

Theory of the direct force in electromigration

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The direct force in electromigration is investigated within the linear-response formalism. Expressions derived by Rimbey and Sorbello are shown to simplify considerably. The result is that the direct force can be obtained from the one-particle Green's function at the Fermi level. Model calculations for hydrogen interstitials in metals indicate that the direct force exerted by the macroscopic electric field on the hydrogen atom may be on the order of 70–90% of the force exerted by the macroscopic field on a bare proton. These results show some similarity to Landauer's theory of the carrier-density–modulation effect, and are in contradiction to the theory of Bosvieux and Friedel.

I. INTRODUCTION

The migration of impurity atoms in a metal that is subjected to an electric field is the phenomenon known as electromigration.¹ It has long been realized that there are two essentially distinct contributions to the driving force exerted on the impurity. First, there is the force associated with the electronic current that accompanies the electric field. This force, which is known as the electron-wind force, is due to the momentum transfer from the electrons to the impurity during collisions.^{1–3} Second, there is the electrostatic force due to the applied, or macroscopic, electric field acting on the impurity. This force, which is known as the direct force, has been a subject of great controversy.¹

The direct-force controversy was spawned by the pioneering work of Bosvieux and Friedel⁴ (BF), who obtained the result that there is no direct force on an interstitial impurity. On one level, the BF result is physically appealing. An impurity is, after all, a locally screened neutral entity in a metal, and thus it should not be subject to a direct force from a uniform electrostatic field. This is a favorite argument of those who would deny the existence of the direct force.⁵ Further study reveals that the argument is flawed, however. It has been pointed out,⁶ for example, that the same argument can be applied to an electron and its accompanying exchange-correlation hole, which is also a neutral entity. One would then be led to conclude that an electron is not subject to force in an electric field, and thus, electron current could not occur. In any case, it should be pointed out that the BF derivation is *not* based on the argument that the impurity is locally neutral. Rather, BF derive their result from some seemingly general quantum-mechanical considerations. The error in their analysis is in assuming that the direct force arises from an equilibrium electrostatic polarization response. As I discuss in Sec. IV, this assumption is not valid. My conclusion is that there is no basis for the BF result despite its continued use by some workers.⁷

An analysis of the direct force is complicated by the presence of the electron-wind force and the accompanying electron-polarization effects. A general, self-consistent

approach is needed to deal with all effects on an equal footing. Such approaches have been provided by Das and Peierls⁶ and by Landauer⁸ from semiclassical points of view. They found that in the formal limit in which the impurity's bare charge is weak ($Z \ll 1$), the direct force is given by the macroscopic field acting on the bare charge. That is,

$$\vec{F}_d = Ze\vec{E} + O(Z^2), \quad (1)$$

where \vec{F}_d is the direct force, Z is the bare valence, e is the magnitude of the electron charge, and \vec{E} is the macroscopic or average field in the metal. To lowest order in Z , Eq. (1) states that there is no screening of the electric field as it acts on the bare charge Ze . This is in contrast to the BF result $\vec{F}_d = 0$.

Landauer goes further to derive an approximate expression for \vec{F}_d based on his carrier-density–modulation effect. The idea is that an attractive impurity potential increases the local density of carriers in the vicinity of the impurity. Continuity of electron current then requires the local electric field to be diminished in the region of higher carrier density, analogous to the situation for macroscopic inhomogeneities of high conductivity. The net result is that the effective valence is diminished. Landauer's result is⁸

$$\vec{F}_d = \frac{Ze\vec{E}}{1 + \frac{1}{3}\beta\Delta n/n_0}, \quad (2)$$

where Δn is the local increase in electron density due to the impurity, n_0 is the average electron density in the metal, and β is an unspecified parameter on the order of unity. Since $\Delta n = Z/\Omega_0$, where Ω_0 is an appropriate atomic volume, Eq. (2) is consistent with Eq. (1).

The use of semiclassical concepts is not expected to be accurate on the atomic scale. Details of electronic wave functions and their polarizability are expected to be important in electromigration, and these are omitted from the analyses by Das and Peierls and by Landauer. To deal with these effects, a general self-consistent quantum-mechanical approach is needed. This was provided by the

introduction by Kumar and Sorbello of linear-response theory in electromigration.⁹ Subsequent development of the linear-response theory of electromigration by Sham¹⁰ and by Schaich¹¹ was particularly important. These papers provided a good deal of insight into the electron-wind force, but did not adequately treat the direct force. The result obtained was $\vec{F}_d = Ze\vec{E}$, which is correct only to lowest order in Z . The reason for the failure to obtain the higher-order corrections to \vec{F}_d was given by Rimbey and Sorbello¹² (RS), who showed that the direct force is contained in some off-shell T -matrix terms neglected by Sham. RS also pointed out that it may be difficult to separate the direct force from some formally higher-order corrections to the wind force. This aspect is not so important, however, because in nearly all practical cases these higher-order corrections are small. (They are of order $1/\epsilon_F\tau$ times the wind force, where ϵ_F is the Fermi energy and τ is the electron relaxation time. Typically, this ratio is on the order of 10^{-2} at room temperature.)

