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Electromigration in transition metals:
I. Computational method

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Abstract. It is shown that, for interstitial impurities in face-centred cubic and body-centred cubic transition metals, electromigration wind valences can be calculated on a microscopic level. The expression for the wind force in metals is discussed and is elaborated within the Korringa–Kohn–Rostoker Green function formalism. Scattering of the electrons by an impurity at positions along possible migration paths, and surrounded by perturbed host atoms, is accounted for up to $l_{max} = 3$. Some basic features of the method are illustrated with the help of the Pd(H) and Nb(H) systems.

1. Introduction

The amount of experimental data on electromigration in various metallic systems is overwhelming [1–3] and demonstrates the intense interest in the subject over the past decades up to the present [4–7]. In electromigration experiments impurity atoms or atoms surrounding vacancies are affected by an electric field through their effective valence in the metal under consideration. The electric field gives rise to a small driving force in addition to the randomly directed forces responsible for diffusion. While in some of the older experiments only the direction of migration [1] (i.e. the sign of the effective valence) was determined, other, more sophisticated, experiments are able to reveal the effective valence itself [1, 4, 7] and even isotope effects therein [8, 9].

Armed with these phenomenological data one could go a step further and ask what is happening at a microscopic level. Several theories for the driving force on an impurity in a jellium in the presence of an electric field have been formulated. Some of them are utilizing semiclassical ideas [10–12] and others [13–18] are on an entirely quantum-mechanical basis. These theories lead to different conclusions concerning the driving force, which evoked the so-called direct force controversy [19–21]. Only as far as the current-induced part of the force is concerned is there agreement in the literature to a large extent, although different points of view exist [22–24].

The aim of the present and subsequent papers is to shed some light on the microscopic origin of the wind force in real metal–impurity systems. For that purpose first of all reliable wavefunctions must be available. For metals containing highly symmetrical substitutional or interstitial impurity clusters (including possible lattice distortion) the scattered Bloch states were calculated as part of investigations on Dingle temperatures [25, 26] and residual resistivities [27]. When dealing with electromigration, clusters of

an oblong shape and, consequently, with a much lower symmetry are met. A substantial amount of extra computational effort is to be expected in calculating the wavefunction at such defects in a dilute alloy. The need for such a state-of-the-art calculation of the wind force in electromigration was expressed by Verbruggen [4, 19] when discussing experimental results for hydrogen in vanadium, niobium and tantalum. Until now interesting qualitative results have been obtained with pseudopotential methods [28–30], which however are only applicable to nearly-free-electron systems, or with a finite-cluster description [31, 32] lacking certain typical features of the infinite lattice.

The present paper is devoted to the method used. In section 2 the basic formulae occurring in the muffin-tin Korringa–Kohn–Rostoker (KKR) method and the KKR Green function description of scattered Bloch states in metal–impurity systems are briefly reviewed. The Brillouin zone integrations for low-symmetry configurations will be discussed. Some conspicuous models dealing with the driving force on an impurity in a jellium are discussed in the first part of section 3. This system always did stand as a model for an interstitial impurity in a real metal. In the last part of section 3 the wind force expression used for the impurity amidst its perturbed surroundings in a real metal is given a sound basis. The elaboration of this expression within the framework of the KKR Green function method in section 4 gives rise to Fermi surface integrals, the numerical evaluation of which is discussed. Section 4 ends with some crude test calculations on two illustrative examples, namely Pd(H) and Nb(H), indicating the correctness of the programs. Some concluding remarks are made in section 5.

Atomic units such that $\hbar = 2m = 1$, m being the electron mass, are used throughout. Note that $e^2 = 2$ in this system of units.

2. Formalism

The electronic structure of an infinite, perfect metal lattice can be calculated following the approach as formulated by Korringa [33] and by Kohn and Rostoker [34]. For that purpose the crystal unit cell is divided into a collection of Wigner–Seitz cells. The potential in a Wigner–Seitz cell is then approximated by the potential inside an inscribed muffin-tin (MT) sphere plus a flat potential in the remaining interstitial region. The heart of the MT approximation is readily recognized in the fact that in the interstitial region the true potential is replaced by the average value. This constant potential, however, then admits the adjustment of free-space solutions in the interstitial region to the regular solutions inside the MT sphere. In this way a formulation in terms of information on the crystal structure, the phase shifts for the MT potentials and a partial-wave sum for the Bloch states becomes feasible. The appropriate expressions and the conventions used are given in section 2.1.

Introduction of a single impurity in a perfect crystal totally destroys the translational symmetry underlying the KKR approach. Application of a Green function technique with the perfect lattice as the unperturbed reference system will yield the scattering states for the electrons in the metal–impurity system. Again the result of the full multiple-scattering treatment [35] of a collection of MT spheres describing a perturbed region in an otherwise perfect lattice can be formulated in terms of structure information on the impurity cluster, impurity phase shifts and a summation over partial waves for the scattered Bloch states. This will be described in section 2.2.

The Brillouin zone integrals encountered in section 2.2 form the subject of section 2.3.

2.1. Muffin-tin method

The method will be described for lattices that can be divided into a collection of identical Wigner–Seitz cells containing a single atomic centre. The Schrödinger equation for an electron moving through the corresponding infinite array of MT potentials is given by

$$(p^2 + V)\Psi_{nk} = \varepsilon_{nk}\Psi_{nk} \tag{1}$$

with

$$V(r) = \sum_j v(r - R_j). \tag{2}$$

The crystal potential $V(r)$ is written as an infinite sum of MT potentials $v(r - R_j)$, located at lattice sites R_j. For the eigenstate $\Psi_{nk}(r)$, around site j the KKR *ansatz* is made

$$\Psi_k(x + R_j) = \sum_L C_{jL}(k)R_L(x). \tag{3}$$

Band index n and crystal wavevector k have been combined into the single label k, whereas L stands for the combination of angular momentum quantum number l and magnetic quantum number m. The regular solutions of the radial Schrödinger equation for one of the (identical) MT potentials, at energy $\varepsilon_k = \kappa^2$,

$$R_L(x) = R_l(\kappa x)Y_L(\hat{x}) \tag{4}$$

are combined by unknown coefficients $C_{jL}(k)$, obeying the Bloch condition

$$C_{j'L}(k) = \exp[ik \cdot (R_{j'} - R_j)]C_{jL}(k). \tag{5}$$

Because for values of x just beyond the MT radius ($x > R_{MT}$) the potential equals the MT constant, the asymptotic form for the regular solution

$$R_L(x) = j_L(x) - i\kappa t_l h^+(x) = [j_l(\kappa x) - i\kappa t_l h_l^+(\kappa x)]Y_L(\hat{x}) \tag{6}$$

can be used there. The $Y_L(\hat{x})$ are real spherical harmonics. The scattering amplitude $-i\kappa t_l = i \sin \eta_l \, e^{i\eta_l}$ contains the host phase shifts η_l. The j_l and h_l^+ are spherical Bessel and Hankel functions respectively.

A wavevector k in the first Brillouin zone is said to fulfil the KKR condition at energy ε_k if the determinant of the KKR matrix

$$M_{LL'}(k) = -\delta_{LL'}/\kappa t_l - ig_{LL'}(k) \tag{7}$$

vanishes. The well known structure matrices $g(k)$ are given by

$$g_{LL'}(k) = \sum_{j'(\neq j)} \exp(-ik \cdot R_{jj'}) \, G_{LL'}(R_{jj'}) \tag{8}$$

where

$$G_{LL'}(R_{jj'}) = 4\pi i^{l-l'} \sum_{L''} i^{l''} C_{LL'L''} h_{L''}^+(R_{jj'}) \tag{9}$$

with $C_{LL'L''}$ a Gaunt coefficient and $R_{jj'} = R_j - R_{j'}$.

For lattices with cubic symmetry the KKR matrix multiplied by a factor $i^{l'-l}$ is real and symmetric, so it can be diagonalized by an orthogonal matrix $V(k)$ with the orthonormal eigenvectors $V^p(k)$ as its columns [36]

$$i^{l'-l}M_{LL'}(k) = [V(k)\Lambda(k)\bar{V}(k)]_{LL'}. \tag{10}$$

The transpose matrix of $V(k)$ is denoted by $\bar{V}(k)$ and $\Lambda(k)$ is the diagonal matrix diag$(\lambda^p(k))$ with $\lambda^p(k)$ the eigenvalues of the KKR matrix.

