Diffusion and segregation at surfaces and interfaces

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It is shown how certain methods developed to treat elementary excitations at surfaces and interfaces can be applied to diffusion and segregation in the presence of surfaces and interfaces.

I. INTRODUCTION

A wide variety of methods is now being used to calculate electronic, vibrational, and magnetic states at surfaces and interfaces. Exact formal solutions for the single-particle excitations can be derived for systems that can be described in terms of pairwise interactions of finite range: electrons in the tight-binding model, phonons in the Born—von Kármán model, and magnons in the Hiesenberg model. Kalkstein and Soven1 showed how to apply Green’s-function methods to this problem, and more recently, several related elaborations and extensions of such Green’s-function approaches have appeared. Without attempting to be exhaustive, we cite here the transfer matrix formalism of Falicov and Yndurain,2 the work of Dy and co-workers,3 and the matrix-continued-fraction development of two of the present authors,4 which will be referred to as MK hereafter.

A simple way to view these methods is as mappings onto linear chains. It is assumed that periodicity is retained parallel to the surface or interface, so that a transform with respect to a two-dimensional wave vector \( \mathbf{q} \), can be performed. For each value of \( \mathbf{q} \), the interplanar elements of the Hamiltonian matrix are zero everywhere except on and near the diagonal, “near” being specified by the particular surface or interface and the range of the interatomic interactions. Surface or interfacial properties are then determined by solving for the Green’s functions of \( \mathbf{q} \)-dependent semi-infinite or infinite linear chains.

In this paper, we show how the same methods can be applied to diffusion and segregation at surfaces and interfaces when these problems are treated in a continuous-time random-walk formulation.5—7 The mathematical formalism is similar to that for elementary excitations, except that the operators are not Hermitian and a Laplace transform with respect to time is taken instead of a Fourier transform. The general theory is outlined in Sec. II, using the notation and results of MK. Specification to an fcc (001) surface, with the diffusing species occupying substitutional sites (e.g., vacancies) or octahedral interstitial sites, and allowing only first-nearest-neighbor hopping, is provided in Sec. III. Applications to thin films are discussed in Sec. IV, where it is shown that enhanced surface layer diffusion can occur in special cases.

The purpose of this paper is to outline and illustrate the mathematical framework of an atomistic description of diffusion and segregation when surfaces or interfaces are present. For clarity of exposition, the theory is presented specifically for surfaces, and two simple choices of initial conditions are considered in the section dealing with an fcc (001) surface. Extensions to interfaces and to other initial conditions are formally straightforward.

Grain boundary diffusion is an area of particular interest for subsequent applications.

II. GENERAL FORMALISM

We consider a crystalline solid in which diffusing particles may move from site to site on a periodic lattice of their own. For vacancies in a Bravais crystal, for example, the diffusion lattice is the same as the crystalline lattice. This is also true for \( \langle 100 \rangle \)-split or dumbbell self-interstitials in fcc metals like Cu and Al,8,9 although for this case there is the additional complication of three possible dumbbell orientations at each site; diffusion of these self-interstitials involves both motion and dumbbell reorientation. We will not explicitly treat
such problems with additional degrees of freedom, but they can be handled within our framework by simply associating a basis with each site. In other systems, the diffusion lattice may be translated from the underlying crystal lattice. This occurs for the octahedral interstitial sites in an fcc crystal, which form an fcc lattice which is displaced from the original by \( \frac{1}{2} \) a cube edge or \( \frac{1}{2} \) the body diagonal. The tetrahedral interstitial sites in an fcc crystal provide a third kind of example; they form a simple cubic lattice of available positions.\(^{10}\)

The lattice of allowed sites for the diffusing particles will be specified by indices \( L, l \), where \( L \)

\[
\delta(L, L')\delta(l, l')\delta(t) = G(L, l, t; L', l', 0) - \sum_{L_1, l_1} \int_0^t d\tau \Psi(L, l; L_1, l_1; \tau) G(L_1, l_1, t - \tau; L', l', 0) .
\]

(1)

The probability that the particle is at \( L, l \) at time \( t \), given that it occupied \( L', l' \) at 0, is denoted by \( P(L, l, t; L', l', 0) \); it will be zero if it arrived at some previous time \( t - \tau \) and stayed for a period \( \tau \),

\[
P(L, l, t; L', l', 0) = \int_0^t d\tau G(L, l, t - \tau; L', l', 0) \Phi(L, l; \tau)
\]

(2)

\[
\Phi(L, l; \tau) = 1 - \sum_{L_1, l_1} \int_0^\tau d\tau \Psi(L_1, l_1; L, l; \tau') .
\]

(3)