The RS expression for the direct force was too complicated to permit evaluation, except for a rather crude separable-potential model which gave rise to some unphysical results.¹² In this paper I show that the RS expression for the direct force can be greatly simplified. The result is a tractable expression for the direct force in terms of the Green's function at the Fermi energy. Explicit calculations are performed for hydrogen impurities in a metal, where the potential is modeled by a three-dimensional square well with s -wave scattering being dominant. It is found that the direct force is typically 10–30% smaller than $Ze\vec{E}$, as one might perhaps expect from Eq. (2), but occasionally \vec{F}_d can be larger than $Ze\vec{E}$. Such deviation of \vec{F}_d from the nominal value $Ze\vec{E}$ may soon be experimentally measurable as more sophisticated measurement techniques are being devised.¹³

II. GREEN'S-FUNCTION EXPRESSION FOR DIRECT FORCE

As shown by Kumar and Sorbello,⁹ the α component of the driving force \vec{F} acting on an impurity whose bare charge is Ze and coordinate is \vec{R} can be written as

$$F_\alpha = ZeE_\alpha + \sum_\beta \lim_{\omega \rightarrow 0} \lim_{\eta \rightarrow 0^+} [\chi_{\alpha\beta}(\omega + i\eta)/i\omega] E_\beta, \quad (3)$$

where $\chi_{\alpha\beta}$ is the force-current response function given by

$$\chi_{\alpha\beta} = i \int_0^\infty dt e^{i(\omega + i\eta)t} \left\langle \left[-\frac{\partial V(t)}{\partial R_\alpha}, J_\beta(0) \right] \right\rangle. \quad (4)$$

Here, $V(t)$ is the interaction potential (operator) between the bare impurity and the electrons, and \vec{J} is the electron-current operator. Both operators are in the Heisenberg representation. The angular brackets denote the statistical ensemble average of the commutator. Units with $\hbar=1$ are assumed.

Expression (3) is formally exact within the context of the Kubo linear-response theory,¹⁴ but it should be pointed out that there is an underlying assumption in the theory. That is, the macroscopic, or average, field \vec{E} is

being treated as an externally applied field. In reality, \vec{E} is a self-consistent field set up dynamically through the conduction process. This is accomplished via "residual-resistivity dipoles" as described by Landauer¹⁵ for the case of defect scattering. Further investigation of this point^{16–18} has indicated that the use of the macroscopic field in Eq. (3) is justifiable, however. The point is that one can focus attention on a very small region \mathcal{R} containing the impurity, and within this region the electrons are driven as if \vec{E} were externally applied. Subsequent scattering by the impurity and its local environment are contained in the response function (4). The dimensions of \mathcal{R} should be smaller than the electron mean free path if the theory is to be consistent. There is no difficulty in imagining such a region containing the impurity, so expression (3) is reasonably "exact."

The model to be considered here is the impurity in jellium model, which is the same model treated by RS in their strong-coupling theory.¹² Following Sham's diagrammatic analysis of the response function (4), RS showed that the driving force \vec{F} can be written in the usual form,

$$\vec{F} = \vec{F}_w + \vec{F}_d, \quad (5)$$

where \vec{F}_w is the wind force, and \vec{F}_d can be expressed in terms of off-the-energy-shell contributions to the response function (4). It is customary to write

$$\vec{F}_d = Z_d e \vec{E}, \quad (6)$$

where Z_d is the effective valence associated with the direct force. The RS expression (3.1) gives

$$Z_d = Z + \Gamma - \frac{2}{3\pi m} \text{Im} \sum_{\vec{k}} k^2 G(\vec{k}, \vec{k}, \epsilon_F), \quad (7)$$

where m is the electron mass and Im denotes imaginary part. $G(\vec{k}, \vec{k}, \epsilon_F)$ is the diagonal part of the Green's function (operator) in the plane-wave representation, i.e.,

$$G(\vec{k}, \vec{k}', \epsilon) = \langle \vec{k} | (\epsilon + i0^+ - H)^{-1} | \vec{k}' \rangle, \quad (8)$$

where $H = -\nabla^2/2m + v$, and v is the screened electron-impurity interaction. The expression for Γ is

$$\Gamma = -\frac{2}{3\pi m} \text{Im} \sum_{\vec{k}, \vec{k}'} \vec{k} \cdot \vec{k}' \int_{-\infty}^{\epsilon_F} d\epsilon G(\vec{k}, \vec{k}', \epsilon) G(\vec{k}', \vec{k}, \epsilon). \quad (9)$$

