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Calculations of the screening of the charge of a proton migrating in a metal

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The amount of screening of a proton in a metal, migrating under the influence of an applied electric field, is calculated using different theoretical formulations. First the lowest order screening expression derived by Sham [Phys. Rev. B **12**, 3142 (1975)] is evaluated. Contrary to Sham, who estimates the screening to be negligible, we find a finite screening of the order of 15%. In addition, "exact" expressions are evaluated which were derived according to different approaches. For a proton in a metal modeled as a jellium the screening appears to be 15±10%, which is neither negligible nor reconcilable with the controversial full-screening point of view of Bosvieux and Friedel [J. Phys. Chem. Solids **23**, 123 (1962)]. In reconsidering the theory of electromigration, a new simplified linear-response expression for the driving force is shown to lead to essentially the same result as found by Sorbello [Phys. Rev. B **31**, 798 (1985)], who has used a rather complicated technique. The expressions allow for a reduction such that only the scattering phase shifts of the migrating impurity are required. Finally it is shown that the starting formula for the driving force of Bosvieux and Friedel leads exactly to the zero-temperature limit of well-established linear response descriptions.

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I. INTRODUCTION

The amount of screening of a hydrogen atom in a current carrying metal has been the subject of a long-standing controversy. In brief, considering the driving force $\mathbf{F}$ on such an atom as being 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 the transfer of momentum of the current carrying electrons to the proton, so

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

Bosvieux and Friedel[1] found a complete cancellation of $\mathbf{F}_\mathrm{d}$, implying full screening of the proton charge and only a wind force being operative, while most other researchers in the field were in favor of at most a very limited screening.[2] According to the convention in electromigration theory, the forces in Eq. (1) are written as being proportional to corresponding valences and the applied electric field $\mathbf{E}$. The effective valence Z^* is the measurable quantity. The wind force has been calculated reliably for many systems with *ab initio* methods for the electronic structure. This has been done not only for migration of interstitials such as hydrogen, but also for substitutional impurities, including self-electromigration.[2–4]

Electromigration is a complicated phenomenon. Its complexity has nothing to do with the many-body nature of the electron-electron interaction. In all electronic structure calculations of pure metals and of alloys, the electron-electron interaction is accounted for using the local density approximation in a standard way, and this is applied in all theoretical treatments of electromigration as well.[4,5] This implies that all theory of electromigration is one-electron theory. We return to this in Sec. II. The complexity of electromigration comes from the fact that both electron transport and ionic transport have to be taken into account. The electron transport leads to the wind force on the migrating ion. Another contribution to the driving force leading to migration is the direct force.

In view of the long history of the controversy regarding the direct force we mention just a few key papers. The linear response expression for the driving force derived by Kumar and Sorbello[6] was considered as a sound starting point for the resolution of the controversy. From an evaluation to lowest order in the impurity potential Sham concluded to a negligible screening.[7] Using an evaluation up to all orders in the potential, in 1985 Sorbello found a screening of at most 25%.[8]

Experiments done in the seventies of the previous century had not been able to determine the value of the direct valence of hydrogen in pure metals unambiguously.[2] After that negligible screening was measured in V(H) and Ta(H), but in Nb(H) a screening of the order of 50% was found.[9] Carefully designed experiments on $\mathrm{Nb}_x V_{1-x}$(H) strongly suggest that Z_d might be close to the value of +1 (Ref. 10). Further, comparison of measured Z^* values in a number of metal hydrides with state-of-the-art calculations of Z_w led to the conclusion that Z_d has a value close to unity.[11] All this led to a consensus at that time.

Nevertheless, Friedel kept defending that only a wind force was operative, the more so as Turban *et al.* had given another support for that point of view.[12] The confusing feature of the latter work is that their starting formula is a well-established form of a linear response expression. But these authors do not evaluate that expression. On the contrary, they just use a proportionality argument regarding the expression for another physical quantity. Another support for the full-screening point of view was given by the present author.[13] However, that result was considered to be valid in the low temperature limit only,[14] and this limit is a rather academic one in view of the relatively high temperatures at which electromigration experiments are carried out. More recently Ishida predicted a screening ranging from 0 to 100%, but his results were depending sensitively on the electron density of the host metal.[15]

We will present a thorough study of the amount of screening. We start with summarizing the main ingredients of the linear response description of the driving force in Sec. II. Although all in this section is standard, including the transition from a many-body expression to a one-electron formula, this section serves as a reference point for further developments in the core of the paper. After that first Sham's screening expression is evaluated numerically for a number of model potentials representing the impurity. The results, given in Sec. III, do not support Sham's conclusion of a negligible screening, but they are in line with Sorbello's result of a screening of 10–30%.

Second, in Sec. IV we will present a very simple evaluation of the linear response description. This evaluation is supplementary to the evaluation given by Rimbey and Sorbello[8,16] and furthermore much more straightforward. The two descriptions are compared in Sec. V. In Sec. VI it appears to be possible to reduce the final expression for the direct force valency $Z_{\rm d}$ to a form containing just the scattering phase shifts of the migrating impurity potential. Numerical results will be presented in Sec. VII, and compared with Sorbello's results.[8]

In Sec. VIII we will show that the starting expression of Bosvieux and Friedel for the driving force is precisely the zero temperature limit of well-established linear response expressions. This is found by describing the switch on of the electric field properly and by giving credit to the Hermitian property of the Hamiltonian of the unperturbed system. It implies that the old claim that only a wind force is operative, is false. Conclusions and suggestions for further research are given in Sec. IX.

II. LINEAR-RESPONSE DESCRIPTION

The linear response expression 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

$$\mathbf{F} = Z_i e\mathbf{E} - ieE_\nu \int_0^\infty dt e^{-at} Tr\left\{\rho(H)\left[\mathbf{F}_{\rm op}(t), \sum_j r_j^\nu\right]\right\} \equiv \mathbf{F}_{\rm d}^{\prime\,\rm bare\,\prime} + \mathbf{F}_{\rm w}^{\rm total}. \tag{2}$$

The first term clearly is the direct force on the bare ion. The Cartesian label ν runs from 1 to 3, the infinitesimally positive number a represents the adiabatical switch on of the electric field represented by the potential

$$\delta V(t) = e\mathbf{E}e^{at}\cdot\left(\sum_j \mathbf{r}_j - Z_i \sum_\alpha \mathbf{R}_\alpha\right) \equiv \delta V e^{at}, \tag{3}$$

with j running over the electrons and α over the ions, and the operator $\rho(H)$ is the grand-canonical density depending on the system Hamiltonian H. The force operator contains the electron-impurity potential

$$V_{ei} = \sum_{j,\alpha} v(\mathbf{r}_j - \mathbf{R}_\alpha) \equiv \sum_{j,\alpha} v_j^\alpha, \tag{4}$$

which is part of the system Hamiltonian, and is given by

$$\mathbf{F}_{\rm op} \equiv -\boldsymbol{\nabla}_{\mathbf{R}_1} V_{ei} = -\sum_j \boldsymbol{\nabla}_{\mathbf{R}_1} v(\mathbf{r}_j - \mathbf{R}_1) \equiv \sum_j \mathbf{f}_j^1. \tag{5}$$

Its time dependence refers to the Heisenberg representation

$$\mathbf{F}_{\rm op}(t) \equiv e^{iHt}\mathbf{F}_{\rm op}e^{-iHt}. \tag{6}$$

It appears that the second term in Eq. (2), 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 $\mathbf{F}_{\rm w}^{\rm total}$, but it is as to the magnitude of that screening contribution that people do not agree. The expression published by Kumar and Sorbello (Ref. 6),

$$\mathbf{F}_{\rm w}^{\rm total} = -\frac{i}{a}E_\nu \int_0^\infty dt e^{-at} Tr\{\rho(H)[\mathbf{F}_{\rm op}(t), J^\nu]\}, \tag{7}$$

follows simply and straightforwardly from a partial integration of Eq. (2) with respect to the time. The current vector is defined

$$\mathbf{J} = ie\left[\sum_j \mathbf{r}_j, H\right] = -e\sum_j \frac{\mathbf{p}_j}{m} = \sum_j \mathbf{j}_j. \tag{8}$$

