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Microscopic theory of the driving force in electromigration

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Kumar and Sorbello have expressed the effective force on an ion in electromigration in terms of a response function, which is evaluated here by the method of quantum field theory. Formulas for the force are derived for the jellium model and for a crystal lattice. Some physical insight can be gained by viewing previous works on this subject through this particular perspective.

I. INTRODUCTION

When a constant and uniform electric field is applied to a solid conductor, it causes a migration of ions. The flux is determined by the mobility times the effective driving forces acting on the ion.[1] The mobility is given by the Einstein relation in terms of the diffusion coefficient. The effective driving force on the ion consists not only of the direct electrical force on the ion but also indirect force via the electrons carrying the current. Much theoretical work on the effective driving force has given us good physical understanding but not unanimity on the subject. Sorbello[2] has given a critical review of all but the most recent theories.

Kumar and Sorbello[3] have provided an excellent framework for the theory of the driving force by using Kubo's theory of linear response.[4] Their evaluation of the response function in terms of the memory functions[5] is, however, of limited validity. A more general formulation in terms of the random-force correlation functions has been given by Schaich.[6] These are, unfortunately, difficult to evaluate even in simple cases. In this paper, we investigate the linear response by the conventional field-theory method.[7,8]

We examine a sequence of systems with increasing complexity. The homogeneous electron gas with a rigid positive background and a dilute random distribution of impurities can be solved completely. There is no need to use the Born approximation for the electron-impurity interaction as was done in Refs. 3 and 6. The formula for the effective force is just that of Fiks[9] and of Huntington and Grone.[10] There is no further screening of the direct force on the ion as found by Bosvieux and Friedel.[11] The modifications due to electron-electron and electron-phonon interaction are considered. In a crystal lattice, a formula is derived for the force on the ion due to scattering by Bloch electrons. Fik's use of crystal momentum transfer including umklapp processes[12] is justified. In the case of a small electron or hole Fermi surface, it follows from our formula that the electron-wind term has the same sign as the Hall mobility.[12]

The advantages of the field-theory method of calculating the driving force are that (i) The fundamental processes contributing to the force are calculated, and when represented by Feynman diagrams, their physical nature is simple to interpret; (ii) The nature of approximations used is easier to delineate than in other methods; (iii) A general formula involving the solution of the Landau-Boltzmann equation (thus including the Fermi-liquid effects) is derived, and the driving force under more general perturbation than an electric field, such as in a combination of electric and magnetic fields or in a temperature gradient, can be calculated.

II. EFFECTIVE FORCE ON AN ION

Consider an ion with charge Ze at $\vec{R}$. e denotes the charge of a proton. The Z electrons which come off the ion are assumed to be in the conduction band of the solid. Then the driving force on the ion due to an electric field $\vec{E}$ is given by[3]

$$F_\alpha = ZeE_\alpha - \langle \partial V/\partial R_\alpha \rangle \,, \qquad (2.1)$$

where V is the interaction energy between this ion and the conduction electrons.

The perturbation on the electron Hamiltonian by the uniform electric field is most conveniently expressed[8] in terms of the vector potential $\vec{A}$,

$$H' = -c^{-1}\vec{J}\cdot\vec{A}\,e^{-i\omega t+\eta t} \,, \qquad (2.2)$$

where c is the speed of light, and $\vec{J}$ is the electron current operator. The infinitesimal positive number η is used to switch on the electric field adiabatically. When the first-order change in the electron density matrix is calculated,[4] the driving force on the ion from Eq. (2.1) becomes, in the limit of the dc field,[3]

$$F_\alpha = ZeE_\alpha + \lim_{\omega\to 0}\,[\chi_{\alpha\beta}(\omega+i\eta)/i\omega]E_\beta \,, \qquad (2.3)$$

where the summation over the Cartesian index β is understood, and $\chi_{\alpha\beta}$ is the force-current response function,

$$\chi_{\alpha\beta}(\omega+i\eta) = \int_0^\infty dt\, e^{i(\omega+i\eta)t}\, i\langle[-\partial V(t)/\partial R_\alpha, J_\beta(0)]\rangle \,, \qquad (2.4)$$

with the time dependence of the dynamical variables

$-\partial V/\partial R_\alpha$ and J_β given in the Heisenberg representation,[7] and the ensemble average taken over the equilibrium electronic state without the electric field. Equations (2.3) and (2.4), first obtained by Kumar and Sorbello,[3] form the starting point of this paper.