The constraint upon the waiting-time density function \( \Psi \) is that a jump must occur to some neighboring site at some time,

\[
1 = \sum_{L_1, l_1} \int_0^\infty dt \Psi(L_1, l_1; L, l; t) .
\]

(4)

As in MK,\(^4\) a two-dimensional transform is taken with respect to a surface wave vector \( \vec{q}_s \) for the diffusion lattice,

\[
f(L, L'; \vec{q}_s) = \frac{1}{N_s} \sum_{L''} e^{i\vec{q}_s \cdot (L - L')} \times f(L, l; L', l') ,
\]

(5)

where \( N_s \to \infty \) is the number of atoms in a layer.

denotes the plane parallel to the surface or interface, and \( l \) position within the plane. For simplicity, we will assume a Bravais diffusion lattice, but non-Bravais lattices can be treated by adding a basis and its attendant extra indices. Let \( \Psi(L, l; L', l'; t)dt \) be the probability that a particle jumps from site \( L', l' \) to \( L, l \) in the time interval \((t, t + dt)\) given that it was at \( L', l' \) at time \( t = 0 \). A Green’s function \( G(L, l, t; L', l', 0) \) is defined as the probability that a particle arrives at site \( L, l \) at time \( t \) given that it was at \( L', l' \) at time \( 0 \). The particle will make its last jump to \( L, l \) from a neighboring site \( L_1, l_1 \), so \( G \) obeys the equation

\[
f(\vec{q}_s) = \int_0^\infty dt e^{-\beta t f(t) .}
\]

(6)

The transformed equations for \( G \) and \( P \) are

\[
\delta(L, L') = \sum_{L_1} [\delta(L, L_1) - \Psi(L_1, l_1; \vec{q}_s, s)]
\]

\[
\times G(L_1, L'; \vec{q}_s, s) ,
\]

(7)

\[
P(L, l; \vec{q}_s, s) = \phi_L(s) G(L, l; \vec{q}_s, s) ,
\]

(8)

\[
\phi_L(s) = \frac{1}{N_s} \sum_L \Phi(L, l; s) = \Phi(L, l, s) .
\]

(9)

The functions \( \Phi(L, l, s) \) do not depend on \( l \), the position in plane \( L \), because of our assumption of a Bravais diffusion lattice. We will outline how to solve Eq. (7) for a semi-infinite solid, following the derivation in MK. Interfaces can be treated along the same lines, as shown in Appendix B of MK.

The elements of the inverse of \( G \) in Eq. (7) are nonzero only on and near the diagonal,
For the simplest case, where the particles can jump to neighboring sites only in the same plane or in nearest-neighbor planes, $G^{-1}$ is tridiagonal,

$$G^{-1}(L,L';q_z,s) = [1 - \Psi(L,L';q_z,s)] \delta(L,L') - \Psi(L,L';q_z,s) [\delta(L-1,L') + \delta(L+1,L')] . \tag{11}$$

This is the inverse Green's function for a random walk on a linear chain with $q_z$-dependent nearest-neighbor jump probabilities.

In general, $G^{-1}$ is block-tridiagonal as in MK,

$$G^{-1} = \begin{bmatrix} 1 - A_{i} & -B_{i} & 0 & 0 \\ -B_{i} & 1 - A_{i} & -B_{i+1} & 0 \\ 0 & -B_{i+1} & 1 - A_{i+1} & -B_{i+2} \\ 0 & 0 & -B_{i+2} & 1 - A_{i+2} \\ \vdots & & & \end{bmatrix} , \tag{12}$$

where $A_{i}, B_{i}, \bar{B}_{i}$ are $(n-1) \times (n-1)$ matrices of elements $\Psi(L,L';q_z,s)$, $1$ is the unit matrix, and $B_{i} (\bar{B}_{i})$ is lower (upper) triangular. Note that unlike in the elementary excitation problem, $G^{-1}$ is not Hermitian. $A_{i} \neq A_{i}'$ and $B_{i} \neq B_{i}'$. We block $G$ in the same way as its inverse, so that $G_{11}$ is the upper left $(n-1) \times (n-1)$ block, $G_{12}$ the block corresponding to $-B_{1}$, and so forth. Note that the Green's function $G$ is not block-tridiagonal, that is, $G_{ij} \neq 0$ for $|i-j| > 1$.

