The starting formula of Bosvieux and Friedel for the force on an ion in a metal due to an applied voltage is shown to lead to the same description as the linear-response approach used in the field since its introduction by Kumar and Sorbello. By this electromigration theory has become a unified theory. It follows after accounting for a treacherous trap term, which at first sight seems to be zero. Up to now Bosvieux and Friedel claimed to predict a completely screened direct force, which means that only a wind force would be operative. In addition the amount of screening has been calculated up to second order in the potential of the migrating impurity, using a finite temperature version of the screening term derived by Sham. For a proton in a metal modeled as a jellium the screening appears to be about 15%, which is neither negligible nor reconcilable with the old full-screening point of view.

Introduction

Electromigration is the motion of an ion in a metal under the influence of an applied voltage. Depending on the metal and the ion its motion is either to the anode or to the cathode. The total driving force on such an ion is known to be the result of two contributions, a direct force and a wind force

\[ \mathbf{F} = \mathbf{F}_{\text{direct}} + \mathbf{F}_{\text{wind}} = (Z_{\text{direct}} + Z_{\text{wind}})e\mathbf{E} = Z^*e\mathbf{E}, \]

in which \( Z^* \) is called the effective valence, which is a measurable quantity. The direct force is due to the direct action of the applied field \( \mathbf{E} \) on the charge of the ion. The wind force comes from the scattering of the current carrying electrons off the ion.

Until 1962 there was a common belief that \( Z_{\text{direct}} \) was equal to the bare valence \( Z_i \) of the ion. At most a small deviation from that value could arise from the electrons in the metallic environment of the ion. In 1962 Bosvieux and Friedel predicted a complete cancellation of the direct force due to screening effects, so that only the wind force would remain. By that prediction a controversy was born. It was not easy to decide matters by a measurement, and a satisfactory theoretical answer was lacking as well.

In 1975 Kumar and Sorbello published an exact linear-response expression for the driving force. After that it was considered as being just a matter of a careful evaluation of that expression in order to settle the problem. It took quite some time to do so though. Finally Sorbello, starting from the complicated treatment given by Rimbev et al., predicted a screening of 10-30%, depending on the potential used for the ion. Support of this result has been given by the present author, starting from a much simpler description. However, in the meantime new support was given for the full-screening point of view.

Interestingly, the original paper by Bosvieux and Friedel (BF) is referred to as being controversial on the one hand, while on the other hand their starting formula is referred to as the first quantum mechanical equation for the wind force, which is seen as a pioneering contribution to the field. Therefore we undertook an evaluation of their starting formula, following the authors as closely as possible, up to a point where we came across a trap. By treating this trap properly the final evaluation ends up at the standard linear-response expression for the driving force. As far as the author knows Sorbello was the first who showed that such traps occur in the theory of electromigration.

The screening itself has been calculated by Sorbello, who used one type of expression for it. Therefore we undertook the evaluation of Sham’s second order expression written in a new form, the more so as a more recent result for the screening, ranging from 0 to 100%, is rather inconclusive. Sham’s expression has never been evaluated numerically, and in his paper he just gives an order of magnitude comparison with his wind force expression. This has led him to the conclusion that the screening is negligible. We find a screening of 5-25%, which is in agreement with Sorbello’s results.

Ryderg atomic units are used, in which the energy is in Rydberg, the distance is in Bohr (1 Bohr \( \approx 0.5 \) \( \text{Å} \)), \( \hbar = 1 \), and the electronic mass is \( \frac{1}{2} \).
Basics of linear-response theory

We first give the standard linear-response expression for the driving force on an ion at position \( \mathbf{R}_i \),

\[
\mathbf{F} = Z_i e \mathbf{E} - i e E_\nu \int_0^\infty dt e^{-at} \text{Tr} \left\{ \rho(H) \left[ \mathbf{F}_{\text{op}}(t); \sum_j r_j^a \right] \right\},
\]

(2)
in which the cartesian label \( \nu \) runs from 1 to 3. The infinitesimally 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 \( \mathbf{F}_{\text{op}} \) stands for

\[
\mathbf{F}_{\text{op}} \equiv -\nabla_{\mathbf{R}_i} V = - \sum_j \nabla_{\mathbf{R}_i} v(\mathbf{r}_j - \mathbf{R}_i) \equiv \sum_j \mathbf{f}_j^i,
\]

(3)
and its time dependence refers to the Heisenberg representation

\[
\mathbf{F}_{\text{op}}(t) \equiv e^{iHt} \mathbf{F}_{\text{op}} e^{-iHt}.
\]

(4)
The expression published by Kumar and Sorbello follows simply after a partial integration in Eq. (2) with respect to the time.