III. HOMOGENEOUS ELECTRON GAS

A. With dilute impurities

For simplicity, consider first the model of a metal in which the lattice of positive ions is replaced by a uniform positively charged background. There are several kinds of dilute impurities randomly distributed in the system with concentration n_j and valence Z_j. For the moment, neglect the electron-electron and electron-phonon interactions. A particular impurity at $\vec{R}$ of the $j=1$ kind is singled out and its driving force is calculated. It is evident that the response function (2.4) has to be averaged over the distribution of all impurities except the one under consideration.

The electron wave function is a plane wave characterized by a wave vector $\vec{k}$. If c_k and $c_k^\dagger$ denote the annihilation and creation operators of the electron in the plane-wave state $\vec{k}$, then the current operator is

$$J_\alpha = -(e/m)\sum_k k_\alpha c_k^\dagger c_k \ , \tag{3.1}$$

where m is the electron mass and the electron-spin states are understood. The potential of the impurity is

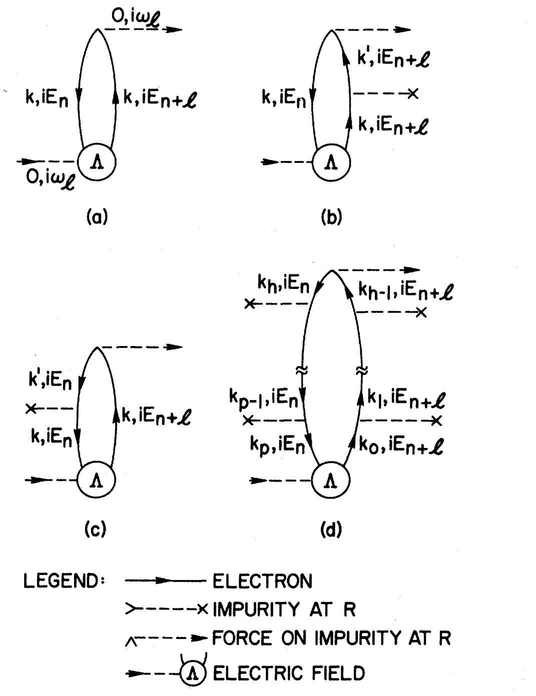

FIG. 1. Contributions to the force-current response function.

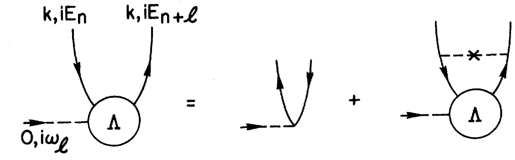

FIG. 2. Integral equation for the current vertex. ---×--- denotes average over all impurity distribution except the one at $\vec{R}$.

$$V(\vec{R}) = \sum_q v_1(\vec{q})\, e^{-i\vec{q}\cdot\vec{R}}\, n(-\vec{q}) \ , \tag{3.2}$$

where $v_1(\vec{q})$ is the Fourier transform of the impurity potential of the first kind, and

$$n(-\vec{q}) = \Omega^{-1}\sum_k c_{k+q}^\dagger c_k \tag{3.3}$$

is the Fourier transform of the electron density operator in the crystal of volume Ω. The force operator on the impurity is, therefore,

$$-\partial V/\partial R_\alpha = \sum_q i q_\alpha v_1(\vec{q})\, e^{-i\vec{q}\cdot\vec{R}}\, n(-\vec{q}) \ . \tag{3.4}$$