The $C_{jL}(k)$ in equation (3) are closely related to the eigenvector $V^0(k)$ pertaining to a vanishing eigenvalue denoted by $\lambda^0(k)$. In principle several eigenvalues with different index p might vanish in different points in reciprocal space. After accounting for normalization of the Bloch wave over the Wigner–Seitz cell [37], the $C_{jL}(k)$ are given by

$$C_{jL}(k) = -i^l V_L^0(k) \, e^{ik \cdot R_j}/\{\sqrt{\kappa[-\partial\lambda^0(k)/\partial\varepsilon]}_{\varepsilon=\varepsilon_k} t_l\}. \tag{11}$$

While combination of equations (3), (6) and (11) yields the wavefunction on the MT sphere, the same wavefunction in the interstitial region is given by [38]

$$\Psi_k(x + R_l) = \sum_L C_{lL}(k) j_L(x) \tag{12}$$

with

$$C_{lL}(k) = -i^l W_L^0(k) \, e^{ik \cdot R_l}/\{\sqrt{\kappa[-\partial\lambda^0(k)/\partial\varepsilon]}_{\varepsilon=\varepsilon_k}\}. \tag{13}$$

Here the interstitial structure matrix $g^l(k)$ enters through

$$i^l W_L^p(k) = \sum_{L'} -i\kappa g_{LL'}^l(k) \, i^{l'} V_{L'}^p(k) \tag{14}$$

and is given by

$$g_{LL'}^l(k) = \sum_j e^{-ik \cdot R_{lj}} G_{LL'}(R_{lj}). \tag{15}$$

While the $V_L^p(k)$ are always real for FCC and BCC systems, the $W_L^p(k)$ are not [39]. This is due to the imaginary part of $g^l(k)$ for an arbitrary interstitial position R_l. In general it only holds that

$$-i\kappa g_{LL'}^l(k) = [-i\kappa g_{LL'}^l(-k)]^* \tag{16}$$

which can be verified most easily using the (Korringa–Kohn–Rostoker–Ziman) KKRZ-like expression for structure factors [39, 40]

$$-i\kappa g_{LL'}^l(k) = \sum_{K_n} e^{iK_n \cdot R_l} \frac{F_L(k + K_n)F_{L'}^*(k + K_n)}{\varepsilon + i\delta - (k + K_n)^2} \tag{17}$$

with

$$F_L(k) = (4\pi i^l/V_{WS}^{1/2})Y_L(\hat{k})[j_l(kx)/j_l(\kappa x)] \tag{18}$$

V_{WS} being the volume of the Wigner–Seitz cell. As a consequence of (16) and the more common property

$$V_L^p(-k) = (-1)^l V_L^p(k) \tag{19}$$

it holds for the $W_L^p(k)$ that

$$W_L^p(-k) = (-1)^l W_L^{p*}(k) \tag{20}$$

which will prove to be of great value in subsection 2.2.

Of course, evaluation of the wavefunction at some point $r = R_I$ in the interstitial region of the Wigner–Seitz cell around a lattice point R_j will give the same result whether one uses either (3) with $x = R_I - R_j$ or (12) with $x = 0$. The angular momentum summation in (3), however, must be carried out far enough, which in practical cases surely will be beyond the value $l = l_{max}$ above which the scattering amplitudes $-i\kappa t_l$ become negligibly small. It is obvious that expression (12) in and around R_I converges much faster with respect to angular momentum. The approach of interstitial positions via (12) has already shown its value [26] compared with earlier attempts [41] starting from (3).

2.2. Scattering states

In the previous section it has been shown that in principle at all positions r in the crystal the Bloch states $\Psi_k(r)$ can be evaluated. Consequently, when an impurity is present in the crystal, the scattering states $\bar{\Psi}_k(r)$ can be obtained from a Lippmann–Schwinger equation

$$\bar{\Psi}_k(r) = \Psi_k(r) + \int d^3r' \, G(r, r')\Delta V(r')\bar{\Psi}_k(r'). \tag{21}$$

In this expression $\Delta V(r)$ stands for the potential difference with respect to the unperturbed system (i.e. the perfect crystal), and will be of a finite range. The crystal Green function $G(r, r')$ at energy ε is defined by

$$[p^2 + V(r) - \varepsilon]G(r, r') = -\delta(r, r') \tag{22}$$

and can be elaborated within the MT description of the crystal potential. With $r = x + R_n$ and $n = j$ for a lattice site or $n = I$ for an interstitial site the host Green function reads as [26]

$$G(x + R_n, x' + R_{n'}) = \sum_{LL'} [-i\kappa h_L^+(x_>)R_{n'L'}(x_<)\delta_{nn'}\delta_{LL'} + R_{nL}(x)\mathcal{G}_{nLn'L'}R_{n'L'}(x')] \tag{23}$$

$x_>$ denoting the vector with the larger modulus and $x_<$ its counterpart. Here x is a point in the interstitial region around R_I or just outside the MT sphere around R_j. When $n = I$, $R_{IL}(x) = j_L(x)$ while $R_{jL}(x)$ is given by (6) for x just outside the MT sphere. The Green function matrix elements $\mathcal{G}_{nLn'L'}$ consist of Brillouin zone integrals and will be discussed in the next subsection. The expression for $\bar{\Psi}_k(r)$ at $r = x + R_{\tilde{n}}$ resulting from the multiple scattering of Bloch states by a potential $\Delta V(r)$ represented by a collection of MT spheres, is assumed to be of the form

$$\bar{\Psi}_k(x + R_{\tilde{n}}) = \sum_L \bar{C}_{\tilde{n}L}(k)R_{\tilde{n}L}(x) \tag{24}$$

where the index $\tilde{n}$ comes from the position vector $R_{\tilde{n}}$ pointing to a, possibly displaced from its original position R_n, atomic centre within the range of $\Delta V(r)$. For the case of substitutional and interstitial impurities, accompanied by moderate lattice distortion,

comparison of (24) with (3), (12) and (23) substituted in (21) results in a relation [35] that connects the scattering coefficients $\bar{C}_{nL}(k)$ through

$$\bar{C}_{nL}(k) = \sum_{n'L'} A_{nLn'L'} C_{n'L'}(k) \tag{25}$$

to the host wavefunction coefficients $C_{nL}(k)$. The back-scattering matrix A incorporates all multiple-scattering effects into the description. Its inverse is given by

$$(A^{-1})_{nLn'L'} = J_{LL'}(-\Delta_n)\delta_{nn'} - \sum_{L''} \mathcal{G}_{nLn'L''}J_{L''L'}(-\Delta_{n'})\Delta t_{l'l'}^{n'}. \tag{26}$$

The matrix $J_{LL'}(\Delta_n)$ accounts for the displacement of the centre at R_n over a small vector Δ_n to $R_n + \Delta_n$ and is given by

$$J_{LL'}(\Delta) = 4\pi i^{l-l'} \sum_{L''} i^{l''} C_{LL'L''} j_{L''}(\Delta) \tag{27}$$

at energy $\varepsilon = \kappa^2$. The matrices $J(\Delta)$ have the property that

$$\sum_{L''} J_{LL''}(\Delta)J_{L''L'}(-\Delta) = \sum_{L''} J_{LL''}(\Delta)J_{L'L''}(\Delta) = \delta_{LL'}. \tag{28}$$

Information concerning $\Delta V(r)$ enters through the differences of t matrices in expression (26)

$$\Delta t_{ll'}^n = t_l^j - t_{l'} \qquad (n = j) \tag{29a}$$

$$\Delta t_{ll'}^n = t_l^I \qquad (n = I). \tag{29b}$$

Apparently the matrix t^j for a perturbed, possibly displaced, host atom as well as the t matrices for the interstitial, t^I, and an unperturbed host atom, t, are degenerate with respect to the magnetic quantum number m. This indicates that they pertain to spherically averaged MT potentials.

It might be worth noting that even in a non-self-consistent treatment the scattered wave $\tilde{\Psi}_k(r)$ reaches over the entire crystal, although $\Delta V(r)$ has a finite range. This can be viewed as a true manifestation of back-scattering effects. The way in which this is realized can be understood most easily by inspection of (26) for the case of a single impurity in an otherwise perfect lattice. The matrix A^{-1} then schematically looks like

$$A^{-1} = \begin{pmatrix} \delta_{LL'} - \mathcal{G}_{jLjL'}t_{l'}^j & 0 \\ -\mathcal{G}_{jLjL'}t_{l'}^j & \delta_{jj'}\delta_{LL'} \end{pmatrix}. \tag{30}$$

Then the matrix A has the same shape, and even around a distant host atom, say at R_α, the coefficients $\bar{C}_{\alpha L}(k)$ differ from $C_{\alpha L}(k)$ because of the admixture of $C_{jL}(k)$ via expression (25).

One also should note from (30) that det A (or det A^{-1}) remains the same, no matter how far the matrix is extended. The determinant essentially is built by atomic centres with $\Delta t_{ll'}^n \neq 0$, lying in the perturbed regions (i.e. $\Delta V(r) \neq 0$) of the crystal. The way in which the matrix A enters the generalized Friedel sum rule [42]

$$\Delta Z = \frac{2}{\pi} \sum_{nL} \Delta \eta_L^n + \frac{2}{\pi} \text{Im} \ln \det A \tag{31}$$

with $\Delta \eta_L^I = \eta_l^I$ and $\Delta \eta_L^j = \eta_l^j - \eta_l$, thus shows that only centres with $\Delta t_{ll'}^n \neq 0$ contribute to the change in the number of electrons ΔZ due to the imperfection. One

can now demand that for a perturbing potential $\Delta V(r)$ it at least must hold that the accompanying phase shifts satisfy (31). Of course a self-consistent treatment of the system would alter the shape of A^{-1} in (30) and give rise to a situation where the contribution to ΔZ of atomic centres beyond a certain range becomes negligible.

For any appropriate approximation of the crystal potential $V(r)$ and the perturbation potential $\Delta V(r)$ in terms of MT potentials it is now possible to determine the Bloch states and the way they are scattered by $\Delta V(r)$. There remains the laborious task of calculating the $G_{nLn'L'}$ in a given impurity cluster.

