Defect and Diffusion Forum Vols. 261-262 (2007) pp. 77-86
online at http://www.scientific.net

Direct Force Controversy in Electromigration Exit

A. Lodder

Faculty of Sciences/Physics and Astronomy, Vrije Universiteit,
De Boelelaan 1081, 1081 HV Amsterdam, The Netherlands
email: A.Lodder@few.vu.nl

Keywords: Electromigration, direct force, controversy, multiple-scattering effects.

Abstract. The last remaining claim of a complete cancellation of the direct force in electromigration is invalidated. In addition new numerical results are given for the magnitude of the direct force on hydrogen in a metallic embedment, showing a screening of at most 40%. The hydrogen potential used is obtained by an *ab initio* method.

Introduction

The driving force **F** on hydrogen in a metal due to an applied electric field is composed of two contributions, a direct force $\mathbf{F}_{\mathrm{d}}$ due to the charge of the proton and a wind force $\mathbf{F}_{\mathrm{w}}$ due to transfer of momentum of the current carrying electrons to the proton:

$$\mathbf{F} = \mathbf{F}_{\mathrm{d}} + \mathbf{F}_{\mathrm{w}} = (Z_{\mathrm{d}} + Z_{\mathrm{w}})\, e\mathbf{E} = Z^{*}e\mathbf{E}. \tag{1}$$

The forces are proportional to corresponding valences and the applied electric field **E**. The effective valence Z^* is the measurable quantity [1]. A basic task of the theory of electromigration is to provide with a microscopically correct expression for the driving force. The wind force is a quantity that has been calculated reliably for many systems with *ab initio* methods for the electronic structure [2]. This has been done not only for migration of interstitials such as hydrogen, but also for substitutional impurities, including self-electromigration [3, 4, 5]. The direct force has been the subject of a long-standing controversy, initiated by the $Z_{\mathrm{d}} = 0$ result of Bosvieux and Friedel [6], which was given support later by Turban et al. [7]. Since about 1985 a consensus has been reached. On the ground of numerical calculations of Z_{d}, in which the hydrogen potential was modeled by a square well, the screening of the direct force was considered to be 25% or less [8]. In spite of that, Friedel and Nozières kept defending their result that only a wind force was operative.

However, recently it has been shown that, although the starting formula of Bosvieux and Friedel was correct, their elaboration failed, and their conclusion of a complete cancellation of the direct force was incorrect [9, 10]. In fact, a correct elaboration of their starting formula led to an expression for the driving force which was equivalent to all linear response expressions used after their introduction by Kumar and Sorbello [11]. By this one of the two $Z_{\mathrm{d}} = 0$ claims has been invalidated.

Turban et al. use a linear response approach which can be analyzed relatively easily [7]. It will be made clear that these authors have not been aware of a treacherous trap which shows up sometimes at some points of the theory of electromigration [9, 12]. We will show that their conclusion of a complete cancellation of the direct force was incorrect as well.

In addition, new results will be presented for the amount of screening of the direct force on hydrogen, using phase shifts of *ab initio* constructed potentials in different metallic host systems.

But we start by giving the main ingedients of the linear-response description of the driving force in electromigration.

Linear-response description

The quantum statistical expectation value for the force on an impurity with chemical valency Z_i at a position $\mathbf{R}_1$ due to an applied electric field is given by [1, 10]

$$\mathbf{F} = Z_i e\mathbf{E} - Tr\Big\{\rho(t)\nabla_{\mathbf{R}_1} V_{ei}\Big\} = \mathbf{F}_{\mathrm{d}}^{\prime\mathrm{bare}\prime} + \mathbf{F}_{\mathrm{w}}^{\mathrm{total}}. \tag{2}$$

in which $\rho(t)$ is the time dependent density operator and the force operator contains the electron-impurity potential $V_{ei} = \sum_{j,\alpha} v(\mathbf{r}_j - \mathbf{R}_\alpha) \equiv \sum_{j,\alpha} v_j^\alpha$. The first term is clearly the direct force on the bare ion. It appears that the second term, which is of course supposed to lead to the wind force, also contains some screening contribution to the direct force. The controversy has not to do with the fact that there is a screening contribution in $\mathbf{F}_{\mathrm{w}}^{\mathrm{total}}$, but it is as to the magnitude of that screening contribution that people don't agree with each other.

