among vacancies.

As is clear from Fig. 2, the diagonal kinetic-transport coefficients $L_{AA}$ and $L_{BB}$ are always larger than the off-diagonal coefficient $L_{AB}$. For a thermodynamically ideal alloy that is also kinetically ideal ($\Gamma_A = \Gamma_B$), the coefficients are symmetric with respect to composition. This symmetry is broken, however, when $\Gamma_A = \Gamma_B$, as can be seen in Fig. 2b and c.

2.3. Fickian flux expressions in a perfect crystal

Gradients in chemical potentials are difficult to measure experimentally. It is more convenient to express fluxes for substitutional diffusion in terms of directly measurable concentration gradients. Starting from the flux expressions, Eq. (10), and using the chain rule of differentiation, we can write for a perfect crystal

$$J_A = -D_{AA} \nabla C_A - D_{AB} \nabla C_B$$
$$J_B = -D_{BA} \nabla C_A - D_{BB} \nabla C_B,$$

with $C_i$ the number of atoms of species $i$ per unit volume (i.e., $C_i = x_i/\Omega$, where $\Omega$ is the volume per substitutional crystal site). These flux expressions can be viewed as generalized Fick equations for substitutional diffusion in a perfect crystal. The matrix of diffusion coefficients $D$ is a product of the matrix of kinetic-transport coefficients $L_{ij}$ with a matrix of thermodynamic factors, $\tilde{\Theta}_{ij}$, according to

$$\begin{pmatrix} D_{AA} & D_{AB} \\ D_{BA} & D_{BB} \end{pmatrix} = \begin{pmatrix} L_{AA} & L_{AB} \\ L_{BA} & L_{BB} \end{pmatrix} \begin{pmatrix} \tilde{\Theta}_{AA} & \tilde{\Theta}_{AB} \\ \tilde{\Theta}_{BA} & \tilde{\Theta}_{BB} \end{pmatrix}.$$  

(36)

The $\tilde{\Theta}_{ij}$ are partial derivatives of the chemical potentials, $\tilde{\mu}_i$ (normalized by $k_BT$), with respect to atomic fractions $x_j$ and are related to the Hessian of the free energy $g(x_A,x_B)$ according to

$$\tilde{\Theta}_{ij} = \frac{1}{k_BT} \frac{\partial \tilde{\mu}_i}{\partial x_j} = \frac{1}{k_BT} \frac{\partial^2 g}{\partial x_i \partial x_j}.$$  

(37)

The elements of the thermodynamic factor matrix can be calculated with grand canonical Monte Carlo simulations using the fluctuation formulas Eq. (24).

2.4. Metrics for substitutional diffusion

While the flux equations in terms of concentration gradients, Eq. (35), are more practical than Eq. (10), expressed in terms of chemical potential gradients, they still do not provide insights into the relevant diffusional processes in a substitutional alloy. In this respect, Kehr et al. [51] demonstrated that the eigenvalues of $D$ lend well to intuitive interpretation. They showed that for regular solution model alloys having a dilute vacancy concentration, the larger eigenvalue of $D$, denoted by $\lambda^+$, becomes a measure for the rate with which density fluctuations due to inhomogeneities in the vacancy concentration dissipate while the smaller eigenvalue, $\lambda^-$, becomes a measure of the rate with which $A$ and $B$ atoms intermix. In this limit, $\lambda^+$ can be viewed as a vacancy diffusion coefficient and $\lambda^-$ as an intermixing coefficient in a perfect crystal.
To provide further insight about binary diffusion in a perfect crystal, it is useful to complement \( \lambda^+ \) and \( \lambda^- \) with two additional parameters expressed in terms of elements of the diffusion coefficient matrix \( \mathbf{D} \) according to
\[
\delta = D_{BB} - D_{AA} + D_{AB} - D_{BA}
\]
and
\[
\phi = \frac{D_{BA}}{D_{AB} + D_{BA}}.
\]

The parameters \( \delta \) and \( \phi \) along with \( \lambda^+ \) and \( \lambda^- \) can serve as an alternative set of coefficients to \( D_{AA}, D_{BB}, D_{AB} \) and \( D_{BA} \) for the purpose of describing binary diffusion in a perfect crystal. This is shown in Appendix D, where expressions for \( D_{ij} \) in terms of \( \lambda^+, \lambda^-, \delta \) and \( \phi \) are derived. While a physical interpretation of \( \delta \) and \( \phi \) will become evident later, we here point out that for a thermodynamically ideal alloy with identical hop frequencies (i.e. \( \Gamma_A = \Gamma_B \)),
\[
\delta = 0; \quad \phi = \frac{x_B}{x_A + x_B}.
\]

Eq. (40) can be verified by substituting the analytical expressions for the thermodynamic and kinetic factors of a thermodynamically and kinetically ideal alloy, Eqs. (25) and (33), into Eq. (36) and subsequently into Eqs. (38) and (39). For non-ideal alloys, \( \delta \) and \( \phi \) deviate from the values given by Eq. (40). The two parameters can therefore serve as measures for the deviation of the alloy from “kinetic” ideality. Appendix C shows that \( \delta \) and \( \lambda^- \) scale linearly with the vacancy concentration, while \( \lambda^+ \) and \( \phi \) have a negligible dependence on the vacancy concentration. The scaling behavior of \( \lambda^+ \) and \( \lambda^- \) with \( x_v \) in the dilute vacancy limit was first determined by Kehr et al. [51] for a regular solution model. This scaling behavior with \( x_v \) is important in order to attribute a physical interpretation to \( \lambda^+, \lambda^-, \delta \) and \( \phi \) for alloys having a dilute vacancy concentration.

The dominant modes of diffusion in a binary, perfect-crystal alloy can be decomposed into a vacancy flux and an intermixing flux between \( A \) and \( B \) atoms. To elucidate these dominant modes, it is convenient to consider a pair of generalized fluxes defined as linear combinations of the fluxes of \( J_A \) and \( J_B \) according to
\[
-(J_A + J_B); \quad \phi J_A - (1 - \phi)J_B.
\]

In a perfect crystal, the first generalized flux is simply equal to the vacancy flux, \( J_V \) (see Eq. (8)). The second generalized flux, which is a linear combination of \( J_A \) and \( J_B \) having \( \phi \) and \( -(1 - \phi) \) as coefficients, will emerge below to be a useful measure of an intermixing flux in a perfect crystal. Both generalized fluxes can be expressed in terms of the four parameters \( \lambda^+, \lambda^-, \delta \) and \( \phi \) according to
\[
J_V = -\lambda^+ \nabla C_V - \delta (\phi \nabla C_A - (1 - \phi) \nabla C_B),
\]
\[
\phi J_A - (1 - \phi) J_B = -\phi (1 - \phi) \delta \nabla C_V - \lambda^- (\phi \nabla C_A - (1 - \phi) \nabla C_B),
\]

which is accurate to first order in the vacancy concentration. These flux expressions were obtained by substituting expressions for \( D_{ij} \) in terms of \( \lambda^+, \lambda^-, \delta \) and \( \phi \) (to first order accuracy in \( x_v \)) derived in Appendix D into Eq. (35) and using \( \nabla C_V = -\nabla (\nabla C_A + \nabla C_B) \) for a perfect crystal. The symmetry inherent to the above flux expressions can be better appreciated when they are expressed in matrix form
\[
\left( \begin{array}{c} J_V \\ \phi J_A - (1 - \phi)J_B \end{array} \right) = -\left( \begin{array}{cc} \lambda^+ & \delta \\ (\phi (1 - \phi) \delta & \lambda^- \end{array} \right) \left( \begin{array}{c} \nabla C_V \\ \phi \nabla C_A - (1 - \phi) \nabla C_B \end{array} \right).
\]

The eigenvalues \( \lambda^+ \) and \( \lambda^- \) of \( \mathbf{D} \) form the diagonal elements of the matrix linking the generalized fluxes to the generalized driving forces, while the two additional metrics, \( \delta \) and \( \phi \), defined by Eqs. (38) and (39), appear as off-diagonal terms.
2.4.1. Generalized flux expressions for a kinetically ideal alloy

A useful starting point to analyze the generalized fluxes, Eqs. (42) and (43), for binary, perfect-crystal diffusion is the kinetically ideal alloy for which \( \Gamma_A = \Gamma_B \). For a kinetically ideal alloy, \( \delta = 0 \), thereby simplifying Eqs. (42) and (43) to yield the following flux expressions

\[
J_V = -\lambda^+ \nabla C_V, \\
\phi J_A - (1 - \phi) J_B = -\lambda^- (\phi \nabla C_A - (1 - \phi) \nabla C_B).
\]

(45)

(46)

For a kinetically ideal binary alloy, it can be verified using Eqs. (25), (33) and (36) that the eigenvalues of the diffusion coefficient matrix are independent of alloy concentration [51].

The first flux expression, Eq. (45), clearly shows that \( \lambda^+ \) for a kinetically ideal binary alloy corresponds to a vacancy diffusion coefficient in a perfect crystal. It directly couples the vacancy flux, \( J_V \), to a vacancy concentration gradient, \( \nabla C_V \). The second flux expression, Eq. (46), describes an intermixing mode between \( A \) and \( B \). This can be understood by considering an initial concentration profile with a constant vacancy concentration throughout the solid, as illustrated by an example in Fig. 3a. This initial concentration profile will activate only the second generalized flux expression, Eq. (46), as the driving force for the first flux expression, \( \nabla C_V \), is zero everywhere. Thus the vacancy flux, \( J_V \), will also be zero everywhere and the vacancy concentration profile will remain unchanged during the diffusion process. In the absence of a vacancy flux, any flux of \( A \) must be equal but opposite to a flux of \( B \), i.e., \( J_A = -J_B \), due to the conservation of crystal sites in a perfect crystal, Eq. (8). Hence, diffusion in a kinetically ideal, perfect-crystal alloy arising from initial conditions that only activate the second flux expression corresponds to a pure intermixing mode between \( A \) and \( B \) atoms.

As the second generalized flux expression, Eq. (46), corresponds to an intermixing mode, we will refer to its generalized flux as an intermixing flux, \( J_A \), for a perfect crystal

\[
\hat{J}_A = \phi J_A - (1 - \phi) J_B.
\]

(47)

where by symmetry \( \hat{J}_A = -\hat{J}_B \). If initial conditions are such that \( J_V = 0 \) and \( \nabla C_V = 0 \), the intermixing flux \( J_A \) reduces to \( J_A \) as then \( \hat{J}_A = -\hat{J}_B \). Furthermore, any concentration modulation of \( A \) must then be compensated by an opposite modulation in that of \( B \) such that \( \nabla C_A = -\nabla C_B \) everywhere (e.g., Fig. 3a). Under these conditions, the second normal mode flux expression, Eq. (46), reduces to

\[
J_A = -\lambda^- \nabla C_A = -\lambda^- (-\nabla C_B),
\]

(48)

Fig. 3. (a) Schematic illustration of concentration profiles that activate an intermixing mode of diffusion in a kinetically ideal alloy. (b) Schematic illustration of concentration profiles in which interdiffusion is suppressed in a kinetically ideal alloy. In order for interdiffusion fluxes to be suppressed, the concentration gradients of \( A \) and \( B \) must satisfy \( \phi \nabla C_A - (1 - \phi) \nabla C_B = 0 \) at each point.
showing that in the absence of vacancy fluxes and vacancy concentration gradients, \( \lambda^- \) for the kinetically ideal alloy can be interpreted as an intermixing coefficient of a perfect crystal, measuring the rate of mixing between \( A \) and \( B \).