It is shown in MK that the upper left or surface block of $G$ is the solution of a recursive sequence of equations,

$$g_{1} = G_{11}(q_z,s) = (1 - A_{i} - B_{i})^{-1} , \tag{13a}$$

$$g_{2} = (1 - A_{2} - B_{2} - B_{2})^{-1} , \tag{13b}$$

$$\vdots$$

It is assumed that the jump probability matrices $A_{i}, B_{i}, \bar{B}_{i}$ settle down to their bulk values $A_{b}, B_{b}, \bar{B}_{b}$ at some level $m$, that is, after $(m-1) \times (n-1)$ planes. The sequence of equations [(13a), (13b), ...] is thus terminated at level $m$ by what we will call the terminated bulk Green's function $g_{b}$,

$$g_{m} = g_{b} = (1 - A_{b} - B_{b} - B_{b})^{-1} . \tag{14}$$

Other blocks of the Green's function can be derived diagrammatically, as shown by Dy et al.\textsuperscript{3} A set of "descending" Green's functions $\chi_{i}$ are defined as the solutions of the equations

$$\chi_{i} = (1 - A_{i} - \bar{B}_{i} - \bar{B}_{i} - \chi_{i+1}[B_{i+1}])^{-1} , \tag{15}$$

where for the semi-infinite solid, $\chi_{1} = (1 - A_{1})^{-1}$ and $\chi_{0} = 0$. The diagonal blocks of $G$ are given by

$$G_{ii} = (1 - A_{i} - B_{i} - g_{i} + \bar{B}_{i} - \bar{B}_{i} - \chi_{i+1}[B_{i+1}])^{-1}$$

$$= g_{i} + g_{i} \bar{B}_{i} - \chi_{i+1} \bar{B}_{i+1} - g_{i} \bar{B}_{i+1} . \tag{16}$$

For $i < i'$,

$$G_{ii'} = G_{ii} \bar{B}_{i} \bar{B}_{i+1} \cdots \bar{B}_{i'-1} \bar{B}_{i'} , \tag{17a}$$

while for $i > i'$,

$$G_{ii'} = G_{ii} \bar{B}_{i} \bar{B}_{i+1} \cdots \bar{B}_{i'-1} \bar{B}_{i'} \chi_{i'} \tag{17b}$$

We are now in a position, at least in principle, to determine any desired element $G(L,L';q_z,t)$ of the Green's function or, from Eqs. (2) or (8), the conditional probability function $P(L,L';q_z,t)$. Measureable quantities will generally involve initial conditions as well. For example, let $c(L,l,t)$ be the concentration of diffusing particles, that is, the probability that a particle is at site $L,l$ at time $t$. Suppose further that the initial concentration is a function only of depth, $c(L,l,t=0) = C_{0}(L)$. Then the concentration in plane $L$ at time $t$ is given by

$$C(L,t) = \frac{1}{N_{a}} \sum_{L'} c(L,l,t)$$

$$= \sum_{L'} P(L,L',q_z,0) \chi_{i} . \tag{18}$$

If $\bar{r}_{\alpha}$ is a unit vector in the $\alpha$ direction parallel to the surface, then a measure of planar diffusion is the mean-square distance a particle moves in a plane from its starting point in that plane in a time $t$,

$$\langle r_{\alpha}^{2}(L,t) \rangle = \sum_{L'} \left[ \bar{r}_{\alpha} \cdot [\bar{R}(L,L) - \bar{R}(L',L')] \right]^{2}$$

$$\times P(L,l,t;L',l',0)$$

$$= \left[ -\frac{d^{2}}{dq_{zz}} P(L,L',q_z,t) \right]_{q_z=0} . \tag{19}$$

The function $\Psi(L,l;L',l';t)$ was defined at the outset as the probability per unit time that a particle at $L',l'$ at time $t = 0$ will jump to site $L,l$ at time $t$. The form for $\Psi$ that we will use separates its spatial and time dependence,\textsuperscript{6,7}

$$\Psi(L,l;L',l';t) = J(L,l;L',l') \chi_{L}(t) , \tag{20}$$

$$\chi_{L}(t) = \frac{1}{\tau_{L}} e^{-t/\tau_{L}} . \tag{21}$$
The constraint in Eq. (4) that no site \( L', l' \) be a trap then requires that the sum of the relative probabilities for jumps from \( L', l' \) to its neighbors be one,

\[
1 = \sum_{L,l} f(L, l; L', l') \tag{22}
\]

and \( \psi_{L'} \) is normalized correctly as defined to integrate to unity over all time. The form given above for \( \Psi(L, l; L', l'; t) \) can be related to thermally activated hopping in a straightforward way.\(^7\)

The transforms needed in Eqs. (7) and (8) for \( G \) and \( P \) are

\[
\Psi(L, l'; \vec{q}_s, s) = J(L, l'; \vec{q}_s) \psi_{L'}(s) \tag{23}
\]

\[
\psi_{L'}(s) = \frac{1}{s \tau_{L'} + 1} \tag{24}
\]

\[
\phi_{L'}(s) = \frac{\tau_{L'}}{s \tau_{L'} + 1} \tag{25}
\]