It was pointed out by RS that, in expression (7), Z should be taken as the number of protons in the nucleus of the impurity. RS also showed that the integral over negative energies in expression (9) corresponds to bound-state contributions which cancel out the corresponding nuclear charges. Thus one can take Z to be the net-ionic-charge number (number of protons minus the number of core electrons) if one takes the lower limit of the ϵ integral in Eq. (9) to be zero, which is the energy of the bottom of the conduction band.

The last two terms on the right-hand side of Eq. (7) are the new contributions to the direct force found by RS. Unfortunately, the complicated nature of expression (9) prevented RS from applying their result to realistic

models for the impurity potential. It turns out, however, that it is unnecessary to calculate the multiple integrals in expression (9) using the explicit form of $G(\vec{k}, \vec{k}', \epsilon)$ for the impurity potential of interest. In the Appendix it is shown that

$$\Gamma = -Z + \frac{2}{3\pi m} \text{Im} \sum_{\vec{k}} k^2 G_0(\vec{k}, \vec{k}, \epsilon_F), \quad (10)$$

where G_0 is the free-electron propagator, i.e.,

$$G_0(\vec{k}, \vec{k}, \epsilon) = \langle \vec{k} | (\epsilon + i0^+ - H_0)^{-1} | \vec{k} \rangle, \quad (11)$$

and $H_0 = -\nabla^2/2m$.

Substitution of expression (10) into Eq. (7) yields

$$Z_d = -\frac{2}{3\pi m} \text{Im} \sum_{\vec{k}} k^2 g(\vec{k}, \vec{k}, \epsilon_F), \quad (12)$$

where $g = G - G_0$ is the change in the Green's function due to the impurity, and thus

$$g(\vec{k}, \vec{k}, \epsilon_F) = G(\vec{k}, \vec{k}, \epsilon_F) - G_0(\vec{k}, \vec{k}, \epsilon_F). \quad (13)$$

Expression (12) is a great simplification over the original RS expression because of the elimination of the multiple integrals. The summation over all \vec{k} values is inconvenient, however. A more practical result can be obtained by expressing the \vec{k} summation, or trace, in the coordinate representation. The result is

$$Z_d = \frac{4}{3\pi} \text{Im} \left[\int [v(\vec{r}) - \epsilon_F] g(\vec{r}, \vec{r}, \epsilon_F) d^3r + \int v(\vec{r}) G_0(\vec{r}, \vec{r}, \epsilon_F) d^3r \right], \quad (14)$$

where

$$g(\vec{r}, \vec{r}, \epsilon_F) = G(\vec{r}, \vec{r}, \epsilon_F) - G_0(\vec{r}, \vec{r}, \epsilon_F)$$

and

$$G(\vec{r}, \vec{r}, \epsilon_F) = \langle \vec{r} | (\epsilon_F + i0^+ - H)^{-1} | \vec{r} \rangle,$$

and similarly for $G_0(\vec{r}, \vec{r}, \epsilon_F)$ with H replaced by H_0 . To obtain Eq. (14) from Eq. (12), one uses the fact that k^2 is the diagonal element of the operator $-\nabla^2$ in the plane-wave representation and makes use of the differential equations satisfied by G and G_0 , namely

$$\left[-\frac{1}{2m} \nabla_{\vec{r}}^2 + v(\vec{r}) - \epsilon - i0^+ \right] G(\vec{r}, \vec{r}', \epsilon_F) = -\delta^3(\vec{r} - \vec{r}'), \quad (15)$$

and similarly for G_0 when v is set equal to zero.

It should be pointed out that to lowest order in Z , expression (14) reduces to $Z_d = Z$. Although this fact is not immediately apparent from expression (14), it can be deduced from the original expressions given by Sham and by RS. These expressions, which were used in obtaining the result (14), show that $\chi_{\alpha\beta}$ is of order v^2 , or, equivalently, of order Z^2 . It then follows from Eq. (3) that $Z_d = Z + O(Z^2)$, which is in agreement with Eq. (1).