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

$$\mathbf{F} = Z_i e\mathbf{E} + \mathbf{F}_{\rm w}^{\rm total} = Z_i e\mathbf{E} + \mathbf{F}_{\rm w}^{\rm scr} + \mathbf{F}_{\rm w}^{\rm BF} = (Z_i + Z^{\rm scr} + Z_{\rm w})e\mathbf{E}$$
$$= (Z_{\rm d} + Z_{\rm w})e\mathbf{E}, \tag{9}$$

containing the result of Bosvieux and Friedel for the wind force $\mathbf{F}_{\rm w}^{\rm BF}$ and a screening contribution.[1] In all treatments available $\mathbf{F}_{\rm w}^{\rm BF}$ can be written in its general form (Refs. 4, 7, and 8)

$$\mathbf{F}_{\rm w}^{\rm BF} = -\int \delta n(\mathbf{r})\boldsymbol{\nabla}_{\mathbf{R}_1} v^1 d^3r, \quad \text{with } v^1 = v(\mathbf{r} - \mathbf{R}_1). \tag{10}$$

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. It is worthwhile to point out that the form (10) is a one-electron expression, completely in line with standard treatments of electronic and transport properties in condensed matter, particularly in metals and metallic alloys. In these treatments the local-density approximation (LDA) is made for the electronic contribution to the potentials used in the description. In the LDA the electron density, which contains a local direct part and a nonlocal exchange term, is given a local form.[5,17] The LDA, being common to most of the treatments of metallic properties, is used in electromigration theory as well.[4] This will be made explicitly below, when the many-body expression in Eq. (2) is reduced legally to a one-electron expression, although it is clear that use is made implicitly of the LDA.[18] From now on we will concentrate on $Z_{\rm d}$.

All previous relevant descriptions have been given for the electron-impurity system,[4] for which the Hamiltonian H can be written as a sum of single particle Hamiltonians h, so

$$H = \sum_j h^j \quad \text{with } h = h_0 + v = h_0 + \sum_\alpha v^\alpha. \tag{11}$$

This form for H is standard for all studies of the electronic structure in condensed matter theory and it is common knowledge that its use implies the application of the LDA.[5,17] The unperturbed one-electron Hamiltonian h_0

stands for the Bloch Hamiltonian, which contains the kinetic energy of the electron and the periodic potential of the metallic atoms in the lattice. For a jellium model, that periodic potential is smeared out to a constant positive background, and one obtains effectively a free-electron Hamiltonian. The full Hamiltonian h contains in addition the potential of the alloying impurities, which may be either substitutional impurities or interstitial impurities, such as hydrogen. For the present problem the form (11) allows for a reduction of the many body expression in Eq. (2) to the following one-electron expression:

$$\mathbf{F}_{\rm w}^{\rm total} = -ieE_\nu \int_0^\infty {\rm d}t e^{-at} tr\{[r^\nu, n(h)]\mathbf{f}^1(t)\}, \tag{12}$$

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

$$n(h) = \frac{1}{e^{\beta(h-\epsilon_{\rm F})}+1}. \tag{13}$$

It has been shown explicitly that if in the right-hand side of Eq. (12) the statistical operator is replaced by this operator for the free particle system, so $n(h) \to n(h_0)$, the Bosvieux-Friedel wind force expression $\mathbf{F}_{\rm w}^{\rm BF}$ arises.[13] That means that the screening part is given by

$$\mathbf{F}_{\rm w}^{\rm scr} = -ieE_\nu \int_0^\infty dt e^{-at} tr\{[r^\nu, n(h)-n(h_0)]\mathbf{f}^1(t)\} = Z^{\rm scr} e\mathbf{E}. \tag{14}$$

The screening valency $Z^{\rm scr}$ is defined

$$Z^{\rm scr} = -\frac{i}{3}\int_0^\infty dt e^{-at} tr\{[\mathbf{r}, n(h)-n(h_0)]\cdot \mathbf{f}^1(t)\}, \tag{15}$$

in which the factor of $\frac{1}{3}$ comes from the fact that all three terms in the inner product of the vectors $\mathbf{r}$ and $\mathbf{f}^1$ contribute equally. In all further evaluations the metallic host is modeled by a jellium, which is the only model used so far in the literature for the study of the direct force problem. This means that the electrons are perturbed by the random distribution of impurities only. Following Sham[7] we now first consider the result to lowest (second) order in the impurity potential v.

III. EVALUATION OF SHAM'S EXPRESSION

The evaluation of Eq. (15) to lowest order in v requires the expansion of the statistical operator $n(h)-n(h_0)$ in v,

$$n(h) = n(h_0) - n(h)\int_0^\beta ds e^{sh} v e^{-sh_0}[1-n(h_0)], \tag{16}$$

while in the time dependence of $\mathbf{f}^1$ one can replace h by h_0. One obtains

$$Z^{scr} = -\frac{4}{3m}\sum_{kk'}(k^2 - \mathbf{k}\cdot\mathbf{k}')\frac{|v_{kk'}|^2}{(\epsilon_k-\epsilon_{k'})^2+a^2}\left(\frac{\partial n_k}{\partial \epsilon_k} - \frac{n_k-n_{k'}}{\epsilon_k-\epsilon_{k'}}\right), \tag{17}$$

where $\mathbf{k}$ is a free electron wave vector and ϵ_k is the corresponding energy. The matrix element $\langle \mathbf{k}|[r^\nu, n(h)-n(h_0)]|\mathbf{k}'\rangle$ is most easily evaluated if one realizes, that it is equal to $i(\frac{\partial}{\partial k_\nu}+\frac{\partial}{\partial k'_\nu})\langle \mathbf{k}|n(h)-n(h_0)|\mathbf{k}'\rangle$. Following Sham and Sorbello[8] the potential v refers to the migrating impurity only. Sham stored part of the presence of the impurities through the replacement $a \to \tau^{-1}$, τ being the transport relaxation time due to the impurities, which can be justified by an average over the distribution of the impurities in the time dependence of the force operator. Both Sham and Sorbello were able to make their complete derivations after taking the $T \to 0$ limit only. It has been shown that Eq. (17) reduces to Sham's expression after taking that limit.[19]

A numerical evaluation of Z^{scr} becomes possible if one employs the spherical wave expansion for a plane wave, converts the summations over the wave vectors to integrals, and carries out the angular integrals over the directions of the wave vectors. After using the relation between k^2 and the energy ϵ_k one ends up at

$$Z^{scr} = -\frac{4}{3\pi^2 m}\int_0^\infty d\epsilon_k \int_0^\infty d\epsilon_{k'} \frac{\dfrac{\partial n_k}{\partial \epsilon_k} - \dfrac{n_k-n_{k'}}{\epsilon_k-\epsilon_{k'}}}{(\epsilon_k-\epsilon_{k'})^2+a^2}\sum_\ell f_\ell(k,k'), \tag{18}$$

in which the function $f_\ell(k,k')$ is defined

$$f_\ell(k,k') = \epsilon_k\sqrt{\epsilon_{k'}}\,v_\ell(k',k)[(2\ell+1)k v_\ell(k',k) - 2(\ell+1)k' v_{\ell+1}(k',k)], \tag{19}$$

containing the information about the ion potential through

$$v_\ell(k',k) = \int_0^\infty r^2 dr j_\ell(k'r)v(r)j_\ell(kr). \tag{20}$$

The integrand has to be treated with care when $\epsilon_{k'}=\epsilon_k$, because then the denominator attains the value a^2 which would imply "singular" behavior. However, precisely then the numerator becomes zero, because $\lim_{\epsilon_{k'}\to\epsilon_k}(n_k-n_{k'})/(\epsilon_k-\epsilon_{k'}) \to \frac{\partial n_k}{\partial \epsilon_k}$. The crucial part of the integrand lies in the square around the point $(\epsilon_k,\epsilon_{k'})=(\epsilon_{\rm F},\epsilon_{\rm F})$. In studying the Z^{scr} integral it appears that in that square one has to keep the Fermi-Dirac distribution function in its finite temperature form. We could not obtain a reliable stable numerical result by using Sham's $T\to 0$ expression. The result of a numerical evaluation for different ion potentials is shown in Fig. 1. We used a screened Coulomb potential

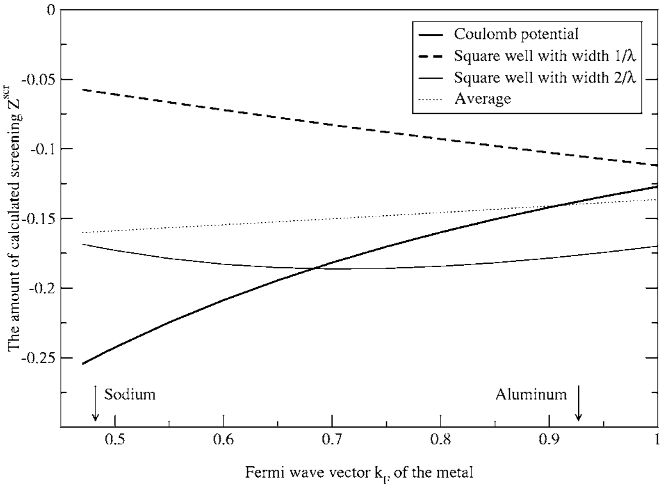

FIG. 1. The amount of screening represented by Z^{scr} according to Eq. (18), for the screened Coulomb potential and for two square well potentials.