Using the linear response expression for $\rho(t)$ one finds for $\mathbf{F}_{\mathrm{w}}^{\mathrm{total}}$

$$\mathbf{F}_{\mathrm{w}}^{\mathrm{total}} = -ieE_\nu \int_0^\infty \mathrm{d}t e^{-at} Tr\Big\{\rho(H)\Big[\mathbf{F}^{\mathrm{op}}(t), \sum_j r_j^\nu\Big]\Big\}, \tag{3}$$

in which the cartesian label ν runs from 1 to 3. The infinitisimally positive number a represents the adiabatical switch-on of the electric field, the operator $\rho(H)$ is the grandcanonical density depending on the system Hamiltonian H, the force operator $\mathbf{F}^{\mathrm{op}}$ stands for

$$\mathbf{F}^{\mathrm{op}} \equiv -\nabla_{\mathbf{R}_1} V_{ei} = -\sum_j \nabla_{\mathbf{R}_1} v(\mathbf{r}_j - \mathbf{R}_1) \equiv \sum_j \mathbf{f}_j^1, \tag{4}$$

and its time dependence refers to the Heisenberg representation

$$\mathbf{F}^{\mathrm{op}}(t) \equiv e^{iHt}\mathbf{F}^{\mathrm{op}}e^{-iHt}. \tag{5}$$

The driving force (2) can be decomposed as follows:

$$\mathbf{F} = Z_i e\mathbf{E} + \mathbf{F}_{\mathrm{w}}^{\mathrm{total}} = Z_i e\mathbf{E} + \mathbf{F}_{\mathrm{w}}^{\mathrm{scr}} + \mathbf{F}_{\mathrm{w}}^{\mathrm{BF}} = (Z_i + Z^{\mathrm{scr}} + Z_{\mathrm{w}})e\mathbf{E} = (Z_{\mathrm{d}} + Z_{\mathrm{w}})e\mathbf{E}, \tag{6}$$

containing the result of Bosvieux and Friedel for the wind force $\mathbf{F}_{\mathrm{w}}^{\mathrm{BF}}$ and a screening contribution [6]. In all treatments available $\mathbf{F}_{\mathrm{w}}^{\mathrm{BF}}$ can be written in its general form

$$\mathbf{F}_{\mathrm{w}}^{\mathrm{BF}} = -\int \delta n(\mathbf{r})\nabla_{\mathbf{R}_1} v^1 d^3r, \qquad \text{with} \qquad v^1 = v(\mathbf{r} - \mathbf{R}_1). \tag{7}$$

The precise explicit form depends on the level of approximation used to represent $\delta n(\mathbf{r})$, which is the local deviation of the electron density from its unperturbed host value due to the applied field and the presence of the impurity. From now on we will concentrate on Z_{d}.

The force expression (3) can be simplified using the fact, that previous relevant descriptions have been given for the electron-impurity system, the Hamiltonian H of which can be be written as a sum of single particle Hamiltonians h, so

$$H = \sum_j h^j \qquad \text{with} \qquad h = h_0 + v = h_0 + \sum_\alpha v^\alpha. \tag{8}$$

This allows for a reduction of the many body expression (3) to the following single particle expression,

$$F_{\mathrm{w}}^{\mathrm{total}} = -ieE \int_0^\infty \mathrm{d}t\ e^{-at}\ tr\Big\{[x, n(h)]f^1(t)\Big\}, \tag{9}$$

where $n(h)$ is the Fermi-Dirac distribution function in operator form

$$n(h) = \frac{1}{e^{\beta(h-\epsilon_{\rm F})} + 1}. \tag{10}$$

In Eq. (9) we adopted the choice of Turban et al. for the x direction, which is allowed because the system is rotationally invariant or, equivalently, isotropic if the position of the impurity is taken as the origin of coordinates.

It has been shown explicitly that if in the right hand side of Eq. (9) the statistical operator is replaced by this operator for the free particle system, so $n(h) \rightarrow n(h_0)$, the Bosvieux-Friedel wind force expression $F_{\rm w}^{\rm BF}$ arises [13]. That means that the screening part is given by

$$F_{\rm w}^{\rm scr} = -ieE \int_0^\infty {\rm d}t\ e^{-at}\ tr\Big\{[x, n(h) - n(h_0)] f^1(t)\Big\} = Z^{\rm scr} eE. \tag{11}$$

A further reduction can be achieved by restricting the evaluation to a system with one impurity in a jellium, which is in accordance with earlier work by others [7, 8]. In that case $f^1 = i[p^x, h] = i[p^x, h_0 + v^1]$. By writing Eq. (11) in terms of eigenstates of $h \rightarrow h_0 + v^1$, labeled by q and q', one finds [10]

$$Z^{\rm scr} = -Z_i + Z_{\rm corr} \equiv -Z_i + i \sum_{qq'}^{\epsilon_q = \epsilon_{q'}} < q|[x, n(h) - n(h_0)]|q' > p^x_{q'q} \equiv -Z_i + Z_{\rm d}. \tag{12}$$

In view of Eq. (6) this would imply a correction term $Z_{\rm corr}$ to the cancellation of the bare direct valency Z_i, by which, effectively, $Z_{\rm corr} = Z_{\rm d}$.