2.3. Brillouin zone integrals

The Green function matrix elements, at energy $\varepsilon = \kappa^2$, in (23) and (26) occur in four forms [38, 39, 41]

$$t_l \mathcal{G}_{jLj'L'} t_{l'} = -t_l \delta_{jj'} \delta_{LL'} - \frac{1}{\kappa V_{BZ}} \int_{BZ} d^3k\, e^{ik \cdot R_{jj'}} [M^{-1}(k)]_{LL'} \tag{32}$$

$$\mathcal{G}_{ILjL'} t_{l'} = -\frac{1}{\kappa V_{BZ}} \int_{BZ} d^3k\, e^{ik \cdot R_{lj}} [(-i\kappa g^I(k)) M^{-1}(k)]_{LL'} \tag{33a}$$

$$t_l \mathcal{G}_{jLIL'} = -\frac{1}{\kappa V_{BZ}} \int_{BZ} d^3k\, e^{ik \cdot R_{jl}} [M^{-1}(k)(-i\kappa \tilde{g}^I(-k))]_{LL'} \tag{33b}$$

$$\mathcal{G}_{ILIL'} = -\frac{1}{\kappa V_{BZ}} \int_{BZ} d^3k [(-i\kappa g^I(k)) M^{-1}(k)(-i\kappa \tilde{g}^I(-k))]_{LL'} \tag{34}$$

when dealing with only one interstitial position. These integrals over the first Brillouin zone with volume V_{BZ} all have singular integrands on the constant energy surface $\varepsilon_k = \kappa^2$, where the KKR condition is satisfied ($\det M(k) = 0$). In addition the integrand of $G_{ILIL'}$ has poles on the free-electron sphere where $k^2 = \varepsilon$. From (10) and (19) it is obvious that

$$M^{-1}_{LL'}(k) = \sum_p i^l V_L^p(k) \frac{1}{\lambda^p(k)} i^{l'} V_{L'}^p(-k) \tag{35}$$

revealing clearly the singularities due to $\det M(k) = 0$ through vanishing eigenvalues $\lambda^0(k)$. These singularities as well as the free-electron poles $(\kappa^2 - k^2)^{-1}$ diverge like $1/x$ with $x = \lambda^0(k)$ or $x = (\kappa^2 - k^2)$ and can therefore be taken care of using

$$\lim_{\varepsilon \to 0} \frac{1}{x + i\varepsilon} = P\left(\frac{1}{x}\right) - i\pi\delta(x). \tag{36}$$

When (36) is applied to (32), (33) and (34) using (35) and (14) one arrives at

$$t_l \mathcal{G}_{jLj'L'} t_{l'} = -t_l \delta_{jj'} \delta_{LL'} - \frac{1}{\kappa V_{BZ}} P \int_{BZ} d^3k \sum_p i^l V_L^p(k) \frac{e^{ik \cdot R_{jj'}}}{\lambda^p(k)} i^{-l'} V_{L'}^p(k)$$

$$- \frac{\pi i}{\kappa V_{BZ}} \int_{FS} dS_k\, i^l V_L^0(k) \frac{e^{ik \cdot R_{jj'}}}{|\nabla_k \lambda^0(k)|} i^{-l'} V_{L'}^0(k) \tag{37}$$

$$\mathscr{G}_{lLjL'}t_{l'} = -\frac{1}{\kappa V_{BZ}} P \int_{BZ} d^3k \sum_p i^l W_L^p(k) \frac{e^{ik\cdot R_{lj}}}{\lambda^p(k)} i^{-l'} V_{L'}^p(k)$$

$$- \frac{\pi i}{\kappa V_{BZ}} \int_{FS} dS_k \, i^l W_L^0(k) \frac{e^{ik\cdot R_{lj}}}{|\nabla_k \lambda^0(k)|} i^{-l'} V_{L'}^0(k) \tag{38a}$$

$$t_l \mathscr{G}_{jLlL'} = -\frac{1}{\kappa V_{BZ}} P \int_{BZ} d^3k \sum_p i^l V_L^p(k) \frac{e^{ik\cdot R_{jl}}}{\lambda^p(k)} i^{-l'} W_{L'}^{p*}(k)$$

$$- \frac{\pi i}{\kappa V_{BZ}} \int_{FS} dS_k \, i^l V_L^0(k) \frac{e^{ik\cdot R_{jl}}}{|\nabla_k \lambda^0(k)|} i^{-l'} W_{L'}^{0*}(k) \tag{38b}$$

$$\mathscr{G}_{lLlL'} = -\frac{1}{\kappa V_{BZ}} P \int_{BZ} d^3k \sum_p i^l W_L^p(k) \frac{1}{\lambda^p(k)} i^{-l'} W_{L'}^{p*}(k)$$

$$- \frac{\pi i}{\kappa V_{BZ}} \int_{FS} dS_k \, i^l W_L^0(k) \frac{1}{|\nabla_k \lambda^0(k)|} i^{-l'} W_{L'}^{0*}(k) - i\varepsilon \delta_{LL'}. \tag{39}$$

The residual part in the above expressions is a Fermi surface integral where it is to be understood that there might be several roots, $\lambda^0(k)$, of the KKR equations that define different sheets of the Fermi surface. The additional singularity at $k^2 = \varepsilon$ in (34) gives rise to a residual part which can be evaluated analytically, resulting in $-i\varepsilon\delta_{LL'}$ in (39). Some important properties of these integrals are [39]

$$\mathscr{G}_{jLj'L'} = \mathscr{G}_{j'L'jL} = \mathscr{G}_{jL'j'L}(-1)^{l+l'} \tag{40}$$

$$\mathscr{G}_{lLjL'} = \mathscr{G}_{jL'lL} \tag{41}$$

$$\mathscr{G}_{lLlL'} = \mathscr{G}_{lL'lL}. \tag{42}$$

These equalities are most easily verified, starting from (32), (33) and (34) and noting that

$$M_{LL'}(k) = (-1)^{l+l'} M_{L'L}(k) = M_{L'L}(-k). \tag{43}$$

While the set of difference vectors $R_{jj'}$ and the KKR matrix $M(k)$ transform according to the cubic group (point group O_h) in FCC and BCC lattices, the point group under which the vectors R_{lj} and consequently the interstitial structure matrices $g^l(k)$ transform can be of much lower order, depending on the position of the migrating atom along its path. It is clear that the computational effort needed to calculate (38) and (39) will be much greater than that for (37). First, the irreducible part of the Brillouin zone over which the integral must be evaluated for a general interstitial position will be larger. Secondly, the complex interstitial structure matrices must be evaluated for a correspondingly larger number of k-vectors. As a third point the evaluation of $g^l(k)$ itself is more complicated, when compared to $g(k)$, owing to the more restricted use of symmetry in the lattice sum over R_{lj} in equation (15).

3. Electromigration

3.1. Introduction

Randomly directed steps of particles in a lattice gas lead to diffusive motion [43]. In metals the diffusion rate of impurities depends heavily on the nature of the diffusion

mechanism. An increase of the temperature in general increases the diffusion rate. In metal–impurity systems in thermodynamic equilibrium there is no net flow of impurity atoms, although the individual atoms still exhibit random thermal motion. By means of an electric field the motion of the individual impurities can be influenced, resulting in a net atomic flow. This phenomenon is the result of both the additional force due to the external field and the mobility of the impurities. The atomic flux is determined by the product of this driving force and the mobility, which is connected to the diffusion coefficient through the Einstein relation [44].

The driving force F exerted on impurities in an electron gas by an external field E, although being an extremely complicated quantity, can be expressed by a stimulus-response relation as simple as

$$F = Z^*eE. \tag{44a}$$

Here Z^* is a completely phenomenological proportionality constant, called the effective valence of the impurity in the electron gas under consideration, and $e \equiv |e|$ is the elementary charge. Usually one distinguishes two different contributions to this total force, a direct force and a wind force. The direct force F_{direct} is due to the direct action of the field on the impurity nucleus and the electrons surrounding it. Further the electrons in the current generated by the electric field are scattered by the impurity. As a result of this interaction the so-called wind force F_{wind} arises. Equation (44a) can be rewritten in terms of these two forces and their accompanying valences Z_{direct} and Z_{wind} as

$$F = F_{direct} + F_{wind} = (Z_{direct} + Z_{wind})eE. \tag{44b}$$

Many attempts have been made to give this relation, or elements of this relation, a more formal basis. They all have in common that the system under consideration is a jellium with a distribution of non-interacting impurities. In general this system serves as a model for interstitial impurities in metals.

The oldest model is due to Fiks [10] and Huntington and Grone [11] and it concerns the wind force. The transport relaxation time τ for the electrons is used to calculate the momentum picked up by an electron gas with density n in an electric field. The frequency of electron impurity collisions is given by $1/\tau_i$, the reciprocal electron–impurity relaxation time. It is assumed that during such a collision the electron transfers all of its momentum to the impurity. For impurity density n_i this ballistic model leads to

$$F_{wind} = -(ne\tau/n_i\tau_i)E \tag{45a}$$

which is always in the direction opposed to the field direction. Equivalently, using $\rho^{-1} = ne^2\tau/m$ and $\rho_i^{-1} = ne^2\tau_i/m$ for the bulk and residual resistivity, ρ and ρ_i, respectively,

$$F_{wind} = -(n\rho_i/n_i\rho)eE. \tag{45b}$$

Bosvieux and Friedel [13] (BF) argued that, within the independent-electron picture, the conduction electrons completely screen out the external field at the position of the impurity. They end up with a quantum-mechanical expression for the total force on the bare (ionic) impurity

$$F_{wind} = -\int d^3r\, n(r)\nabla_{R_1} v_{bare}(r - R_1) \tag{46a}$$

with electron density

$$n(r) = \sum_k f(\varepsilon_k)|\bar{\Phi}_k(r)|^2 \tag{46b}$$

and an unscreened ionic impurity potential $v_{bare}(r - R_1)$ for an impurity at position R_1.