$$v(r) = -\frac{Z_i e^2 e^{-\lambda r}}{r} \quad \text{while} \quad v_{k'k} \equiv \frac{1}{8\pi^3}\int d^3 r e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}} v(r), \tag{21}$$

with $Z_i = 1$ representing a proton in a jellium and the inverse screening length λ given by the Thomas-Fermi expression (Ref. 20)

$$\lambda^2 = 4\pi e^2 \mathcal{N}(\epsilon_F) \quad \text{with } \mathcal{N}(\epsilon) = \frac{m\sqrt{2m\epsilon}}{\pi^2} \to v_{kk} = -\frac{Z_i}{8\pi^3 \mathcal{N}(\epsilon_F)}. \tag{22}$$

In addition square well potentials were employed in the same spirit as Sorbello did.[8] The width r_0 of the square well potential was chosen to be equal to the screening length $1/\lambda$ and twice as large. The corresponding well depth v_0 was determined by the condition $v_0/v_c = 0.999$, where $v_c = \pi^2/8mr_0^2$ is the critical value of the well depth for which a bound state forms. For further details, see Ref. 8. The value of λ is determined by the Fermi energy. While Sorbello chose five values for the Fermi energy, typical for metals ranging from sodium to aluminum, we have done the calculation for a whole range of Fermi energies. The results are plotted as a function of the Fermi wave number k_F. The k_F values of sodium and aluminum are indicated.

Because λ increases monotonically with the Fermi energy, the range of the corresponding screened Coulomb potential decreases with increasing k_F, whose reduction in strength is seen clearly in the solid curve. In Fig. 2 the v_{kk}^2 curves are plotted for the three potentials. A clear decrease is seen for the Coulomb potential, and a rather flat behavior for the square well potentials, while the one with $2/\lambda$ is markedly stronger than the one with the smaller width. Apparently, the screening to second order in the impurity potential is not negligible at all, but on the average as large as 15±10%. As a guide for the eye we gave the average of Z^{scr} for the three potentials as a dotted line.

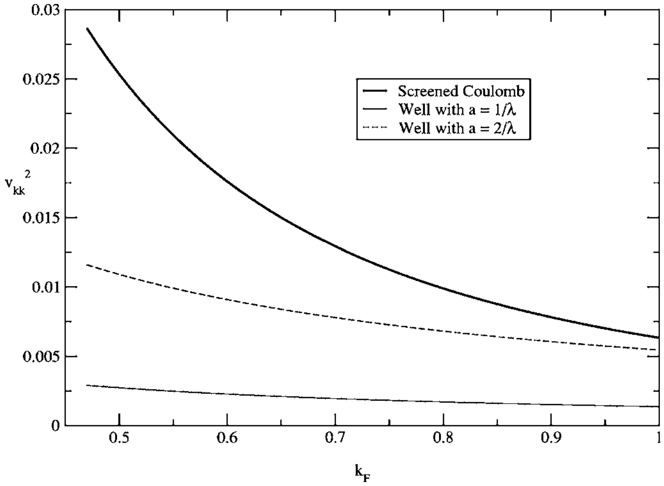

FIG. 2. v_{kk}^2 plotted as a function of k_F, for the two square well potentials and the screened Coulomb potential.

For security we evaluated an alternative expression for Z^{scr}, given by

$$Z^{scr} = -\frac{4}{3m}\sum_{kk'} (k^2 - \mathbf{k}\cdot\mathbf{k}')|v_{kk'}|^2 \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} \frac{(\epsilon_k - \epsilon_{k'})^2 - a^2}{[(\epsilon_k - \epsilon_{k'})^2 + a^2]^2}. \tag{23}$$

This expression follows if Eq. (15) is modified such that the dipole operator $\mathbf{r}$ commutes with the force operator $\mathbf{f}^1(t)$ instead of with the statistical operator. While Z^{scr} given by Eq. (17) reduces to Sham's expression after taking the $T \to 0$ limit, such a proof is not available for Z^{scr} given by Eq. (23). On the other hand, the two expressions (17) and (23) are equivalent, being related to each other through a partial integration for the derivatives with respect to the $\mathbf{k}$ and $\mathbf{k}'$ vectors. The alternative for Eq. (18) becomes

$$Z^{scr} = -\frac{4}{3\pi^2 m}\int_0^\infty d\epsilon_k \int_0^\infty d\epsilon_{k'} \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} \frac{(\epsilon_k - \epsilon_{k'})^2 - a^2}{[(\epsilon_k - \epsilon_{k'})^2 + a^2]^2} \times \sum_{\ell} f_\ell(k,k'). \tag{24}$$

If one takes proper care of the higher sensitivity of the expression (24) to the choice of the infinitesimal parameter a the results turn out to be the same. It can be taken relatively small, much smaller than a typical value of 0.01 for the inverse transport relaxation time. In fact, it is the mesh of the integration that determines the lower limit of a. For the expressions (18) and (24) it was never larger than 0.00015 and 0.005, respectively. On the other hand, for $a = 0.01$ the screening represented by the curves in Fig. 1 reduces by at most 2%.

IV. REDUCTION OF LINEAR-RESPONSE FORMULA FOR THE SCREENING

The evaluation of the linear-response formula (15) to all orders in the impurity potential 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.[8] In that case $\mathbf{f}^1 = i[\mathbf{p}, h] = i[\mathbf{p}, h_0 + v^1]$. By writing Eq. (15) in terms of eigenstates of $h \rightarrow h_0 + v^1$, labeled by q and q', one can carry out the time integral and finds

$$Z^{scr} = \frac{i}{3}\sum_{qq'} \langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle \cdot \frac{\epsilon_q - \epsilon_{q'}}{\epsilon_{q'} - \epsilon_q + ia}\mathbf{p}_{q'q}$$
$$= \frac{i}{3}\sum_{qq'} \langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle \cdot \left(-1 + \frac{ia}{\epsilon_{q'} - \epsilon_q + ia}\right)\mathbf{p}_{q'q} = -\frac{i}{3} tr\{[\mathbf{r}, n(h) - n(h_0)] \cdot \mathbf{p}\}$$
$$+ \frac{i}{3}\sum_{qq'}^{\epsilon_q = \epsilon_{q'}} \langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle \cdot \mathbf{p}_{q'q}. \qquad (25)$$

The first term in the last line reduces to $-Z_i$ because $itr\{[r^\nu, n(h) - n(h_0)]p^\mu\} = itr\{[n(h) - n(h_0)][p^\mu, r^\nu]\} = tr\{n(h) - n(h_0)\}\delta_{\nu,\mu} = Z_i\delta_{\nu,\mu}$. One arrives at

$$Z^{scr} = -Z_i + Z_{\mathrm{corr}}$$

with

$$Z_{\mathrm{corr}} \equiv \frac{i}{3}\sum_{qq'}^{\epsilon_q = \epsilon_{q'}} \langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle \cdot \mathbf{p}_{q'q}. \qquad (26)$$

In view of Eq. (9) this would imply a correction term $Z_{\mathrm{corr}} = Z_{\mathrm{d}}$ due to the cancellation of the bare direct valency Z_i. The step of subtracting and adding an ia term in the numerator in the second line of Eq. (25) may look somewhat artificial, and the ia factor creates the impression to lead to a zero result in the $a \rightarrow 0$ limit. We have to admit that, in earlier work, we overlooked this rather hidden trap. It is to the merit of Sorbello that he discovered the trap.[18] At that time we could not go along with Sorbello's suggestion yet.[21] But after a rigorous search we now follow him by noting, that for the $\epsilon_q = \epsilon_{q'}$ terms in the third line the ia factor cancels, and the remaining terms give a finite contribution.[18]

Sorbello[8] starts from a result obtained by Rimbey and Sorbello[16] through an evaluation of Eq. (7) and finds after some rewritings for Z_{d}

$$Z_{\mathrm{d}} = -\frac{2}{3\pi m}\,\mathrm{Im}\, tr\{p^2[G(\epsilon_{\mathrm{F}}) - G^0(\epsilon_{\mathrm{F}})]\}. \qquad (27)$$

The single particle Green's function $G(\epsilon)$ for one impurity in a jellium, with $h = h_0 + v^1$, and the free electron Green's function $G^0(\epsilon)$ are given by

$$G(\epsilon) = \frac{1}{\epsilon + ia - h} \quad \text{and} \quad G^0(\epsilon) = \frac{1}{\epsilon + ia - h_0}$$

with

$$h_0 = \frac{p^2}{2m}. \qquad (28)$$

This form for Z_{d} is Sorbello's Eq. (12) and it implies a cancellation of Z_i present in his Eq. (7). In order to distinguish our result for Z_{d} from Sorbello's Z_{d} we keep the notation Z_{corr}.