Summary of the treatment by Turban et al. [7]

Turban et al. concentrate on the equality

$$Z^* e = \Big(\frac{\mathbf{J}}{\mathbf{J}_i}\Big)_{\mathbf{E}=0}, \tag{13}$$

which can be derived using the principles of the thermodynamics of irreversible processes. The effective valence Z^* is directly related to the total flux $\mathbf{J}$ of electric charge, ionic as well as electronic, associated with a unit flux of the impurity, in the absence of an applied electric field. They first calculate the total electron flux J_e induced by an impurity with charge $Z_i e$ moving with a constant velocity u in the x direction. According to their Eq. (16) they find that

$$\Big(\frac{J_e}{u}\Big)_{\mathbf{E}=0} = -\sum_{mn} \frac{\nu_m - \nu_n}{E_m - E_n - ia} F^{\rm op}_{mn} X_{nm}, \tag{14}$$

in which $\nu_m =< m|\rho(H)|m >$ is the occupation number of the level E_m corresponding to the eigenvector $|m>$ of the Hamiltonian of the electron system with the impurity at some position, and $X = \sum_j x_j$ is the position operator for the electron system. Because of the equality

$$i \int_0^\infty dt < m|F^{\rm op}(-t)|n > e^{-at} = \frac{F^{\rm op}_{mn}}{E_m - E_n - ia}, \tag{15}$$

Eq. (14) can be rewritten as

$$\begin{aligned} (\frac{J_e}{u})_{\mathbf{E}=0} &= -i \int_0^\infty dt\ e^{-at} \sum_{mn} (\nu_m - \nu_n) < m|F^{\rm op}(-t)|n > X_{nm} \\ &= -i \int_0^\infty dt\ e^{-at} Tr\{\rho(H)[F^{\rm op}(-t), X]\}. \end{aligned} \tag{16}$$

Note that this latter form differs from $F_{\mathrm{w}}^{\mathrm{total}}/eE$ according to Eq. (3) only by the sign of the time dependence of the force operator. After that Turban et al. argue that J_e, representing the total electron current, can be decomposed as

$$J_e = Z_i u + J_e^{\mathrm{w}} \equiv (Z_i - Z_{\mathrm{w}})u, \tag{17}$$

in which J_e^{w} represents the friction current due to the scattering of the free carriers by the moving impurity, being equal to $-Z_{\mathrm{w}}u$ in the notation of the present paper. It may be worth while to mention that, for a simple metal, $Z_{\mathrm{w}} < 0$, because the electric current flows in a direction opposite to the electric field direction and the current determines the direction of the wind force. Subsequently, the authors evaluate Eq. (3) using their own notation, and they find that

$$F_{\mathrm{w}}^{\mathrm{total}} = eE\sum_{mn}\frac{\nu_m - \nu_n}{E_m - E_n + ia}F_{mn}^{\mathrm{op}}X_{nm} = -eE\Big(\frac{J_e}{u}\Big)_{\mathbf{E}=0}. \tag{18}$$

If one looks away from the difference in sign of the infinitesimal term ia in the denominator, the second equality can be read rightaway from Eq. (14). Substitution into Eq. (6) leads to

$$F = eE\Big(Z_i - \Big(\frac{J_e}{u}\Big)_{\mathbf{E}=0}\Big). \tag{19}$$

In view of their conjectured Eq. (17) Turban et al. end up with a total force

$$F = -eE\Big(\frac{J_e^{\mathrm{w}}}{u}\Big)_{\mathbf{E}=0}, \tag{20}$$

which is just the wind force. The authors conclude that by this result they have clarified and demonstrated Eq. (13) and further that the direct electrostatic force on the impurity vanishes.

Analysis of the treatment by Turban et al.

Although the derivations reproduced above are correct, there is one weak point in the analysis, namely Eq. (17). By now there is an overwhelming evidence that that equation is incomplete [8, 10, 14]. Instead of conjecturing Eq. (17), Sham evaluated $F_{\mathrm{w}}^{\mathrm{total}}$, by that effectively evaluating J_e explicitly, see Eq. (18) [14]. To lowest order in the impurity potential he finds Eq. (6) with a vanishing Z^{scr}, so that according to that work $Z_{\mathrm{d}} \approx Z_i$. From a description to all orders in the impurity potential, Sorbello found that $-Z^{\mathrm{scr}}/Z_i \leq 0.25$ [8]. A recent, rather thorough calculation leads to Eq. (12) [10]. Eq. (17) is equivalent to the equality $Z^{\mathrm{scr}} = -Z_i$, which would imply a complete screening of the direct force. One way or the other Eq. (17) gives a picture of the actual physical process which is too simple.