We evaluate the response function (2.4) in powers of the potential of the impurity under consideration. The first-, second-, and pth-order terms are given in Fig. 1. In this manner, the dependence on the potential $V(\vec{R})$ of this particular impurity ion is explicitly shown. The parts of the diagrams without this impurity line are understood to contain the effect of all other impurities except this one. Consider the electron Green's function. Since it is averaged over the random distribution of all impurities except one, it regains the full translation symmetry of the system,

$$G(k, iE_n) = 1/(iE_n - \mathcal{E}_k + i\sigma_n/2\tau') \ , \tag{3.5}$$

where $E_n = (2n+1)\pi T$, n being an integer, T being the temperature in energy units. $\sigma_n = \mathrm{sgn} E_n$, $\hbar = 1$. $\mathcal{E}_k$ is the electron energy measured from the Fermi level and τ' is the lifetime of the electron due to impurity scattering,

$$1/\tau' = \sum_j 1/\tau'_j \ , \tag{3.6a}$$

with

$$1/\tau'_j = n_j m \int \frac{dS_{k'}}{(2\pi)^2 k'} \left| T_j(k, k'; -i0)\right|^2 \ , \tag{3.6b}$$

where $\vec{k}$ and $\vec{k}'$ are on the Fermi surface, and $\int dS_{k'}$ is an integration over the Fermi surface. T_j is the T matrix of the electron scattering against an impurity of the jth kind.

The current vertex denoted by Λ in Fig. 1 contains the vertex correction expressed as an integral equation in Fig. 2. Again, it contains the effects of all impurities except the one under consideration averaged over their distributions. The solution for the vertex[7,8,13] is of the form $(-e/m)k_\alpha \times\Lambda(iE_n,iE_{n+l})$, with

$$\Lambda(iE_n,iE_{n+l})=\frac{i\omega_l+i(\sigma_{n+l}-\sigma_n)/2\tau'}{i\omega_l+i(\sigma_{n+l}-\sigma_n)/2\tau}\ , \tag{3.7}$$

where $\omega_l=2l\pi T$ and τ is the transport lifetime, given by a similar sum as Eq. (3.6a) with

$$1/\tau_j=mn_j\int\frac{dS_{k'}}{(2\pi)^2k'}\,|T_j(k,k',-i0)|^2(1-\hat{k}\cdot\hat{k}')\ , \tag{3.8}$$

where $\hat{k}$ and $\hat{k}'$ denote unit vectors. The vertex corrections around the impurity potential at $\vec{\mathrm{R}}$ are negligible for low-concentration impurities.

The first-order term for the response function, depicted by Fig. 1(a), vanishes in the uniform electric field case since it selects out the zero-momentum transfer ($q=0$) component of the force $-\partial V/\partial R_\alpha$ which vanishes by Eq. (3.4). The second-order term has two contributions given by Figs. 1(b) and 1(c); thus

$$\begin{aligned}\chi^{(2)}_{\alpha\beta}(i\omega_l)=(2e/m)T\Omega^{-2}\sum_{nkk'}&i(\vec{\mathrm{k}}'-\vec{\mathrm{k}})_\alpha\\ &\times|v_1(k'-k)|^2k_\beta[G(k',iE_n)-G(k',iE_{n+l})]\\ &\times G(k,iE_n)G(k,iE_{n+l})\Lambda(iE_n,iE_{n+l}). \end{aligned}\tag{3.9}$$

The frequency sum over n is considered in detail in the Appendix. After analytically continuing $i\omega_l$ to $\omega+i\eta$ and taking the zero-temperature and low-frequency limit, we obtain, by Eq. (A4),

$$\begin{aligned}\chi_{\alpha\beta}(\omega+i\eta)=-\delta_{\alpha\beta}\left(\frac{2e\omega}{3m}\right)\Omega^{-2}\sum_{kk'}&i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\cdot\vec{\mathrm{k}}|v_1(\vec{\mathrm{k}}-\vec{\mathrm{k}}')|^2\\ &\times\left(\int_{-\infty}^{\infty}\frac{dx}{2\pi}\mathrm{sgn}(x)\,\mathrm{Im}[G(k',x+i0)^2G(k,x+i0)^2]\right.\\ &\left.+\frac{2\tau}{\pi}[\mathrm{Im}G(k',i0)][\mathrm{Im}G(k,i0)]\right)\ ,\end{aligned}\tag{3.10}$$

where Im stands for the imaginary part of. Both terms on the right-hand side can be evaluated. The first term, involving the integral over x, is of the order $1/\tau\mathcal{E}_F$, where $\mathcal{E}_F$ is the Fermi energy and is thus negligible. The second term yields