An alternative form for the sum rule (22) is

\[
1 = \sum_{L} J(L, l; \vec{q}_s) = 0 .
\]

This sum rule for diffusion is analogous to the Goldstone rule that reflects translational invariance for lattice vibrations and spin waves. Substituting Eq. (25) in Eq. (8), we can express the Laplace transforms of the planar concentration and diffusion functions in Eqs. (18) and (19) in the form

\[
C(L, s) = \frac{\tau_{L'}}{s \tau_{L'} + 1} \sum_{L'} G(L, l'; \vec{q}_s = 0, s) C_{0}(L') \tag{26}
\]

\[
\langle r^2_a(L, s) \rangle = \frac{\tau_{L'}}{s \tau_{L'} + 1} \left[ - \frac{d^2}{dq_s^2} G(L, l; \vec{q}_s, s) \right]_{\vec{q}_s = 0} \tag{27}
\]

### III. THE fcc (001) SURFACE

To illustrate the general formalism described in the preceding section, we will show how it applies to the (001) surface of a fcc diffusion lattice. This lattice is appropriate for diffusion in a fcc crystal if the diffusing particles occupy the crystalline atomic sites (e.g., vacancies) or the octahedral interstitial sites, which are the cube centers and the midpoints of the cube edges. Nearest-neighbor hopping is assumed, and for simplicity it is also assumed that only the first plane differs from the bulk. This example then is one for which Eq. (11) applies, that is, for which the matrices \( A_i, B_i, \bar{B}_i \) in (12) and subsequent equations are in fact scalars, and the algebra reduces to that for a \( \vec{q}_s \)-dependent linear chain with nearest-neighbor hopping. Solutions for systems such as a fcc (110) surface where the matrices are 2 × 2's can be derived along the lines followed in Mostoller and Rajagopal.\(^{11}\) For cases where the blocks are \((n - 1) \times (n - 1)\)'s, \(n > 3\), \(g_b\) can be determined by transforming Eq. (14) to a \( \lambda \)-matrix problem.\(^3\)

The two-dimensional wave vector for the fcc (001) surface is

\[
\vec{q}_s = (2\pi/a)(\xi_1 + \xi_2, -\xi_1 + \xi_2, 0) \tag{28}
\]

where \(-\frac{1}{2} \leq \xi_1, \xi_2 \leq \frac{1}{2}\). In the bulk, the probability of jumping from a site to any of its twelve nearest neighbors is the same, so that \(j_b = J(L, l; L', l') = \frac{1}{12}\) between nearest neighbors in the bulk. For an atom at site \(L', l'\) in plane 1, there are four nearest neighbors in plane 1 and four in plane 2, so there are two relative jump probability parameters \(j_{11}\) and \(j_{21}\), and they must satisfy the sum rule

\[
1 = 4(j_{11} + j_{21}) .
\]

From Eqs. (5), (10)–(12), and (23) and (24), the functions \(A_i, B_i, \bar{B}_i\) are as follows:

\[
A_i(\vec{q}_s, s) = \frac{1}{3(s \tau_{1} + 1)} \left( j_{11}/j_b \right) \times (\cos^2 \pi \xi_1 + \cos^2 \pi \xi_2 - 1) \tag{29a}
\]

\[
\bar{B}_i(\vec{q}_s, s) = \frac{1}{3(s \tau_{1} + 1)} \times (j_{21}/j_b) \cos \pi \xi_1 \cos \pi \xi_2 \tag{29b}
\]

\[
A_b(\vec{q}_s, s) = \frac{1}{3(s \tau_{b} + 1)} \times (\cos^2 \pi \xi_1 + \cos^2 \pi \xi_2 - 1) \tag{29c}
\]

\[
B_b(\vec{q}_s, s) = \bar{B}_b(\vec{q}_s, s) = \frac{1}{3(s \tau_{b} + 1)} \cos \pi \xi_1 \cos \pi \xi_2 \tag{29d}
\]

\(A_i\) and \(\bar{B}_i\) are the only elements of \(Q^{-1}\) in Eq. (12) that differ from \(A_b\) and \(B_b\).

From Eqs. (13a) and (14), the surface and terminated bulk Green's functions are the solutions of

\[
g_1 = (1 - A_1 - B_b \bar{B}_b)^{-1} , \tag{30}
\]

\[
g_b = (1 - A_b - B_b^2)^{-1} . \tag{31}
\]

In addition, the intraplanar Green's function \(G_b\) for the infinite bulk crystal can be obtained from Eq. (16),

\[
G_b = (1 - B_b^2)^{-1} g_b \tag{32}
\]
The solution of these equations is straightforward, and we will give only some of the final results.