Before discussing the physical situation it may be interesting to point at a specific feature of the contributions after Sham's work. While Sham finds just one term for Z^{scr}, which to lowest order in the impurity potential is small compared to Z_i, both Sorbello and the present author find two terms of about the same magnitude which have to be subtracted. Sorbello wrote

$$Z^{\mathrm{scr}} = -Z_i + Z_{\mathrm{d}}, \tag{21}$$

which is equivalent to Eq. (12). Initially, the present author found the Turban et al. result $Z^{\mathrm{scr}} = -Z_i$ [13]. It is only recently that a treacherous hidden trap was discovered and a second term was found, which was called a correction term Z_{corr}, see Eq. (12).

Because of this surprising result, and because of the fact that the different elaborations for $F_{\mathrm{w}}^{\mathrm{total}}$ are spread over the literature, we will give the main steps for the evaluation of J_e/u, see Eq. (16). To that end we first write down the corresponding single particle expression,

$$\Big(\frac{J_e}{u}\Big)_{\mathbf{E}=0} = -i\int_0^\infty \mathrm{d}t\; e^{-at}\; tr\Big\{[x, n(h) - n(h_0) + n(h_0)]f^1(-t)\Big\}. \tag{22}$$

Note that this expression differs from $F_{\rm w}^{\rm total}/eE$ in Eq. (9) merely in the sign of the time dependence of the force operator. This is another reason for giving the explicit evaluation, because from these expressions equality (18) is not completely obvious, although it will turn out to be correct. If one follows Sham's approach, he obtained two lowest order terms in the impurity potential, which are v^2 terms. Because the force operator is proportional to v, one of the v^2 terms comes from the time dependence of the force operator, to be combined with the $n(h_0)$ operator in Eq. (22). The other one comes from the operator difference $n(h) - n(h_0)$, while then in the time dependence operators h can be replaced by h_0. Using the expansion

$$n(h) = n(h_0) - n(h_0)\int_0^\beta ds\; v(s)(1-n(h_0)) + \text{ higher order in } v, \tag{23}$$

one finds straightforwardly, that

$$\begin{aligned} -i\int_0^\infty \mathrm{d}t\; e^{-at}\; tr\Big\{[x, n(h)-n(h_0)]f^1(-t)\Big\} &= \\ = \frac{4}{m}\sum_{kk'} k_x(k_x-k'_x)\frac{|v_{kk'}|^2}{(\epsilon_k-\epsilon_{k'})^2+a^2}\left(\frac{\partial n_k}{\partial \epsilon_k} - \frac{n_k-n_{k'}}{\epsilon_k-\epsilon_{k'}}\right) &= -Z^{\rm scr(2)}. \end{aligned} \tag{24}$$

This is precisely the opposite of $Z^{\rm scr}$ in Eq. (17) of Ref. [10]. The superscript (2) indicates that it is the expression to lowest (= second) order in the impurity potential. Using the expansion

$$e^{iht} = \left(1 + i\int_0^t dsv(s) + \cdots\right)e^{ih_0t}, \tag{25}$$

one finds for the other term in Eq. (22)

$$\begin{aligned} -i\int_0^\infty \mathrm{d}t\; e^{-at}\; tr\Big\{[x, n(h_0)]f^1(-t)\Big\} &= \\ -\frac{2\pi\tau}{m}\sum_{kk'}\frac{\partial n_k}{\partial\epsilon_k}k_x(k_x-k'_x)|v_{kk'}|^2\delta(\epsilon_k-\epsilon_{k'}) &= -Z_{\rm w}^{(2)}, \end{aligned} \tag{26}$$

in which the artificial demping parameter a in front has been replaced by the inverse of the system transport relaxation time τ, in accordance with Sham's paper and a remark of the same tenor in the paper of Turban et al. This is precisely the opposite of the lowest order evaluation of the wind valence expression, Eq. (7), rewritten as

$$Z_{\rm w}^{\rm BF} = \frac{1}{eE}\int d^3r\;\delta n(\mathbf{r})f^1 = \frac{\tau}{m}\sum_k k_x\frac{\partial n_k}{\partial\epsilon_k}\int d^3r|\psi_k(\mathbf{r})|^2 f^1, \tag{27}$$

in which ψ_k is the exact wave function of the electron as it is perturbed locally by the presence of the impurity. Substituting Eqs. (24) and (26) in Eq. (22) we find for the lowest order result

$$\left(\frac{J_e}{u}\right)^{(2)}_{\mathbf{E}=0} = -Z^{\rm scr(2)} - Z_{\rm w}^{(2)}. \tag{28}$$