All important studies of the driving force have been done for the electron-impurity system, the Hamiltonian \( H \) of which can be written as a sum of single particle Hamiltonians \( h \), so

\[
H = \sum_j h^j \quad \text{with} \quad h = h_0 + v = h_0 + \sum_\alpha v^\alpha,
\]

(5)
in which the summation in the electron-impurity potential runs over the positions \( \mathbf{R}_\alpha \) of the impurities. This allows for a reduction of the many body expression (2) to the following single particle expression,

\[
\mathbf{F} = Z_i e \mathbf{E} - i e E_\nu \int_0^\infty dt e^{-at} \text{tr} \left\{ n(h) \left[ \mathbf{F}^i(t); r^\nu \right] \right\},
\]

(6)
where \( n(h) \) is the Fermi-Dirac distribution function in operator form

\[
n(h) = \frac{1}{e^{\beta(h - \epsilon_F)} + 1}.
\]

(7)

The treatment of Bosvieux and Friedel (BF)

We start to follow BF’s treatment, by writing down their system Hamiltonian

\[
H = - \sum_{\mu=1}^N \frac{\Delta^\mu}{2m^\mu} + V(\mathbf{r}_1, \ldots, \mathbf{r}_\mu, \ldots, \mathbf{r}_N).
\]

(8)
In applying a small perturbation denoted as \( \delta V \) they write down the perturbed wave function \( \Psi \). In their appendix BF employ the idea of switching on the field adiabatically. For the sake of clarity we give the explicit form of the perturbing potential due to an applied field,

\[
\delta V(t) = e \mathbf{E} e^{at} \cdot \left( \sum_j \mathbf{r}_j - \sum_\alpha Z_\alpha \mathbf{R}_\alpha \right) \equiv \delta V e^{at} \equiv (\delta V(\mathbf{r}) + \delta V(\mathbf{R})) e^{at},
\]

(9)
which is zero in the limit \( t \to -\infty \). The position dependent potentials have been defined for later use. BF’s force expression reads as

\[
\tilde{\phi} = - < \Psi | \nabla_{\mathbf{r}_i} (V + \delta V) | \Psi >,
\]

(10)
in which \( | \Psi > \) represents the state of the system as it develops from its unperturbed ground state \( | \psi_0 > \) due to the perturbation \( \delta V \). In order to find \( | \Psi > \) we solve the time dependent Schrödinger equation

\[
i \frac{\partial \Psi(t)}{\partial t} = \mathcal{H}(t) \Psi(t)
\]

(11)
for the total Hamiltonian
\[ \mathcal{H}(t) = H + \delta V(t) \] (12)

by working in the interaction representation for \( \Psi(t) \), defined as
\[ \Psi_I(t) \equiv e^{iH_I t} \Psi(t). \] (13)

The equation for \( \Psi_I(t) \) becomes
\[ i \frac{\partial \Psi_I(t)}{\partial t} = e^{iH_I (-H + i \frac{\partial}{\partial t})} \Psi(t) = e^{iH_I \delta V(t)} e^{-iH_I t} \Psi_I(t). \] (14)

After integrating this equation one finds for \( \Psi(t) \) linearly in \( \delta V \)
\[ \Psi(t) = -ie^{-iH_I t} \int_0^t dt' e^{iH_I t'} \delta V(t') e^{-iH_I t} \Psi_I(-\infty) + e^{-iH_I t} \Psi_I(-\infty). \] (15)

With \( \delta V(t) = \delta Ve^{at} \), applying the substitution \( t - t' \equiv s \), and considering an arbitrary time in the present, so \( t = 0 \), this becomes
\[ \Psi(0) \equiv \Psi = -i \int_{-\infty}^\infty dt e^{-(iH+\alpha)t} \delta Ve^{iHt} \Psi_I(-\infty) + \Psi_I(-\infty). \] (16)

If one calculates matrix elements with this \( \Psi \) the factor \( e^{-iE_0 0} \) in the state \( |\Psi_I(-\infty)\rangle \) drop out so that just the ground state \( |\psi_0\rangle \) remains. BF’s Eq. (1.2) for \( |\Psi_I(-\infty)\rangle \) is reproduced by inserting the complete set of eigenstates of the system Hamiltonian \( H \), denoted by \( |\psi_n\rangle \). The only difference is the presence of the infinitesimal number \( a \). BF have omitted it and just denote that in the summation over \( n \) the value \( n = 0 \), corresponding to the ground state, has to be excluded. It will become clear that this difference has a dramatic influence on the final results.