We can assign an interpretation to \( \phi \) as well by again considering the first flux expression, Eq. (45), in the absence of an intermixing flux, \( \tilde{J}_A = 0 \). Fig. 3b schematically illustrates concentration profiles in a perfect crystal in which intermixing is suppressed: the non-uniform concentration profiles for \( A \) and \( B \) have gradients in the same direction at each point, which are both opposite to the vacancy concentration gradient (due to \( x_V = 1 - x_A - x_B \) in a perfect crystal). Setting \( \tilde{J}_A \) to zero in Eq. (47) and using Eq. (8) for a perfect crystal we can write

\[
J_A = -(1 - \phi)J_V; \quad J_B = -\phi J_V. \tag{49}
\]

These relations indicate that without intermixing fluxes, \( \phi \) is equal to the fraction of the vacancy flux exchanging with \( B \) atoms, and \( (1 - \phi) \) is equal to the fraction of the vacancy flux exchanging with \( A \) atoms. For a kinetically ideal alloy, \( \phi = x_B/(x_A + x_B) \), which corresponds to the fraction of non-vacant sites occupied by \( B \) atoms (likewise, \( (1 - \phi) = x_A/(x_A + x_B) \) corresponds to the fraction of non-vacant sites occupied by \( A \) atoms). At the atomic scale, the vacancies in a kinetically ideal alloy perform unbiased exchanges with \( A \) and \( B \) atoms as \( \Gamma_A = \Gamma_B \). Hence the fraction of \( B \) (\( A \)) atoms exchanging with a net vacancy flux, \( J_V \), is equal to the local fraction of \( B \) (\( A \)) atoms, as it emerges in Eq. (49).

With this interpretation of \( \phi \) and \( (1 - \phi) \), we can better understand the meaning of the intermixing flux \( \tilde{J}_A \) during general diffusion processes that simultaneously activate both flux expressions, Eqs. (45) and (46), by rewriting Eq. (47) as

\[
\tilde{J}_A = J_A + (1 - \phi)J_V, \tag{50}
\]

where the conservation of crystal sites, Eq. (8), was used. In this form, the intermixing flux \( \tilde{J}_A \) can be understood as the total flux of \( A \) minus the flux of \( A \) stemming from exchanges with vacancies. This difference corresponds to the flux of \( A \) caused by exchanges with \( B \) and is thus the part of the total flux of \( A \) participating in intermixing with \( B \).

Clearly, for a kinetically ideal alloy, the vacancy flux expression, Eq. (45), and the intermixing flux expression, Eq. (46), each in isolation describe a normal mode diffusion process in a binary, perfect-crystal alloy. The decay rates of each normal mode are the eigenvalues \( \lambda^+ \) and \( \lambda^- \) [51]. The gradient in the vacancy concentration, \( \nabla C_V \), is a driving force for the first normal mode diffusion process resulting in vacancy fluxes, while \( \phi \nabla C_A - (1 - \phi) \nabla C_B \) is the driving force for the second normal mode diffusion process corresponding to intermixing between \( A \) and \( B \). The intermixing flux expression possesses a symmetry between \( A \) and \( B \) where \( \phi \) weights both the flux of \( A \) and the concentration gradient of \( A \) while \( (1 - \phi) \) weights the flux of \( B \) and the concentration gradient of \( B \).

### 2.4.2. Generalized flux expressions for non-ideal binary alloys in the dilute vacancy limit

For a kinetically non-ideal alloy, \( \delta \) deviates from zero, and the vacancy flux and intermixing flux expressions, Eqs. (42) and (43), become more complicated. When expressed in matrix form as in Eq. (44), the vacancy and intermixing fluxes, \( J_V \) and \( \phi J_A - (1 - \phi)J_B \), are no longer diagonal in terms of the vacancy concentration gradient, \( \nabla C_V \), and intermixing driving force, \( \phi \nabla C_A - (1 - \phi) \nabla C_B \). The interpretations assigned to \( \lambda^+ \) and \( \lambda^- \) for a kinetically ideal alloy are therefore no longer strictly valid. Nevertheless, we can still interpret \( \lambda^- \) as a vacancy diffusion coefficient and \( \lambda^+ \) as an intermixing coefficient in the asymptotic limit of a dilute vacancy concentration (provided that the \( L_{ij} \) scale with \( x_V \) and that the alloy is thermodynamically well-behaved as defined in Appendix C). We illustrate this by considering the generalized flux expressions, Eqs. (42) and (43), under conditions where either the vacancy flux is absent or the intermixing flux is absent.

The absence of a vacancy flux, \( J_V = 0 \), corresponds to a pure intermixing mode since, due to the conservation of crystal sites, Eq. (8), \( \tilde{J}_A = -J_B \). Setting the vacancy flux to zero in Eq. (42) imposes a constraint on the vacancy concentration gradient according to

\[
\nabla C_V = -\frac{\delta}{\lambda} (\phi \nabla C_A - (1 - \phi) \nabla C_B) \tag{51}
\]

which, when substituted into Eq. (43) for the intermixing flux, yields
\[ \phi J_A - (1 - \phi) J_B = -\lambda^+ (1 - \epsilon) (\phi \nabla C_A - (1 - \phi) \nabla C_B) \]

(52)

where

\[ \epsilon = \frac{\phi (1 - \phi) \delta^2}{\lambda^+ \lambda}. \]

(53)

Eq. (52) is only valid in the absence of a vacancy flux and therefore describes a pure intermixing mode \( (J_A = -J_B) \). It relates an intermixing flux, \( \phi J_A - (1 - \phi) J_B \), to an intermixing driving force, \( \phi \nabla C_A - (1 - \phi) \nabla C_B \), with as diffusion coefficient \( \lambda^+ (1 - \epsilon) \). The parameter \( \epsilon \) scales with the vacancy concentration and vanishes as the vacancy concentration \( x_V \) approaches zero. Hence, also for kinetically non-ideal alloys, \( \lambda^+ \) can be interpreted as a perfect-crystal intermixing coefficient in the asymptotic limit of a dilute vacancy concentration \( x_V \rightarrow 0 \).

Since crystalline solids of technological importance often have finite vacancy concentrations, it is of interest to estimate the size of the dimensionless parameter \( \epsilon \) for typical vacancy concentrations of binary substitutional alloys. We can calculate \( \epsilon \) exactly for thermodynamically ideal but kinetically non-ideal alloys using the analytical expressions for the kinetic-transport coefficients \( \tilde{L}_{ij} \) (derived by Moleko et al. [79], see Appendix B) and thermodynamic factors \( \theta_{ij} \) (Eq. (25)). For thermodynamically ideal alloys, \( \epsilon \) is a function of the ratio of hop frequencies \( \Gamma_B/\Gamma_A \) as well as the alloy concentration, \( x_B \) and \( x_V \) (with \( x_A = 1 - x_B - x_V \)). For small vacancy concentrations, \( \epsilon \) scales linearly with the vacancy concentration \( x_V \). At constant \( \Gamma_B/\Gamma_A \) ratio and vacancy concentration \( x_V \), the parameter \( \epsilon \) exhibits a maximum at intermediate alloy concentration. Fig. 4 illustrates the maximum value of \( \epsilon/x_V \) with respect to alloy concentration plotted versus \( \Gamma_B/\Gamma_A \) ratio for thermodynamically ideal alloys. The ratio \( \epsilon/x_V \) is zero for the kinetically ideal alloy where \( \Gamma_B/\Gamma_A = 1 \) and steadily increases as the alloy deviates from kinetic ideality (i.e., with increasing \( \Gamma_B/\Gamma_A \) ratio), reaching a plateau close to 4.5 for very large \( \Gamma_B/\Gamma_A \) ratios. Hence an upper bound on \( \epsilon \) for small vacancy concentrations is \( \epsilon \approx 5x_V \). For \( \epsilon \) to be at most 0.01 (i.e., a 1% error if \( \epsilon \) were neglected), the vacancy concentration must be 0.002, which is significantly larger than typical vacancy concentrations in most metal alloys. For \( x_V = 10^{-6} \), which is approximately the vacancy concentration in Al at 600 K, \( \epsilon \) is of the order of \( 5 \times 10^{-6} \). It is clear that even for kinetically non-ideal alloys having a dilute vacancy concentration, \( \lambda^+ \) can be interpreted as a perfect-crystal intermixing coefficient, describing mixing between \( A \) and \( B \) in the absence of vacancy fluxes.

To assign a physical interpretation to \( \lambda^+ \) for a kinetically non-ideal alloy, it is useful to analyze the flux expressions Eqs. (42) and (43) in the absence of an intermixing flux. Setting the intermixing flux \( J_A = \phi J_A - (1 - \phi) J_B \) equal to zero in Eq. (43) imposes a constraint on the concentration profiles.

\[ \frac{\epsilon}{x_V} \]

\[ \frac{\Gamma_B}{\Gamma_A} \]

Fig. 4. The maximum value of \( \epsilon \), Eq. (53), normalized by the vacancy concentration \( x_V \) versus the \( \Gamma_B/\Gamma_A \) ratio. For small vacancy concentrations, \( \epsilon \) scales linearly with the vacancy concentration.
\[
\phi \nabla C_A - (1 - \phi) \nabla C_B = -\frac{\phi(1 - \phi)\delta}{\lambda_v} \nabla C_V
\]  
(54)

which when substituted into the vacancy flux expression Eq. (42) yields
\[
J_V = -\lambda_v'(1 - \epsilon) \nabla C_V
\]  
(55)

where \(\epsilon\) is again given by Eq. (53). In the absence of an intermixing flux, a fraction \((1 - \phi)\) of the vacancy flux exchanges with \(A\) atoms while a fraction \(\phi\) of the vacancy flux exchanges with \(B\) atoms. Under these conditions, Eq. (55) shows that the vacancy flux, \(J_V\), is proportional to a gradient in the vacancy concentration, \(\nabla C_V\), with as proportionality constant \(\lambda_v'(1 - \epsilon)\). This proportionality constant can be interpreted as a vacancy diffusion coefficient. In alloys having a dilute vacancy concentration, \(\epsilon\) is negligible compared to 1, and \(\lambda_v'(1 - \epsilon) \approx \lambda_v\). Hence, even in kinetically non-ideal binary alloys, \(\lambda_v\) can be interpreted as a vacancy diffusion coefficient.

For general non-equilibrium concentration profiles, both modes of perfect-crystal diffusion corresponding to vacancy fluxes and intermixing will participate. Furthermore, a pure intermixing mode cannot be sustained over time in a non-ideal alloy as off-diagonal elements in the diffusion matrix of Eq. (44) will activate vacancy fluxes.

### 2.4.3. Physical interpretation of \(\delta\)

As with \(\lambda^+\), \(\lambda^-\), and \(\phi\), it is also possible to assign a physical interpretation to the parameter \(\delta\) to characterize the transport properties of a non-ideal alloy having a perfect crystal. The generalized flux expressions, Eqs. (42) and (43), show that for a kinetically non-ideal alloy, \(\delta\) couples the vacancy flux, \(J_V\), to the intermixing driving force, \(\phi \nabla C_A - (1 - \phi) \nabla C_B\), while \(\phi(1 - \phi)\delta\) couples an intermixing flux, \(\phi f_A - (1 - \phi)f_B\), to a gradient in the vacancy concentration, \(\nabla C_V\). In a kinetically ideal alloy, \(\delta = 0\) and vacancy fluxes therefore cannot emerge due to intermixing driving forces. Hence the Kirkendall effect, which results in vacancy fluxes during intermixing, will not occur in a kinetically ideal alloy. The Kirkendall effect only occurs when differences in the hop frequencies of \(A\) and \(B\) exist. In kinetically non-ideal alloys, \(\Gamma_A \neq \Gamma_B\) such that \(\delta \neq 0\) and vacancy fluxes then can emerge in the presence of intermixing driving forces. The parameter \(\delta\), in addition to measuring the deviation from kinetic ideality, therefore also serves as a metric for the Kirkendall effect. In fact, by examining Eq. (42) under the condition of \(\nabla C_V = 0\), it is evident that \(\delta\) can be interpreted as a Kirkendall diffusion coefficient.

The second generalized flux expressions, Eq. (43), also shows that intermixing fluxes can be caused by a gradient in the vacancy concentration even in the absence of an intermixing driving force. The strength of this coupling is \(\phi(1 - \phi)\delta\), which is again proportional to the degree with which the alloy deviates from kinetic ideality, \(\delta\).