$$\chi_{\alpha\beta}(\omega+i0)=-\delta_{\alpha\beta}i\omega env_F\tau S_1\ , \tag{3.11}$$

where $v_F=k_F/m$ is the Fermi speed, n is the total conduction-electron density, and S_1 is the "transport" scattering cross section of the impurity in the Born approximation,

$$S_1=\frac{1}{(2\pi v_F)^2}\int dS_{k'}\,|v_1(k'-k)|^2(1-\hat{k}\cdot\hat{k}'),\tag{3.12}$$

with both $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$ on the Fermi surface. This is equivalent to the results obtained by Kumar and Sorbello[3] and by Schaich,[6] using a different method for evaluating the response function to second order in the impurity potential.

It is possible to evaluate all higher-order terms. The pth-order term, typified by Fig. 1(d), contains p terms with different number of impurity lines on each side of the current and force vertices. With $k_p=k_0$, we have

$$\begin{aligned}\chi^{(0)}_{\alpha\beta}(i\omega_l)=\frac{2e}{m}iT\sum_n\Omega^{-p}&\sum_{k_1\cdots k_p}\left(\prod_{h=1}^{p}v_1(k_h-k_{h-1})\right)\\ &\times k_{0\beta}\sum_{h=1}^{p}[(k_h-k_{h-1})_\alpha G(k_0,iE_{n+l})\cdots G(k_{h-1},iE_{n+l})G(k_h,iE_n)\cdots G(k_p,iE_n)\Lambda(iE_n,iE_{n+l})]\ .\end{aligned}\tag{3.13}$$

The frequency sum over n is evaluated by Eq. (A4) for $T=0$ and small ω. The first term, involving an integral over x, is negligible when $1/\tau\ll\mathcal{E}_F$, and the second term yields

$$\begin{aligned}\chi^{(p)}_{\alpha\beta}(\omega+i0)&=\delta_{\alpha\beta}(e\omega\tau/3m\pi\tau')\Omega^{-p}\sum_{k_1\cdots k_p}\left(\prod_{h=1}^{p}v_1(k_h-k_{h-1})\right)\\ &\quad\times\vec{\mathrm{k}}_0\cdot\sum_{h=1}^{p}[(\vec{\mathrm{k}}_h-\vec{\mathrm{k}}_{h-1})G(k_0,i0)\cdots G(k_{h-1},i0)G(k_h,-i0)\cdots G(k_p,-i0)]\\ &=i\omega ne\tau\delta_{\alpha\beta}\times2\int\frac{d^3k'}{(2\pi)^3}\sum_{h=1}^{p}(1-\hat{k}\cdot\hat{k}')T_1^{(n-h)}(k,k'-i0)[\mathrm{Im}G(k',-i0)]T_1^{(h)}(k',k,i0)\ ,\end{aligned}\tag{3.14}$$

where $\vec{\mathrm{k}}$ is on the Fermi surface and $T_1^{(h)}$ is the hth-order term in the impurity potential v_1 of the T matrix given by

$$T_1(k,k';iE_n)=v_1(k-k')+\int\frac{d^3k''}{(2\pi)^3}\times v_1(k-k'')G(k'',iE_n)T_1(k'',k';iE_n)\ .\tag{3.15}$$

Summing over all orders in the impurity potential, we obtain the same expression as in Eq. (3.11), except that the scattering cross section of the impurity whose driving force is being calculated is given by

$$S_1=(2\pi v_F)^{-2}\int dS_{k'}(1-\hat{k}\cdot\hat{k}')\,|T_1(k,k';-i0)|^2\,, \quad (3.16)$$

with both $\vec{k}$ and $\vec{k}'$ on the Fermi surface. Substituting Eq. (3.11) into Eq. (2.3), we obtain the driving force

$$F_\alpha=(Z-nv_F\tau S_1)eE_\alpha\;. \quad (3.17)$$

This is the result of Fiks[9] and of Huntington and Grone.[10]