Before we give the evaluation of the left hand side of Eq. (24) to all orders in the impurity potential, we comment on this lowest order result. First of all, Sham gave an order of magnitude estimate of $Z^{\rm scr(2)}/Z_{\rm w}^{(2)} \approx 1/(E_{\rm F}\tau)$, which is negligible. Recently $Z^{\rm scr(2)}$ has been calculated numerically, and the conclusion was that the screening was at most 25% [10]. Secondly, the result (24) has been used as a strong argument against a complete screening, represented by $Z^{\rm scr} = -Z_i$. For, $Z^{\rm scr(2)}$, being the lowest order result and being quadratic in the potential, is quadratic in Z_i. This means that there is no room theoretically for a $Z^{\rm scr}$, which is linear in Z_i.

Now we give the evaluation to all orders, and this will reveal a treacherous trap. As above we use the equality $f^1 = i[p^x, h]$ and the eigenstates of $h \to h_0 + v^1$, labeled by q and q'. By this one can carry out the time integral and finds

$$\begin{aligned} &-i\int_0^\infty \mathrm{d}t\; e^{-at}\; tr\Big\{[x, n(h) - n(h_0)]f^1(-t)\Big\} \\ &= i\sum_{qq'} < q|[x, n(h) - n(h_0)]|q'> \frac{\epsilon_q - \epsilon_{q'}}{\epsilon_q - \epsilon_{q'} + ia} p^x_{q'q} \\ &= i\sum_{qq'} < q|[x, n(h) - n(h_0)]|q'> \left(1 - \frac{ia}{\epsilon_q - \epsilon_{q'} + ia}\right) p^x_{q'q} \\ &= Z_i - i\sum_{qq'}^{\epsilon_q = \epsilon_{q'}} < q|[x, n(h) - n(h_0)]|q'> p^x_{q'q} \equiv Z_i - Z_\mathrm{d} = -Z^\mathrm{scr}. \end{aligned} \qquad (29)$$

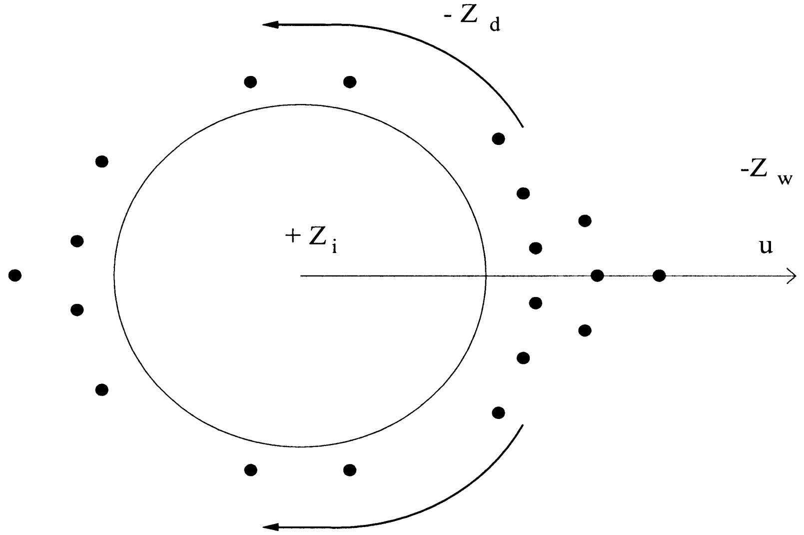

Figure 1: The impurity with charge $Z_i e$ moves to the right with a velocity u and is surrounded by electrons, depicted as solid circles. This motion induces an electron flux due to friction proportional to -Z_w to the right and a backflow proportional to -Z_d, while the impurity carries with it the screening charge $Z_i e$. The full electron flux J_e is represented by Eq. (30).

In the result for Z^scr quoted in Eq. (12) the second term was still denoted as Z_corr, as it emerged as a correction term to the full screening result Z_i. But here we denote it as Z_d, because it stands for the direct valence indeed. Note, that Z_d in Eq. (29) is the result of a seemingly artificial rewriting of the energy ratio in the second line as a sum of two terms. Naively one would expect the term proportional to the infinitisemal parameter a to be zero, but Sorbello has shown that it has a finite value if one just keeps the $\epsilon_q = \epsilon_{q'}$ terms [12]. Further, interestingly, both in the description by Sorbello and in the present most simplified description Z^scr consists of two terms which are of the same order of magnitude.