The summation over k includes the two spin eigenstates. Clearly the BF wind force is rooted in the non-equilibrium distribution for the conduction electrons, as expressed by the field-dependent part of the distribution function

$$f(\varepsilon_k) = f_0(\varepsilon_k) + e\tau v_k \cdot E[\partial f_0(\varepsilon)/\partial \varepsilon]_{\varepsilon = \varepsilon_k}. \tag{46c}$$

In the original paper the single-particle wavefunctions $\bar{\Phi}_k(r)$ satisfy a Schrödinger equation, with potential

$$v(r - R_1) = v_1(r - R_1) + v_E(r - R_1), \tag{46d}$$

only to first order in $v(r - R_1)$. Here $v_1(r - R_1)$ is the electron–impurity interaction in the absence of the electric field E. Owing to the field, a slightly altered Fermi–Dirac distribution brings about a change in electron density around the impurity, thus introducing an extra potential $v_E(r - R_1)$.

Landauer and Woo [22] heuristically derived contributions that are second-order in $v(r - R_1)$. The physically appealing concept of residual resistivity dipoles [45] (RRD) plays an important role. The RRD set up an electric field around an impurity just strong enough to make the electrons overcome the local increase in resistivity. It is clear that on average this additional field must point in the same direction as the external field. Landauer and Woo thus show that the RRD field gives a contribution to the wind force aligned in the direction of the external field. Note that neither Bosvieux and Friedel nor Landauer and Woo take the electron–impurity interaction in the absence of the field into account to all orders. This limitation can be removed, as shown by Sham [15] and discussed more explicitly by Sorbello [23].

Sorbello performed model calculations on an s scatterer in a jellium. The electron–impurity scattering was treated up to all orders in $v_1(r - R_1)$. The electron density that he found after insertion of the scattered wave into (46b) clearly revealed the BF contribution as well as the RRD contribution. After applying Thomas–Fermi screening to this non-equilibrium electron density the formal separation into BF and RRD contributions was retained in the new expression for the density. At the position of the impurity, however, the RRD field turned out to point in a direction opposite to what Landauer and Woo predicted. From this Sorbello concluded that for more complex (higher angular momentum) scatterers a t-matrix treatment will yield the complete electron density, not admitting such a clear distinction between BF and RRD contributions. Contrary to what Landauer and Woo assumed the RRD charge distribution for the s scatterer was found to be spatially extended: '. . . the RRD is hidden, chameleonlike, within the Friedel oscillations . . .', as Sorbello puts it.

After this outline of the basic models in electromigration theory, section 3.2 introduces more recent developments based on linear response theory. The implications for the expression for the wind force in dealing with a real metal–impurity system, compared with a simple jellium system, are considered in section 3.3.

3.2. Linear response

More recent theoretical investigations on the driving force in electromigration all start from an important result due to Kumar and Sorbello [14]. After decoupling the electronic coordinates from the impurity coordinates through the Born–Oppenheimer approximation, they arrived at a formally exact expression within Kubo's linear response theory. The driving force is given by a response function describing the response of

the unperturbed system, with Hamiltonian H, to an oscillating external field $E(t) = E\,e^{-i\omega t + at}$,

$$F(t) = ZeE(t) - ie \sum_{\nu} E_{\nu}(t) \int_0^\infty dt'\, e^{(i\omega - a)t'}\, \mathrm{Tr}\left(\rho_0(H)\left[-\nabla_{R_1} V(t'), \sum_j r_j^\nu\right]\right) \qquad (47a)$$

in which $a = +0$ assures adiabatic switching on of the field. The summation over ν indicates a dot product of the field with the coordinate r_j of the jth electron. The great advantage of such an approach is that the grand canonical density operator for the equilibrium system $\rho_0(H)$ can have a very realistic Hamiltonian as its argument. The total interaction between the impurities, numbered by α, and the electrons is given by

$$V = \sum_{j,\alpha} v_{\mathrm{bare},\alpha}(r_j - R_\alpha) \qquad (47b)$$

in the r representation and is also contained in H. Differentiation of V with respect to R_1, the coordinate of the impurity under consideration, constitutes the force operator. In $(47a)$ this operator occurs in the Heisenberg picture

$$-\nabla_{R_1} V(\tau) = e^{+iH\tau}(-\nabla_{R_1} V)\,e^{-iH\tau}. \qquad (47c)$$

Although formally exact, expression $(47a)$ contains a trace over a commutator weighted with the full many-body density operator and can therefore be considered as intractable. By treating the electron–electron interaction in an approximate way and neglecting certain inelastic effects in the electron–phonon interaction, it is possible to replace H by a sum of single-particle Hamiltonians

$$H = \sum_j h_j. \qquad (48)$$

It is still possible to account for the phonon field by averaging over the canonical phonon ensemble afterwards [18]. Application of (48) to (47) results in the expression

$$F(t) = ZeE(t) - ie \sum_{\nu} E_{\nu}(t) \int_0^\infty dt'\, e^{(i\omega - a)t'}\, \mathrm{tr}\{f_0(h)[f_1(t'), r^\nu]\} \qquad (49)$$

containing a single-particle trace. Here $f_0(h)$ is the equilibrium Fermi–Dirac distribution function in operator form and f_1 the force operator for the impurity under consideration

$$f_1 = -\nabla_{R_1} v_1 \qquad (50)$$

where v_1 in the r representation equals $v_1(r - R_1)$ being one term of the right-hand side of $(47b)$ but by now self-consistently dressed with screening electrons due to the transition to a single-particle description (see equation (48)). This dressed potential is therefore different from the bare potential used by Bosvieux and Friedel in their expression $(46a)$ for the total force.

If the phonon field is left out of consideration h can be taken to be

$$h = h_0 + v_1 + \sum_{\alpha \neq 1} v_\alpha \qquad (51)$$

with h_0 the single-particle Hamiltonian for the electron in the absence of the impurity potentials. The electron–electron interaction is supposed to be accounted for in h at, for instance, the local density level. The replacement of electrons with mutual interaction by independently moving quasi-particles always did prove to work remarkably well even

in rather complicated metallic electron gas systems. In the case of low impurity density it can be shown that the v_α ($\alpha \neq 1$) take care of the dissipation in the system, while it is v_1 that accounts for the local situation around R_1. Hence it might be conjectured that the phonon field, previously discarded, can be regarded as contributing to the dissipation as well and, consequently, to the inverse electrical transport relaxation time τ^{-1}. Using Liouville operators with the commutator generating property when acting on another operator A

$$\hbar A = [h, A] \tag{52a}$$

and consequently

$$e^{i\hbar t} A = e^{+i\hbar t} A \, e^{-i\hbar t} \tag{52b}$$

expression (49) can be rewritten in the DC limit ($\omega = 0$) as [18]

$$F = ZeE - e \sum_\nu E_\nu \mathrm{tr}\!\left([f_0(h_1) - f_0(h_0), r^\nu] \frac{1}{\hbar_1 + i/\tau} f_1 \right)$$

$$- e \sum_\nu E_\nu \, \mathrm{tr}\!\left([f_0(h_0), r^\nu] \frac{1}{\hbar_1 + i/\tau} f_1 \right). \tag{53}$$

The seemingly superfluous division made in (53) has a twofold purpose. In the first place it can be shown that, in the low dissipation limit ($\tau \to \infty$), the sum of the first two members of the right-hand side of (53) vanishes. Secondly, for a system containing only one impurity, in the same low dissipation limit it can be shown that the third member, when evaluated in the basis of eigenkets $|k\rangle$ of h_0 at eigenvalues ε_k, exactly equals [45]

$$\frac{2e}{a} \sum_k E \cdot k \left[\frac{\partial f_0(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon = \varepsilon_k} \langle \bar{\Psi}_k(r) | - \nabla_{R_1} v_1(r - R_1) | \bar{\Psi}_k(r) \rangle \tag{54}$$

with $\bar{\Psi}_k$ the exact local wavefunction. This expression strongly resembles the Bosvieux–Friedel expression for the wind force, the difference being the replacement of v_{bare} by v_1. Further it can be demonstrated [46] that (54) reduces to the ballistic wind force expression (45a) with $\tau = a^{-1}$, upon substitution of

$$\bar{\Psi}_k(r) = \frac{4\pi}{\Omega^{1/2}} \sum_L i^l Y_L(\hat{k}) R_L(r) \tag{55}$$

with the regular solution of the Schrödinger equation $R_L(r)$ having the asymptotic form (6) for an independent particle in jellium.

The evaluation of (47a) described above strongly benefits from the use of Liouville operators. The time integration in (49) can be carried out leading to the resolvent $(\hbar + ia)^{-1}$. Another approach to the evaluation of (47a) makes use of the method of quantum field theory [15, 16] involving temperature Green functions [47]. Following Sham's analysis of the response function in terms of Feynman diagrams, Sorbello showed [48] that the results of Rimbey and Sorbello [16] could be simplified to

$$F = -\frac{4}{3\pi} \mathrm{Im} \sum_k k^2 [G(k, k, \varepsilon_F) - G_0(k, k, \varepsilon_F)] eE + F_{\mathrm{wind}} \tag{56}$$

with zero-temperature Green functions at the Fermi energy ε_F

$$G_0(k, k, \varepsilon_F) = \langle k | 1/(\varepsilon_F^\pm - h_0) | k \rangle \tag{57a}$$

$$G(k, k, \varepsilon_F) = \langle k | 1/[\varepsilon_F^\pm - (h_0 + v_1)] | k \rangle. \tag{57b}$$

The direct force term in (56) is what remains after exact cancellation of nuclear charges corresponding to negative energy states (bound states). Unfortunately it is not easy to make a comparison of (56) with (53) for there is no dissipation present in (56). Clearly the vanishing of the direct force in (56) upon taking $\tau \to \infty$ cannot be reproduced. However, (53) as well as (56) in general predict only a partially screened direct force, contrary to complete screening as found by Bosvieux and Friedel.