V. COMPARISON OF THE TWO DESCRIPTIONS

While the description by Rimbey and Sorbello is rather involved and the result (26) is obtained in a few lines, it is worthwhile to compare the final expressions. We first evaluate Z_{corr} to lowest order in the impurity potential, for which we take a screened Coulomb potential, Eq. (21). By using Eq. (16) and the equality

$$[\mathbf{r}, n(h)] = -\frac{i}{m}\int_0^\beta ds\; n(h)e^{sh}\mathbf{p}e^{-sh}[1 - n(h)], \qquad (29)$$

in which the electron mass $m = \frac{1}{2}$ in atomic units, one finds straightforwardly for Z^0_{corr}

$$Z^0_{\mathrm{corr}} = \frac{i}{3}\sum_k \langle k|[\mathbf{r}, n(h) - n(h_0)]|k\rangle \cdot \mathbf{k}$$
$$= -4\pi\sqrt{\epsilon_{\mathrm{F}}}v_{kk} = Z_i \equiv Z_i(\mathrm{pot}), \qquad (30)$$

in which a quantity $Z_i(\mathrm{pot}) = -4\pi\sqrt{\epsilon_{\mathrm{F}}}v_{kk}$ is defined to be used below. For the screened Coulomb potential this quantity is equal to $Z_i = 1$, but this is not the case for other potentials. This result from an explicit calculation follows also if one writes the sum over the free space states $|k\rangle$ as a trace and uses the equality given in the sentence just below Eq. (25).

Similarly one finds for Sorbello's Z_{d} to lowest order in the impurity potential, writing the trace in Eq. (27) in terms of free space states labeled by k,

$$Z_d^{(0)} = -\frac{2}{3\pi m}\,\mathrm{Im}\int d^3k k^2 G^0_k(\epsilon_{\mathrm{F}})v_{kk}G^0_k(\epsilon_{\mathrm{F}}) = -4\pi\sqrt{\epsilon_{\mathrm{F}}}v_{kk} = Z_i. \qquad (31)$$

This is obtained by using the following two equalities,

$$\frac{\partial}{\partial\epsilon_k}G^0_k(\epsilon) = \frac{\partial}{\partial\epsilon_k}\frac{1}{\epsilon - \epsilon_k + ia} = G^0_k(\epsilon)G^0_k(\epsilon) \quad \text{and} \quad \lim_{a\rightarrow 0}\mathrm{Im}\, G^0_k(\epsilon_{\mathrm{F}}) = -\pi\delta(\epsilon_{\mathrm{F}} - \epsilon_k). \qquad (32)$$

Apparently, to lowest order in the impurity potential the two final expressions Z_{corr} and Z_{d} are equal and they reproduce the bare valency of the migrating ion. Although the complete expressions are not equal, an "almost" equality can be derived. We rewrite Z_{corr} by applying Eq. (29) both for h and h_0. After inserting a complete set of free electron states in the h_0 term in Eq. (26) and carrying out the integral over s, one finds

$$Z_{\mathrm{corr}} = \frac{\beta}{3m}\sum_{qq'}^{\epsilon_q=\epsilon_{q'}}\left[n_q(1-n_q)\mathbf{p}_{qq'} - \sum_{k''} n_{k''}(1-n_{k''})\right.$$
$$\left.\times\langle q|k''\rangle\mathbf{k}''\langle k''|q'\rangle\right]\cdot\mathbf{p}_{q'q}\rightarrow$$
$$-\frac{1}{3\pi m}\sum_{qq'}^{\epsilon_q=\epsilon_{q'}}\left[\mathrm{Im}\,G_q(\epsilon_{\mathrm{F}})\mathbf{p}_{qq'} - \sum_{k''}\mathrm{Im}\,G^0_{k''}(\epsilon_{\mathrm{F}})\right.$$
$$\left.\times\langle q|k''\rangle\mathbf{k}''\langle k''|q'\rangle\right]\cdot\mathbf{p}_{q'q} = -\frac{1}{3\pi m}\,\mathrm{Im}\sum_{qq'}^{\epsilon_q=\epsilon_{q'}}\langle q|\mathbf{p}[G(\epsilon_{\mathrm{F}})$$
$$-G^0(\epsilon_{\mathrm{F}})]|q'\rangle\cdot\mathbf{p}_{q'q}. \tag{33}$$

In the transition from the first to the second line the $T\rightarrow 0$ limit was taken, for which $\beta n_q(1-n_q) = -\frac{\partial}{\partial\epsilon_q}n_q \rightarrow \delta(\epsilon_q-\epsilon_{\mathrm{F}}) = -\frac{1}{\pi}\,\mathrm{Im}\,G_q(\epsilon_{\mathrm{F}})$. Both Sham and Sorbello give their elaborated expressions in this $T\rightarrow 0$ limit. The similarity of this last line with Sorbello's Z_{d}, Eq. (27), is striking. The factor of 2 reflects whether the electron spin degeneracy has been accounted for explicitly or not. In fact, if in the last line of Eq. (33) the states q and q' are replaced by the unperturbed ones k and k', it reduces to Sorbello's expression. This implies an intriguing equality indeed, and it shows that the two descriptions are closely related.

VI. THE CORRECTION TERM IN TERMS OF PHASE SHIFTS

For the evaluation of the correction term Z_{corr} as it is defined in Eq. (26) one needs the states $|q\rangle$. These states are the eigenstates of a system with one impurity in free space. It is known that the scattering states $|\psi_k\rangle$ for this system, which have a one-to-one correspondence to the free space states $|k\rangle$, are exact solutions of the Schrödinger equation for one impurity in free space as well. It appears that the evaluation of Z_{corr} becomes relatively simple if one uses the scattering states instead of the true eigenstates. We return to this point below.

The expansion of the scattering state $\langle\mathbf{r}|\psi_k\rangle \equiv \psi_k(\mathbf{r})$ in terms of spherical harmonics is given by

$$\psi_k(\mathbf{r}) = \frac{4\pi}{\sqrt{\Omega}}\sum_L i^{\ell}Y^*_L(\hat{k})R_{\ell}(r,k)Y_L(\hat{r}). \tag{34}$$

The angular momentum label L combines the labels ℓ and m, so $L\equiv\ell m$, and $R_{\ell}(r,k)$ is the radial solution of the Schrödinger equation at the energy ϵ_k for a spherically symmetric potential v centered at the origin. For r outside the range of the potential $R_{\ell}(r,k)$ can be written in terms of the scattering t matrix $t_{\ell} = -\frac{1}{k}\sin\delta_{\ell}\exp(i\delta_{\ell})$ as $j_{\ell}(kr) - ikt_{\ell}h^+_{\ell}(kr)$, where δ_{ℓ} are the phase shifts. This means that for a plane wave $R_{\ell}(r,k)\rightarrow j_{\ell}(kr)$. The box normalization in the system volume Ω induces a discrete set of k values. In the properties to be presented below a delta function normalization will be used, which means that in Eq. (34) the system volume Ω has to be replaced by $8\pi^3$. Using the expansion Eq. (16), the equality $\langle k'|v|\psi_k\rangle = t_{k'k}$ which holds for scattering states $|q\rangle\rightarrow|\psi_k\rangle$, and the overlap property for scattering states

$$\langle k'|\psi_k\rangle = \frac{\delta(k-k')}{k^2}\sum_L Y_L(\hat{k}')Y^*_L(\hat{k})(1-ikt_{\ell}), \tag{35}$$