Because the wind force has never been a subject of dispute, we refer to the literature for the proof, that the left hand side of Eq. (26), evaluated to all orders in the impurity potential, leads to -Z^BF_w as it is given in the right hand side of Eq. (27) [13]. We denote this exact result as -Z_w. Combining this result and Eq. (29) with Eq. (22) we find that

$$(\frac{J_e}{u})_{\mathbf{E}=0} = -Z^{\mathrm{scr}} - Z_\mathrm{w} = Z_i - Z_\mathrm{d} - Z_\mathrm{w}. \tag{30}$$

Taking everything together we end up at a picture shown schematically in Fig. 1. An impurity moving to the right induces a friction term proportional to Z_w and a backflow term proportional to Z_d. It can be concluded that the conjectured Eq. (17) is incomplete in that a backflow term proportional to Z_d is not represented in it. There is no cancellation of the direct force. On top of that, Eq. (13) is by now even more clarified, in that also an ionic charge flow is represented in it explicitly, which is proportional to Z_d.

Numerical results for Z_d

Recently Z_d as given in the Eqs. (12) or (29) has been calculated numerically [10]. It was shown that this Z_d expression could be elaborated such that only the scattering phase shifts of the impurity were required for its numerical evaluation. Till now only model square well potentials were used in the spirit of Sorbello's calculation [8]. A metal is represented by its Fermi energy, and the corresponding square wells were chosen such, that their width was either $1/\lambda$ or $2/\lambda$, where λ is the Thomas-Fermi screening parameter. In the present text we will make a first step towards using real-metal ionic phase shifts. For the metals which Sorbello represented merely by their Fermi energies, we constructed muffin-tin potentials for the metal atoms, both as they reproduce their Fermi surfaces and as they are perturbed by the presence of the impurity, which in the present work is the hydrogen atom. For the way it is done starting from *ab initio* calculated atomic potentials, which is rather standard, we refer the interested reader to work by van Ek and the present author [15]. A full account of the real metallic embedment of the hydrogen will be subject of future work, but a possible approach to achieve that has already been mentioned earlier [16].

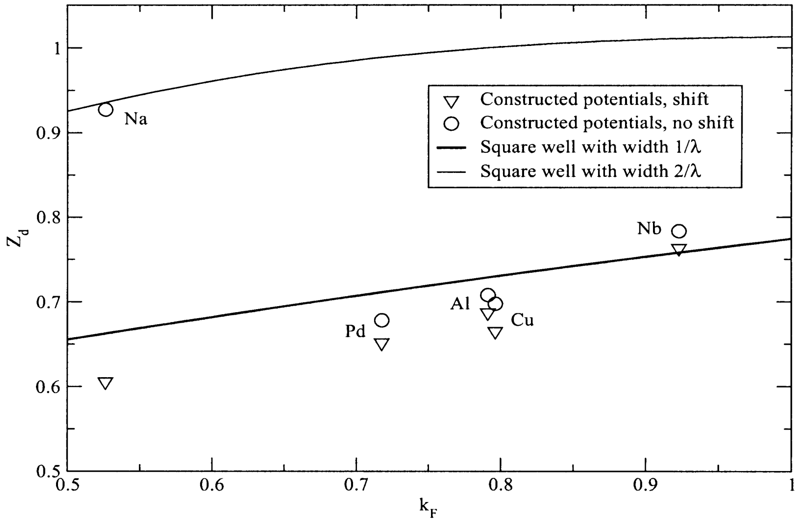

Figure 2: Z_d for hydrogen in the metals Na, Pd, Al, Cu and Nb, using *ab initio* constructed potentials and shifted ones, such that $Z_\mathcal{F} = 1$.