Expression (14) is very practical because the Green's function $G(\vec{r}, \vec{r}, \epsilon_F)$ can be readily determined numerically from the differential equation (15) for any given spherically symmetric impurity potential $v = v(r)$. In that case, the standard partial-wave analysis simplifies the calculation of G . This is illustrated in the next section for a simple square-well model for hydrogen interstitials in metals. In this model, the differential equation (15) for the Green's function can be solved analytically.

III. MODEL CALCULATION

In this section, expression (14) is evaluated for the simple model of a three-dimensional square-well potential. The model is used to estimate the direct force for the case of hydrogen interstitial impurities in metals. The potential is taken to be

$$v(r) = \begin{cases} -v_0 & \text{for } r \leq r_0, \\ 0 & \text{for } r > r_0, \end{cases} \quad (16)$$

where v_0 is a positive constant for an assumed attractive impurity potential ($Z > 0$).

Substitution of this potential in expression (14) gives

$$Z_d = \frac{2}{3} \epsilon_F \Delta n_T(\epsilon_F) + \frac{2}{3} v_0 \Delta n_L(\epsilon_F) + \frac{8}{9} m v_0 k_F r_0^3 / \pi, \quad (17)$$

where $\Delta n_T(\epsilon_F)$ and $\Delta n_L(\epsilon_F)$ are, respectively, the changes in the total and local densities of states at ϵ_F due to the introduction of the impurity. Explicitly,

$$\Delta n_T(\epsilon_F) = -\frac{2}{\pi} \text{Im} \int g(\vec{r}, \vec{r}, \epsilon_F) d^3r \quad (18)$$

and

$$\Delta n_L(\epsilon_F) = -\frac{2}{\pi} \text{Im} \int g(\vec{r}, \vec{r}, \epsilon_F) \Theta(r_0 - r) d^3r, \quad (19)$$

where $\Theta(x)$ equals unity for $x \geq 0$ and vanishes for $x < 0$. In obtaining Eq. (17), use was made of the standard form of G_0 in terms of spherical Bessel functions and Hankel functions. This allowed the last term on the right-hand side of Eq. (14) to be evaluated, resulting in $\frac{8}{9} m v_0 k_F r_0^3 / \pi$, where $k_F = (2m\epsilon_F)^{1/2}$ is the Fermi wave vector.

Self-consistency is imposed in this model by use of the Friedel sum rule, which states that

$$Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \delta_l(\epsilon_F), \quad (20)$$

where the $\delta_l(\epsilon)$ are the phase shifts at energy ϵ . The phase shifts can also be used to determine $\Delta n_T(\epsilon_F)$ by the usual expression,

$$\Delta n_T(\epsilon_F) = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1) \left. \frac{d\delta_l(\epsilon)}{d\epsilon} \right|_{\epsilon=\epsilon_F}. \quad (21)$$

The local density of states, unlike the total density of states, is not simply related to $\delta_l(\epsilon)$. According to Eq. (19), the Green's function $G(\vec{r}, \vec{r}, \epsilon_F)$ needs to be calculated for $r < r_0$. This is readily accomplished by the standard technique of matching the homogeneous solutions to the differential equation (15) using the Wronskian. After some tedious algebra, one can obtain analytical results.

TABLE I. Calculated values for square-well model of hydrogen interstitials in metals. The well radius r_0 is chosen to equal the Thomas-Fermi screening length. Atomic units assumed.

Metal	k_F	r_0	v_0/v_c	$\delta_0(\epsilon_F)$ (deg)	$\Delta n_L(\epsilon_F)$	$\Delta n_T(\epsilon_F)$	Z	Z_d	Z_d/Z
Na	0.4816	1.277	0.25	8.44	0.225	0.303	0.094	0.105	1.12
			0.50	22.1	0.624	0.578	0.245	0.309	1.26
			0.75	44.0	1.160	0.368	0.489	0.628	1.28
			1.00	72.5	1.263	-0.827	0.806	0.788	0.98
Pd	0.7176	1.046	0.25	9.70	0.154	0.133	0.108	0.117	1.08
			0.50	24.3	0.384	0.207	0.270	0.311	1.15
			0.75	45.0	0.606	0.032	0.500	0.543	1.09
			1.00	68.8	0.592	-0.450	0.763	0.630	0.83
Cu	0.7962	0.993	0.25	10.0	0.138	0.106	0.111	0.120	1.08
			0.50	24.8	0.332	0.152	0.275	0.390	1.12
			0.75	45.0	0.503	-0.004	0.500	0.521	1.04
			1.00	67.6	0.479	-0.383	0.751	0.594	0.79
Nb	0.8532	0.959	0.25	10.2	0.128	0.090	0.113	0.122	1.08
			0.50	25.0	0.301	0.122	0.278	0.307	1.10
			0.75	45.0	0.443	-0.022	0.500	0.506	1.01
			1.00	66.8	0.414	-0.345	0.743	0.572	0.77
Al	0.9273	0.920	0.25	10.5	0.116	0.074	0.116	0.124	1.07
			0.50	25.4	0.266	0.092	0.282	0.304	1.08
			0.75	44.9	0.378	-0.037	0.499	0.488	0.98
			1.00	65.9	0.345	-0.303	0.732	0.546	0.75