Now we evaluate BF’s force expression, Eq. (10), linearly in the applied field \( \delta V \).
\[ \vec{F} = -\langle \psi_0 | \nabla_i (\delta V) | \psi_0 \rangle + i \int_0^\infty dt e^{-at} \langle \psi_0 | (\nabla_i V) e^{-iHt} \delta V e^{iHt} | \psi_0 \rangle + \text{c.c.} \]
\[ = Z_i eE + i \int_0^\infty dt e^{-at} \langle \psi_0 | (\nabla_i V), e^{-iHt} \delta V e^{iHt} | \psi_0 \rangle, \] (17)
in which we used Eq. (10) for \( |\Psi\rangle \) and Eq. (9) for evaluating the matrix element \( \langle \psi_0 | \nabla_i (\delta V) | \psi_0 \rangle \).

In the further evaluation of this equation we want to follow BF’s evaluation given in their §1. The integral over the time in the first line of Eq. (17) is carried out after inserting a complete set \( |\psi_n\rangle \) of eigenstates. Further, use is made of the equality \( (\nabla_i V) = [\nabla_i, H] \). This way one obtains
\[ \vec{F} = Z_i eE - \sum_n (E_n - E_0) \langle \psi_0 | \nabla_i | \psi_n \rangle \frac{\langle \psi_n | \delta V | \psi_0 \rangle}{E_0 - E_n + ia} + \text{c.c.} \]
\[ = Z_i eE - \sum_n \langle \psi_0 | \nabla_i | \psi_n \rangle \langle \psi_n | \delta V | \psi_0 \rangle \frac{E_n - E_0 - ia + ia}{E_0 - E_n + ia} + \text{c.c.} \]
\[ = Z_i eE + \sum_n \langle \psi_0 | \nabla_i \delta V | \psi_0 \rangle - ia \sum_n \langle \psi_0 | \nabla_i | \psi_n \rangle \frac{\langle \psi_n | \delta V | \psi_0 \rangle}{E_0 - E_n + ia} + \text{c.c.} \]
\[ = -ia \sum_n \langle \psi_0 | \nabla_i | \psi_n \rangle \frac{\langle \psi_n | \delta V | \psi_0 \rangle}{E_0 - E_n + ia} + \text{c.c.} \] (18)

We want to comment on Eq. (18) in view of the results of BF. First, in evaluating the matrix element \( \langle \psi_0 | [\nabla_i, H] | \psi_0 \rangle \) in the first line of Eq. (18) BF create in addition surface integral terms corresponding to Green’s theorem, by that not appreciating the hermitian property of \( H \). These surface integral terms represent flow of probability out of the system, which is obviously zero for a finite system and for an isolated metal, as BF admit. But this flow is zero also for a metal carrying a steady electric current, which is denied in practice by BF. Secondly, in their treatment the last line of Eq. (18) is missing, because BF have put \( a = 0 \) from the beginning. We want to point out that regarding this last line a treacherous, hidden trap in the formalism is involved, which has shown up earlier in electromigration theory\(^9\). This term seems to be zero because of the proportionality with the infinitesimal number \( a \), but we will show that this term in fact is a rich one.
In rewriting the last line of Eq. (18) we first write the energy denominator as coming from a time integral as follows

\[
\tilde{\phi} = -a \int_0^\infty dt \ e^{-at} \sum_n <\psi_0|\nabla_i|\psi_n><\psi_n| e^{-iHt}\delta V e^{iHt}|\psi_0> + c.c.
\]

\[
= -a \int_0^\infty dt \ e^{-at} <\psi_0| \left[ e^{iHt} \nabla_i e^{-iHt} \delta V(R) \right] |\psi_0>.
\]  

(19)