B. Modification due to electron-electron and electron-phonon interaction

The inclusion of the electron-electron Coulomb interaction is done in the same way as Langer.[8] Modification of the diagrams for the force-current response function results in corresponding modification of the formula for the scattering cross section, Eq. (3.16). For example, three types of modification of the response function are illustrated in Fig. 3(a), and the corresponding modification in the T matrix is shown in Fig. 3(c): (i) screening of the impurity potential such that $v(q)$ is replaced by $v(q)/\epsilon(q,0)$, where $\epsilon(q,0)$ is the static dielectric function of the electron gas; (ii) vertex correction of the impurity potential; and (iii) dressing of the electron propagator which results in a factor of wave-function renormalization[8] on the right-hand side of Eq. (3.16). The effect of the impurity at $\vec{R}$ on the dielectric screening, as illustrated by Fig. 3(b), should also be included in the T matrix as shown in Fig. 3(d). We shall return to discuss the physical significance of these types of processes in Sec. III D.

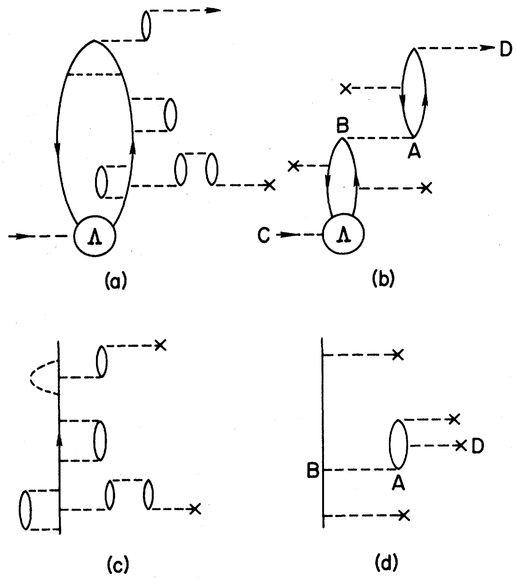

FIG. 3. Electron-electron interaction, denoted by dashed lines, modifying the force-current response function.

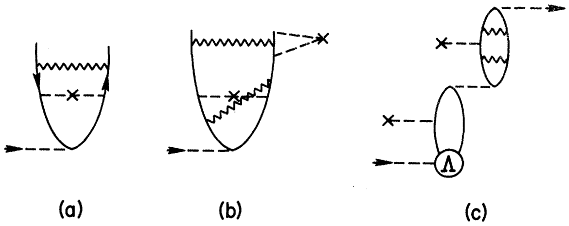

FIG. 4. Electron-phonon dressing of the response function. The wavy lines denote phonons.

The modification due to the electron-phonon interaction is formally the same as that due to the electron-electron interaction in the sense that in the diagrams considered above, we simply have to replace the Coulomb line by a phonon propagator. The scattering cross section S_1 has to include the electron-phonon modification as discussed above. Furthermore, the electron-phonon interaction contributes to the electron-transport lifetime. At the high temperature where ion diffusion is important, (usually much higher than the Debye temperature), the electron-phonon scattering in transport can be treated in the elastic approximation[14,15] resulting in a transport lifetime τ_{ep}. If the interference term between the phonon-scattering and the impurity-scattering events [such as in Fig. 4(b)] are neglected, and only the processes in Fig. 4(a) are included, the reciprocal scattering times due to the different sources are additive, whence Matthiessen's rule follows. Whether this approximation is used or not, τ in Eq. (3.17) is the total relaxation time. If τ_0 represents the relaxation time without the impurities of type 1, we have

$$\tau^{-1}-\tau_0^{-1}=n_1v_FS_1\;, \quad (3.18)$$

provided that S_1 represents the scattering cross section by an impurity of type 1, including the interference effects of phonons and other impurity scatterings.

C. Screening of the direct electrical force on the ion

Since the electric field is uniform ($q=0$), there is no electronic screening of the field and the direct force $Ze\vec{E}$ in Eq. (2.1) is modified only through the electron-wind term (the second term) in Eq. (3.17). Bosvieux and Friedel[11] argued that for an impurity, the direct force is completely screened by the electrons. We have shown above that this is not correct. Consider the impurity potential at $\vec{R}$ as a function of the valence Z. The electron screening which completely compensates the direct force $Ze\vec{E}$ must contribute a term to the response function $\chi_{\alpha\beta}$ of first order in Z. The first-order term, Fig. 1(a), is shown to be zero. The electron-wind term is at least $O(Z^2)$.