### 2.5. Classification of substitutional alloys based on kinetic metrics

The parameters \(\lambda^+\), \(\lambda^-\), \(\phi\) and \(\delta\) are useful metrics to characterize the transport properties of binary alloys having a perfect crystal (i.e., in the absence of dislocations and grain boundaries). They provide direct information about the relevant modes of diffusion in a substitutional alloy related to intermixing and vacancy fluxes responsible for the Kirkendall effect, which is not as easily discerned from inspection of the matrix of diffusion coefficients \(D_{ij}\). We emphasize, however, that the interpretations assigned to \(\lambda^+\), \(\lambda^-\) and \(\phi\) for kinetically non-ideal alloys are based on an analysis of equations that are asymptotically valid in the dilute vacancy limit where \(x_V \to 0\). In this limit, \(\lambda^+\) is equivalent to a vacancy diffusion coefficient in the binary alloy, \(\lambda^-\) is an intermixing coefficient describing mixing between \(A\) and \(B\), and \(\phi\) represents the fraction of a vacancy flux that exchanges with \(B\) atoms in the absence of intermixing (by symmetry, \((1 - \phi)\) represents the fraction of a vacancy flux that exchanges with \(A\) atoms). The fourth metric \(\delta\), which is equal to zero for a thermodynamically and kinetically ideal alloy (i.e., \(\Gamma_A = \Gamma_B\)), can be interpreted as a Kirkendall diffusion coefficient, linking a vacancy flux to an intermixing driving force.

While the vacancy concentration in most metallic alloys is very small, it is not infinitesimally small. Nevertheless, the interpretations assigned to \(\lambda^+\), \(\lambda^-\), \(\phi\) and \(\delta\) are still meaningful for vacancy concentrations as high as 0.002, as discussed in Section 2.4.2. An inspection of these kinetic metrics provides
invaluable insights about the diffusional processes in a perfect-crystal alloy, allowing comparisons and classifications of alloys having differing thermodynamic and kinetic properties.

In this section, we explore the behavior of the kinetic metrics in thermodynamically ideal but kinetically non-ideal alloys, as well as a thermodynamically non-ideal alloy. As a thermodynamically non-ideal alloy, we consider fcc Al$_{1-x}$Li$_x$, which exhibits both a solid solution and L1$_2$ ordering for compositions around Al$_3$Li. To facilitate the comparison between the thermodynamically ideal A–B model alloys and fcc Al$_{1-x}$Li$_x$, we assume that pure A has the same vacancy concentration as that predicted for Al with a first-principles cluster expansion [31] at 600 K (i.e., $x_V = 1.4 \times 10^{-6}$ corresponding to a vacancy formation energy of almost 700 meV). We also assign the A atoms a vacancy exchange frequency $\Gamma_A$ similar to that predicted for Al at 600 K from first principles (i.e., $\Delta E_b = 600$ meV and $\nu^* = 4.0 \times 10^{13}$ appearing in Eq. (27)) [38].

### 2.5.1. Thermodynamically ideal substitutional alloys

In the ideal reference alloy (i.e., thermodynamically as well as kinetically ideal), the eigenvalues are independent of alloy concentration, $\delta = 0$ and $\phi = x_B/(x_A + x_B)$. Once a thermodynamically ideal alloy departs from kinetic ideality (i.e. $\Gamma_A \neq \Gamma_B$), the coefficients $\delta$ and $\phi$ deviate from 0 and $x_B/(x_A + x_B)$, respectively. Furthermore, the kinetic coefficients $\lambda^+$, $\lambda^-$ and $\delta$ become concentration dependent.

Fig. 5 illustrates the composition dependence of $\lambda^+$ and $\lambda^-$ for thermodynamically ideal alloys with $\Gamma_B = \Gamma_A$, $\Gamma_B = 10 \times \Gamma_A$ and $\Gamma_B = 100 \times \Gamma_A$. These were calculated by diagonalizing the diffusion coefficient matrix $D$, Eq. (36), using the analytical expressions for $L_{AA}, L_{AB}$ and $L_{BB}$ derived by Moleko et al. [79] (see Fig. 2 and Appendix B) along with the thermodynamic factors for a random alloy, Eq. (25). Fig. 5a shows that $\lambda^+$ increases with the concentration of the fast diffuser (B in this case) when $\Gamma_B > \Gamma_A$. Also plotted in Fig. 5a (circles) are values for the vacancy tracer diffusion coefficient for each of the three random alloys defined by

$$D_V = \frac{\langle (\Delta \bar{R}_V)^2 \rangle}{(2d)t}$$

where $\Delta \bar{R}_V$ is a vector connecting the end points of a vacancy trajectory after time $t$ in a crystal with dimension $d$. The vacancy tracer diffusion coefficients were calculated with kinetic Monte Carlo simulations. As is clear from Fig. 5a, the vacancy tracer diffusion coefficients coincide with $\lambda^+$, confirming the interpretation of $\lambda^+$ as a measure of the vacancy mobility within the binary alloy in the dilute vacancy limit (the kinetic Monte Carlo simulations to calculate $D_V$ were performed with a vacancy concentration of 0.002).

While the addition of a fast diffuser to an alloy leads to an increase of $\lambda^+$, its effect on the perfect-crystal interdiffusion coefficient $\lambda^-$ is more complicated. Fig. 5b shows that for the random alloy with $\Gamma_B = 10 \times \Gamma_A$, $\lambda^-$ decreases with the concentration of the fast diffuser B. If the difference in vacancy exchange frequencies between A and B is very large (e.g., $\Gamma_B = 100 \times \Gamma_A$), Fig. 5b shows that low concentrations of the fast diffuser (B atoms) cause a slight increase of $\lambda^-$, followed by a decrease of $\lambda^-$ as more of the fast diffuser is added to the alloy. This implies that high concentrations of a fast diffuser actually reduces the efficacy of intermixing in the perfect crystalline state.

Fig. 6a illustrates the concentration dependence of $\phi$ for the three thermodynamically ideal alloys having different $\Gamma_B/\Gamma_A$ ratios. For the kinetically ideal alloy ($\Gamma_B = \Gamma_A$), $\phi$ is equal to $x_B/(x_A + x_B)$ and approaches $x_B$ as $x_V \to 0$ (or equivalently $x_A + x_B \to 1$). Fig. 6a shows that $\phi$ deviates from its linear dependence on $x_B$ (when $x_V \to 0$) as the $\Gamma_B/\Gamma_A$ ratio deviates from 1. In systems for which $\Gamma_B > \Gamma_A$, $\phi$ exceeds $x_B$ as illustrated in Fig. 6a. In view of the interpretation of $\phi$ as the fraction of the vacancy flux exchanging with B (in the absence of interdiffusion fluxes), Fig. 6a shows that a larger fraction of the fast diffuser exchanges with an unbalanced vacancy flux than in the kinetically ideal alloy.

The Kirkendall effect arises from a net vacancy flux as a result of concentration gradients and can only occur in alloys in which the components have different hop frequencies with vacancies. Any metric for the Kirkendall effect in a binary alloy should therefore increase as the ratio of hop frequencies of the fast and slow diffuser increases. The analysis of the previous section suggests that $\delta$ can serve as a metric for the tendency of an alloy to exhibit the Kirkendall effect. For the ideal reference alloy, $\delta = 0$ and the Kirkendall effect is absent. However, when $\Gamma_B \neq \Gamma_A$, the alloy becomes susceptible to the
Kirkendall effect and $\delta$ should deviate from zero. Fig. 6b illustrates the concentration dependence of $\delta$ for the two random alloys with $\Gamma_B = 100 \times \Gamma_A$, $\Gamma_B = 10 \times \Gamma_A$ and $\Gamma_B = 100 \times \Gamma_A$. Both $\lambda^+$ and $\lambda^-$ are independent of concentration in a random alloy that is also kinetically ideal, i.e., $\Gamma_A = \Gamma_B$. The lines are obtained using analytical expressions for $L_\delta$ derived by Moleko et al. [79] and the ideal solution thermodynamic factors to calculate the diffusion coefficient matrix, while the circles in (a) are vacancy tracer diffusion coefficients calculated with kinetic Monte Carlo simulations.

Fig. 5. Concentration dependence of (a) $\lambda^+$ and (b) $\lambda^-$ for a random alloy with $\Gamma_B = \Gamma_A$, $\Gamma_B = 10 \times \Gamma_A$ and $\Gamma_B = 100 \times \Gamma_A$. Both $\lambda^+$ and $\lambda^-$ are independent of concentration in a random alloy that is also kinetically ideal, i.e., $\Gamma_A = \Gamma_B$. The lines are obtained using analytical expressions for $L_\delta$ derived by Moleko et al. [79] and the ideal solution thermodynamic factors to calculate the diffusion coefficient matrix, while the circles in (a) are vacancy tracer diffusion coefficients calculated with kinetic Monte Carlo simulations.

Correlation factors offer valuable information about atomic mechanisms of diffusion [104–107] and provide insight about the concentration dependence of the various kinetic coefficients depicted in Figs. 5 and 6. A correlation factor, Eq. (34), measures the average of the square of the displacement of a particular component relative to that of a random walker having the same hop frequency. Fig. 7 illustrates the correlation factors for the A, B and V species (referred to as $f_A$, $f_B$ and $f_V$ respectively) for random fcc alloys with $\Gamma_B/\Gamma_A = 10$ and $\Gamma_B/\Gamma_A = 100$ (calculated with kinetic Monte Carlo having $x_V = 0.002$). The maximum value that a correlation factor can attain is 1 as this corresponds to a perfect random walk. In a single component fcc crystal in which diffusion occurs via the vacancy mechanism, the correlation factor of atomic diffusion is 0.781 [108]. This is the value of $f_A$ as $x_B \to 0$ as can be seen in Fig. 7. The correlation factor for vacancy diffusion in a single component solid (e.g., $x_B \to 0$) containing a dilute concentration of vacancies is 1 since an isolated vacancy performs a random walk.
However, as is evident in Fig. 7, the vacancy correlation factor drops rapidly upon addition of a small concentration of a fast diffuser $B$.

The dramatic reduction in $f_V$ upon alloying with a fast diffuser indicates that the presence of a very mobile component introduces important correlations between successive vacancy hops. For small $B$ concentration, $B$ atoms are typically isolated, i.e., separated by a significant distance from other $B$ atoms. Once a vacancy wanders into the nearest neighbor shell of an isolated $B$ atom, it will on average undergo many back and forth exchanges with that $B$ atom before departing its nearest neighbor shell. However, while the vacancy and an isolated $B$ atom may perform many hops, these are essentially restricted to back and forth movements between a pair of sites as opposed to a more extended trajectory characteristic of a random walk. As the concentration of $B$ reaches a critical value leading to interconnected networks of $B$ atoms, however, the vacancy can migrate more freely along the percolating network of $B$ atoms, rather than predominantly hopping back and forth with an isolated $B$. This causes an increase of both $f_V$ and $f_B$.

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in the perfect-crystal interdiffusion coefficient $λ^−$. As more fast diffusing $B$ atoms become available with increasing $x_B$, the vacancy has more $B$ atoms to exchange with, making it even less likely to exchange with $A$ and to rearrange $A$ and $B$ atoms relative to each other.

2.5.2. Thermodynamically non-ideal substitutional alloy

Most multi-component solids deviate from thermodynamic ideality. A solid exhibits different degrees of short- and long-range order depending on its temperature and composition, as well as the strength of the interactions between its constituents. Varying degrees of order occur because the energy of a solid depends on the arrangement of the different constituents, with certain arrangements energetically more favored than most others. Likewise, the activation barrier, $ΔE_b$, and vibrational prefactor, $ν^*$, that determine the hop frequency according to Eq. (27) also depend on the local degree of order. A typical atom migrating within a multi-component solid samples many different local environments along its trajectory and executes hops with frequencies that change with the local environment.

The fcc Al–Li alloy serves as a useful example to analyze diffusion in a binary substitutional solid that deviates from thermodynamic ideality. While Al$_{1−x}$Li$_x$ is predominantly stable in the bcc crystal structure, it is metastable in fcc when Al-rich and exhibits L1$_2$ ordering around $x = 0.25$. A first-principles investigation has shown that diffusion in this alloy is strongly affected by its thermodynamic properties [38]. As demonstrated elsewhere, it is possible to accurately describe the configurational energy of the Al$_{1−x}$Li$_x$ alloy with a cluster expansion parameterized to reproduce the first-principles energies (density functional theory within the local density approximation) of a small set of periodic arrangements of Al and Li over fcc [21,31]. When implemented in Monte Carlo simulations, this cluster
expansion predicts the phase stability of the L1$_2$ phase at finite temperature as illustrated in the calculated phase diagram in Fig. 8a [31]. The L1$_2$ phase is predicted to be stable over a large concentration interval, undergoing an order–disorder transition around 730 K. By accounting for the configuration dependence of the vacancy formation energy, it is also possible to calculate the equilibrium vacancy concentration in Al$_{1-x}$Li$_x$ as a function of the bulk alloy concentration as illustrated in Fig. 8b at 600 K [31]. The Monte Carlo simulations also predict significant short-range order around the vacancy within the solid solution phase, with the vacancy preferring a nearest neighbor shell rich in Al atoms. In the L1$_2$ ordered phase, where Li occupies the corner points of the conventional cubic fcc unit cell, the vacancy predominantly occupies the Li-sublattice, as this allows the vacancy to be surrounded by Al [31].