3.3. Wind force

The aforementioned expressions for the driving force all reveal a contribution proportional to the deviation from the equilibrium Fermi–Dirac distribution, termed the wind force. This force can be pictured as arising from the unequal occupation numbers for incident electrons in states $\Psi_k(r)$ and $\Psi_{-k}(r)$. Consequently the occupation of the scattering states $\bar{\Psi}_k(r)$ and $\bar{\Psi}_{-k}(r)$ will be influenced, giving rise to an anisotropic charge density around the impurity

$$\rho(r) = -en(r) = -e \sum_k f(\varepsilon_k) |\bar{\Psi}_k(r)|^2. \tag{58}$$

All authors agree about the form of the quantum-mechanical expression for the wind force, namely the Bosvieux–Friedel expression (46a). There remains only one point of discussion, for in equation (46a) the bare (ionic) potential is used in the force operator while in expression (54) it is the screened electron–impurity potential which shows up. The reason for this is that in the original paper [13] Bosvieux and Friedel only paid attention to the electric field at the position of the migrating ion, which has not always been realized in later work [19]. Within the single-particle approximation, however, an electron moves in the self-consistent field of all other charged particles. It therefore has interaction with the combined fields of the impurity and all other electrons. The correct expression for the wind force then reads

$$F_{\text{wind}} = \sum_k f(\varepsilon_k) \langle \bar{\Psi}_k(r) | - \nabla_{R_1} v_1(r - R_1) | \bar{\Psi}_k(r) \rangle \tag{59}$$

with $\bar{\Psi}_k(r)$ related to $v_1(r - R_1)$ through the self-consistent solution of the Schrödinger equation

$$[p^2 + v_1(r) - \varepsilon_k] \bar{\Psi}_k(r) = 0. \tag{60a}$$

More explicitly, in the independent-electron approximation electrons in single-particle states $\bar{\Psi}_k(r)$ only have a self-consistent interaction with

$$v_1(r - R_1) = v_{\text{bare}}(r - R_1) + v_{\text{screen}}(r - R_1) \tag{60b}$$

where v_{screen} is due to the effect of all electrons. Because the Born–Oppenheimer approximation was invoked at an early stage it is automatically assumed that v_{screen} instantaneously moves along with the nucleus of the impurity. In this way it is assured that $-\nabla_{R_1}$ acts on both v_{bare} and v_{screen} in the same way. It should be precisely this kind of self-consistent electron–impurity potential that appears upon changing from the true system Hamiltonian H to a sum of single-particle Hamiltonians in equation (48) with (51).

Once this matter has been settled it is interesting to investigate the applicability of (59) to interstitial impurities in real metals. A difference between a jellium and a real metal that immediately leaps to mind is the anisotropy at a general position in the latter

system. As a consequence plane waves $|k\rangle$ must be replaced by Bloch states $|nk\rangle \equiv |k\rangle$, describing the independent-electron states in a translationally invariant metal lattice. The anisotropy also brings about that not all interstitial positions are equally accessible to the impurity, that is, only a restricted number of migration paths, defined by the symmetry of the lattice, are walked. Of course, in an anisotropic system the wind force on an impurity becomes position-dependent,

$$F_{\text{wind}} = Z_{\text{wind}}(R_1)eE \tag{61}$$

with $\underline{Z}_{\text{wind}}(R_1)$ a 3×3 symmetric tensor. The reduction of this theoretical wind valence tensor to a scalar quantity, which can be compared to what an experimentalist measures for FCC and BCC crystals, involves some ideas about diffusion mechanisms and will be addressed extensively in a subsequent paper. At the present stage all attention will be devoted to the justification of the adaption of equation (59) to the band structure of real metals,

$$F_{\text{wind}}(R_1) = \sum_k f(\varepsilon_k)\langle \bar{\Psi}_k(r; R_1)| - \nabla_{R_1} v_1(r - R_1)|\bar{\Psi}_k(r; R_1)\rangle. \tag{62a}$$

The functions $\bar{\Psi}_k(r; R_1)$ are the exact local wavefunctions obeying

$$[p^2 + V(r) + \Delta V(r; R_1) - \varepsilon_k]\bar{\Psi}_k(r; R_1) = 0. \tag{62b}$$

Both $\bar{\Psi}_k$ and ΔV carry the impurity position in the spirit of the Born–Oppenheimer approximation, that is to say, they depend on R_1 only in a parametric way. All dynamics involving the coupling of R_1 and $\dot{R}_1$ to electronic coordinates has been neglected. The calculation of $\bar{\Psi}_k$ is performed with fixed positions of the nuclei determining ΔV.

Given a perturbing potential ΔV which includes the migrating interstitial nucleus, there remain two important questions. First, one could ask to what extent the band index n holds back the derivation of (54) as performed by Lodder [46]. There the third member of the right-hand side of (53), before the time integration has been carried out, is evaluated for the case of a single impurity in an otherwise unperturbed system. For a real metal, matrix elements occurring in the trace

$$\sum_{nk} \langle nk|[f_0(h_0), r^\nu]f_1(t)|nk\rangle \tag{63a}$$

have to be evaluated. After insertion of a complete set of eigenstates just after the commutator, non-diagonal factors

$$\langle nk|[f_0(h_0), r^\nu]|n'k'\rangle \tag{63b}$$

emerge. When the Bloch states are evaluated in the coordinate representation, diagonality in k can be demonstrated through the transformation $r = r' + R$, where R is a lattice vector. Application of the Bloch theorem yields a factor $e^{i(k' - k) \cdot R}$ that must be equal to one, which constitutes the desired result in the first Brillouin zone. Using the well known identity [49]

$$[f_0(h), r^\nu] = \frac{\mathrm{i}}{m} \int_0^\beta \mathrm{d}\lambda \, f_0(h)p^\nu(-\mathrm{i}\lambda)e^{\beta(h-\mu)} f_0(h) \tag{63c}$$

where $\beta = (kT)^{-1}$ and μ is the chemical potential, (63b) can be expressed as

$$(\mathrm{i}/m)\langle nk|p^\nu|n'k\rangle\{-[f_0(\varepsilon_{nk}) - f_0(\varepsilon_{n'k})]/(\varepsilon_{nk} - \varepsilon_{n'k})\}. \tag{63d}$$

In metals, at moderate temperatures, μ can be safely approximated by ε_F.

A closer look at the statistical part in (63d) immediately reveals that the matrix elements diagonal in the band index (i.e. $\varepsilon_{n'k} \rightarrow \varepsilon_{nk}$) give the usual elastic or recoilless single-band contributions, weighted by the energy derivative of the Fermi–Dirac distribution function. At $T = 0$ only diagonal matrix elements at ε_F need to be accounted for. At finite temperatures more of these diagonal terms, weighted by $-\partial f_0(\varepsilon)/\partial \varepsilon$, contribute. In addition inelastic inter-band matrix elements, between states with the same wavevector k, may arise. Of course the availability of states that are moderately separated in energy determines the importance of this effect relative to the delta-function-like intra-band contributions in (63d). From the band structure of various metals (Al, Cu, Ag, Pd, V and Nb) [50] it can be seen that inelastic inter-band contributions arise only from limited regions in k-space. This ocurs, for instance, when a degenerate energy band starts to split up around the Fermi level. Intra-band contributions, however, extend over the entire constant energy surface $\varepsilon = \varepsilon_{nk} = \varepsilon_{n'k}$ and are therefore expected to be of much more importance. In fact, as mentioned by Sorbello [28], the electron–impurity scattering events themselves turn out to be predominantly recoilless ($>99\%$). This means that all dynamics of the impurity can be ignored, although recently some doubt was cast upon this assumption [51].

For diagonal matrix elements of the force operator

$$\int_0^\infty dt \, e^{-at} \langle nk | e^{ih_1 t} f_1 \, e^{-ih_1 t} | nk \rangle \tag{64}$$

with

$$h_1 = h_0 + \Delta V(r; R_1) \tag{65}$$

it can be shown that the time-dependent factors in (64) transform the Bloch states into the exact local wavefunctions. Because in the original proof [46] nothing more than the requirement that $|nk\rangle$ be an eigenvector of h_0 and $|\Psi_{nk}\rangle$ be an eigenvector of h_1 was used, it also holds in (64) that $e^{-ih_1 t} |nk\rangle$ can be replaced by $e^{-i\varepsilon_{nk}t} |\Psi_{nk}\rangle$. This establishes that (62a) is applicable to interstitial impurities in real metals. Inter-band terms are not included; all intra-band contributions are accounted for to their full extent.