The expressions are rather unweildy. Consequently, I have restricted by numerical calculations to cases where only the $l=0$ phase shifts are appreciable. This is the situation that is to be expected for the strong, localized potential characterizing a hydrogen interstitial impurity in a metal.

The well radius r_0 is chosen to equal the Thomas-Fermi screening length, λ_{TF} , where $\lambda_{TF}=(6\pi n_0 e^2/\epsilon_F)^{-1/2}$. For each value of v_0 there is a definite value of Z determined by the Friedel sum rule (20) at the assumed Fermi level of the metal of interest. The calculated values of Z and Z_d are shown in Table I for a series of host metals with $v_0/v_c=0.25, 0.50, 0.75$, and 1.00 , where $v_c=\pi^2/8mr_0^2$ is the critical value of v_0 for which a bound state forms. (The $v_0/v_c=1.00$ case actually refers to a v_0/v_c value that is very slightly less than unity, so as to avoid the bound-state formation.) Values of k_F were chosen between 0.4816 and 0.9273 a.u., corresponding to the cases of sodium and aluminum, respectively. Between these limits, the k_F values chosen correspond to ϵ_F values appropriate to band-structure calculations for palladium, copper, and niobium.¹⁹ The Pd and Nb results should be regarded only as rough estimates for these metals with complicated band structures, since band-structure effects are not contained in the jellium model. The intent here is primarily to examine a reasonable spread of k_F values rather than to claim quantitative accuracy for transition metals.

Our numerical results show that both Z and Z_d vary smoothly and essentially monotonically with v_0 . As v_0/v_c approaches zero, the ratio Z_d/Z approaches unity,

which is the general result for the weak-charge limit. This ratio increases somewhat as v_0/v_c increases, then begins to decrease for v_0/v_c values between 0.50 and 0.75 . The relevant choice of v_0/v_c for a hydrogen interstitial should give a value of Z as near to unity as possible, if the use of only s -wave contributions is to be reasonable. The appropriate value of v_0/v_c is thus the largest value consistent with no bound-state formation, i.e., v_0/v_c should be just less than unity. For Na this choice gives $Z=0.806$, with Z_d being within 2% of this value. At the other extreme of k_F values, the Al result is $Z=0.732$ with Z_d about 25% lower than this.

The values of $\delta_0(\epsilon_F)$ for the cases of Pd, Cu, and Nb with v_0/v_c near unity are within a few percent of values obtained by Lodder¹⁹ from impurity-potential calculations for hydrogen in these metals. This lends further support to the choice of v_0/v_c just less than unity as the relevant potential strength in modeling hydrogen interstitials. (Stronger potentials would create a bound state, and this would result in a negative ion, which is not expected to be the case for hydrogen interstitials in the metals considered here.)

To provide an indication of the sensitivity of the results to r_0 , the calculations were repeated with r_0 taken to be twice as large as before. These results are shown in Table II. In all calculations, only the s -wave contributions were considered. Although this is an excellent approximation for the case that $r_0=\lambda_{TF}$ (Table I results), the approximation is not so good for the $r_0=2\lambda_{TF}$ case. In the former case, $\delta_1(\epsilon_F)$ is no more than a few percent of $\delta_0(\epsilon_F)$, whereas in the latter case, $\delta_1(\epsilon_F)$ is on the order of

TABLE II. Same calculation as in Table I except that r_0 is chosen to be twice the Thomas-Fermi screening length.