First-principles calculations of migration barriers for various Al–Li configurations and concentrations showed that the average migration barrier (averaged between forward and backward hops)
for a Li atom into an adjacent vacancy is less by almost 200 meV than that for Al. This shows that in addition to exhibiting non-ideal thermodynamic properties, the alloy deviates from kinetic ideality. In fact, the non-idealities tend to work in opposite directions: while Li is kinetically more mobile, having a lower migration barrier than Al when next to a vacancy, it is nevertheless thermodynamically deprived of diffusion mediating vacancies as the vacancies prefer to be surrounded by Al.

By combining the first-principles calculated activation barriers with the cluster expansion for the energies of end states in kinetic Monte Carlo simulations as described in Ref. [38], it is possible to evaluate the Kubo-Green expressions for the $L_{ij}$ coefficients (with $i,j = \text{Li or Al}$). These are illustrated in Fig. 8c at 600 K. Although the fcc solid solution of $\text{Al}_{1-x}\text{Li}_x$ has kinetic coefficients that are qualitatively similar to those of an ideal solution (Fig. 2), within the L1$_2$ phase, the kinetic coefficients exhibit more structure as a function of concentration. In the L1$_2$ phase, the off-diagonal kinetic coefficient, $\tilde{L}_{\text{LiAl}}$, which reflects correlations between the trajectories of the center of mass of Al atoms with that of Li atoms, is significantly smaller than the diagonal kinetic coefficients, $\tilde{L}_{\text{LiLi}}$ and $\tilde{L}_{\text{AlAl}}$. Its small magnitude leads to large statistical scatter. The diagonal kinetic coefficients exhibit a minimum at the stoichiometric composition ($x = 0.25$) of L1$_2$ where the number of anti-site defects that disrupt ordering is minimized. Beyond the stoichiometric composition of the L1$_2$ phase, the kinetic coefficient $\tilde{L}_{\text{LiLi}}$ increases significantly due to an anti-site structural bridge diffusion mechanism [109,110]. For $x > 0.25$, the excess Li occupy the Al sublattice of L1$_2$ and form a bridge to allow vacancies, which predominantly occupy the Li-sublattice, to more easily depart one Li-sublattice site and migrate to the next.

![Graph showing concentration dependence of the eigenvalues $\lambda^+$ and $\lambda^-$ of the diffusion coefficient matrix for the metastable fcc $\text{Al}_{1-x}\text{Li}_x$ alloy.](image1.png)

![Graph showing concentration dependence of $\phi$ for the metastable fcc $\text{Al}_{1-x}\text{Li}_x$ alloy at $T = 600$ K.](image2.png)

**Fig. 9.** (a) Concentration dependence of the eigenvalues $\lambda^+$ and $\lambda^-$ of the diffusion coefficient matrix for the metastable fcc $\text{Al}_{1-x}\text{Li}_x$ alloy. (b) Concentration dependence of $\phi$ for the metastable fcc $\text{Al}_{1-x}\text{Li}_x$ alloy at $T = 600$ K.
To obtain the Fickian diffusion coefficients $D_{ij}$ as well as the metrics for substitutional diffusion $\lambda^+, \lambda^-, \delta$ and $\phi$, it is also necessary to calculate the components of the thermodynamic factor matrix $\bar{\Theta}$ appearing in Eq. (36). This can be done with Eq. (24) in terms of ensemble averages of fluctuations in the number of $A = Al$ and $B = Li$ atoms, numerically evaluated within grand canonical Monte Carlo simulations. Multiplying the thermodynamic factor matrix with the matrix of kinetic coefficients according to Eq. (36) then yields the matrix of diffusion coefficients $D$. Fig. 9a illustrates the eigenvalues, $\lambda^+$ and $\lambda^-$ of this matrix as a function of the Li concentration. In the solid solution of $Al_{1-x}Li_x$, both $\lambda^+$ and $\lambda^-$ exhibit a negligible concentration dependence, while in the $L1_2$ phase, both eigenvalues drop significantly. The thermodynamic preference of the vacancies for the lithium sublattice sites of $L1_2$ constrains the trajectory of the vacancies, leading to a drop in overall mobility of Li, Al and vacancies. Nevertheless, $\lambda^+$, which is a measure for the vacancy diffusivity, rapidly increases above $x = 0.25$ in the $L1_2$ phase as a result of the anti-site structural bridge mechanism [109,110] that becomes viable once excess Li occupies the Al sublattice.

Fig. 9b illustrates the concentration dependence of $\phi$ defined as

$$\phi = \frac{D_{LiAl}}{D_{AlLi} + D_{LiAl}}.$$  (57)

which, as explained in Sections 2.4.1 and 2.4.2, can be interpreted as the fraction of a vacancy flux that exchanges with Li atoms (in the absence of intermixing). In the solid solution, $\phi$ is greater than that for the kinetically ideal alloy, $\phi_{\text{ideal}}$ (ideal solution and $I_a = I_b$). This can be attributed to the lower activation barrier for Li hops into an adjacent vacancy as compared to that of Al. A net flux of vacancies (e.g., after a quench when supersaturated vacancies diffuse to surfaces and extended defects) will preferentially exchange with Li atoms (compared to a kinetically ideal alloy). In $L1_2$, $\phi$ is slightly less than $\phi_{\text{ideal}}$ below $x = 0.25$ but becomes larger than $\phi_{\text{ideal}}$ above $x = 0.25$.

Numerical errors on the individual Fickian diffusion coefficients $D_{ij}$ due to statistical noise inherent to Monte Carlo techniques prevent us from extracting reliable values for the Kirkendall diffusion coefficient, $\delta$. The metric $\delta$ is a small quantity as it scales with the vacancy concentration (which is small in $Al_{1-x}Li_x$) and is a difference between much larger quantities of approximately the same magnitude. Thus, a different approach must be developed in order to obtain this quantity from first principles.

3. The role of vacancy sources and sinks

The treatment of substitutional diffusion has so far been restricted to perfect crystals. In this limiting case, we can make direct contact with diffusion coefficients that are calculated from first principles using a cluster expansion for the configurational energy and kinetic Monte Carlo simulations within a defect-free crystal (i.e., without extended defects that can serve as vacancy sources and sinks). The assumption of a perfect crystal may be valid for very precisely synthesized heterostructures, or for a study of diffusion at low temperatures where vacancy creation or annihilation at sources and sinks could be kinetically suppressed. Most solids, however, contain defects that can locally regulate the vacancy concentration, complicating the task of linking kinetic properties calculated for perfect crystals with non-equilibrium phenomena observed in real solids. As a first approximation for solids containing vacancy sources and sinks, we can examine the other extreme in which sources and sinks are assumed to exist uniformly (at least on a continuum scale) such that the vacancy concentration is locally always equilibrated. This approximation is conventionally made in textbook treatments of substitutional diffusion [2,76].

3.1. A continuous and dense distribution of sources and sinks

In the limit of a continuous distribution of vacancy sources and sinks, the assumption can be made that the vacancy chemical potential is zero throughout the solid and that therefore $d\mu_V = 0$. This condition implies a sufficiently high density of vacancy sources and sinks to regulate the vacancy concentration at its equilibrium value. Despite the high concentration of vacancy sources and sinks, we nevertheless assume (as is done in standard treatments of substitutional diffusion) that diffusion
happens through crystalline regions, thereby neglecting contributions from grain boundary diffusion and diffusion along dislocation cores. The perfect-crystal diffusion coefficients, $D_{ij}$, then still describe transport in the bulk alloy. The only role of defects is to impose the thermodynamic constraint that $\mu_V = 0$ throughout the solid, which, using Eq. (4) and the fact that $C_i = x_i/\Omega$, allows us to express the concentration gradient of one atomic species in terms of the other according to

$$\nabla C_A \bigg/ \nabla C_B = - \frac{x_A}{x_B} \left( \frac{\partial^2 g}{\partial x_B \partial x_A} \right) + x_B \left( \frac{\partial^2 g}{\partial x_A^2} \right) \tag{58}$$

where the concentration dependence of the volume per substitutional site, $\Omega$, has been neglected. With Eq. (58) the Fickian flux equations for a perfect crystal, Eq. (35), can be rewritten in terms of the concentration gradient of either $A$ or of $B$ (but not both). Expressing the diffusion coefficients $D_{ij}$ in terms of the kinetic coefficients $L_{ij}$ and thermodynamic factors $\Theta_{ij}$ and using Eq. (58) we obtain

$$J_A = -D_A \nabla C_A$$
$$J_B = -D_B \nabla C_B \tag{59}$$

with the self-diffusion coefficients $D_A$ and $D_B$ defined as

$$D_A = \left( \frac{L_{AA}}{x_A} - \frac{L_{AB}}{x_B} \right) \frac{x_A}{k_B T} \left( \frac{d \mu_A}{dx_A} \right)_{\mu_V = 0}$$
$$D_B = \left( \frac{L_{BB}}{x_B} - \frac{L_{BA}}{x_A} \right) \frac{x_B}{k_B T} \left( \frac{d \mu_B}{dx_B} \right)_{\mu_V = 0}. \tag{60}$$

The derivatives of the chemical potentials are taken under the constraint that $\mu_V = 0$ (along the line in composition space corresponding to an equilibrium vacancy concentration, Fig. 1b). In terms of the Hessian elements of the free energy, these derivatives can be written as

$$\left( \frac{d \mu_A}{dx_A} \right)_{\mu_V = 0} = x_B \left( \frac{\partial^2 g}{\partial x_B^2} - \frac{x_A \partial^2 g}{\partial x_A \partial x_B} \right) \left( \frac{\partial^2 g}{\partial x_A \partial x_B} \right)^2$$
$$\left( \frac{d \mu_B}{dx_B} \right)_{\mu_V = 0} = x_A \left( \frac{\partial^2 g}{\partial x_A^2} + \frac{x_B \partial^2 g}{\partial x_A \partial x_B} \right)^2. \tag{61}$$

where the Hessian elements of the free energy are to be evaluated at concentrations $x_A$ and $x_B$ for which $\mu_V = 0$. These expressions can be derived starting with Eq. (2) and differentiating under the constraint that $x_A$ and $x_B$ are functionally related to each other according to Eq. (4) when holding $\mu_V = 0$. It should be emphasized that the above derivatives of the chemical potentials are not partial derivatives, but rather derivatives with respect to one concentration variable $x_i$ performed at constant vacancy chemical potential (i.e., $\mu_V = 0$). In a perfect binary crystal with vacancies, there are two independent concentration variables. However, once the constraint of an equilibrium vacancy concentration is imposed (i.e., $\mu_V = 0$), only one composition variable is independent (either $x_A$ or $x_B$, but not both). For an ideal solution having a vacancy concentration independent of alloy composition, Eq. (61) becomes

$$\left( \frac{d \mu_A}{dx_A} \right)_{\mu_V = 0} = \frac{k_B T}{x_A}, \quad \left( \frac{d \mu_B}{dx_B} \right)_{\mu_V = 0} = \frac{k_B T}{x_B}. \tag{62}$$
As is clear from Eq. (59), the assumption of an equilibrium vacancy concentration leads to flux equations for each component $A$ and $B$ that depend only on their own concentration gradient. This does not, however, mean that gradients in the vacancy concentration are absent or that $\nabla C_A = -\nabla C_B$. Since the equilibrium vacancy concentration can vary depending on the local alloy concentration, any gradients in $A$ and/or $B$ will lead to a gradient in the vacancy concentration, even when vacancies are locally in equilibrium.

The above flux equations are identical to those derived in the standard textbook treatment of substitutional diffusion based on the assumption that a continuous and dense distribution of vacancy sources exist to locally maintain an equilibrium vacancy concentration throughout the solid [2,75,69,76]. The standard derivation of Eq. (59) starts with Eq. (10) and then uses the constraint that $d\mu_i = 0$ along with the Gibbs–Duham relation. The derivation here clarifies the precise meaning of the derivatives of the chemical potentials, Eq. (61), in terms of quantities that can be calculated with grand canonical Monte Carlo simulations (i.e., the Hessian of $g(x_A, x_B)$ related to the variances in the number of atoms at constant chemical potentials, Eq. (24)).