Here we just give the results, without reproducing the published formalism [10]. The Z_{d} values obtained by using the phase shifts for the constructed potentials are shown in Fig. 2. The circles correspond to the hydrogen potentials as they come out of the construction. That is the way they are used in earlier work [15]. The reason was, that these potentials represent the hydrogen as it is embedded by the metallic host atoms as completely as possible. The tail of the atomic hydrogen potential is incorporated in the potentials of the first and second shell of embedding host atoms, by which these atoms have phase shifts differing slightly from the unperturbed-host atom phase shifts. But here the hydrogen potential is used with just a constant potential around it, being the so-called muffin-tin zero. Therefore we also applied a shifting procedure. The potentials were shifted by a constant in order to give a Friedel sum $Z_{\mathcal{F}} = 1$. Results for these shifted potentials are given by the triangles. As a reference we show in addition the results for the two model square well potentials mentioned above, with well width r_0 equal to $1/\lambda$ and $2/\lambda$, which have formed part of the results in Ref. [10]. It is seen that the results corresponding to the original and shifted potentials do not differ much, apart from the case of sodium. Further, the model square well potential with $r_0 = 1/\lambda$ leads to Z_{d} values which are just slightly larger than those for the constructed potentials. However, while the square well values are monotonic with k_{F}, because λ decreases monotonically with k_{F}, such a systematic monotonic behaviour is not present for the metals indicated. This must be a reflection of the difference in metallic environment of the hydrogen, although the effect is not strong. So far we conclude that the picture arising from the use of *ab initio* constructed potentials does not really differ from the picture which came out of the use of model potentials. The calculated Z_{d} values lie much closer to unity than to zero, and only the latter value would imply a complete screening of the direct force.

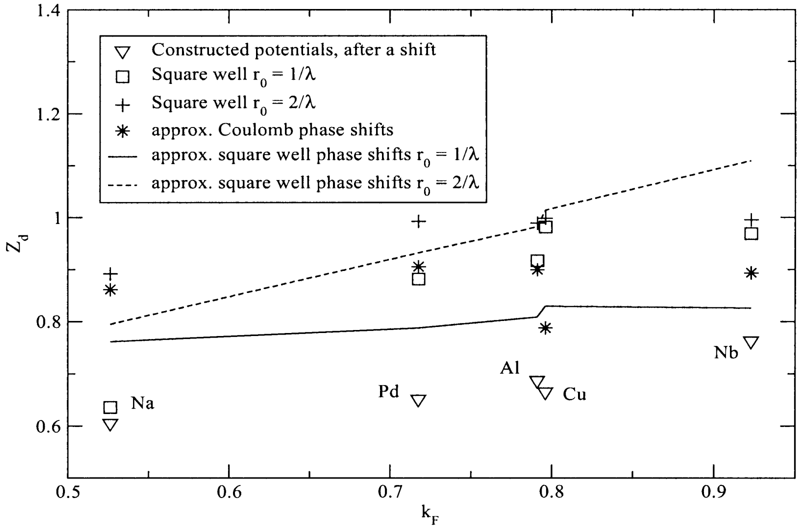

Figure 3: Z_{d} for hydrogen in the five metals indicated, using potentials derived in various ways from the *ab initio* constructed potentials after a shift, such that $Z_{\mathcal{F}} = 1$.

In order to make the present study complete we do additional calculations for potentials derived from the *ab initio* constructed potentials in various ways. Results are shown in Fig. 3. First of all we fitted these potentials to a screened Coulomb potential, by that obtaining the corresponding values for the screening parameter λ. Using the above indicated model-square-well potential procedure the Z_d values represented by a square and a plus sign are obtained. We only show the results corresponding to the shifted potential. The original values, shown in Fig. 2, are here reproduced, again as triangles. Further we use appoximate phase shifts obtained as follows. We start from the exact equality for the scattering t matrix t_ℓ

$$t_\ell = \int_0^\infty r^2 dr j_\ell(kr) v(r) R_\ell(r) = -\frac{1}{k} \sin \delta_\ell e^{i\delta_\ell}, \tag{31}$$

in which $R_\ell(r)$ is the exact solution of the Schrödinger equation for the spherical potential $v(r)$ at the energy $E = k^2$ and δ_ℓ are the scattering phase shifts. In the Born approximation $R_\ell(r)$ is replaced by the spherical Bessel function $j_\ell(kr)$ and we read from Eq. (31) the following approximate equality

$$v_\ell = \int_0^\infty r^2 dr j_\ell(kr) v(r) j_\ell(kr) \approx -\frac{1}{k} \sin \delta_\ell \cos \delta_\ell. \tag{32}$$

This way approximate phase shifts can be calculated for the potentials available, which are the screened Coulomb potential as mentioned above and the two corresponding square well potentials. The Z_d values obtained this way for the screened Coulomb potential are represented by the stars in Fig. 3, while the square well results are given by the solid and broken lines. It is seen that Z_d values for $1/\lambda$ square wells are smaller than those for the $2/\lambda$ square wells, which is in line with earlier results. Further, again all Z_d values obtained this way lie above a value of 0.6.