Metal	r_0	v_0/v_c	$\delta_0(\epsilon_F)$ (deg)	$\Delta n_L(\epsilon_F)$	$\Delta n_I(\epsilon_F)$	Z	Z_d	Z_d/Z
Na	2.554	0.25	12.0	0.593	0.087	0.133	0.133	1.00
		0.50	26.2	1.018	-0.163	0.291	0.266	0.91
		0.75	41.4	1.034	-0.781	0.460	0.359	0.78
		1.00	55.8	0.631	-1.542	0.619	0.390	0.63
Pd	2.092	0.25	12.0	0.211	-0.044	0.133	0.133	1.00
		0.50	24.8	0.268	-0.228	0.276	0.248	0.90
		0.75	37.4	0.143	-0.511	0.416	0.326	0.78
		1.00	48.8	-0.102	-0.805	0.542	0.367	0.68
Cu	1.986	0.25	11.8	0.144	-0.056	0.131	0.134	1.02
		0.50	24.2	0.153	-0.219	0.269	0.246	0.91
		0.75	36.1	0.024	-0.447	0.402	0.323	0.80
		1.00	46.8	-0.187	-0.677	0.521	0.370	0.71
Nb	1.919	0.25	11.7	0.106	-0.061	0.130	0.134	1.03
		0.50	23.8	0.091	-0.210	0.264	0.245	0.93
		0.75	35.2	-0.037	-0.407	0.392	0.324	0.83
		1.00	45.5	-0.227	-0.602	0.506	0.375	0.74
Al	1.841	0.25	11.5	0.067	-0.064	0.128	0.134	1.05
		0.50	23.1	0.031	-0.197	0.257	0.245	0.95
		0.75	34.1	-0.093	-0.362	0.379	0.326	0.86
		1.00	43.8	-0.261	-0.521	0.487	0.383	0.79

10–30% of $\delta_0(\epsilon_F)$. The smaller values of $\delta_0(\epsilon_F)$ for the case $r_0 = 2\lambda_{TF}$ result in smaller values of Z and Z_d , but the Z_d/Z ratios are similar to those for the $r_0 = \lambda_{TF}$ case. Again, it is found that Z_d is on the order of 20–30% smaller than Z at the maximum $\delta_0(\epsilon_F)$, although the Z_d/Z ratio for Na is considerably smaller than this.

IV. DISCUSSION

The numerical results showing that $Z_d < Z$ for $v_0/v_c \lesssim 1$ are consistent with Landauer's expression (2). However, for smaller values of v_0/v_c and for $r_0 = \lambda_{TF}$ (Table I), it is found that $Z_d > Z$, which is in conflict with expression (2). It is possible that Landauer's result, being based on a semiclassical viewpoint, is more appropriate to a long-range potential, i.e., large r_0 . For the larger choice of r_0 (Table II), the calculations give $Z_d < Z$, with Z_d approaching Z in the $v_0 \rightarrow 0$ limit. This is consistent with the Landauer expression (2).

The contributions to Z_d from each of the three terms in expression (17) are of comparable magnitude, and if the changes in the local and total densities of states are positive for an attractive potential, each of the terms in expression (17) is positive. It is apparent from Tables I and II, however, that $\Delta n_T(\epsilon_F)$ is often negative, thus diminishing Z_d . [The correlation between negative $\Delta n_T(\epsilon_F)$ and smaller Z_d/Z values is apparent in the tables.] According to Eq. (21), negative $\Delta n_T(\epsilon_F)$ for an s -wave potential occurs when $\delta_0(\epsilon)$ vs ϵ has a negative slope at ϵ_F . For an attractive impurity this can only occur outside the weak-scattering (first-order perturbation-theory) regime.

The importance of the impurity-induced change in the density of states is also apparent from the general expression (12). Were it not for the k^2 factor in Eq. (12), Z_d would be proportional to $\Delta n_T(\epsilon_F)$, since the latter equals

$$-(2/\pi) \text{Im} \sum_{\vec{k}} g(\vec{k}, \vec{k}, \epsilon_F).$$

The k^2 factor gives stronger weight to the local density of states because the kinetic energy is larger in the region where the impurity potential is deepest. This weighting effect is more obvious in expression (14).

It would be useful to evaluate Z_d for impurity potentials more realistic than the square-well model. This can be accomplished with expression (14) once $G(\vec{r}, \vec{r}, \epsilon_F)$ has been determined. The latter could be readily obtained as a by-product of impurity-potential calculations. Lacking $G(\vec{r}, \vec{r}, \epsilon_F)$, one might resort to a cruder approximation if $\Delta n_T(\epsilon_F)$ and $\Delta n_L(\epsilon_F)$ were available. Here one might use the square-well-model result (16) with v_0 being estimated by averaging a screened Coulomb potential over an appropriate atomic volume.