3.1.1. The Darken approximation

Fig. 2 illustrates that the off-diagonal kinetic coefficients $\tilde{L}_{AB}$ are always smaller than the diagonal kinetic coefficients $L_{AA}$ and $L_{BB}$. We could therefore neglect the off-diagonal term $\tilde{L}_{AB}$ to simplify Eq. (60). Inspection of the Kubo-Green expression for $\tilde{L}_{AB}$ shows that this coefficient measures the degree to which the trajectories of $A$ atoms are correlated with the trajectories of $B$ atoms. A further simplification to Eq. (60) becomes possible if each diagonal kinetic coefficient, for example $L_{AA}$, is written as

$$
\frac{L_{AA}}{x_A} = \frac{\left\langle \sum_{i=1}^{N_A} (\Delta R_i^A(t))^2 \right\rangle}{2dnAt} + \frac{\left\langle \sum_{i=1}^{N_A} \sum_{l \neq 1} \frac{\Delta R_i^A \Delta R_l^A}{\Delta^2} \right\rangle}{2dnAt},
$$

where we have used the fact that $x_A = N_A/M$. The ratio $L_{AB}/x_B$ can be written in a similar manner. The first term in Eq. (63) is equal to the well-known tracer diffusion coefficient defined as

$$
D_i^T = \frac{\left\langle (\Delta \vec{R}_i)^2 \right\rangle}{(2d) t},
$$

where $\Delta \vec{R}_i$ is the vector that connects the endpoints of the trajectory of an atom of type $i$. The second term in Eq. (63) is similar in nature to the off-diagonal kinetic coefficient $\tilde{L}_{AB}$ except that it measures the degree with which the trajectories of different atoms of the same type are correlated.

By neglecting all terms that measure correlations between the trajectories of different diffusing particles (i.e., $L_{AB}$ and the second term in Eq. (63)), the self-diffusion coefficients $D_A$ and $D_B$ reduce to

$$
D_A = D_A^T \frac{x_A}{k_BT} \left( \frac{d\mu_A}{dx_A} \right)_{\mu_i = 0},
$$

$$
D_B = D_B^T \frac{x_B}{k_BT} \left( \frac{d\mu_B}{dx_B} \right)_{\mu_i = 0},
$$

where $D_A^T$ and $D_B^T$ are tracer diffusion coefficients of $A$ and $B$. These expressions for the self-diffusion coefficients correspond to the well-known Darken approximation [111].

3.1.2. The Kirkendall effect and interdiffusion

The Kirkendall effect arises from a difference in hop frequencies between $A$ and $B$ atoms. If, for example, $B$ exchanges more frequently with vacancies than $A$, then a gradient in the concentrations of $A$ and $B$ should lead to a net vacancy flux in a direction opposite to the flux of $B$. In the presence of active vacancy sources and sinks that accommodate any resultant deviation of the vacancy concentration from its equilibrium value, the crystal will locally shrink or expand (e.g., through dislocation climb). This leads to a local movement of the crystalline frame of reference relative to the laboratory frame and is referred to as a Kirkendall shift. The local velocity of the crystal frame of reference relative to the laboratory frame is proportional to the net flux of atoms at that point according to [2,75,69,76]
Using Eqs. (59) and (60) to eliminate the fluxes \( J_A \) and \( J_B \) and Eq. (58) to relate \( \nabla C_A \) to \( \nabla C_B \) for an equilibrium vacancy concentration, the local crystal frame velocity, \( v_l \), can be written as

\[
v_l = -\Omega \delta_{\mu_V=0} \nabla C_B, \tag{67}
\]

where

\[
\delta_{\mu_V=0} = \left[ \left( \frac{L_{AA}}{X_A} - \frac{L_{AB}}{X_B} \right) - \left( \frac{L_{BB}}{X_B} - \frac{L_{AB}}{X_A} \right) \right] x_B \frac{k_B T}{\mu_B} \left( \frac{d\mu_B}{dx_B} \right)_{\mu_V=0}.
\tag{68}
\]

For alloys in which the vacancy concentration is independent of the alloy concentration,

\[
\delta_{\mu_V=0} = D_A - D_B, \tag{69}
\]

as then

\[
x_A \left( \frac{d\mu_A}{dx_A} \right)_{\mu_V=0} = x_B \left( \frac{d\mu_B}{dx_B} \right)_{\mu_V=0}
\tag{70}
\]

according to the Gibbs–Duhem relation \[84\] and the fact that \( dx_A = -dx_B \). Eq. (69) is a result commonly derived in standard treatments of substitutional diffusion \[2,75,69,76\] and is strictly valid only if the equilibrium vacancy concentration is independent of the bulk alloy concentration, which is a reasonable approximation for most alloys but not for intermetallic compounds such as B2 NiAl \[36\].

Local Kirkendall shifts of the lattice frame in solids containing a continuous distribution of vacancy sources and sinks only occur in regions having concentration gradients. In regions far away from the interdiffusion zone of a diffusion couple, concentration gradients are absent and hence no fluxes of \( A \) and \( B \) exist. The crystal frame in these regions is then locally fixed to the laboratory frame. The local migration of the lattice frame within the interdiffusion zone can be measured by attaching inert markers to the lattice frame, as was first done by Kirkendall \[78,77\].

For diffusion couples, it is often desirable to work with flux expressions formulated within the laboratory frame of reference, as it is in this frame that measurements of concentration profiles are made. The flux of \( B \) atoms within the laboratory frame, \( J_B \), is equal to the flux of \( B \) in the crystal frame, \( J_B \), (given by Eq. (59)) plus a flux of \( B \) due to a local shift of the crystal frame with velocity \( v_l \) \[75,69,2,76\]

\[
\tilde{J}_B = J_B + x_B \left( \frac{\nu_l}{\Omega} \right) = -x_B J_A + x_A J_B, \tag{71}
\]

where the last identity is only valid as \( x_V \to 0 \). A similar expression can be formulated for \( \tilde{J}_A \). As before, we can apply Eqs. (58) and (59) to eliminate \( J_A \) and \( J_B \) and Eq. (58) to relate \( \nabla C_A \) to \( \nabla C_B \) for an equilibrium vacancy concentration, yielding

\[
\tilde{J}_B = -\tilde{D} \nabla C_B, \tag{72}
\]

where

\[
\tilde{D} = \left[ x_B \left( \frac{L_{AA}}{X_A} - \frac{L_{AB}}{X_B} \right) + x_A \left( \frac{L_{BB}}{X_B} - \frac{L_{AB}}{X_A} \right) \right] x_B \frac{k_B T}{\mu_B} \left( \frac{d\mu_B}{dx_B} \right)_{\mu_V=0}.
\tag{73}
\]

This expression can be viewed as a Fickian flux equation for interdiffusion within the laboratory frame of reference. \( \tilde{D} \) is commonly referred to as the interdiffusion coefficient. If the equilibrium vacancy con-
centration is independent of alloy composition then \( \nabla C_A = -\nabla C_B \) and the interdiffusion coefficient takes the familiar form
\[
\bar{D} = x_B D_A + x_A D_B, \tag{74}
\]
as a result of Gibbs-Duhem and the fact that \( dx_A = -dx_B \) when \( x_V \) is independent of alloy composition. If the vacancy concentration is not independent of alloy concentration, this identity no longer holds \cite{113,114} and Eq. (73) must be used to calculate the interdiffusion coefficient \( \bar{D} \). The interdiffusion coefficient \( \bar{D} \) describes intermixing between \( A \) and \( B \) in the laboratory frame of reference under the thermodynamic constraint that \( \mu_V = 0 \) at each point of the solid. It therefore is different from \( \lambda^- \), which describes intermixing in a perfect crystal within the crystal frame of reference (in alloys having a dilute vacancy concentration).

3.2. Comparison between the perfect crystal and the uniform source-sink approximation

3.2.1. Thermodynamically ideal alloy

It is useful to compare the intermixing coefficient for a perfect-crystal with a dilute concentration of vacancies (\( \lambda^- \)) and the interdiffusion coefficient within the uniform source–sink approximation (\( \bar{D} \)). Both metrics describe the same physical phenomenon of intermixing between \( A \) and \( B \) of a binary alloy. Nevertheless, \( \lambda^- \) describes intermixing within a perfect crystal in the crystal frame of reference while \( \bar{D} \) describes intermixing in the laboratory frame of reference of a crystal containing abundant vacancy sources and sinks to maintain a uniform equilibrium vacancy concentration.

An appropriate starting point for a comparison between \( \lambda^- \) and \( \bar{D} \) is the ideal reference alloy, which is both thermodynamically ideal as well as kinetically ideal (i.e., \( \Gamma_A = \Gamma_B \)). For this alloy, it can be verified using Eqs. (25), (62) and (33) that \( \lambda^- \) and \( \bar{D} \) are not only independent of concentration, but are actually equal to each other as \( x_V \rightarrow 0 \). This is due to the absence of the Kirkendall effect in a kinetically ideal alloy. In the absence of initial gradients in the vacancy concentration, it is impossible to generate a vacancy flux in a kinetically ideal alloy as a result of gradients of \( A \) and \( B \) concentrations. Therefore the crystal need not locally expand or contract to accommodate local supersaturations in vacancy concentration. The lattice frame of reference does not move relative to the laboratory frame of reference and \( \bar{D} \) therefore describes the same mode of intermixing as \( \lambda^- \).

The two metrics of interdiffusion become concentration dependent and diverge from each other once a thermodynamically ideal alloy deviates from kinetic ideality (i.e., \( \Gamma_A \neq \Gamma_B \)). This is illustrated in Fig. 10. While \( \lambda^- \) and \( \bar{D} \) approximate each other in the dilute limits, they deviate at intermediate concentrations. In an alloy with \( \Gamma_B = 100 \times \Gamma_A \) where \( A \) has similar properties to \( Al \) at 600 K (\( x_V = 1.4 \times 10^{-6}, \Delta E_V = 600 \text{ meV and } v^* = 4 \times 10^{13} \text{ Hz, see Section 2.5} \)), the difference is more than an order of magnitude when using the analytical kinetic-transport coefficients \( \bar{D}_V \) derived by Moleko et al. \cite{79} (see Appendix B). For this alloy, \( \bar{D} \) exhibits a maximum at intermediate concentration.

The difference between \( \bar{D} \) and \( \lambda^- \) for alloys having large \( \Gamma_B/\Gamma_A \) ratios can be understood as follows. An alloy having very different vacancy exchange frequencies for the two components will exhibit a strong Kirkendall effect. Once a percolating network of the fast diffuser is established within a perfect crystal, the vacancies can predominantly wander along this network, exchanging rarely with the slow diffuser and thereby leading to a reduction in the efficiency of intermixing. Hence, \( \lambda^- \) can decrease as the concentration of the fast diffuser is increased (Fig. 10a and b). If, however, abundant vacancy sources and sinks are available, intermixing can be mediated by the Kirkendall effect. The spatial redistribution of the fast diffuser can then occur, not by intermixing with the slow diffuser within the crystal, but by exchanging with net vacancy fluxes. The fast diffuser then accumulates at grain boundaries and climbing dislocations where their concentration is low. The departure of fast diffusers from regions in which they have a high concentration causes local contraction of the crystal, while the arrival of the fast diffuser in regions in which their concentration is low causes local expansion of the crystal. Hence \( \bar{D} \), which describes this mechanism of interdiffusion, can be large in alloys in which the components have very different hop frequencies.

For comparison, Fig. 10 also shows the interdiffusion coefficient \( \bar{D}_{\text{Darhen}} \) calculated within the Darken approximation in which Eq. (65) is used as an approximation for \( D_A \) and \( D_B \). In a random alloy,
3.2.2. Thermodynamically non-ideal alloy

We again consider fcc $\text{Al}_{1-x}\text{Li}_x$ for the purpose of comparing $\tilde{D}$ and $\lambda^-$ in a thermodynamically non-ideal alloy. Fig. 11 shows $\tilde{D}$ and $D_{\text{Darken}}$ as a function of Li concentration $x$, calculated at 600 K. The various interdiffusion metrics do not differ substantially except within the L1$_2$ phase in which $D_{\text{Darken}}$ is now larger than both $\tilde{D}$ and $\lambda^-$. However, the concentration interval in which the solid solution of $\text{Al}_{1-x}\text{Li}_x$ is stable, is limited to $x < 0.15$. A comparison with the thermodynamically ideal alloys of Fig. 10a and b, shows that for small concentrations of the fast diffuser, the difference between $\tilde{D}$ and $\lambda^-$ is also small in thermodynamically ideal alloys.