The appropriate dimensionless Laplace transform variable for the bulk is \( u = \tau_b \). For \( \frac{1}{3} \neq \xi_1 \) or \( \xi_2 \), the terminated bulk and bulk Green's functions are

\[
g_b = \frac{3(u+1)}{2\cos^2\xi_1 \cos^2\xi_2} \left[ 3(u+1) - (\cos^2\xi_1 + \cos^2\xi_2 - 1) - \sigma \right],
\]

\[
G_b = \frac{3(u+1)}{\sigma},
\]

\[
\sigma^2 = [3(u+1) - \{(\cos^2\xi_1 + \cos^2\xi_2)^2 - 1\}] \left\{ 3(u+1) - \{(\cos\pi\xi_1 - \cos\pi\xi_2)^2 - 1\} \right\}.
\]

In the limit \( \xi'_a \rightarrow 0 \) (\( \xi \rightarrow 0 \)) appropriate for the planar concentration and diffusion functions, \( g_b \) and \( G_b \) reduce to

\[
g_b = \frac{9}{2}(u+1) \left[ u + u_0 - [u(u+2u_0)]^{1/2} + u + 1 - \left( \frac{1}{3u} + 1 \right) \left[ u(u+2u_0) \right]^{1/2} \right] \pi^2 \xi^2,
\]

\[
G_b = \frac{u+1}{[u(u+2u_0)]^{1/2}} \left[ 1 - \frac{1}{3u} \pi^2 \xi^2 \right],
\]

where \( u_0 = \frac{2}{3} \).

To express the surface plane Green's function \( g_1 = G_{11} \) for \( \xi \rightarrow 0 \) in a compact fashion, we introduce some additional notation involving the surface:bulk ratios of the waiting times and relative jump probabilities,

\[
\alpha_1 = \tau_1 / \tau_b,
\]

\[
c_{L1} = j_{L1} / j_b = 12j_{L1}, \quad 3 = c_{11} + c_{21}.
\]

In terms of these ratios and of \( u = \tau_b \) and \( u_0 = \frac{2}{3} \), the Laplace transform of the surface plane Green's function can be written as

\[
G_{11} = (\alpha_1 u + 1) \left[ \frac{1}{D(u)} - \frac{1}{2} \pi^2 \xi^2 \frac{N(u)}{D^2(u)} \right],
\]

\[
D(u) = (\alpha_1 - \frac{1}{2} c_{21}) u + \frac{1}{2} c_{21} [u(u+2u_0)]^{1/2},
\]

\[
N(u) = 2 - c_{21} + c_{21} \left[ \frac{u(u+2u_0)}{u^{1/2}} \right].
\]

The quantities whose behavior with time we will discuss are surface concentrations and planar diffusion. For the former, two initial distributions will be considered. First, if all diffusing particles are initially in the surface layer, that is, if \( C_0(L) = c_0 \delta(L,1) \) in Eqs. (18) and (26), then the transform of the concentration in the surface layer, normalized to the initial value, is

\[
\Gamma_1(s) = \frac{C(1,s)}{c_0} = \frac{\tau_1}{\alpha_1 u + 1} G_{11}(\xi_s = 0, s).
\]

On the other hand, if the initial concentration is uniform throughout the semi-infinite solid, \( C_0(L) = c_{0b} \), we obtain

\[
\Gamma_b(s) = \frac{C(1,s)}{c_{0b}} = \frac{\tau_1}{\alpha_1 u + 1} \left[ \sum_{m=0}^{\infty} (B_b g_b)^m \right] \xi_s = 0
\]

\[
= \frac{\tau_1}{\alpha_1 u + 1} \left[ \frac{G_{11}}{1 - B_b g_b} \right] \xi_s = 0
\]

Substituting from (36) and (40) to (42), these reduce to

\[
\Gamma_1(s) = \frac{\tau_1}{D(u)},
\]

\[
\Gamma_b(s) = \frac{1}{2} \left[ \frac{u + 2u_0}{u^{1/2}} + 1 \right] \left[ \frac{\tau_1}{D(u)} \right]
\]

From Eqs. (27), (28), and (40), the surface planar diffusion transform is

\[
\langle r^2_{sa}(1,s) \rangle = \frac{1}{4} a^2 \tau_1 \frac{N(u)}{D^2(u)}.
\]