The second question that has to be answered concerns the potential v_1 for the migrating atom. If one imagines an interstitial impurity, surrounded by perturbed host atoms, it is not immediately clear what in fact constitutes the migrating entity. Alternatively formulated, one may ask to which part of $\Delta V(r; R_1)$ the gradient operator should be applied in order to obtain f_1. This certainly is not a trivial question. Although there will exist a wind force on $\Delta V(r; R_1)$ as a whole, owing to the immobility of the perturbed host atoms in $\Delta V(r; R_1)$, work will be performed on matter in the interstitial region around the impurity nucleus only. It is the electrons and the impurity nucleus in this region that contribute to v_1 and hence to f_1, while the use of $\Delta V(r; R_1)$ as a whole in equation (62b) should assure a correct description of the local wavefunction. When preparing for actual wind force calculations in the subsequent paper, the choice of suitable potentials will be outlined and discussed extensively. Only determination of the force on the moving entity in $\Delta V(r; R_1)$ will lead to $Z_{\text{wind}}(R_1)$ values that can be compared to experimental Z^* values, after a proper reduction of the 3×3 tensor to a scalar Z_{wind}.

4. Muffin-tin multiple-scattering description of $Z_{\text{wind}}(R_1)$

4.1. Basic expressions

In real metals the deviation from the equilibrium distribution function, linear in the applied field, is given by

$$f(\varepsilon_k) - f_0(\varepsilon_k) = (-e)\boldsymbol{\lambda}_k \cdot \boldsymbol{E}[-\partial f_0(\varepsilon)/\partial\varepsilon]_{\varepsilon=\varepsilon_k} \tag{66}$$

in which $\boldsymbol{\lambda}_k$ is the vector mean free path. Only this part of $f(\varepsilon_k)$ is responsible for the wind force and enters (62a) as can be seen from (63d). When (66) is substituted in (62a), after conversion of the summation over spin states k into integrations over surfaces of constant energy in the first Brillouin zone and neglecting inter-band contributions, one arrives at

$$\boldsymbol{F}_{\text{wind}}(\boldsymbol{R}_1) = \frac{2}{V_{\text{BZ}}}\int d\varepsilon\,\frac{\partial f_0(\varepsilon)}{\partial\varepsilon}\int_{\varepsilon_k=\varepsilon}\frac{dS_k}{v_k}\,\langle\bar{\Psi}_k(r;\boldsymbol{R}_1)|$$

$$- \nabla_{\boldsymbol{R}_1}v_1(r-\boldsymbol{R}_1)|\bar{\Psi}_k(r;\boldsymbol{R}_1)\rangle \otimes \boldsymbol{\lambda}_k e\boldsymbol{E} \tag{67}$$

where $\times$ denotes the dyadic product.

Although thermal broadening of the Fermi–Dirac distribution function could be accounted for in (67), for the time being zero temperature will be assumed, so $\partial f_0(\varepsilon)/\partial\varepsilon \approx -\delta(\varepsilon - \varepsilon_{\text{F}})$. After substitution of (24), the matrix element in (67) can be shown (see appendix) to equal

$$2\varepsilon_{\text{F}}\sum_L\sum_{m_1=-l-1}^{l+1}(\cot\eta_{l+1}^l - \cot\eta_l^l)D_{Ll+1,m_1}\,\text{Re}[t_{l+1}^{l*}t_l^l\bar{C}_{ll+1,m_1}^*(k)\bar{C}_{lL}(k)]. \tag{68}$$

After substitution of this expression in (67) and comparing with (61) the wind valence tensor for the impurity at $\boldsymbol{R}_1$ is given by

$$\underline{Z}_{\text{wind}}(\boldsymbol{R}_1) = 2\varepsilon_{\text{F}}\sum_L\sum_{m_1=-l-1}^{l+1}(\cot\eta_{l+1}^l - \cot\eta_l^l)D_{Ll+1,m_1}\,\text{Re}(t_{l+1}^{l*}t_l^lW_{l+1,m_1,L}) \tag{69a}$$

with

$$D_{LL'} \equiv \int d\hat{r}\,Y_L(\hat{r})\hat{r}Y_{L'}(\hat{r}) \tag{69b}$$

and the vectorial matrix

$$W_{LL'} = -\frac{2}{V_{\text{BZ}}}\int_{\text{FS}}\frac{dS_k}{v_k}\,\bar{C}_{lL}^*(k)\boldsymbol{\lambda}_k\bar{C}_{lL'}(k). \tag{69c}$$

In general no k-dependent mean free paths including all scattering processes are available and the Ziman approximation [52] $\boldsymbol{\lambda}_k = \tau\boldsymbol{v}_k$ must be invoked. Furthermore the alloy wavefunction coefficients can be replaced by the right-hand side of (25) leaving an integral over the Fermi surface with an integrand that comprises only host quantities,

$$W_{LL'} = -2\tau\sum_{\substack{n_1L_1\\n_2L_2}}A_{lLn_1L_1}^*A_{lL'n_2L_2}\left(\frac{1}{V_{\text{BZ}}}\int_{\text{FS}}dS_k\,C_{n_1L_1}^*(k)\hat{v}_kC_{n_2L_2}(k)\right). \tag{70}$$

The host integral in (70) has an integrand that behaves regularly over the entire Fermi surface. This integral can be evaluated in terms of eigenvectors of the KKR matrix and interstitial structure constants, as will be shown in the next section.

4.2. Properties of the Fermi surface integrals

In order to arrive at some general properties of the integrals occurring in (70), with the help of (11) and (13) the following notation is introduced:

$$\frac{1}{V_{BZ}} \int_{FS} dS_k \, C_{jL}^*(k) \hat{v}_k C_{j'L'}(k) = \frac{1}{t_j^* t_{j'}} \frac{i^{l'-l}}{\kappa V_{BZ}} \int_{FS} dS_k \, V_L^0(k)$$

$$\times \frac{\hat{v}_k}{|\partial \lambda^0(k)/\partial \varepsilon|} V_{L'}^0(k) \, e^{-ik \cdot R_{jj'}} \equiv \frac{1}{t_j^* t_{j'}} I_{jLj'L'} \tag{71a}$$

$$\frac{1}{V_{BZ}} \int_{FS} dS_k \, C_{IL}^*(k) \hat{v}_k C_{jL'}(k) = \frac{1}{t_{j'}} \frac{i^{l'-l}}{\kappa V_{BZ}} \int_{FS} dS_k \, W_L^{0*}(k)$$

$$\times \frac{\hat{v}_k}{|\partial \lambda^0(k)/\partial \varepsilon|} V_{L'}^0(k) \, e^{-ik \cdot R_{Ij}} \equiv \frac{1}{t_{j'}} I_{ILjL'} \tag{71b}$$

$$\frac{1}{V_{BZ}} \int_{FS} dS_k \, C_{IL}^*(k) \hat{v}_k C_{IL'}(k) = \frac{i^{l'-l}}{\kappa V_{BZ}} \int_{FS} dS_k \, W_L^{0*}(k)$$

$$\times \frac{\hat{v}_k}{|\partial \lambda^0(k)/\partial \varepsilon|} W_{L'}^0(k) \equiv I_{ILIL'}. \tag{71c}$$

It is easy to demonstrate the Hermitian property

$$I_{nLn'L'} = I_{n'L'nL}^* \tag{72a}$$

with respect to the indices $(nL, n'L')$. This property equally well applies to $W_{LL'}$ with respect to (L, L'), which can be trivially established from equation (69c). Furthermore it is worth noting that the vectorial matrices I are purely imaginary, which follows from (72a) on the one hand and from the equality

$$I_{nLn'L'} = -I_{n'L'nL} \tag{72b}$$

on the other. Property (72b) is readily derived by explicit interchange of the appropriate factors in the integrands of (71) and using (19) and (20).

The reader might have noticed a superficial similarity between $I_{nLn'L'}$ and the residual parts of the $\mathcal{G}_{nLn'L'}$ in (37) to (39). When for instance $I_{ILjL'}$ is rewritten as

$$I_{ILjL'} = \frac{i^{l'-l}}{\kappa V_{BZ}} \left((-1)^{l+l'+1} \int_{FS} dS_k \, \frac{\hat{v}_k}{|\partial \lambda^0(k)/\partial \varepsilon|} W_L^0(k) V_{L'}^0(k) \, e^{+ik \cdot R_{Ij}} \right)$$

and compared to the residual part of $\mathcal{G}_{ILjL'}$ (see (38a))

$$-i\pi \frac{i^{l-l'}}{\kappa V_{BZ}} \int_{FS} dS_k \, \frac{1}{|\nabla_k \lambda^0(k)|} W_L^0(k) V_{L'}^0(k) \, e^{+ik \cdot R_{Ij}}$$

one notices that a major part of the integrands is equal and therefore has to be calculated only once, which reduces the computational effort to some extent when dealing with low-symmetry impurity clusters. Of course the same applies to $I_{jLj'L'}$ and $I_{ILjL'}$.

The vectorial character of l is carried by the unit vector in the direction of the velocity. On the Fermi surface, being the constant energy surface at $\varepsilon = \varepsilon_F$, it holds that

$$d\varepsilon_k = dk \cdot \nabla_k \varepsilon_k + d\lambda^0(k) \, \partial \varepsilon_k / \partial \lambda^0(k) \equiv 0 \tag{73a}$$

and consequently

$$v_k = [-\nabla_k \lambda^0(k)][\partial \varepsilon_k / \partial \lambda^0(k)] \tag{73b}$$

and

$$\hat{v}_k = -\hat{\nabla}_k \lambda^0(k). \tag{73c}$$

The numerical determination of $[\partial \lambda^0(k)/\partial \varepsilon_k]^{-1}$ of course needs solutions of the KKR equations at energies just around $\varepsilon = \varepsilon_F$.