Although the model calculations were performed for interstitial impurities, the same calculations could have been performed for substitutional impurities. In that case, Z would refer to the difference in ionic-charge number between solute and host atoms. The situation becomes more complicated, however, as the impurity atom migrates. There are then atomic-configuration effects to consider during the diffusion jump, as, for example, in the vacancy mechanism of diffusion where the solute is at some posi-

tion \vec{R} between two vacancies. As a first approximation, one could regard the solute as an isolated interstitial when it is halfway between the vacancies. A numerical average could then be performed to obtain an effective Z_d value. Such complications do not occur for interstitial electromigration.

The role of band structure is more difficult to assess. The original RS expression (7) and the resulting expression (14) were obtained within a jellium model. The latter expression, however, involves Green's functions and impurity potentials which could be calculated beyond the jellium model. It is tempting to use Eq. (14) with the Green's functions obtained for a realistic model of a crystalline lattice. Determining whether or not this procedure is justified requires further study. An analysis of the response function (4) within a Bloch representation would be required.

A fundamental aspect of the direct force deserves emphasis. The basic point is that Z_d is a dynamic entity and cannot simply be calculated from the static response to an electric field. This is obvious from Landauer's discussion of the carrier-density-modulation effect,⁸ but it can also be deduced from the form of Eq. (7). The Γ contribution in Eq. (7) formally corresponds to the electrostatic screening response to the applied field. This fact emerges when a disguised version of the response function for electrostatic polarizability is recognized to be lurking in Eq. (9). This function is²⁰

$$\chi(\vec{r}, \vec{r}') = -\frac{2}{\pi} \text{Im} \int_{-\infty}^{\epsilon_F} G(\vec{r}, \vec{r}', \epsilon) G(\vec{r}', \vec{r}, \epsilon) d\epsilon. \quad (22)$$

For the static-polarizability problem, the induced electron density δn is related to the electrostatic potential ϕ according to²⁰

$$\delta n(\vec{r}) = \int \chi(\vec{r}, \vec{r}') \phi(\vec{r}') d^3r'. \quad (23)$$

The cancellation of Z with the part of Γ that depends on the impurity potential as expressed by Eq. (10) can be shown from Eqs. (22) and (23) to be a reflection of the following fact: A uniform electric field [$\phi(\vec{r}) = -\vec{r} \cdot \vec{E}$] exerts no force on an isolated neutral entity under conditions of static thermodynamic equilibrium. This statement ties in with the popular argument that is invoked for the vanishing of the direct force and explains why the BF approach is incorrect. The point is that the last term on the right-hand side of Eq. (7) (or, more precisely, the part of that term which depends on the existence of the impurity) is the only surviving contribution to Z_d . This term appears only in a dynamic calculation, and is therefore missing in static-equilibrium calculations such as that of BF.

The special dynamic nature of Z_d has also been appreciated by Huntington,²¹ Froberg,²² Landauer,^{8,23} Das and Peierls,²⁴ and Sorbello and Dasgupta.¹⁶ In the present work, I have presented a tractable theoretical expression that permits a quantum-mechanical calculation of Z_d . According to expression (14), or the square-well-model result (17), accurate experimental determination of Z_d can provide important information on alloy potentials in metals.

V. SUMMARY

The direct force has been related through Eqs. (6) and (14) to the one-particle Green's function for impurity scattering at the Fermi energy. Expression (14) allows the direct force to be calculated from quantities that are readily available from impurity-potential studies. Model calculations for hydrogen interstitials in metals give values of the direct force that are on the order of 70–90% of $Ze\vec{E}$. These results show some similarity with Landauer's result, Eq. (2), which he obtained from an analysis based on his carrier-density-modulation effect. In Landauer's analysis and mine the direct force arises from dynamic contributions which are not contained in a standard electrostatic-polarizability calculation, such as that of BF. The major limitation of my analysis is that it is based on the model of an isolated impurity in a jellium background. Further work is needed to determine the effects of band structure and atomic configurations for general defect complexes.

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APPENDIX

Expression (10) is now derived. To do this, I recast the defining equation (9) for Γ into the following form, which is independent of representation:

$$\Gamma = -\frac{2}{\pi m} \int_{-\infty}^{\epsilon_F} \text{Im} \text{Tr} p G(\epsilon) p G(\epsilon), \quad (A1)$$

where Tr stands for trace, $p = -i(\partial/\partial x)$ is the x component of the momentum operator, and $G(\epsilon) = 1/(\epsilon + i0^+ - H)$ is the operator form of the Green's function. It is convenient to express the trace in Eq. (A1) in the representation in which H is diagonal. This gives

$$\text{Tr} p G(\epsilon) p G(\epsilon) = \sum_{n, n'} p_{nn'} G_n(\epsilon) p_{n'n} G_n(\epsilon), \quad (A2)$$

where $p_{nn'} = \langle n | p | n' \rangle$ and $G_n(\epsilon) = \langle n | G(\epsilon) | n \rangle$, and similarly for $G_{n'}(\epsilon)$. The eigenstates of H are denoted $|n\rangle$ and $|n'\rangle$.