For comparison, we can also define mean-square planar diffusion distances for the bulk and the terminated bulk by substituting \( G_b \) and \( g_b \), respectively, for \( G(L,L) \) in Eq. (27),

\[
\langle R^2_{ba}(L) \rangle = \frac{\tau_b}{\tau_b + 1} \left[ -\frac{d^2}{d\xi^2} G_b(\xi_s,s) \right] \xi_s = 0
\]

\[
= \frac{1}{4} a^2 \tau_b \frac{1}{u^{3/2}(u + 2u_0)^{1/2}}
\]
\[
\langle r_{ba}(1,s) \rangle = \frac{\tau_b}{s \tau_b + 1} \left[ -\frac{d^2}{dq_{sa}^2} g_b(q_s,s) \right]_{q_s=0}
\]
\[
= \frac{9}{8} a^2 \tau_b \left[ \frac{1}{3u} + 1 \right] \left[ u(u+2u_0) \right]^{1/2}
- (u+1)
\]  
(49)

The inverse Laplace transforms of Eqs. (45)-(49) can all be written down in closed form. These general results are given in Appendix A. Several limiting cases of interest are discussed below.

We first consider the special case where there is no hopping from plane 1 to plane 2, that is, \(0 = j_{21} = c_{21}\). From Eqs. (41) and (42), we then have \(D(u) = \alpha_1 u = s \tau_1\) and \(N(u) = 2\). With the surface decoupled from the bulk, the mean-square surface planar diffusion distance increases linearly with time,

\[
\langle r_{a}(1,t) \rangle = \frac{1}{3} a^2 (t/\tau_1).
\]
(50)

If all diffusing particles are initially in the surface layer, then reassuringly, they remain there, \(\Gamma_s(t) = 1\). For a uniform initial concentration of the diffusing particles, however, the concentration in the surface plane increases without limit,

\[
\Gamma_b(t) = 1 + \frac{1}{3} \int_0^{2t/3 \tau_b} dx e^{-x[I_0(x)+I_1(x)]}.
\]
(51)

This occurs because we have assumed that there is no hopping from plane 1 to plane 2, but have allowed hopping from plane 2 to plane 1, \(j_{21} = j_b = \frac{1}{12}\). For the general case in which hopping from surface to bulk is allowed, we will discuss the short- and long-time limits of the general expressions given in Appendix A. At very short times, that is, for \(t/\tau_b \rightarrow 0\) and \(u_1(t/\tau_b) \rightarrow 0\), the concentration ratios and mean-square diffusion distances are linear in \(t\):

\[
\Gamma_s(t) = 1 - \frac{1}{3} c_{21}(t/\tau_1),
\]
(52)

\[
\Gamma_b(t) = 1 + \frac{1}{3}(\alpha_1 - c_{21})(t/\tau_1),
\]
(53)

\[
\langle r_{a}^2(1,t) \rangle = \frac{1}{3} a^2 \left( 1 - \frac{1}{3} c_{21}(t/\tau_1) \right),
\]
(54)

\[
\langle R_{ba}^2(L,t) \rangle = \frac{1}{3} a^2 (t/\tau_b).
\]
(55)

These results exhibit the behavior expected. The time scale for the surface properties \(\Gamma_s\), \(\Gamma_b\), and \(\langle r_{a}^2 \rangle\) is \(\tau_1\) at small times, and for the bulk property \(\langle R_{ba}^2 \rangle\) it is \(\tau_b\). If all diffusing particles are initially in the surface layer, then the surface concentration can only decrease, and \(\Gamma_s(t)\) does so. For a uniform initial concentration, however, Eq. (53) shows that \(\Gamma_b(t)\) may either increase or decrease according to whether \(\alpha_1 = \tau_1/\tau_b\) is greater or less than \(c_{21} = j_{21}/j_b\). The value of \(\langle r_{a}^2(1,t) \rangle\) is less than it would be for no hopping from plane 1 to plane 2 [cf. Eq. (50)] by the factor \(1 - c_{21}/3\), reflecting the fact that a particle in the surface plane can now hop into the bulk as well as in the surface.

The long-time behavior of the various functions can be found either directly from Eqs. (A1)-(A10), or by keeping only the most singular terms in their Laplace transforms in the limit \(s,u \rightarrow 0\), then inverting the transforms. The results are as follows:

\[
\Gamma_s(t) \sim \frac{\alpha_1}{c_{21}} \frac{1}{\left[ \pi(t/\tau_b)/3 \right]^{1/2}},
\]
(56)

\[
\Gamma_b(t) \sim \frac{\alpha_1}{c_{21}},
\]
(57)

\[
\langle r_{a}^2(1,t) \rangle \sim \frac{2\alpha_1}{c_{21}} a^2 \left( t/\tau_b \right)/12\pi)^{1/2},
\]
(58)

\[
\langle R_{ba}^2(L,t) \rangle \sim a^2 \left( t/\tau_b \right)/12\pi)^{1/2},
\]
(59)

\[
\langle R_{ba}^2(1,t) \rangle \sim a^2 \frac{1}{[(4\pi/3)(t/\tau_b)]^{1/2}}.
\]
(60)

\(\Gamma_s(t)\) goes to zero at long times as it should; if all diffusing particles are initially in the surface layer, they will eventually all diffuse into the bulk. The surface layer concentration reaches a steady-state value larger or smaller than the initial value by \(\Gamma_b = \alpha_1/c_{21}\) if the initial concentration is uniform. Both the surface and bulk planar diffusion functions have the same \(t^{1/2}\) power-law dependence, in contrast to the case of a surface isolated from the bulk, where \(\langle r_{a}^2(1,t) \rangle\) was proportional to \(t\). Equation (59) corresponds to a bulk diffusion constant of \(D_b = a^2 / 3 \tau_b\).