one finds for Z_{corr}

$$Z_{\mathrm{corr}} = -\frac{4}{3\pi m}\int_0^{\infty}k^3dk\left[\frac{\partial}{\partial\epsilon_k}\delta(\epsilon_k-\epsilon_{\mathrm{F}})\right]F(\epsilon_k)$$
$$= \frac{2}{\pi}\left[F(\epsilon_{\mathrm{F}}) + \frac{2}{3}\epsilon_{\mathrm{F}}^{3/2}\frac{\partial}{\partial\epsilon_{\mathrm{F}}}\bar{F}(\epsilon_{\mathrm{F}})\right], \tag{36}$$

in which the function $F(\epsilon_k)$ is given by

$$F(\epsilon_k) = \frac{1}{4}\sum_{\ell}(\ell+1)(\sin 2\delta_{\ell} + \sin 2\delta_{\ell+1})[\cos^2(\delta_{\ell}-\delta_{\ell+1})+1], \tag{37}$$

and $\bar{F}(\epsilon_k) \equiv \frac{1}{k}F(\epsilon_k)$. Crucial steps of the derivation of Eq. (36) are given in the Appendix. This expression can be evaluated simply, because it is just a function of the phase shifts of the impurity potential at the Fermi energy. Z_{corr} as it is given by Eq. (36) has to be compared with the lowest order expression, obtained by the replacements $|q\rangle\rightarrow|k\rangle$ and $|q'\rangle\rightarrow|k'\rangle$. For the sake of a proper comparison this expression has to be evaluated in a similar way, by the use of scattering states. This way one obtains

$$Z^0_{\mathrm{corr}} = -\frac{4}{3\pi m}\int_0^{\infty}k^3dk\left[\frac{\partial}{\partial\epsilon_k}\delta(\epsilon_k-\epsilon_{\mathrm{F}})\right]F^0(\epsilon_k)$$
$$= \frac{2}{\pi}\left[F^0(\epsilon_{\mathrm{F}}) + \frac{2}{3}\epsilon_{\mathrm{F}}^{3/2}\frac{\partial}{\partial\epsilon_{\mathrm{F}}}\bar{F}^0(\epsilon_{\mathrm{F}})\right], \tag{38}$$

in which the function $F^0(\epsilon_k)$ is given by

$$F^0(\epsilon_k) = \frac{1}{2}\sum_{\ell}(2\ell+1)\sin 2\delta_{\ell} = \sum_{\ell}(2\ell+1)\sin\delta_{\ell}\cos\delta_{\ell}, \tag{39}$$

and $\bar{F}^0(\epsilon_k) \equiv \frac{1}{k}F^0(\epsilon_k)$. The right-hand sides of Eqs. (38) and (30) can have different numerical values, because the two elaborations are different in character. Comparison of these numerical values can be considered as a test of the error made in using scattering states instead of the true eigenstates. Another test of this error is obtained by evaluating the simplified lowest order result for Z_{corr} explicitly, to be denoted as Z^{00}_{corr}, using the expansion (16). One finds

$$Z^{00}_{\mathrm{corr}} = tr\{n(h)-n(h_0)\} = \frac{2}{\pi}\sum_{\ell}(2\ell+1)\sin\delta_{\ell}\cos\delta_{\ell}$$
$$= \frac{2}{\pi}F^0(\epsilon_k) \neq \frac{2}{\pi}\sum_{\ell}(2\ell+1)\delta_{\ell} = Z_{\mathrm{F}}, \tag{40}$$

in which Z_{F} stands for the Friedel sum. The inequality in Eq. (40) must be attributed to the use of scattering states instead of the true eigenstates. The difference between these two types of states has been stressed by Fenton[22] and commented on by the present author.[23] A scattering state is prepared such that it is an unperturbed state at $t=-\infty$, which develops under the influence of a scattering potential located at some position in the system. An eigenstate has to be constructed using the boundary conditions of the system in addition to the properties of the potential. In terms of scattering theory, eigenstates contain the influence of backscattering by the boundaries in addition to the information about the scattering by the potential. It is clear that the third member of Eq. (40) reduces to $Z_{\rm F}$ in the small phase-shifts limit $\delta_\ell \to 0$.

Sorbello's equation for $Z_{\rm d}$, Eq. (27), can be evaluated through the use of scattering states as well. We first give the form corresponding to the eigenstates of h, denoted as usual by $|q\rangle$, followed by the result obtained by using scattering states.

$$Z_d = -\frac{2}{3\pi m}\,\mathrm{Im}\sum_q \sum_{k'} \langle q|k'\rangle k'^2 G^0_{k'}(\epsilon_{\rm F})\langle k'|v|q\rangle G_q(\epsilon_{\rm F})$$
$$\to \frac{4}{3\pi}\frac{\partial}{\partial \epsilon_{\rm F}}\int_0^\infty \epsilon_k^{3/2} d\epsilon_k \delta(\epsilon_{\rm F}-\epsilon_k)\bar{F}^0(\epsilon_k) = \frac{4}{3\pi}\frac{\partial}{\partial \epsilon_{\rm F}}\epsilon_{\rm F}^{3/2}\bar{F}^0(\epsilon_{\rm F}). \tag{41}$$

As above, for scattering states the potential matrix element becomes equal to the t matrix element $t_{k'k}$. The energies ϵ_k and ϵ_q are equal, being connected by a delta function as shown in Eq. (35). Interestingly, this rewritten Z_d is equal to our $Z^0_{\rm corr}$ given by Eq. (38). This again shows the close relationship between the results obtained through the simplified approach presented here and Sorbello's results.

Sorbello calculated Z_d of Eq. (27) using the square well potentials described in Sec. III. To that end he derives his rewritten form Eq. (17), which we reproduce in a slightly different notation as follows:

$$Z_d = \frac{4v_0 k_{\rm F}}{3\pi}\int_0^{r_0} r^2 dr \sum_\ell (2\ell+1)\left(R_\ell^2(r,k_{\rm F}) - j_\ell^2(k_{\rm F}r)\right)$$
$$+ \frac{4\epsilon_{\rm F}}{3\pi}\sum_\ell (2\ell+1)\frac{\partial \delta_\ell}{\partial \epsilon}\rfloor_{\epsilon_{\rm F}} + \frac{4k_{\rm F}v_0 r_0^3}{9\pi}. \tag{42}$$

In the derivation has been used, that $\frac{p^2}{2m}=h-v=h-\epsilon_{\rm F}+\epsilon_{\rm F}-v$, $G-G^0=GvG^0$, $(h-\epsilon_{\rm F})G=-1$, $-\mathrm{Im}\,Tr\{G-G^0\}=\Sigma_\ell(2\ell+1)\frac{\partial\delta_\ell}{\partial\epsilon}\rfloor_{\epsilon_{\rm F}}$, $\mathrm{Im}\,G^0(\mathbf{r},\mathbf{r})=-k_{\rm F}\Sigma_L j_L^2(\mathbf{r})$, and $\mathrm{Im}\,G(\mathbf{r},\mathbf{r})=-k_{\rm F}\Sigma_L R_L^2(\mathbf{r})$, with $R_L(\mathbf{r})\equiv R_\ell(r,k_{\rm F})Y_L(\hat{r})$. For $r\le r_0$ the radial solution $R_\ell(r,k_{\rm F})\propto j_\ell(k_v r)$, with $k_v=\sqrt{k_{\rm F}^2+v_0}$. For reasons of a proper comparison we evaluated Z_d according to Eq. (42) up to $\ell=2$, because Sorbello restricted himself to $\ell_{\rm max}=0$.

VII. NUMERICAL RESULTS

The expressions obtained will be evaluated for the same square well model potentials as were used in Sec. III, in that employing a slight generalization of the potentials used by Sorbello.[8] Results for $Z_d/Z_{\rm F}$ and $Z_{\rm corr}/Z^0_{\rm corr}$ are shown in Fig. 3. Because the Friedel sum for the model square well potentials is rarely equal to unity, the use of ratios gives the proper measure for the screening, in which we follow Sorbello.

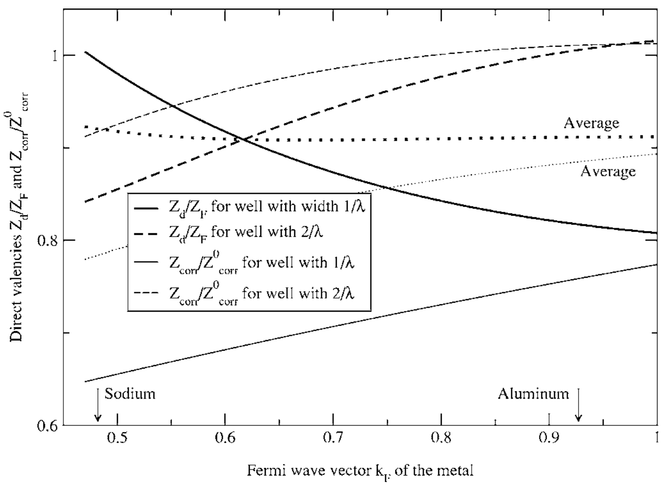

FIG. 3. $Z_d/Z_{\rm F}$ and $Z_{\rm corr}/Z^0_{\rm corr}$ plotted as a function of $k_{\rm F}$, for the two square well potentials.