Taking everything together, these results are in agreement with earlier findings, which gave $Z_\mathrm{d} = 0.75 \pm 0.15$. Therefore, the present results, which are the first being based on the use of *ab initio* constructed hydrogen potentials, can be seen of a support for these findings. Apparently, by now there is an overwhelming evidence for a non-negligible screening, but a complete screening is really out of the picture.

Conclusions and perspectives

After falsifying the famous claim of Bosvieux and Friedel of a complete screening of the direct force [6, 9], now the other claim, put forward by Turban et al., has been shown to be not valid [7]. By this, from now on both $Z_\mathrm{d} = 0$ claims can be discarded, and one can say indeed: the direct force controversy in electromigration exit. In this respect Zwerger's remark, that the *total* force on the impurity is proportional to the additional resistivity it causes, is rather confusing [17]. Zwerger studies the electronic charge distribution around a fixed impurity induced by a steady electron flow. He finds an electronic backflow, and it would be interesting to study its relationship with the backflow calculated in the present work, see Fig. 1. In addition, he calculates the force on the impurity due to the steady flow, given by his Eq. (15), which is equivalent to Eq. (7) above. By that it is clear that he just considers the wind force, and his remark holds for the wind force anyhow. In his treatment an applied electric field is not in the picture, by which he does not even touch on the direct force problem.

Further, explicit calculations of the direct valence Z_d are done, this time based on the use of *ab initio* constructed hydrogen potentials, and no longer on model square well potentials. It appears that the predictions in the literature, giving $Z_\mathrm{d} = 0.75 \pm 0.15$, are reliable [8, 10].

A few problems are left in the field. For hydrogen in niobium a value $Z_\mathrm{d} < 0.5$ has been measured, while for hydrogen in tantalum values have been measured which are significantly larger than unity [18, 19]. This has never been explained, but up to now only calculations are available for hydrogen in a jellium. In a proper approach one would have to do calculations in which the metallic embedment of the hydrogen is accounted for. It has been shown earlier that in transition metals strong multiple scattering effects can lead to surprising results for the wind force [20]. Similarly, for Z_d a first attempt would be to represent the migrating impurity including its metallic environment by a finite cluster. Initial hints for a possible approach have been given already [16]. Such a program will the subject for further research.

Acknowledgements

The author wishes to thank Dr B.L.G. Bakker for providing him phase shifts for a screened Coulomb potential, which formed the stimulant to start the construction of *ab initio* potentials. The author is grateful to Dr. Istvan Nagy for pointing him at the work of Zwerger.

References

[1] For a recent review, see R. S. Sorbello, in Solid State Physics, Vol. 51, Eds. H. Ehrenreich and F. Spaepen (Academic Press, San Diego, 1997), p. 159.

[2] J. van Ek and A. Lodder: Defect and Diff. Forum **115-116** (1994), p. 1.

[3] J.P. Dekker, A. Lodder and J. van Ek: Phys. Rev. B **56** (1997) p. 12167.

[4] J.P. Dekker and A. Lodder: J. Phys.: Cond. Matter **10** (1998), p. 6687.

[5] J.P. Dekker and A. Lodder: J. Appl. Phys. **84** (1998), p. 1958.

[6] C. Bosvieux and J. Friedel: J. Phys. Chem. Solids **23**, (1962), p. 123.

[7] L. Turban, P. Nozières and M. Gerl: Journal de Physique **37** (1976), p. 159.

[8] R. S. Sorbello: Phys. Rev. B **31** (1985), p. 798.

[9] A. Lodder: Europhys. Lett. **72** (2005), p. 774.

[10] A. Lodder: Phys. Rev. B **74** (2006), p. 045111.

[11] P. Kumar and R.S. Sorbello: Thin Solid Films **25** (1975), p. 25.

[12] R.S. Sorbello: Solid State Commun. **76** (1990), p. 747.

[13] A. Lodder: J. Phys. Chem. Solids **51** (1990), p. 19.

[14] L.J. Sham: Phys. Rev. B **12** (1975), p. 3142.

[15] J. van Ek and A. Lodder: J. Phys.: Cond. Matter **3** (1991), p. 7331.

[16] A. Lodder: Defect and Diff. Forum **237-240** (2005), p. 695.

[17] W. Zwerger: Phys. Rev. Lett. **79** (1997), p. 5270.

[18] A.H. Verbruggen and R. Griessen: Phys. Rev. B **32** (1985), p.1426.

[19] K. Hashizume, Y. Kawabata, K. Matsumoto, N. Tsutsumi and M. Sugisaki: Defect and Diff. Forum **95-98** (1993), p. 329.

[20] A. Lodder and M.G.E. Brand: J. Phys. F: Met. Phys. **14** (1984), p. 2955.