3.3. Discrete distribution of sources and sinks

So far, we have considered two extremes of substitutional diffusion: binary diffusion in a perfect crystal and binary diffusion assuming a continuous and dense distribution of vacancy sources. Within the continuous source approximation, the presence of vacancy sources is assumed to only impose a thermodynamic constraint on the driving forces for diffusion resulting from the condition that

\[ D_{\text{Darken}} \]
\( \mu = 0 \) throughout the solid. Any role that a high density of vacancy sources may play in promoting short-circuit diffusion is neglected. The uniform source/sink approximation is conventionally made in textbook treatments of substitutional diffusion [2,69,76] and is also commonly used in quantitative analyses of diffusion couples [112,115].

A treatment of substitutional diffusion in a solid that contains a low density of vacancy sources and sinks is possible at a continuum level if we consider the alloy as consisting of regions that are perfect crystals (e.g., grains) explicitly decorated and or bounded by discrete vacancy sources and sinks (dislocations, grain boundaries and surfaces). Diffusion within the grains is then to be described with the perfect crystal Fickian flux expressions (35) while the vacancy sources and sinks serve as boundary conditions to Eq. (35). This approach requires an accurate characterization of the spatial distribution of dislocations and grain boundaries within the solid.

We can distinguish between ideal vacancy sources, which maintain an equilibrium vacancy concentration in its immediate vicinity, and non-ideal sources that require some degree of vacancy supersaturation or depletion before vacancies are annihilated or created. Dislocations accommodate vacancies through climb processes, which usually requires the recombination of partial dislocations through thermal fluctuations. The effectiveness of this climb process is therefore sensitive to the stacking fault energy of the solid. Dimensionality of the source can be another factor that plays a role in the effectiveness of accommodating vacancy supersaturations. Dislocations are one-dimensional sources while grain boundaries are two-dimensional sources. Although dislocations are usually more abundant and uniformly distributed throughout a solid as compared to grain boundaries, only simulations containing explicit sources and sinks will accurately indicate the relative effectiveness between dislocations and grain boundaries in accommodating supersaturations in vacancy. A rough estimate for the grain size at which grain boundaries would dominate dislocations as vacancy sources can be obtained when simplifying assumptions, such as a simple geometry of the grain, are made [121].

As an illustration of a continuum simulation with explicit sources, we consider below an idealized diffusion couple initially containing equally spaced parallel grain boundaries and investigate the degree with which the evolution of the concentration profile predicted for a perfect crystal deviates from that of a solid with a continuous and dense distribution of sources.

Grain boundaries that act as ideal vacancy sources will locally pin the vacancy concentration at its equilibrium value. Furthermore, the concentration profiles of \( A \) and \( B \) will be continuous across each grain boundary if they are ideally permeable to both \( A \) and \( B \). These constraints on the various concentrations impose a set of boundary conditions on the continuity equation for diffusion within each grain.
as described in Ref. [116]. The continuity equations within each grain can be solved numerically with a finite-difference scheme, accounting for the composition dependence of the diffusion coefficients.

The annihilation or creation of vacancies at each source can lead to local expansions or contractions of the crystal. Accounting for this in a numerical simulation is possible by adjusting the distance between grid points adjacent to the source by an amount that ensures that the vacancy concentration at the source maintains its equilibrium value. The technical details of this numerical approach to treat discrete sources and sinks within a diffusion couple are described in Ref. [116].

Fig. 12 shows a concentration profile at intermediate time in the laboratory frame of reference predicted with a continuum simulation of a diffusion couple initially containing five equal-sized grains (dashed line). The horizontal axis $\hat{y}$ in Fig. 12 is the position in dimensionless length (scaled with the total length of the crystal) and the vertical axis $\hat{C}_B$ is the dimensionless concentration (scaled with lattice site density) as a function of position $\hat{y}$. The hats indicate dimensionless quantities. The fast diffuser $B$ is initially located within the left half of the diffusion couple, while the slow diffuser $A$ occupies the right half of the diffusion couple. The diffusion coefficients used to describe transport within the grains are for a thermodynamically ideal alloy with $C_B = \frac{100}{C_A^2}$. Notice that the concentration profile is not smooth in the vicinity of a vacancy source. The spikes in concentration around the vacancy source arise from a difference in vacancy exchange frequencies between $A$ and $B$ atoms. The fast diffuser $B$ accumulates at the source where vacancies are created and is depleted around sources (sinks) that annihilate vacancies. Uphill diffusion, whereby atoms diffuse up their concentration gradient, is only possible in a strictly binary system if the diffusion coefficient is negative. The apparent uphill diffusion in Fig. 12, emerges because each grain is effectively a ternary system and the large flux of vacancies in the vicinity of the vacancy sources preferentially exchanges with the fast diffuser.

The presence of explicit vacancy sources also leads to a Kirkendall shift of the diffusion couple. Furthermore, differences in vacancy fluxes at the ends of each grain can lead to a Kirkendall-effect-in-

\[
\begin{align*}
\frac{\partial C_A}{\partial t} &= \nabla(D_{AA}\nabla C_A + D_{AB}\nabla C_B) \\
\frac{\partial C_B}{\partial t} &= \nabla(D_{BA}\nabla C_A + D_{BB}\nabla C_B)
\end{align*}
\]
duced coarsening phenomenon [116], whereby some grains shrink in size and others grow, even in the absence of capillarity effects (which are not present in this case since each grain boundary is assumed planar). In the example of Fig. 12, the left two grains shrink due to vacancy ejection at sources in the initially B-rich (left) side, while the other three grains grow due to vacancy injection at sources there. In a three-dimensional crystal with grains having complex three-dimensional shapes, any Kirkendall shift as well as grain size and shape change will cause stresses within the solid and increase the driving force for void formation and decohesion along grain boundaries.

The profile of Fig. 12 illustrates the role of the Kirkendall effect in mediating intermixing in the presence of vacancy sources. Due to a difference by a factor of 100 in vacancy exchange frequencies between A and B, the fast diffuser B migrates to the A-rich regions by predominantly exchanging with a net vacancy flux (see Fig. 6a for the $\Gamma_B = 100 \times \Gamma_A$ alloy, showing that $\phi_b$, which measures the fraction of the vacancy flux that exchanges with B, is close to 1 above $x_b = 0.2$). The influx of B atoms in the A-rich regions is accommodated by a lengthening of the A-rich grains. The depletion of B on the B-rich side is accommodated by a shrinkage of the B-rich grains. Due to the discrete nature of the vacancy sources, enrichment of B on the A-rich side occurs predominantly in the vicinity of the sources (spikes in concentration), while depletion of B in the B-rich region also occurs close to the sources and results in a contraction of the adjacent grains. Interdiffusion in the presence of vacancy sources clearly relies on the Kirkendall effect for alloys with a large $\Gamma_B/\Gamma_A$ ratio, occurring to an important extent by an exchange of the fast diffuser with net vacancy fluxes and a rigid shift of the slow diffuser through Kirkendall-effect-induced grain shrinkage or growth.

Also illustrated in Fig. 12, are concentration profiles of the diffusion couple at intermediate time calculated for a perfect crystal without any vacancy sources, $\bar{C}_{\text{cs}}^B$, and within the continuous source approximation, $C_{\text{cs}}^B$. The concentration profile for $\bar{C}_{\text{cs}}^B(\bar{y})$ was obtained by solving the continuity Eq. (75) with zero fluxes at the surfaces. The concentration profile $C_{\text{cs}}^B(\bar{y})$ is determined by solving a continuity equation applied to the interdiffusion flux expression, Eq. (72), for the uniform source sink approximation

$$\frac{\partial C_{\text{cs}}^B}{\partial t} = \nabla \bar{D} \nabla C_{\text{cs}}^B$$

within the laboratory frame of reference. In both continuity equations, the diffusion coefficients $D_{ij}$ and $\bar{D}$ are derived from the same set of transport coefficients $L_{ij}$ and therefore describe the same system, but within different approximations with respect to the treatment of vacancy sources and sinks. Fig. 12 shows that the profile with a finite number of vacancy sources is intermediate between the two extremes, $\bar{C}_{\text{cs}}^B$ and $C_{\text{cs}}^B$. Intermixing for an alloy with a large difference in hop frequencies between A and B is the slowest in a perfect crystal, where hops of both A and B atoms are required. Intermixing increases with the density of vacancy sources, and becomes most effective when the vacancy source density is high enough to regulate an equilibrium vacancy concentration throughout the solid.

As noted in Section 3.2.1, the perfect-crystal interdiffusion coefficient $\bar{\lambda}^-$ is equal to the continuous source approximation interdiffusion coefficient $\bar{D}$ for the kinetically ideal reference alloy ($\Gamma_A = \Gamma_B$) in the dilute vacancy limit, as it does not exhibit the Kirkendall effect. Hence concentration profiles determined for diffusion couples containing discrete vacancy sources will be identical to those predicted within the continuous source approximation in kinetically ideal alloys.

The time dependence of the concentration profile of a diffusion couple with discrete vacancy sources should converge to that predicted by the uniform source approximation as the density of discrete sources is increased. A measure of the deviation between simulation results that account for explicit sources and the solution using the continuous source approximation is a norm of the difference in the concentration profiles defined as

$$N_{\Delta C} = \sqrt{\int_0^L \left( \bar{C}_B(\bar{y}) - C_{\text{cs}}^B(\bar{y}) \right)^2 \, d\bar{y}}$$

(77)
where \( \hat{L} \) is the dimensionless length of the one-dimensional diffusion couple (i.e., \( \hat{L} = 1 \)), \( \hat{C}_B(\hat{y}) \) is the concentration from the simulation with discrete sources and sinks and \( C^{sim}_{B}(\hat{y}) \) is the concentration predicted within the uniform source-sink approximation.

Fig. 13 illustrates the norm, Eq. (77), as a function of a dimensionless time, \( \hat{t} \), for diffusion couples having different numbers of grains with grain boundaries acting as ideal vacancy sources. The time evolution of the norm \( N_{\Delta \hat{C}} \) for thermodynamically ideal alloys depends on the \( \Gamma_B/\Gamma_A \) ratio when plotted versus the dimensionless time, defined according to

\[
\hat{t} = \hat{t} \frac{a^2 \Gamma_A}{L^2},
\]  

where \( L \) is the total length of the diffusion couple and \( a \) is the atomic hop distance. The actual time dependence of the norm for a thermodynamically ideal alloy can be extracted from Fig. 13 by multiplying the dimensionless time \( \hat{t} \) by \( L^2/a^2 \Gamma_A \). Since the initial concentration profiles are identical for

![Diagram](image1.png)

**Fig. 13.** The norm of the difference between the concentration profiles in systems with discrete sources and that in a system with continuous sources as a function of dimensionless time for a variety of source densities for thermodynamically ideal alloys with (a) \( \Gamma_B = 10 \times \Gamma_A \) and (b) \( \Gamma_B = 100 \times \Gamma_A \).
each diffusion couple (left half pure B and right half pure A), the norm in all cases is zero at t=0. As diffusion proceeds, \( \bar{N}_{DC} \) initially increases, reaches a maximum and then decreases to zero with increasing time. In the long time limit, all diffusion couples converge to a uniform concentration profile. The norms in Fig. 13 are overall smaller and converge more rapidly to zero as the source density increases, showing, as expected, that the time evolution of the concentration profile approaches that predicted by the continuous source approximation with increasing density of vacancy sources. Fig. 13 also shows that the deviation between the discrete vacancy source concentration profile and that predicted within the continuous source approximation increases with the \( I_B/I_A \) ratio.