It is seen that for the stronger potentials, with $r_0=2/\lambda$, Sorbello's boldly dashed curve lies somewhat lower than the dashed curve for the present description, while they display almost equal results for the higher $k_{\rm F}$ values. The curves for the weaker potentials lie lower than those for $r_0=2/\lambda$. Although they differ considerably for smaller $k_{\rm F}$ values, the curves approach each other for higher $k_{\rm F}$. Both results imply a decrease of the inaccuracy related to the $|q\rangle \to |\psi_k\rangle$ replacement in the present description for states with increasing k values. This is reasonable, because larger k values correspond to smaller wave lengths, which probe the scattering potential more precisely, while the boundary effect decreases. As a guide for the eye the average for the two well widths are drawn as dotted lines. From the present description one comes to a direct valency of 0.85±0.15 on the average, while this is 0.91±0.10 for Sorbello's description. So it appears that the $|q\rangle \to |\psi_k\rangle$ replacement is not too crude in determining a measure for the amount of screening. The screening mentioned by Sorbello is based mainly on the $r_0=1/\lambda$ potentials, because for these potentials his restriction to $\ell_{\rm max}=0$ is reasonable. If we correct for the higher ℓ values we find 0.82 for $Z_d/Z_{\rm F}$ in aluminum instead of his 0.75. He used the latter value in mentioning a screening of 25%. For the sake of completeness we remark, that if one would compare the boldly dashed curve with the values given in Sorbello's Table II one would observe considerable differences. This is due to the fact that for the $r_0=2/\lambda$ potentials the $\ell=1$ and 2 terms contribute significantly. Taking everything together the available models and descriptions end up at a screening between 5 and 30%. Comparing with the largely metallic-density dependent result of Ishida, covering the entire range of no screening to complete screening, the present result can be considered as rather conclusive, in that complete screening is excluded.[15]

In order to get some more insight in the $k_{\rm F}$ dependences shown in Fig. 3 we display the quantities $Z^0_{\rm corr}$, Z_i(pot), and $Z_{\rm F}$ in Fig. 4. It is seen that all curves have a positive slope, apart from the one for $Z_{\rm F}$ for the weaker $r_0=1/\lambda$ potential. This is certainly related to the seemingly deviant $Z_d/Z_{\rm F}$ curve in Fig. 3 and the fact that the $Z_d/Z_{\rm F}$ curves have been ob-

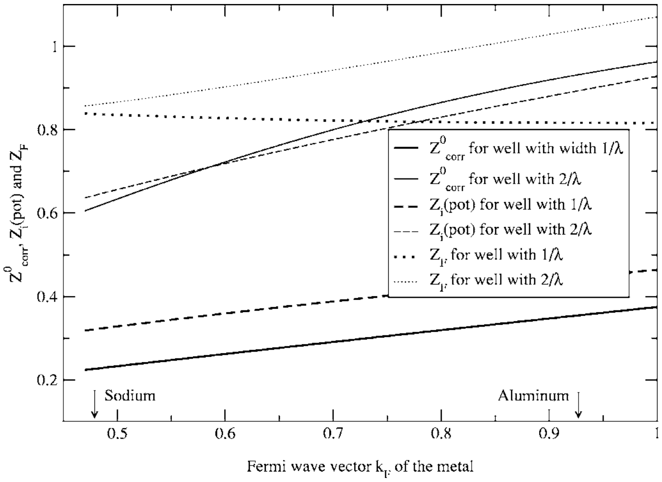

FIG. 4. Z^0_{corr}, Z_i(pot), and Z_{F} plotted as a function of k_{F}, for the two square well potentials.

tained by an accurate numerical evaluation of Eq. (42), while the $Z_{\mathrm{corr}}/Z^0_{\mathrm{corr}}$ results "suffer" from the $|q\rangle \rightarrow |\psi_k\rangle$ replacement. The effect of this replacement is larger for the weaker potential, which can be seen from both $Z_{\mathrm{corr}}/Z^0_{\mathrm{corr}}$ curves in Fig. 3 and the Z^0_{corr} curves in Fig.4. This is understandable if one realizes that the effect of the potential on the wave functions increases with its strength, while the effect of the boundaries remains unchanged. Further we observe that Z^0_{corr}, Z_i(pot), and Z_{F} lead to different curves. The difference between Z^0_{corr} and Z_i(pot) as shown in Fig. 4 is certainly due to the $|q\rangle \rightarrow |\psi_k\rangle$ replacement. However, Eq. (30) implies that for the screened Coulomb potential one should find $Z_i(\mathrm{pot}) = Z^0_{\mathrm{corr}} = Z_i = Z_{\mathrm{F}} = 1$. This means that a difference between Z_i(pot) and Z_{F} uncovers some limitation of the use of the model square well potential. Although the differences in shape of the three potentials are known, in Fig. 5 we show their shapes for a certain k_{F} value, for which we choose a value in the middle of 0.7.

VIII. THE FORCE EXPRESSION OF BOSVIEUX AND FRIEDEL

The starting expression of Bosvieux and Friedel for the driving force is

$$\mathbf{F}_{T=0} = -\langle \Psi | \boldsymbol{\nabla}_{\mathbf{R}_1} (V_{ei} + \delta V) | \Psi \rangle, \tag{43}$$

in which the state $|\Psi\rangle$ is a solution of the Schrödinger equation for the system in the presence of an applied field. This means that one has to solve the time dependent Schrödinger equation

$$i\frac{\partial \Psi(t)}{\partial t} = \mathcal{H}(t)\Psi(t) \equiv [H + \delta V(t)]\Psi(t). \tag{44}$$

The subscript $T=0$ is added by the present author in order to distinguish this force from the force given in Eq. (2). The derivation of Eq. (2), in which a solution of the Liouville equation is used, has been given in the literature many times. Because the approach through the system wave function is typical for the theory of Bosvieux and Friedel, and because some questions can be raised about their solution, we give crucial steps of the derivation. We solve Eq. (44) by using the interaction representation for $\Psi(t)$, defined by

$$\Psi_I(t) \equiv e^{iHt}\Psi(t). \tag{45}$$

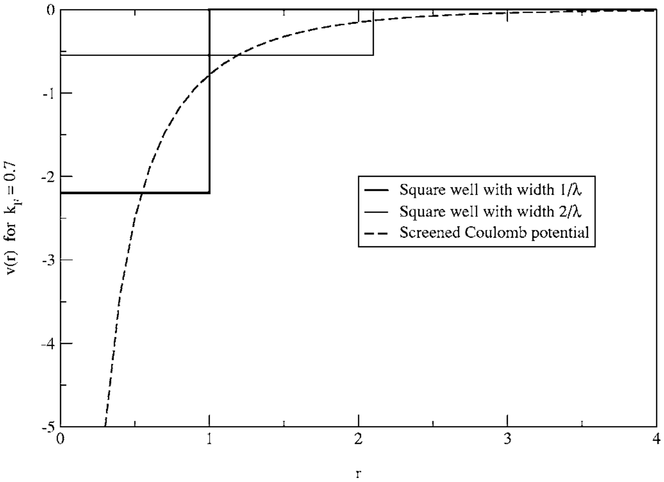

FIG. 5. $v(r)$ for the three potentials plotted as a function of r.

The equation for $\Psi_I(t)$ becomes

$$i\frac{\partial \Psi_I(t)}{\partial t} = e^{iHt}\delta V(t) e^{-iHt}\Psi_I(t). \tag{46}$$

After integrating this equation and using that for $t \rightarrow -\infty$ the system is in the ground state of the unperturbed system Hamiltonian H, one finds for $\Psi(t)$ linearly in δV,

$$\Psi(t) = -ie^{-iHt}\int_{-\infty}^{t} dt' e^{iHt'}\delta V(t') e^{-iHt'}\Psi_I(-\infty) + e^{-iHt}\Psi_I(-\infty). \tag{47}$$

With $\delta V(t) = \delta V e^{at}$, applying the substitution $t - t' \equiv s$, and considering an arbitrary time in the present, so $t=0$, this becomes

$$\Psi(0) \equiv \Psi = -i\int_{0}^{\infty} dt e^{-(iH+a)t}\delta V e^{iHt}\Psi_I(-\infty) + \Psi_I(-\infty). \tag{48}$$

If one calculates matrix elements with this $|\Psi\rangle$, the factor $e^{-iE_0\infty}$ in the state $|\Psi_I(-\infty)\rangle$ drops out so that just the ground state $|\psi_0\rangle$ of H remains.