The relation $p = -im[x, H]$ implies that $p_{n'n} = -im(\epsilon_n - \epsilon_{n'})x_{n'n}$, where ϵ_n and $\epsilon_{n'}$ are the energy eigenvalues, i.e., $H|n\rangle = \epsilon_n|n\rangle$. Substitution of this $p_{n'n}$ form into Eq. (A2) gives

$$\text{Tr} p G(\epsilon) p G(\epsilon) = -im \sum_{n, n'} [G_n^{-1}(\epsilon) - G_{n'}^{-1}(\epsilon)] \times G_n(\epsilon) G_{n'}(\epsilon) p_{nn'} x_{n'n}, \quad (A3)$$

where

$$G_n^{-1}(\epsilon) = \langle n | G^{-1} | n \rangle = \epsilon + i0^+ - \epsilon_n,$$

and similarly for $G_{n'}^{-1}(\epsilon)$.

Using $G^{-1}G = 1$ and introducing the commutator relation $[p, x] = -i$ in the $|n\rangle$ representation, one can easily obtain, from Eq. (A3), the result

$$\text{Im Tr}pG(\epsilon)pG(\epsilon) = -m \text{Tr}G(\epsilon). \quad (\text{A4})$$

Substitution into Eq. (A1) yields

$$\Gamma = \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \text{Im Tr}g(\epsilon)d\epsilon + \frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \text{Im Tr}G_0(\epsilon)d\epsilon, \quad (\text{A5})$$

where $g(\epsilon) = G(\epsilon) - G_0(\epsilon)$ and $G_0(\epsilon) = 1/(\epsilon + i0^+ - H_0)$ is the free-electron propagator ($H_0 = -\nabla^2/2m$).

The first term on the right-hand side of Eq. (A5) is the negative of the net change in the number of occupied states due to the introduction of the impurity [compare Eq. (18)]. Local neutrality in a metal guarantees that this equals $-Z$. That is,

$$Z = -\frac{2}{\pi} \int_{-\infty}^{\epsilon_F} \text{Im Tr}g(\epsilon)d\epsilon. \quad (\text{A6})$$

The desired result (10) is thus proved if the second terms on the right-hand sides of Eqs. (A5) and (10) can be shown to be equal.

To establish this equality, one can parallel the development from Eqs. (A1)–(A4) starting with the quantity

$$\Gamma_0 \equiv -\frac{2}{\pi m} \int_{-\infty}^{\epsilon_F} \text{Im Tr}pG_0(\epsilon)pG_0(\epsilon)d\epsilon, \quad (\text{A7})$$

and using the plane-wave representation $|\vec{k}\rangle$ in place of

the $|n\rangle$ representation. Instead of Eq. (A4), one finds

$$\text{Im Tr}pG_0(\epsilon)pG_0(\epsilon) = -m \text{Tr}G_0(\epsilon), \quad (\text{A8})$$

which establishes the fact that the last term on the right-hand side of Eq. (A5) equals Γ_0 .

It is now simple to obtain the desired relation

$$\Gamma_0 = \frac{2}{3\pi m} \text{Im} \sum_{\vec{k}} k^2 G_0(\vec{k}, \vec{k}, \epsilon_F), \quad (\text{A9})$$

which will finally prove expression (10). To derive Eq. (A9), I recast Eq. (A7) in the \vec{k} representation as follows:

$$\Gamma_0 = -\frac{2}{\pi m} \text{Im} \int_{-\infty}^{\epsilon_F} \sum_{\vec{k}} k_x^2 G_0^2(\vec{k}, \vec{k}, \epsilon)d\epsilon. \quad (\text{A10})$$

Note that

$$G_0^2(\vec{k}, \vec{k}, \epsilon) = -\frac{\partial}{\partial E} G_0(\vec{k}, \vec{k}, \epsilon), \quad (\text{A11})$$

which allows the ϵ integration of $G_0^2(\vec{k}, \vec{k}, \epsilon)$ in Eq. (A10) to be trivially performed to give $-G_0(\vec{k}, \vec{k}, \epsilon_F)$. The desired relation (A9) is now obtained upon replacement of k_x^2 by $\frac{1}{3}k^2$.

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