It is also instructive to consider the time required to reach equilibrium in a planar diffusion couple as a function of the number of discrete vacancy sources. The following norm

\[
\eta = \frac{\sqrt{\int_0^L (\hat{C}_B(y, t) - \hat{C}_B^{eq})^2 dy}}{\sqrt{\int_0^L (\hat{C}_B(y, 0) - \hat{C}_B^{eq})^2 dy}}
\]

measures the deviation of a diffusion couple from its final equilibrium state characterized by a uniform concentration of all its components: in the initial state \( \eta = 1 \) while in the final equilibrium state \( \eta = 0 \). Fig. 14 illustrates the elapsed time (normalized according to Eq. (78)) for the norm, Eq. (79), to reach \( \eta = 0.001 \) as a function of the number of grains in a one-dimensional diffusion couple. The limiting case corresponds to the continuous source (cs) approximation. The simulations were performed for a diffusion couple of length \( L = 1 \) \( \mu \)m using values for \( C_A, a \) and the vacancy concentration \( x_V \) representative of Al. The fast diffuser \( B \) was assumed to have a hop frequency \( I_B = 10 \times I_A \). As is clear from Fig. 14, the time to reach equilibrium converges quite rapidly to that of the continuous source approximation, leveling off around 10 grains (e.g., 11 discrete vacancy sources). For this particular simulation, this implies that continuous source approximation behavior is nearly reached when planar vacancy sources are separated from each other by 100 nm. Larger separations between vacancy sources for this model system lead to equilibration times that are sensitive to the inter-vacancy source spacing. These results clearly illustrate a transition of diffusion behavior from a perfect-crystal model to a continuous-vacancy-source model as the vacancy source density increases.

**Fig. 14.** Elapsed time to reach the final equilibrium state of a planar diffusion couple (defined by \( \eta = 0.001 \)) as a function of the number of grains that act as discrete vacancy sources. The fast diffuser hop frequency is 10 times larger than that of the slow diffuser (\( I_B = 10 \times I_A \)). The continuous source approximation is denoted by (cs).
4. Conclusion

The aim of this paper has been to clarify the link between macroscopic transport properties in binary substitutional alloys and atomistic hop frequencies that can be calculated from first principles. We have restricted the focus to crystalline binary substitutional solids in which diffusion is mediated by vacancies. The presence of vacancies in a binary crystalline alloy renders the solid a ternary system. A complicating factor in real substitutional alloys is the presence of vacancy sources and sinks, which can annihilate and create vacancies. Diffusion in a binary substitutional alloy is sensitive to the density of vacancy sources and sinks and different metrics for diffusion can be formulated depending on whether the alloy more closely approximates a perfect crystal or whether it can be assumed to contain a continuous distribution of vacancy sources and sinks to maintain an equilibrium vacancy concentration throughout the solid.

Our starting point has been a description of a formalism to calculate kinetic-transport coefficients in a perfect crystal without vacancy sources and sinks. The diffusion coefficients in non-dilute substitutional alloys are derived from a matrix product of a thermodynamic factor and a kinetic factor. Here, we have derived expressions relating the thermodynamic factor to the Hessian of the free energy of substitutional solids and shown how this Hessian can be calculated within the grand canonical ensemble using Monte Carlo simulations applied to a cluster expansion of the configurational energy of the alloy. The kinetic factor is a matrix of Onsager kinetic-transport coefficients, which can be calculated with Kubo-Green expressions, first derived by Allnatt [67–69] for diffusion in a perfect crystal. These expressions are based on ensemble averages of the square of the displacement of the center of mass of diffusing A and B atoms at equilibrium. With this statistical mechanical formalism laid out, it is possible to predict perfect-crystal diffusion coefficients of binary substitutional alloys from first principles using well-established techniques from alloy theory based on the cluster expansion formalism.

While the matrix of diffusion coefficients describing transport in a crystalline binary alloy is essential input for realistic continuum simulations of diffusional processes, it does not provide direct information about the dominant modes of diffusion in a substitutional solid, namely intermixing and vacancy fluxes that can lead to the Kirkendall effect. In this respect Kehr et al. [51] demonstrated that, for perfect crystalline binary solids having regular solution model thermodynamics, the eigenvalues of the diffusion coefficient matrix are related to the vacancy mobility and the rate of intermixing in the dilute-vacancy limit. Here, we have extended the analysis of Kehr et al. [51] and introduced two additional metrics derived from the diffusion coefficient matrix, $\phi$ and $\delta$, that provide additional insight into the dominant modes of binary substitutional diffusion. These metrics, which serve to characterize the Kirkendall effect, have been defined such that they also measure the deviation of the alloy from both thermodynamic and kinetic ideality.

Knowledge of perfect crystal kinetic-transport coefficients and diffusion coefficients also allows us to analyze diffusion in solids containing vacancy sources and sinks such as grain boundaries and climbing dislocations. This is possible if any contribution to transport from short-circuit diffusion due to crystalline defects can be neglected. At the continuum level, two approaches were described to account for vacancy sources and sinks. The first, which is the standard textbook treatment of substitutional diffusion, relies on the assumption that the solid contains a sufficiently dense vacancy source and sink distribution to regulate an equilibrium vacancy concentration throughout the solid. Within this approximation, two metrics are defined: One measures the drift of the crystal frame of reference relative to the laboratory frame of reference and a second describes interdiffusion within the laboratory frame of reference. An alternative approach to account for vacancy sources and sinks within a continuum description is to assume a discrete distribution of sources which serve as boundary conditions to the Fickian flux expressions for a perfect crystal.

We have shown here that the interdiffusion coefficient in the continuous source/sink approximation differs substantially from the intermixing coefficient of a perfect crystal in alloys with a high susceptibility to the Kirkendall effect. In a perfect crystal, intermixing requires both the fast and slow diffuser to migrate in order to dissipate a concentration gradient among the components of the solid. In a solid containing a continuous distribution of vacancy sources and sinks, interdiffusion can be
mediated by the Kirkendall effect whereby only the fast diffuser migrates and the slow diffuser is redistributed in space by a rigid shift of the lattice.

With the formalism of substitutional diffusion established, we are now in a position to explore a wide variety of alloys from first principles to shed light on the relationship between complex atomic hop mechanisms and macroscopic metrics for diffusion. This will provide guidance in the development of physically motivated mobility matrices to conveniently and self-consistently parameterize experimental diffusion data [117]. At the macroscopic level, three-dimensional continuum simulations of perfect crystals surrounded and decorated by one and two dimensional vacancy sources and sinks will resolve important questions about the precise role of these defects on diffusion. Such simulations will indicate critical densities of sources required before the commonly used continuous source/sink approximation becomes valid. They will also indicate how sensitive substitutional diffusion is to the nature of vacancy sources and sinks (e.g., one dimensional versus two dimensional) [120].

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Appendix A. Here we derive an expression for the thermodynamic factor for perfect crystal diffusion in terms of particle number fluctuations that can be calculated with grand canonical Monte Carlo simulations. The thermodynamic factor is defined by

$$\tilde{\Theta} = \frac{1}{k_B T} \begin{pmatrix} \frac{\partial \mu_A}{\partial x_A} & \frac{\partial \mu_A}{\partial x_B} \\ \frac{\partial \mu_B}{\partial x_A} & \frac{\partial \mu_B}{\partial x_B} \end{pmatrix}. \quad (80)$$

It is convenient to consider the inverse of this matrix, which can be expressed as

$$\tilde{\Theta}^{-1} = k_B T \begin{pmatrix} \frac{\partial x_A}{\partial \mu_A} & \frac{\partial x_B}{\partial \mu_A} \\ \frac{\partial x_A}{\partial \mu_B} & \frac{\partial x_B}{\partial \mu_B} \end{pmatrix}. \quad (81)$$

Within the grand canonical ensemble, this matrix can be expressed in terms of the variances of the number of A and B atoms within the perfect crystal at fixed $\mu_A$ and $\mu_B$ according to (see for example Hill [99])

$$\tilde{\Theta}^{-1} = \frac{1}{M} \begin{pmatrix} \langle N_A^2 \rangle - \langle N_A \rangle^2 & \langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle \\ \langle N_A N_B \rangle - \langle N_A \rangle \langle N_B \rangle & \langle N_B^2 \rangle - \langle N_B \rangle^2 \end{pmatrix}. \quad (82)$$

Taking the inverse of this matrix yields Eq. (24).

Appendix B. Moleko et al. [79] derived a set of analytical expressions for $\tilde{L}_{ij}$ for a random alloy in which $\Gamma_A \neq \Gamma_B$. In the notation and formalism developed here, these expressions take the form

$$\tilde{L}_{AA} = x_V x_A \rho a^2 \Gamma_A \left(1 - \frac{2x_B \Gamma_A}{\Lambda} \right),$$

$$\tilde{L}_{BB} = x_V x_B \rho a^2 \Gamma_B \left(1 - \frac{2x_A \Gamma_B}{\Lambda} \right),$$

$$\tilde{L}_{AB} = \frac{2 \rho a^2 \Gamma_A \Gamma_B x_V x_A x_B}{\Lambda}.$$ \quad (83)
where

\[
\Lambda = \frac{1}{2} (F + 2)(x_A \Gamma_A + x_B \Gamma_B) - \Gamma_A - \Gamma_B + 2(x_A \Gamma_B + x_B \Gamma_A) \\
+ \sqrt{\left( \frac{1}{2} (F + 2)(x_A \Gamma_A + x_B \Gamma_B) - \Gamma_A - \Gamma_B \right)^2 + 2F \Gamma_A \Gamma_B}
\]

(84)

and

\[
F = \frac{2f}{1 - f}.
\]

(85)

As with the kinetically ideal expressions for \( \tilde{L}_{ij} \), \( f \) is the correlation factor for a single component solid having the crystal structure of the \( A-B \) alloy, and is a function of \( x_i \).

As has been shown by Hartmann et al. [55] and illustrated in Fig. 2, these coefficients agree very well with kinetic Monte Carlo approximations of the \( \tilde{L}_{ij} \). The circles in Fig. 2 were calculated using a Monte Carlo cell having dimensions of \( 8 \times 8 \times 8 \) primitive fcc unit cells, containing one vacancy. This means that a vacancy never meets other vacancies in these simulations, which is a reasonable approximation in the dilute vacancy limit.

The analytical expressions, Eq. (83), show that for a thermodynamically ideal alloy, the \( \tilde{L}_{ij} \) scale linearly with the vacancy concentration for dilute vacancy concentrations. This dependence on vacancy concentration should persist for thermodynamically non-ideal alloys as long interactions among different vacancies are negligible (i.e. atomic transport is dominated by single vacancy hops). The \( \tilde{L}_{ij} \) can therefore be calculated at a convenient vacancy concentration in kinetic Monte Carlo simulations and then adjusted to a value consistent with the actual vacancy concentration by multiplying the calculated \( \tilde{L}_{ij} \) by \( (x_{V_{\text{actual}}} / x_{V_{\text{simulation}}}) \) where \( x_{V_{\text{simulation}}} \) is the vacancy concentration in the simulation cell and \( x_{V_{\text{actual}}} \) is the vacancy concentration in the actual system.

Both ensemble averages and time averages were performed to numerically evaluate the Kubo-Green expressions, Eq. (32), plotted in Fig. 2. At each concentration, 4000 different random initial configurations were used. For each one of these initial configurations, 1000 Monte Carlo passes were performed, of which the first 500 were equilibriation steps for each random starting configuration. Each Monte Carlo pass corresponds to a sequence of hops of the vacancy equal to the number of lattice sites formed, of which the first 500 were equilibriation steps for each random starting configuration. Each Monte Carlo pass corresponds to a sequence of hops of the vacancy equal to the number of lattice sites in the simulation cell. Averaging was performed by sampling values for \( \tilde{L}_{ij} \) at different times for all the different initial configurations.

**Appendix C.** In this appendix, we show that for alloys having a dilute vacancy concentration, \( \lambda^- \) and \( \delta \) scale with \( x_V \), while \( \lambda^+ \) and \( \phi \) do not. We demonstrate this for alloys in which the kinetic-transport coefficients \( \tilde{L}_{ij} \) are proportional to \( x_V \) in the dilute vacancy limit (see Appendix B).