Because \( H \) commutes with \( \delta V(R) \) the second term reduces to \( Z_i eE \), and one finds that

\[
\tilde{\phi} = Z_i eE - a \int_0^\infty dt \ e^{-at} <\psi_0| \left[ e^{iHt} (\nabla_i V) e^{-iHt}, eE \cdot \sum_j r_j \right] |\psi_0>.
\]  

(20)

After a partial integration with respect to time, using that \( [\nabla_i, H] = (\nabla_i V) \), and substituting \( \delta V(r) \) according to Eq. (9), one finds

\[
\tilde{\phi} = Z_i eE + i \int_0^\infty dt \ e^{-at} \sum_q <q| \left[ e^{iht} (\nabla_i V) e^{-iht}, eE \cdot r \right] |q>.
\]  

(21)

We are back at the second line of Eq. (17), but only the electron coordinates in \( \delta V \) have survived the operations. The influence of the electric current on the total force is taken care of by the second term in the right hand side of Eq. (21). In retrospection this result follows right away from Eq. (17) as well, but we wanted to go along with BF’s way of evaluation first.

Eq. (21) is a very interesting result. It is precisely the zero temperature equivalent of Eq. (2). This becomes even more clear if we write down the form which shows up after the reduction of Eq. (21) to single particle states denoted by \( |q> \).

\[
\tilde{\phi} = Z_i eE + i \int_0^\infty dt \ e^{-at} \sum_q <q| \left[ e^{iht} (\nabla_i V) e^{-iht}, eE \cdot r \right] |q>.
\]  

(22)

At \( T = 0 \) the sum over the single particle states has a sharp cut-off at \( \epsilon_q = \epsilon_F \). The finite temperature equivalent of Eq. (22) can be written as

\[
\tilde{\phi} = Z_i eE + i \int_0^\infty dt \ e^{-at} \sum_q n(\epsilon_q) <q| \left[ e^{iht} (\nabla_i V) e^{-iht}, eE \cdot r \right] |q>
\]

\[
= Z_i eE - i \int_0^\infty dt \ e^{-at} \sum_q \sum_j \left( n(h) \left[ f^i(t), eE \cdot r \right] \right) \equiv (Z_i + Z_{\text{wind}} + Z^{\text{scr}}) eE,
\]  

(23)

in which the Fermi-Dirac distribution \( n(\epsilon) \) has been inserted, see Eq. (4). The force operator \( f^i \) is defined in Eq. (3). Clearly, Eq. (23) is completely equivalent to Eq. (3) of the present text. By this electromagnet theory can be considered as being unified. Apparently, BF’s starting formula was correct, but these authors did not recognize its precise contents. This became more clear recently BF used Eq. (10) for their result regarding the direct force only. They treated the wind force separately, applying a semi-classical standard approach in describing the current carrying electrons and accounting for the scattering of the electrons by the migrating impurity quantum mechanically.

The formal Eqs. (22) or (23), or forms which have been shown to be equivalent to them, have been used since Kumar and Sorbello published their linear-response approach to the electromigration problem. The result of all this research is, that the second term of these equations contains two contributions, as it has been indicated explicitly in the right hand side of Eq. (23). One can be identified as the wind force. The other one implies some screening of the bare direct force \( Z_i eE \). The wind force expression has been studied thoroughly and has been applied to calculate \( Z_{\text{wind}} \) for both interstitial and substitutional impurities in many metals. Because the present paper is devoted to the settlement of the controversy regarding the direct force, we want to add a calculation of \( Z^{\text{scr}} \) starting from Sham’s contribution. But first one more comment on Eq. (23) and its interpretation. BF claim to have proven that for an isolated system the force on an ion is zero. The present author agrees that this force is zero, but this fact does not follow from an explicit proof, but from the knowledge that internally any applied field \( E \) is screened out by an electronic surface charge that is built up. This is a general result from the theory of electromagnetism. That is why then \( \tilde{\phi} \), which is proportional to \( E \), is zero, because \( E = 0 \).
Calculation of $Z^{scr}$

If one evaluates Eq. (23) to lowest order in the potential $v$ of the ion, for a jellium model of the metal, one finds that

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

(24)
in which a $k$ label refers to a plane wave. It has been shown that the $T \to 0$ limit is equivalent with Sham’s expression. Sham gave an order of magnitude estimate by comparing it with the wind force expression. $Z_{wind}$ is proportional to the transport relaxation time $\tau$ of the system, while $Z^{scr}$ is proportional to the inverse of an energy, for which the Fermi energy can be chosen. By that he came out at a ratio of $(\epsilon_F \tau)^{-1} \approx 0.01$, being negligible.