The long-time behavior of the terminated bulk planar diffusion in Eq. (60) reflects an unphysical property of the terminated bulk Green's function \(g_b\). It is the surface Green's function for a semi-infinite crystal in which the sum rule (4) or (22) is not obeyed in the surface layer; as previously noted, this sum rule is the analog of the Goldstone rule for phonons and magnons. The relative jump probabilities for a particle at \(L',l'\) in the surface layer of the "terminated bulk" have the same value, \(J(L,1|L',l') = \frac{1}{12}\); as in the bulk, but there are only eight sites to which jumps can be made. \(\langle r_{ba}^2(1,t) \rangle\) therefore exhibits a \(t^{-1/2}\) rather than a
dependence.

Between the short-time behavior in Eqs. (52)–(54) and the very long-time behavior in Eqs. (56)–(58), surface segregation and diffusion go through an intermediate range determined primarily by the ratio of \( \alpha_1 = \tau_{1}/\tau_{0} \) to \( c_{21} = j_{21}/j_{0} \). Here the solutions can be found numerically from Eqs. (A4)–(A8).

IV. THIN FILMS

The general theory described in Sec. II can be applied to thin films as well as to surfaces of semi-infinite solids and interfaces in infinite crystals. Mathematically, the primary difference is that the recursive sequence of equations [(13b), (13b), \ldots] is not ended with a terminated bulk Green's function \( g_{N} \) that satisfies Eq. (14), but rather with

\[
g_{N} = (1 - \Delta N)^{-1}
\]

(61)

for a film of \( N \) blocks. Also, the blocking into \((n - 1) \times (n - 1)\)'s requires that films of \( N(n - 1) \) planes be considered.

To illustrate such applications, we will give a few results for a film of \( N \) layers in which only hopping in the same plane and between nearest-neighbor planes is allowed. The inverse Green's-function matrix \( \mathcal{G}^{-1}(\bar{q}, s) \) then is tridiagonal, just as for a finite linear chain with \((q, \text{dependent})\) nearest-neighbor hopping. We restrict our interest to the long-time limit, \( t/\tau_{L} \to \infty \), so we keep only the most singular terms in the Laplace transforms in the limit \( s \to 0 \). Equation (7) for \( \mathcal{G} \) is rewritten as an equation for the conditional probability \( \mathcal{P} \) using Eqs. (8) and (23)–(25). Solutions in the limit \( \bar{q}, s \to 0 \) are then found by employing appropriately transformed versions of Eqs. (13a), (13b), \ldots and (15)–(17).

In the long-time limit, the conditional probability that a particle is in plane \( L \) given that it began in plane \( L' \) is

\[
P(L, L'; \bar{q}, s = 0, t) = \frac{\tau_{L}}{T_{L}},
\]

(62)

\[
T_{L} = \tau_{L} + \frac{L}{m = 1} \left[ \sum_{n = m+1}^{L} \frac{1}{\mu_{n}} \right] \tau_{m}
\]

(63)

In the above, \( \mu_{L} \) is defined as the ratio

\[
\mu_{L} = \left[ \frac{J(L, L' - 1; \bar{q}, s)}{J(L' - 1, L; \bar{q}, s)} \right]_{\bar{q}, s = 0}.
\]

(64)

Equation (62) describes the steady-state concentration of diffusing particles in the film. It does not and should not depend on the initial layer-dependent concentration distribution, because enough time has elapsed to allow the planar concentrations to find equilibrium.

The same lack of dependence on the starting point occurs for the intra- and interplanar mean-square displacements,

\[
\frac{d^{2}}{d\bar{q}_{a}^{2}} \mathcal{P}(L, L'; \bar{q}, s) = \Delta_{L} t,
\]

(65)

\[
\Delta_{L} = \frac{T_{L}}{T_{L', L_1}} \sum_{L_1} \left[ \frac{d^{2}}{d\bar{q}_{a}^{2}} J(L, L'; \bar{q}) \right]_{\bar{q}_{a} = 0} \frac{1}{T_{L_1}}.
\]

(66)

For an fcc (001) diffusion film, this can be written in the form

\[
\Delta_{L} = \delta_{L} \frac{a^{2}}{2\tau_{L}};
\]

(67)

\[
\delta_{L} = \frac{\tau_{L}}{2T_{L}} \sum_{L'} \frac{1}{T_{L'}} (1 + 4j_{L/L'})
\]

(68)

For a single layer, \( \delta_{1} = 1 \) and \( \Delta_{1} = a^{2}/2\tau_{1} \), as in Eq. (50).