4.3. Computational aspects

If the methods outlined in the preceding sections are to be applied to interstitial impurities in FCC or BCC metals, first of all MT potentials describing the metallic host are needed. The Fermi energy is then determined by demanding that the electron-like volumes inside the different sheets of the Fermi surface add up to the chemical valence of the metal. The phase shifts η_l ($l_{max} = 3$) at the Fermi energy are used to produce an integration mesh in the first Brillouin zone with an increasing density of k-points upon approaching the singularities at the Fermi surface and the free-electron sphere (section 2.3). This mesh is produced by a program KKRMESH that iteratively approaches the singular surfaces, thereby dividing the 1/48th irreducible part of the Brillouin zone into a large number of tetrahedra [53]. For each of the four k-points defining the corners of a tetrahedron the matrix $V(k)$ (see (10)) and the eigenvalues $\lambda^p(k)$ are stored. The Fermi surface itself is given in terms of triangular surface elements defined by three k-points, for which the $V^0(k)$, $\nabla_k \lambda^0(k)$ and $\partial \lambda^0(k)/\partial \varepsilon_k$ are stored. A special program (LINMESH) reduces the number of k-points that occur more than once in adjacent tetrahedra or triangles. This compressed mesh consists of a collection of unique k-points and corresponding eigenvectors, eigenvalues and gradients plus information on how to build the original mesh from this collection.

Using the 48 orthogonal transformations O_i ($i = 1, \ldots, 48$) of the point group O_h, the mesh can be extended to the entire Brillouin zone,

$$
\begin{aligned}
O_i k = k' \qquad & V^p(k') = U_i V^p(k) \\
\lambda^p(k') = \lambda^p(k) \qquad & M(k') = U_i M(k) U_i^{-1}
\end{aligned} \tag{74}
$$

where U_i are the corresponding transformations in the function space spanned by the real spherical harmonics. When dealing with the Green function for a general interstitial position, the integrals must be evaluated over the correspondingly larger irreducible part of k-space belonging to the point group of the interstitial position in the crystal. This necessity comes from the interstitial structure matrices $g^I(k)$ through $W^p(k)$ in (38b), (39), (71b) and (71c). The structure matrices are evaluated with the efficient Ewald summation method [54] but nevertheless demand the major part of the computer time needed to calculate the integrals. In a detailed study of the de Haas–van Alphen effect in Pd(H), Oppeneer *et al* [26, 55, 56] already calculated the aforementioned integrals for the special case of a hydrogen atom at an octahedral site in the FCC lattice. In that work explicit use was made of the fact that the irreducible part remains 1/48th

of the Brillouin zone and that $i^{l'-l}[-i\kappa g^l(k)]$ is purely real. These results served as a test for the new programs. When applied to the octahedral position the new programs give the same results for $\mathcal{G}_{lL_jL'}$ and $\mathcal{G}_{lL_jL'}$.

The actual evaluation of the integrals is much in the spirit of Oppeneer's approach although the programs were designed in such a way that optimal use could be made of the vector facilities on a Cyber 995E computer under the NOS/VE operating system of CDC. Vectorization was done on the index labelling the k-vector in the Brillouin zone mesh throughout the program INTEG. In this way even integrations over 1/4th part of the Brillouin zone could be performed within an acceptable computer time span.

Finally integrals over irreducible parts are converted to integrals over the entire Brillouin zone by applying all elements in the point group. For example $G_{lL_jL'}$ and $I_{lL_jL'}$ are assembled through

$$\mathcal{G}_{lL_jL'} t_{l'} = \sum_{i=1}^{h} \left[U_i \left(-\frac{1}{\kappa V_{BZ}} \int_{BZ, \text{irred}} \mathrm{d}^3 k \, \mathrm{e}^{\mathrm{i}k \cdot \hat{O}_i R_{lj}} (-\mathrm{i}\kappa g^l) M^{-1} \right) \bar{U}_i \right]_{LL'}$$

and

$$I_{lL_jL'} = \sum_{i=1}^{h} \frac{\mathrm{i}^{l'-l}}{\kappa V_{BZ}} O_i \begin{bmatrix} \left[U_i \left(\int_{FS, \text{irred}} \mathrm{d}S_k \, W^0 \frac{\hat{v}_x}{|\nabla_k \lambda^0|} V^0 \, \mathrm{e}^{-\mathrm{i}k \cdot \hat{O}_i R_{lj}} \right) \bar{U}_i \right]_{LL'} \\ \left[U_i \left(\int_{FS, \text{irred}} \mathrm{d}S_k \, W^0 \frac{\hat{v}_y}{|\nabla_k \lambda^0|} V^0 \, \mathrm{e}^{\mathrm{i}k \cdot \hat{O}_i R_{lj}} \right) \bar{U}_i \right]_{LL'} \\ \left[U_i \left(\int_{FS, \text{irred}} \mathrm{d}S_k \, W^0 \frac{\hat{v}_z}{|\nabla_k \lambda^0|} V^0 \, \mathrm{e}^{-\mathrm{i}k \cdot \hat{O}_i R_{lj}} \right) \bar{U}_i \right]_{LL'} \end{bmatrix}$$

where h denotes the order of the point group. Note that integrals over irreducible parts for different vectors $\hat{O}_i R_{lj}$ ($i = 1, \ldots, h$) are mixed together to give the desired complete integral for R_{lj}. The program SYMMETRY performing this last step consumes a negligible amount of computer time when compared with the previous programs.

Now with appropriate phase shifts η_l^n the matrix A^{-1} (see (26)) can be constructed. After inversion of A^{-1} the vectorial matrix W is built and the wind valence tensor (69a) can be calculated in a last step. In the next, final subsection the operation and the relative time consumption of the programs will be illustrated by Pd(H) and Nb(H) serving as representative examples of FCC and BCC systems.

4.4. Examples: Pd(H) and Nb(H)

Palladium, being an FCC metal with lattice parameter $a = 7.351$ Bohr, has a complicated Fermi surface consisting of three separate sheets when neglecting spin–orbit coupling [57]. There are the central Γ sheet, the jungle gym (JG) sheet, often encountered when dealing with d electrons, and the X-hole pockets. Further it is known that hydrogen occupies the octahedral position. Migration might take place along the [1 1 1] direction pointing towards the tetrahedral position [58]. Along this path the symmetry operations defining the point group C_{3v} are present ($h = 6$). The potentials used by Oppeneer *et al* [26] give $\varepsilon_F = 0.515$ Ryd above the MT zero. An angular momentum cut-off at $l_{max} = 3$ was used. The Brillouin zone mesh inside the 1/48th irreducible part consists of 11 138 tetrahedra giving rise to a reduced set of 4610 k-vectors. An additional reduced set of 767 k-vectors for the different sheets of the Fermi surface represent 269 (Γ), 471 (JG)

Table 1. Phase shifts η_l in radians at $\varepsilon_F = 0.515$ Ryd for host Pd atoms, the octahedral impurity cluster and the tetrahedral impurity cluster. The last column displays the MT radii for the different atoms in Bohr.

Atom	η_0	η_1	η_2	η_3	R_{MT}
Pd host	−0.460 649	−0.094 864	−0.298 246	0.001 546	2.3891
H octahedral	1.259 393	0.024 300	0.000 440	0.000 005	1.2864
Pd first shell	−0.049 794	−0.091 142	−0.291 735	0.001 589	2.3891
H tetrahedral	0.872 207	0.005 979	0.000 045	$<10^{-6}$	0.7939
Pd first shell	−0.433 511	−0.085 589	−0.282 298	0.001 654	2.3891

and 56 (X) triangles enclosing volumes of 0.309, 1.704 and 1.991 electrons respectively. Together with six electrons in filled Brillouin zones this adds up to 10.004 valence electrons. Note that for the numerical evaluation of (38a), (38b) and (39) a total number of $8(4610 + 767) = 43\,016$ complex interstitial structure matrices had to be calculated. After having calculated the integrals G and I for the octahedral and tetrahedral positions the A-matrix is constructed. The phase shifts used for the interstitial atom at the octahedral position and for the first shell of perturbed host atoms surrounding it are those given by Oppeneer in the Pd(H) paper [26]. For the tetrahedral position phase shifts were calculated for potentials that have been constructed following the same recipe. Both sets of phase shifts are given in table 1. They do not include lattice distortion nor do they satisfy the Friedel sum rule. For the present purpose of showing the feasibility of wind valence calculations this is not important.

The resulting 3×3 tensor for an octahedral hydrogen atom is

$$\frac{\underline{Z}_{wind}^{oct}}{\tau} = \begin{pmatrix} -0.010\,97 & 0.000\,00 & 0.000\,00 \\ 0.000\,00 & -0.010\,97 & 0.000\,00 \\ 0.000\,00 & 0.000\,00 & -0.010\,97 \end{pmatrix}$$

while at the tetrahedral position it is

$$\frac{\underline{Z}_{wind}^{tet}}{\tau} = \begin{pmatrix} 0.001\,26 & 0.000\,03 & 0.000\,03 \\ 0.000\,03 & 0.001\,26 & 0.000\,03 \\ 0.000\,03 & 0.000\,03 & 0.001\,26 \end{pmatrix}.$$

Although the free-electron picture certainly does not apply to Pd, one might get an impression of the magnitude of the wind valence by multiplying these matrices with a τ value of about 10 as derived from the bulk resistivity [59] at room temperature using the free-electron expression for the resistivity [52]. Symmetry demands diagonality at both the octahedral and tetrahedral positions. This is realized at the tetrahedral position only in an approximate way. The small off-diagonal elements are due to the specific way in which the interstitial structure matrices are evaluated. The direct-space part of the Ewald summation has the octahedral position as its origin. Vectors R_{lj} are grouped in shells around this position. It is readily imaginable that upon leaving the first (octahedral) shell this grouping of the R_{lj} is no longer an appropriate choice to achieve fastest convergence in the Ewald summation.