![Graph showing $Z^{scr}$ for different potentials](image)

**FIG. 1:** The amount of screening represented by $Z^{scr}$ according to Eq. (24), with $a = \tau^{-1}$, for the screened Coulomb potential and for two square well potentials.

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 $\epsilon_k$ one ends up at

$$Z^{scr} = -\frac{4}{3\pi^2 m} \int_{0}^{\infty} d\epsilon_k \int_{0}^{\infty} d\epsilon_{k'} \frac{\partial n_k}{\partial \epsilon_k} \frac{n_k - n_{k'}}{\epsilon_k - \epsilon_{k'}} + a^2 \sum_{f} f_{f}(k, k') ,$$

(25)
in which the function $f_{f}(k, k')$ is defined as

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

(26)
containing the information about the ion potential through

$$v_{f}(k', k) = \int_{0}^{\infty} r^2 dr \ j_{f}(k'r) v(r) j_{f}(kr) .$$

(27)
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' behaviour. 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 $(\epsilon_k, \epsilon_{k'}) = (\epsilon_F, \epsilon_F)$. 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. A calculation for $a \ll \tau^{-1}$ has been presented elsewhere. Here we want to follow Sham more closely. He replaced $a$ by $\tau^{-1}$, by that accounting for the entire distribution of impurities in the metal and for the possible presence of other scattering mechanisms.
The result of a numerical evaluation for different ion potentials is shown in FIG. 1. In addition to a screened Coulomb potential\textsuperscript{12},

\[ v(r) = -\frac{Z_i e^2 e^{-\lambda r}}{r}, \]  

(28)

with the Thomas-Fermi screening parameter \( \lambda \), square well potentials were employed in the same spirit as Sorbello did\textsuperscript{5}. The choice \( Z_i = 1 \) represents a proton in a jellium. The width of the square well potential was chosen to be equal to the screening length \( 1/\lambda \) and twice as large. The corresponding well depth was limited by the condition that just no bound state could be formed. The value of \( \lambda \) 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 \( \lambda \) increases monotonically with the Fermi energy, the range of the corresponding screened Coulomb potential decreases with increasing \( k_F \), which reduction in strength is seen clearly in the bold solid curve. We compared \( v_{kk} \) for the three potentials and found a clear decrease for the Coulomb potential with increasing \( k_F \), and a rather flat behaviour for the square well potentials, the one with \( 2/\lambda \) being markedly stronger than the one with the smaller width. The screening to second order in the impurity potential appears to be not negligible, but on the average \( 15 \pm 10\% \). For comparison we mention, that the result for a very small \( a \) value shows a screening which is at most 2\% larger then the present result for \( a = \tau^{-1} = 0.01 \). As a guide for the eye we gave the average of \( Z_{scr} \) for the three potentials as a dotted line. Interestingly, this result does not imply that Sham’s conclusion of a negligible screening is entirely wrong. If fact, he compared \( Z_{scr} \) with \( Z_{wind} \). The ratio \( Z_{scr}/Z_{wind} \) is small indeed, but this comes from the large value of \( \tau \). It may be clear that a comparison with \( Z_i \) would have been more appropriate.

In conclusion, we have shown that the starting formula of Bosvieux and Friedel gives the right driving force on an ion in a metal under the influence of an applied voltage. Because it always has been recognized as the first time that a quantummechanical form for that force was written down, their contribution can still be characterized as a pioneering one. On the other hand, their prediction of a complete cancellation of the direct force has been falsified, because it was based on surface integral terms, which are zero due to the hermiticity of the system Hamiltonian. Further, the expression for the magnitude of the screening due to Sham does not give a negligible screening, but a screening of about 15\%. This is in agreement with an earlier result based on another approach\textsuperscript{2}.

Taking all this together, the controversy regarding the magnitude of the direct force can be regarded as being resolved by now, and a unification of the various descriptions has been achieved.

Acknowledgments

Discussions with Jacques Friedel and an extended recent correspondence is greatly appreciated.

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