In thin films, it is possible for the underlying layers to give enhanced surface diffusion. For an fcc (001) film of two layers, for example,

\[
\delta_{1} = \left[ \frac{\tau_{1}}{\tau_{1} + \mu_{2} \tau_{2}} \right]^{2} (1 + \mu_{2} - 4j_{21}),
\]

(69)

where \( \mu_{2} = j_{21}/j_{12} \). This will be greater than one, and \( \langle r_{a}^{2}(1, t) \rangle \) will be greater than \( \langle a^{2}/2\tau_{1} \rangle t \), if

\[
(1 - 4j_{12})^{2} = 4j_{22}^{2} \left[ \frac{\tau_{2}}{\tau_{1} + \mu_{2} \tau_{2}} \right]^{2} > \tau_{1}(\mu_{2} \tau_{2} + 2\tau_{1})
\]

(70)

Roughly speaking, an atom that begins in the surface layer can drop into plane 2 where more rapid diffusion occurs and return to the surface further from its starting point than if it had remained in plane 1 the whole time. This cannot happen in the true long-time limit (\( t \gg \tau_{L} \)) for a semi-infinite solid, because for that case, the probability that the particle will be found in plane 1, where it began, vanishes as \( t^{-1/2} \) for \( t \to \infty \) [cf. Eq. (56) for a semi-infinite solid and Eq. (62) for a thin film]. Practically, however, there may be situations in which diffusion on and just below the surface of a semi-infinite solid occurs on a time scale orders of magnitude faster than in the bulk and between the bulk and the surface region. In such situations, a thin-film treatment would be appropriate.
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APPENDIX: GENERAL TIME-DEPENDENT RESULTS FOR fcc (001)

The Laplace transforms (45) – (49) can be inverted with the aid of tables12,13 and considerable algebra. We first make a few definitions,

\[ T = \frac{t}{\tau_b} , \]

\[ a = a_1 - \frac{1}{2} c_{21}, \quad b = \frac{1}{2} c_{21}, \quad d = -(a^2 - b^2) , \]

\[ u_1 = \frac{2b^2}{d} u_0 , \]

and recall that \( u_0 = \frac{2}{a} \). The surface plane concentration and diffusion functions then are

\[ \Gamma_s(t) = \frac{\alpha_1}{d} [ bF(T, u_0, u_1) - ae^{-u_1 T} ] , \]

\[ \Gamma_B(t) = \frac{1}{2} \left[ F(T, u_0, u_1) + \frac{a}{b} (1 - e^{-u_1 T}) + 1 \right] , \]

\[ \langle r_a^2(1, t) \rangle = \frac{1}{2} a^2 \frac{\alpha_1}{d} \left[ b \theta(T, u_0, u_1) F(T, u_0, u_1) + \frac{1}{u_1} (1 - b - au_0)(1 - e^{-u_1 T}) + \frac{a^2}{d} [ 2(1 - b) - au_0 ] Te^{-u_1 T} \right] \]

where the function \( F \) and operator \( \theta \) are defined by

\[ F(T, u_0, u_1) = e^{-u_1 T} I_0(u_0 T) + (2u_0 - u_1) e^{-u_1 T} \int_0^T dT' e^{-(u_0 - u_1)T'} I_0(u_0 T') , \]

\[ \theta(T, u_0, u_1) = u_0 T + \frac{1}{2} u_0 \frac{\partial}{\partial u_0} + \left[ u_0 + \frac{a}{d} [ 2(1 - b) - au_0 ] \right] \frac{\partial}{\partial u_1} . \]

Planar diffusion in the bulk and at the surface of the terminated bulk are given by

\[ \langle R_{ba}^2(L, t) \rangle = \frac{1}{2} a^2 u_0 T e^{-u_0 T} [ I_0(u_0 T) + I_1(u_0 T) ] , \]

\[ \langle r_{ba}^2(1, t) \rangle = \frac{1}{2} a^2 e^{-u_0 T} \left[ I_0(u_0 T) + 1 - \frac{2}{u_0 T} I_1(u_0 T) \right] . \]

8For a review, see F. W. Young, Jr., J. Nucl. Mater. 69-70, 310 (1978).