It is useful to express the chemical potentials more explicitly in terms of the concentration variables. \( \tilde{\mu}_A = \mu_A - \mu_V \), where both \( \mu_V \) and \( \mu_A \) can be written as \( \mu_V(T) + k_B T \ln(\gamma_V x_V) \) and \( \mu_A(T) + k_B T \ln(\gamma_A x_A) \), respectively. The activity coefficients \( \gamma_V \) and \( \gamma_A \) are each a function of \( x_A \) and \( x_B \) and serve as a measure for the deviation from ideality (i.e., \( \gamma_V \) and \( \gamma_A \) equal 1 in an ideal solution). The chemical potential \( \tilde{\mu}_A \) can be expressed as

\[
\tilde{\mu}_A = \mu_A^0 - \mu_V^0 + k_B T \ln(\gamma_A) + k_B T \ln x_A - k_B T \ln(\gamma_V) - k_B T \ln x_V.
\]

(86)

\( \tilde{\mu}_B \) can be written in a similar way. The natural logarithms of the activity coefficients \( \gamma_i \) are referred to as excess partial molar free energies and can be Taylor expanded in terms of the independent concentration variables around a reference concentration [118,119]. Our scaling analysis of \( \lambda^- \), \( \lambda^+ \), \( \delta \) and \( \phi \) relies on the assumption that the Taylor expansions of \( \ln \gamma_i \) do not diverge in the limit of a dilute vacancy concentration \( x_V \rightarrow 0 \) (i.e., they do not scale as \( \ln x_V \) or \( 1/x_V^b \) where \( b \) is a positive number). We will refer to such alloys as “thermodynamically well-behaved.”

Using expressions for \( \tilde{\mu}_i \) in the form of Eq. (86), we can write the elements of the thermodynamic factor matrix such as \( \Theta_{AA} \) as
\[ \bar{\Theta}_{AA} = \frac{\partial \left( \frac{\mu_A}{k_B T} \right)}{\partial x_A} = \frac{1}{x_V} + \frac{1}{x_A} + f_{AA}, \]  
(87)

where \( f_{AA} \) is defined according to

\[ f_{ij} = \frac{\partial \ln \gamma_i}{\partial x_j} - \frac{\partial \ln \gamma_V}{\partial x_j}. \]  
(88)

Note that all partial derivatives with respect to \( x_A \) are taken at constant \( x_B \) and constant number of lattice sites \( M \). In a similar manner

\[ \bar{\Theta}_{BB} = \frac{\partial \left( \frac{\mu_B}{k_B T} \right)}{\partial x_B} = \frac{1}{x_V} + \frac{1}{x_B} + f_{BB}, \]  
(89)

While

\[ \bar{\Theta}_{AB} = \frac{\partial \left( \frac{\mu_A}{k_B T} \right)}{\partial x_B} = \frac{1}{x_V} + f_{AB}, \]  
(90)

\[ \bar{\Theta}_{BA} = \frac{\partial \left( \frac{\mu_B}{k_B T} \right)}{\partial x_A} = \frac{1}{x_V} + f_{BA}. \]

With the elements of the thermodynamic factor matrix written as in Eqs. (87), (89) and (90), we can express the elements of the diffusion coefficient matrix as

\[ D_{AA} = \frac{1}{x_V} \left( \bar{L}_{AA} + \bar{L}_{AB} \right) + \bar{L}_{AA} \left( \frac{1}{x_A} + f_{AA} \right) + \bar{L}_{AB} f_{AB}, \]
\[ D_{AB} = \frac{1}{x_V} \left( \bar{L}_{AA} + \bar{L}_{AB} \right) + \bar{L}_{AA} f_{AB} + \bar{L}_{AB} \left( \frac{1}{x_B} + f_{BB} \right), \]
\[ D_{BA} = \frac{1}{x_V} \left( \bar{L}_{BB} + \bar{L}_{AB} \right) + \bar{L}_{BB} f_{AB} + \bar{L}_{AB} \left( \frac{1}{x_A} + f_{AA} \right), \]
\[ D_{BB} = \frac{1}{x_V} \left( \bar{L}_{BB} + \bar{L}_{AB} \right) + \bar{L}_{BB} \left( \frac{1}{x_B} + f_{BB} \right) + \bar{L}_{AB} f_{AB}. \]
(91)

We can then use these expressions for \( D_{ij} \) to determine the scaling with vacancy concentration of \( \delta, \phi, \lambda^- \) and \( \lambda^+ \).

**C.1. Scaling of \( \delta \)**

Substituting the above \( D_{ij} \) into \( \delta = D_{BB} + D_{AB} - D_{BA} - D_{AA} \), we obtain

\[ \delta = - (\bar{L}_{AA} + \bar{L}_{AB}) \left( \frac{1}{x_A} + f_{AA} \right) + (\bar{L}_{AB} + \bar{L}_{BB}) \left( \frac{1}{x_B} + f_{BB} \right) - (\bar{L}_{BB} - \bar{L}_{AA}) f_{AB}. \]  
(92)

In the dilute vacancy limit, the \( \bar{L}_{ij} \) scale linearly with the vacancy concentration \( x_V \) while the coefficients of \( \bar{L}_{ij} \) in this expression to first order should be independent of \( x_V \). This is true for the terms \( 1/x_A \) and \( 1/x_B \) and should be true for the \( f_{ij} \) if the alloy is thermodynamically well-behaved as defined above. Hence \( \delta \) to first order scales linearly with \( x_V \).

**C.2. Scaling of \( \phi \)**

The parameter \( \phi \) is defined as the ratio of \( D_{BA} \), an off-diagonal diffusion coefficient for perfect crystal binary diffusion, and the sum of the off-diagonal diffusion coefficients \( D_{AB} + D_{BA} \). Using Eq. (91), we can write
The first term in Eq. (93), \((\tilde{L}_{AA} + \tilde{L}_{BB} + 2\tilde{L}_{AB})/x_V\), is independent of the vacancy concentration, as the \(\tilde{L}_y\) in the dilute vacancy limit are proportional to \(x_V\). The other terms do scale linearly with \(x_V\) in the dilute vacancy limit. Likewise for \(D_{BA}\), the first term in Eq. (91), \((\tilde{L}_{BB} + \tilde{L}_{AB})/x_V\), is independent of \(x_V\). The ratio of \(D_{BA}\) to \(D_{AB} + D_{BA}\) therefore does not scale with the vacancy concentration.

C.3. Scaling of \(\lambda^+\) and \(\lambda^-\)

To determine the scaling with \(x_V\) of \(\lambda^+\) and \(\lambda^-\), we follow the same approach used by Kehr et al. [51], which they applied to a regular-solution model. The eigenvalues of the diffusion coefficient matrix \(D_{ij}\) are related to its elements according to

\[
\tilde{L}_{ij} = D_{ij} \left( 1 + \frac{4 D_{AB} D_{BA} - D_{AA} D_{BB}}{(D_{AA} + D_{BB})^2} \right) \tag{94}
\]

Using the Eq. (91) for the \(D_{ij}\), the following relations can be derived

\[
D_{AA} + D_{BB} = \frac{1}{x_V} (\tilde{L}_{AA} + \tilde{L}_{BB} + 2\tilde{L}_{AB}) + O(x_V), \tag{95}
\]

which to first order in \(x_V\) is independent of the vacancy concentration, while

\[
D_{AB} D_{BA} - D_{AA} D_{BB} = -\frac{1}{x_V} (\tilde{L}_{AA} \tilde{L}_{BB} - \tilde{L}_{AB}^2) \times \left( \frac{1}{x_A} + \frac{1}{x_B} + f_{AA} + f_{BB} - 2f_{AB} \right) + O(x_V^2). \tag{96}
\]

This expression scales linearly with the vacancy concentration \(x_V\). The second factor in Eq. (96) can be written as partial derivatives of chemical potentials according to

\[
\Theta_{mix} = \frac{1}{k_B T} \left( \frac{\partial (\mu_A - \tilde{\mu}_A)}{\partial x_A} - \frac{\partial (\mu_B - \tilde{\mu}_B)}{\partial x_B} \right) = \frac{1}{k_B T} \left( \frac{\partial^2 g}{\partial x_A^2} + \frac{\partial^2 g}{\partial x_B^2} - 2 \frac{\partial^2 g}{\partial x_A \partial x_B} \right), \tag{97}
\]

where the second equality follows from the fact that \(\tilde{\mu}_i = \partial g / \partial x_i\) with \(g(x_A, x_B)\) being the free energy normalized per crystal site of the solid containing \(A, B\) and vacancies. The second equality in Eq. (97) shows that \(\Theta_{mix}\) is equal to the curvature of \(g(x_A, x_B)\) along the direction of a constant vacancy concentration, i.e., \(dx_A = -dx_B\).

The ratio of diffusion coefficients appearing under the square root in Eq. (94)

\[
\frac{D_{AB} D_{BA} - D_{AA} D_{BB}}{(D_{AA} + D_{BB})^2} = \frac{-x_V (\tilde{L}_{AA} \tilde{L}_{BB} - \tilde{L}_{AB}^2) \left( \frac{1}{x_A} + \frac{1}{x_B} + f_{AA} + f_{BB} - 2f_{AB} \right)}{(\tilde{L}_{AA} + \tilde{L}_{BB} + 2\tilde{L}_{AB})} + O(x_V^2) \tag{98}
\]

scales linearly with \(x_V\) and is much smaller than one. This remains true even when \(x_A \rightarrow 0\) or \(x_B \rightarrow 0\) where \(1/x_A\) or \(1/x_B\) diverge respectively. In these dilute limits, the alloy can be treated as thermodynamically ideal, allowing us to equate the kinetic coefficients \(L_{ij}\) to the analytical expressions of Moleko et al. [79] (see Eq. (83) in Appendix B). The analytical expressions of \(L_{AA}\) and \(L_{AB}\) contain a factor \(x_A\), which cancel the \(1/x_A\) term, while the analytical expressions of \(L_{BB}\) and \(L_{AB}\) contain a factor \(x_B\), which cancel the \(1/x_B\) term. Hence even in the dilute limits \((x_A \rightarrow 0\ or \ x_B \rightarrow 0)\), the ratio, Eq. (98), scales with \(x_V\) allowing us to Taylor expand the square root in Eq. (94) in the dilute vacancy limit. Keeping all terms up to order \(x_V\), yields expressions, similar to the results of Kehr et al. [51].

\[
\lambda^+ = \frac{1}{x_V} (\tilde{L}_{AA} + \tilde{L}_{BB} + 2\tilde{L}_{AB}) + O(x_V) \tag{99}
\]

and

\[
\lambda^- = \frac{\tilde{L}_{AA} \tilde{L}_{BB} - \tilde{L}_{AB}^2}{L_{AA} + 2L_{AB} + L_{BB}} \Theta_{mix} + O(x_V^2). \tag{100}
\]
This shows that for dilute vacancy concentrations, $\lambda^+$ is independent of $x_V$, while $\lambda^-$ is linearly proportional to $x_V$.

As was pointed out by Kehr et al. [51], the expression for $\lambda^-$, Eq. (100), can be viewed as a factorization of the perfect-crystal interdiffusion coefficient into a product of a kinetic factor and a thermodynamic factor, $\theta_{mix}$. The derivation here extends the treatment of Kehr et al. [51] beyond a simple regular solution model.

**Appendix D.** Here we derive relationships between the matrix of diffusion coefficients, $D_{AA}$, $D_{AB}$, $D_{BA}$ and $D_{BB}$, and the metrics for perfect crystal substitutional diffusion, $\lambda^+$, $\lambda^-$, $\delta$ and $\phi$. The parameters $\lambda^+$ and $\lambda^-$ are the eigenvalues of the diffusion coefficient matrix and are given by Eq. (94) while $\delta$ and $\phi$ are defined in terms of the $D_0$ according to Eqs. (38) and (39). By inverting these four relations, the following expressions can be derived for $D_{AA}$, $D_{AB}$, $D_{BA}$ and $D_{BB}$ in terms of $\lambda^+$, $\lambda^-$, $\delta$ and $\phi$.

\[
D_{AA} = \frac{1}{2} \left[ (\lambda^+ + \lambda^-) - \delta - \left( \frac{2\phi - 1}{1 - \phi} \right) D_{AB} \right]
\]
\[
D_{BB} = \frac{1}{2} \left[ (\lambda^+ + \lambda^-) + \delta + \left( \frac{2\phi - 1}{1 - \phi} \right) D_{AB} \right]
\]
\[
D_{AB} = (1 - \phi) \left[ -2\phi + 1 - \delta + \sqrt{\left( \lambda^+ - \lambda^- \right)^2 - 4\phi(1 - \phi)\delta^2} \right]
\]
\[
D_{BA} = \frac{\phi}{1 - \phi} D_{AB}.
\]

**References**