By this one finds for Eq. (43)

$$\begin{aligned}\mathbf{F}_{T=0} &= -\langle \psi_0 | \boldsymbol{\nabla}_{\mathbf{R}_1}(\delta V) | \psi_0 \rangle \\ &\quad + i\int_{0}^{\infty} dt e^{-at}\langle \psi_0 | (\boldsymbol{\nabla}_{\mathbf{R}_1} V_{ei}) e^{-iHt}\delta V e^{iHt} | \psi_0 \rangle + \mathrm{c.c.} \\ &= Z_i e\mathbf{E} + i\int_{0}^{\infty} dt e^{-at}\langle \psi_0 | [(\boldsymbol{\nabla}_{\mathbf{R}_1} V_{ei}), e^{-iHt}\delta V e^{iHt}] | \psi_0 \rangle.\end{aligned} \tag{49}$$

Because H commutes with the coordinates $\mathbf{R}_\alpha$ in δV only the electron coordinates survive. Using the definition of the force operator, Eq. (5), and the Hermitian property of H it is clear that the time dependence can be applied to $\mathbf{F}_{\mathrm{op}}$ as well, and Eq. (49) can be written as

$$\mathbf{F}_{T=0} = Z_i e\mathbf{E} - ie\int_0^\infty dt e^{-at}\langle\psi_0|[\mathbf{F}_{\mathrm{op}}(t),\mathbf{E}\cdot\sum_j \mathbf{r}_j]|\psi_0\rangle. \tag{50}$$

Interestingly, Eq. (50) is precisely the zero-temperature equivalent of Eq. (2). This becomes even more clear if one writes down the form which shows up after the reduction of Eq. (50) to single particle states denoted by $|q\rangle$.

$$\mathbf{F}_{T=0} = Z_i e\mathbf{E} - ie\int_0^\infty dt\, e^{-at}\sum_q \langle q|[\mathbf{f}^1(t),\mathbf{E}\cdot\mathbf{r}]|q\rangle. \tag{51}$$

The force operator $\mathbf{f}^1$ is defined in Eq. (5). At $T=0$ the sum over the single particle states has a sharp cutoff at $\epsilon_q=\epsilon_{\mathrm{F}}$. The finite temperature equivalent of Eq. (51) can be written

$$\mathbf{F} = Z_i e\mathbf{E} - ie\int_0^\infty dt e^{-at} tr\{n(h)[\mathbf{f}^1(t),\mathbf{E}\cdot\mathbf{r}]\}, \tag{52}$$

in which the Fermi-Dirac distribution $n(\epsilon)$ has been inserted, see Eq. (13). Clearly, Eq. (52) is completely equivalent to Eq. (12) of the present text. By this, electromigration theory can be considered as being unified. Apparently, the starting formula of Bosvieux and Friedel was correct, but these authors did not recognize its precise contents. In fact, they wrote down surface-integral terms, by this not appreciating the Hermitian property of the system Hamiltonian. This property implies that these terms are zero, but their full-screening results were derived from these terms. In addition, they missed the power of their starting formula, Eq. (43), by taking the $a\to 0$ limit in too early a stage of the derivation. A detailed account of these statements, in which the original paper is followed as closely as possible, can be read elsewhere.[24]

IX. CONCLUDING REMARKS AND PERSPECTIVES

The amount of screening of the direct force on a proton in an electric-current carrying metal has been shown to lie between 5 and 25%. By this the full-screening prediction of Bosvieux and Friedel has been invalidated, completely in agreement with an earlier result obtained by Sorbello.[1,8] On top of that, the surface integral terms used by Bosvieux and Friedel to derive their full-screening result appear to be zero, due to the Hermitian property of the Hamiltonian. Interestingly, it has been shown explicitly that the starting expression of Bosvieux and Friedel for the driving force is the zero-temperature limit of all linear-response expressions used in the literature since their introduction by Kumar and Sorbello.[6]

All existing calculations use a jellium model for a metal, or are not applicable to transition metals.[15] In view of the description presented it becomes feasible to account for real metallic effects. These effects have been accounted for in the calculations of the wind force to a large detail,[3] but for the direct force this was much too involved up to now.[4] Such a development would be interesting, because this may lead to an explanation of a measured result which has not been understood yet. For most hydrides a direct valency for the hydrogen has been measured which is of the order of unity. However, in Nb(H) a direct valency was found of about 0.44. Such a deviating value may arise from multiple scattering effects of the electrons around a proton surrounded by metallic atoms, which can be accounted for in a finite-cluster description. It is worthwhile to investigate this possibility, because in the development of the description of the wind force surprising positive values for the wind valence in V(H) and Nb(H) were found, which were in agreement with the experiment.[25] The surprise comes from the fact that in a system composed of a finite cluster embedded in a jellium the electron dispersion relation is still free electronlike, from which one would expect a negative wind valence. The calculated result must be due to the rather strong multiple scattering effects, which were accounted for explicitly. A finite cluster description for the direct valency would be a straight generalization of the impurity in a jellium description implemented so far. This is a feasible development if one uses the simplified treatment presented above, of which it has been shown that the expressions can be evaluated in terms of the scattering phase shifts of the constituent atoms.

ACKNOWLEDGMENT

I want to thank Jacques Friedel for an interesting conversation and an extended correspondence over the recent months.

APPENDIX: CRUCIAL STEPS IN THE DERIVATION OF EQ. (36)

For the evaluation of Z_{corr} defined in Eq. (26) one needs the momentum matrix element $\mathbf{p}_{q'q}$ and the matrix element of the commutator with the statistical distributions. For $\mathbf{p}_{q'q}$ one writes

$$\mathbf{p}_{q'q} = \frac{(4\pi)^2}{8\pi^3}\sum_{LL'} i^{\ell-\ell'} Y_{L'}(\hat{k}')Y_L^*(\hat{k}) \int d^3r R_{L'}^*(\mathbf{r})\mathbf{p}R_L(\mathbf{r}), \tag{A1}$$

in which Eq. (34) with $\Omega\to 8\pi^3$ has been used for the wave functions and $R_L(\mathbf{r})\equiv R_\ell(r,k)Y_L(\hat{r})$. If one represents the scattering potential by a square well with depth v_0 the inner radial solution is a Bessel function as well, so $R_\ell(r,k) = A_\ell j_\ell(k_v r)$, with $k_v=\sqrt{k^2+v_0}$, and one finds

$$\int Y_{L'}^*(\hat{r})\mathbf{p}R_L(\mathbf{r})d\hat{r} = i^{\ell'-\ell}k_v\mathbf{D}_{L'L}R_{\ell'\ell}(r,k), \tag{A2}$$

in which the equality

$$\int Y_{L'}^*(\hat{r})\mathbf{p}j_L(\mathbf{r})d\hat{r} = i^{\ell'-\ell}k\mathbf{D}_{L'L}j_{\ell'}(kr) \tag{A3}$$

has been used and

$$\mathbf{D}_{L'L} \equiv \int d\hat{k} Y^*_{L'}(\hat{k}) \hat{k} Y_L(\hat{k}). \tag{A4}$$

The double-ℓ label in Eq. (A2) refers to the fact that the factor A_ℓ is not changed by the momentum operation and the angular integration, so that

$$k_v R_{\ell'\ell}(r,k) = k_v \frac{A_\ell}{A_{\ell'}} R_{\ell'}(r,k) \to k[j_{\ell'}(kr) - ikt_\ell h^+_{\ell'}(kr)]. \tag{A5}$$