Table 2. Phase shifts η_l in radians at $\varepsilon_F = 0.852$ Ryd for host Nb atoms, the tetrahedral impurity cluster and the octahedral impurity cluster. The last column displays the MT radii for the different atoms in Bohr.

Atom	η_0	η_1	η_2	η_3	R_{MT}
Nb host	−1.227 907	−0.526 527	0.897 286	0.006 503	2.0922
H tetrahedral	1.164 623	0.060 603	0.002 139	0.000 051	1.3948
Nb first shell	−1.225 550	−0.525 584	0.926 668	0.006 565	2.0922
H octahedral	1.059 525	0.026 228	0.000 520	0.000 007	1.0267
Nb first shell	−1.223 287	−0.524 705	0.956 334	0.006 651	2.0922
Nb second shell	−1.227 439	−0.526 326	0.903 123	0.006 494	2.0922

In niobium ($a = 6.238$ Bohr) the hydrogen atom occupies a nearly tetrahedral site with point symmetry D_{2d}. When leaving this site along the [100] direction towards the so-called octahedral site (point group D_{4h}) the symmetry is reduced to C_{2v} ($h = 4$). Table 2 shows the phase shifts and MT radii used for the Nb(H) system at the different sites. The host phase shifts give rise to a mesh consisting of 8086 tetrahedra (a reduced set of 3607 k-points). The Fermi energy is 0.852 Ryd and the Fermi surface comprises a central Γ sheet enclosing holes (153 k-points, 177 triangles) and a JG sheet (612 k-points, 915 triangles). Note that the JG sheet incorporates both the hole tubes and the N-hole pockets [60] for they come from the same root of the KKR equation. The enclosed electron volumes are 1.898 and 1.100 for the Γ sheet and the JG sheet respectively. Together with one completely filled Brillouin zone this gives a total of 4.998 electrons in the valence band. The wind valence tensor for a hydrogen atom at the tetrahedral position is

$$\frac{\underline{Z}_{wind}^{tet}}{\tau} = \begin{pmatrix} 0.052\,85 & 0.000\,00 & 0.000\,00 \\ 0.000\,00 & -0.058\,90 & 0.000\,00 \\ 0.000\,00 & 0.000\,00 & -0.058\,90 \end{pmatrix}.$$

For an octahedral hydrogen atom the tensor is

$$\frac{\underline{Z}_{wind}^{oct}}{\tau} = \begin{pmatrix} 0.072\,15 & 0.000\,00 & 0.000\,00 \\ 0.000\,00 & 0.072\,15 & 0.000\,00 \\ 0.000\,00 & 0.000\,00 & -0.241\,38 \end{pmatrix}.$$

Note the anisotropy at the tetrahedral position as well as at the octahedral position. Just as for Pd(H) no lattice distortion was accounted for and the Friedel sum rule was not satisfied. At the average electron density in niobium we find a transport relaxation time of about 20 at room temperature.

The programs are designed to deal with an extra shell of surrounding atoms, although this is expected to be of little importance for the electron scattering, as already noticed by Oppeneer *et al* [26]. The computer time consumption of the various programs is dominated by the calculation of the integrals. Unfortunately this is a program that must be executed repeatedly for several positions along the migration path.

5. Concluding remarks

In the context of multiple scattering of Bloch electrons by impurity clusters, a method for the calculation of the electromigration wind force on interstitial impurities in FCC and BCC metals has been implemented in the form of a FORTRAN computer program. Starting from a well founded theoretical expression for the wind force on an impurity in a jellium, an equivalent expression in a real metal could be justified. When elaborated in terms of scattering by MT potentials, vectorial integrals over constant energy surfaces in *k*-space emerge. These vectorial integrals, together with Brillouin zone integrals, must be evaluated for general interstitial positions in order to follow the impurity during a migration jump. Although an enormous number of interstitial structure matrices have to be calculated at each position of the interstitial, the required computer time remains within acceptable limits. The result of a calculation at a certain interstitial position is the 3×3 wind valence tensor, which of course needs additional interpretation before making a comparison with experimental effective valences.

In the following paper the electromigration of small interstitials like H, C, B and O in non-magnetic FCC (Cu, Ag, Ni, Pd, Al) and BCC (V, Nb, Ta) metals will be investigated with the tools developed in this paper.

Many experiments on electromigration of substitutional impurities have been reported on. It is therefore interesting to consider to what extent the programs developed for interstitials could apply to these systems. Although this will be a subject of a future publication, it can be stated that at the initial position (i.e. all atoms at lattice positions) there is no point at all in calculating the wind force on, for instance, an atom next to a vacancy. No interstitial structure matrices are needed, only the integrals connecting lattice vectors have to be calculated. However, as pointed out clearly by Lodder [61], things get entirely different upon walking the migration path. Nevertheless application of the present formalism to the initial position already might reveal valuable information concerning the magnitude of the wind valence and its alteration upon leaving the initial position by only a small distance.

Appendix

In this appendix the matrix element

$$\langle \bar{\Psi}_k(r) | -\nabla_{R_1} v_1(r - R_1) | \bar{\Psi}_k(r) \rangle$$

as it occurs in (67) will be elaborated for MT potentials.

The single-particle alloy wavefunction $\bar{\Psi}_k(r)$ obeys

$$[-\nabla^2 + V_{\text{MTZ}} + v_1(x) - \varepsilon_k] \bar{\Psi}_k(x) = 0 \tag{A1}$$

in the interstitial region where V_{MTZ} is the MT constant. Application of ∇_x from the left side yields

$$[-\nabla^2 + V_{\text{MTZ}} + v_1(x) - \varepsilon_k][\nabla_x \bar{\Psi}_k(x)] = [-\nabla_x v_1(x)] \bar{\Psi}_k(x) \tag{A2}$$

for only $v_1(x)$, the local perturbation due to the impurity, and $\bar{\Psi}_k(x)$ depend on x.

Multiplication of (A2) by $\bar{\Psi}_k^*(x)$ from the left-hand side and adding and subtracting $[\nabla_x \bar{\Psi}_k(x)][\nabla^2 \bar{\Psi}_k^*(x)]$ gives

$$\bar{\Psi}_k^*(x)[-\nabla_x v_1(x)]\bar{\Psi}_k(x) = -\bar{\Psi}_k^*(x)\nabla^2[\nabla_x \bar{\Psi}_k(x)]$$
$$+ [\nabla_x \bar{\Psi}_k(x)][\nabla^2 \bar{\Psi}_k^*(x)] - [\nabla_x \bar{\Psi}_k(x)][\nabla^2 \bar{\Psi}_k^*(x)]$$
$$+ [V_{MTZ} + v_1(x) - \varepsilon_k]\bar{\Psi}_k^*(x)[\nabla_x \bar{\Psi}_k(x)]. \tag{A3}$$

The last two members of the right-hand side of (A3) vanish because of (A1).

Integration of the left-hand side of (A3) over all space can be restricted to the volume inside the muffin-tin sphere of v_1 with radius R_{MT}. Using Green's theorem to convert the volume integration to an integration over the surface enclosing this volume, (A3) can be integrated

$$\int_{x \leqslant R_{MT}} d^3x\, \bar{\Psi}_k^*(x)[\nabla_x v_1(x)]\bar{\Psi}_k(x) = R_{MT}^2 \int_{x = R_{MT}} d\hat{x}\, [\bar{\Psi}_k^*(x), \nabla_x \bar{\Psi}_k(x)]_{x = R_{MT}}. \tag{A4}$$

Realizing that $\nabla_x v_1(x) = -\nabla_{R_1} v_1(r - R_1)$, one additionally needs expression (24) with $n = I$ and

$$\nabla_x[f_l(\kappa x)Y_L(\hat{x})] = \kappa \sum_{L'} f_{l'}(\kappa x)Y_{L'}(\hat{x})(\delta_{l',l-1} - \delta_{l',l+1})D_{LL'}$$
$$D_{LL'} = \int d\hat{x}\, Y_L(\hat{x})\hat{x}Y_{L'}(\hat{x}) \tag{A5}$$

where $f_l = j_l$ or n_l, and the Wronskian

$$[j_l(\kappa x), n_l(\kappa x)] = 1/\kappa x^2 \tag{A6}$$

to show that

$$\int_{x \leqslant R_{MT}} d^3x\, \bar{\Psi}_k^*(x)[-\nabla_{R_1} v_1(r - R_1)]\bar{\Psi}_k(x)$$

$$= 2\varepsilon_F \sum_L \sum_{m_1 = -l-1}^{l+1} (\cot \eta_{l+1}^I - \cot \eta_l^I)D_{Ll+1,m_1}$$
$$\times \mathrm{Re}[t_{l+1}^{l''} t_l^I \bar{C}_{ll+1,m_1}^*(k)\bar{C}_{lL}(k)]. \tag{A7}$$

This result has been derived earlier for finite clusters [62, 63].

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