If one substitutes Eq. (A2) in Eq. (A1) one obtains

$$\mathbf{p}_{q'q} = \frac{2}{\pi} \sum_{LL'} Y_{L'}(\hat{k}') Y^*_L(\hat{k}) \mathbf{D}_{L'L} I^{RR}_{\ell'\ell}(k',k) \tag{A6}$$

with

$$I^{RR}_{\ell'\ell}(k',k) = \int_0^\infty r^2 dr k_r R^*_{\ell'}(r,k') R_{\ell'\ell}(r,k), \tag{A7}$$

and in which $k_r = k_v$ inside the range of the potential and $k_r = k = k_F$ outside of it. Using the equality

$$\int_0^\infty r^2 dr j_\ell(k'r) j_\ell(kr) = \frac{\pi \delta(k-k')}{2k^2}, \tag{A8}$$

it appears to be possible to reduce the integral $I^{RR}_{\ell'\ell}(k',k)$ to

$$I^{RR}_{\ell'\ell}(k',k) = \frac{k\pi}{2} \frac{\delta(k-k')}{k^2} \overline{I}^{RR}_{\ell'\ell}, \tag{A9}$$

in which

$$\overline{I}^{RR}_{\ell'\ell} \equiv 1 - ikt_\ell + ikt^*_{\ell'} - 2ikt_\ell ikt^*_{\ell'}. \tag{A10}$$

Now we turn to the other matrix element in Eq. (26). Using Eq. (16) one finds

$$\langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle = -\int_0^\beta ds \langle q|[\mathbf{r}, n(h) e^{sh} v e^{-sh_0}(1 - n(h_0))]|q'\rangle. \tag{A11}$$

We remind the reader that in this equation h and v just refer to the system with one impurity, so to h^1 and v^1. Now we use the equality (29) and the following related equality:

$$[e^{\beta h}, \mathbf{r}] = -\frac{i}{m} \int_0^\beta ds \mathbf{p}(s) e^{\beta h} \tag{A12}$$

twice, one time for h and one time for h_0. By that the commutator in the right-hand side of Eq. (A11) can be written as follows:

$$\begin{aligned}
&[\mathbf{r}, n(h) e^{sh} v e^{-sh_0}(1 - n(h_0))] \\
&= -\frac{i}{m} n(h) \left\{ \int_0^\beta ds' \mathbf{p}(s')[1 - n(h)] e^{sh} v e^{-sh_0} \right. \\
&\quad \left. - \int_0^s ds' \mathbf{p}(s') e^{sh} v e^{-sh_0} + e^{sh} v e^{-sh_0} \mathbf{p}[s - \beta n(h_0)] \right\} \\
&\quad \times [1 - n(h_0)].
\end{aligned} \tag{A13}$$

It will be clear that $\mathbf{p}(s)$ in the first and second term refers to h.

Now we develop the qq' matrix element of this operator as it occurs in Eq. (A11). In that we will make use of the property proven above through Eq. (A6) with (A9), namely that the energies ϵ_q and $\epsilon_{q'}$ in the matrix element $\mathbf{p}_{qq'}$ are equal, and of the equality of the energies ϵ_k and ϵ_q in the overlap $\langle k|q\rangle$, see Eq. (35). In the first and second term we have to insert two complete sets, one q set $|q'''\rangle\langle q'''|$ and one k set $|k''\rangle\langle k''|$. In the third and fourth term one needs the complete k set only. This way one writes for the qq' matrix element in the left-hand side of Eq. (A11)

$$\begin{aligned}
\langle q|[\mathbf{r}, n(h) - n(h_0)]|q'\rangle = \frac{i\beta^2}{m} n_q &\left[\sum_{q'''} \sum_{k''} \mathbf{p}_{qq'''} \left(\frac{1}{2} - n_{q'''}\right) t^*_{k''k'''} \right. \\
&\left. + \sum_{k''} t^*_{k''k} \mathbf{k}'' \left(\frac{1}{2} - n_{k''}\right) \right] (1 - n_{k''}) \\
&\times \langle k''|q'\rangle,
\end{aligned} \tag{A14}$$

in which the potential matrix element $v_{qk'} = v^*_{k'q}$, between an exact scattered state $|q\rangle = |\psi_k\rangle$, see Eq. (34), and an unperturbed state, a plane wave $|k'\rangle$, has been replaced by the corresponding t matrix element $t^*_{k'k}$.

By now we have developed the means for bringing Z_{corr} in a manageable form. One has to take the inner product of the matrix element given by Eq. (A14) with $\frac{i}{3}\mathbf{p}_{q'q}$ and to carry out the summations. Because the summations are equivalent to integrals and the absolute values of *all* k vectors involved are equal through delta functions, one just has to carry out the angular integrations. We write for Z_{corr} in Eq. (26)

$$\begin{aligned}
Z_{\text{corr}} = \frac{i}{3} \int d\hat{k} \int d\hat{k}' \int d\hat{k}'' \left(\int d\hat{k}''' \right) &\langle q|[\mathbf{r}, n(h^1) \\
&- n(h_0)]|q'\rangle \cdot \mathbf{p}_{q'q},
\end{aligned} \tag{A15}$$

in which the right-hand side of Eq. (A14) is supposed to have been substituted. The angular integration over $\hat{k}'''$ applies to the first term in the right-hand side of Eq. (A14) only. The product of statistical factors which shows up can be simplified and in the $T \to 0$ limit be written as follows:

$$\begin{aligned}
&-\beta^2 n_k (1 - n_k)\left(\frac{1}{2} - n_k\right) \\
&= \frac{1}{2} \beta \frac{\partial}{\partial \epsilon_k} [n_k (1 - n_k)] \to \frac{1}{2} \frac{\partial}{\partial \epsilon_k} \delta(\epsilon_k - \epsilon_F).
\end{aligned} \tag{A16}$$

If one substitutes this equality, uses Eqs. (A6), (A9), (A10), and (A14), accounts for the factor of 2 due to the spin degeneracy, and carries out all angular integrations, one finds for Z_{corr} of Eq. (A15)

$$\begin{aligned} Z_{\text{corr}} &= \frac{2}{3\pi m}\int_0^\infty k^2 dk \frac{\partial}{\partial \epsilon_k}\delta(\epsilon_k - \epsilon_{\text{F}})\sum_{LL'} \mathbf{D}_{LL'}\cdot \mathbf{D}_{L'L}(1 - ikt_{\ell'}) \\ &\quad \times (t^*_{\ell'}\bar{I}^{RR}_{\ell\ell'} + t^*_{\ell})k^2 \bar{I}^{RR}_{\ell'\ell} \\ &= -\frac{4}{3\pi m}\int_0^\infty k^3 dk \left[\frac{\partial}{\partial \epsilon_k}\delta(\epsilon_k - \epsilon_{\text{F}})\right]F(\epsilon_k), \end{aligned} \tag{A17}$$

in which it has been used that

$$\bar{I}^{RR}_{\ell\ell'} = \cos(\delta_\ell - \delta_{\ell'})e^{-i(\delta_\ell - \delta_{\ell'})}, \tag{A18}$$

and

$$\sum_{mm'} D^{\nu}_{LL'}D^{\mu}_{L'L} = \frac{1}{3}\delta_{\mu\nu}((\ell + 1)\delta_{\ell',\ell+1} + \ell\ \delta_{\ell',\ell-1}). \tag{A19}$$

In the right-hand side of Eq. (A17) one recognizes the second member of Eq. (36), by which the derivation has been completed. The derivations leading to Eqs. (38), (40), and (41) are similar, and they are simpler as well.

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

[2] For a review, see J. van Ek and A. Lodder, Defect Diffus. Forum **115-116**, 1 (1994).

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

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

[5] R. Zeller and P. H. Dederichs, Phys. Rev. Lett. **42**, 1713 (1979).

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

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

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

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

[10] R. C. Brouwer and R. Griessen, Phys. Rev. Lett. **62**, 1760 (1989).

[11] J. van Ek and A. Lodder, J. Phys.: Condens. Matter **3**, 7331 (1991).

[12] L. Turban, P. Nozières, and M. Gerl, J. Phys. (Paris) **37**, 159 (1976).

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

[14] A. Lodder, Solid State Commun. **79**, 143 (1991).

[15] H. Ishida, Phys. Rev. B **51**, 10345 (1995).

[16] P. R. Rimbey and R. S. Sorbello, Phys. Rev. B **21**, 2150 (1980).

[17] P. J. Braspenning, R. Zeller, A. Lodder, and P. H. Dederichs, Phys. Rev. B **29**, 703 (1984).

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

[19] A. Lodder, Physica A **158**, 723 (1989).

[20] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, 1992), Ch. 5.

[21] A. Lodder, Solid State Commun. **79**, 147 (1991).

[22] E. W. Fenton, Solid State Commun. **22**, 63 (1977).

[23] A. Lodder, Physica B **97**, 156 (1979).

[24] A. Lodder, Europhys. Lett. **72**, 774 (2005).

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