Let us further examine the issue of screening by treating the $q \to 0$ and $\omega \to 0$ limits of the spatial and temporal varying external electric potential $\phi(\mathrm{q}, \omega) \times e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{r}}-i\omega t}$, producing a perturbation on the electron system,

$$H' = -en(-\vec{\mathrm{q}})\phi(\vec{\mathrm{q}}, \omega)\, e^{-i\omega t+\eta t} . \tag{3.19}$$

The external electric field acting on the impurity at $\vec{\mathrm{R}}$ is

$$D_\alpha = -iq_\alpha \phi(\vec{\mathrm{q}}, \omega)\, e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{R}}} . \tag{3.20}$$

By the same reasoning as in Sec. II, the driving force on the ion is

$$F_\alpha = ZeD_\alpha + e\chi_\alpha(\vec{\mathrm{q}}, \omega + i\eta)\phi(\vec{\mathrm{q}}, \omega) , \tag{3.21}$$

where χ_α is the force-density response function, defined by Eq. (2.4) with the number density $n(-\vec{\mathrm{q}})$ in place of the current J_β.

To the first order in the impurity potential at $\vec{\mathrm{R}}$,

$$\chi_\alpha^{(1)}(q, \omega) = -iq_\alpha v_1(-\vec{\mathrm{q}})\chi_{nn}(\vec{\mathrm{q}}, \omega)\, e^{i\vec{\mathrm{q}}\cdot\vec{\mathrm{R}}} , \tag{3.22}$$

where χ_{nn} is the density-response function of the electron gas averaged over the impurity distribution, related to the dielectric function by[16]

$$1 - v(q)\chi_{nn}(q, \omega) = 1/\epsilon(q, \omega) , \tag{3.23}$$

where $v(q) = 4\pi e^2/q^2$ is the Coulomb interaction between electrons. If we take the impurity potential to be $-Zv(q)$, the driving force to first order in Z is

$$F_\alpha^{(1)} = ZeD_\alpha/\epsilon(q, \omega) , \tag{3.24}$$

when Eq. (3.22) is substituted into Eq. (3.21) using Eq. (3.23).

In the uniform and static-field limit, for a metal, ϵ diverges,[16] and thus the direct force of the external field D_α on the ion is completely screened out. However, the same argument can clearly be applied to any point charge, including an electron in the metal. Thus, the external field creates no current. If we wish to maintain a current, we must have the total electric field inside a metal to be nonvanishing, i.e., taking the finite field to be

$$E_\alpha = -iq_\alpha \phi(\vec{\mathrm{q}}, \omega)\, e^{-i\vec{\mathrm{q}}\cdot\vec{\mathrm{R}}}/\epsilon(q, \omega) , \tag{3.25}$$

which yields again,

$$F_\alpha^{(1)} = ZeE_\alpha . \tag{3.26}$$

The direct force cannot be screened by the electron gas, not considering the wind effect.

D. Residual resistivity dipoles and spatial conductivity modulation[17]

Landauer[17] has pointed out two physical effects which need be considered in electromigration as well as in conductivity when both impurity and electron-phonon scatterings are present. It is interesting to see what physical processes in the field theoretic notation correspond to these effects. A typical process which corresponds to the residual resistivity dipoles[18] is depicted by Fig. 3(b). The part of the diagram from the point C to A may be regarded as a contribution to the electric field at A due to a charge distribution around the impurity at $\vec{\mathrm{R}}$ caused by the current. Alternatively, we group the diagram from D to B as a screening of the T matrix, described by Fig. 3(d).

Figure 4(c) is an example of the spatial-conductivity-modulation effect.[19] The part from C to A yields a spatially varying internal electric field around the impurity at $\vec{\mathrm{R}}$. Electron-phonon scattering in the neighborhood will be modified. We again group such terms in the T matrix. In principle, we have the means to calculate these effects. An exhaustive evaluation of such terms is, however, beyond the scope of this paper.

E. Conservation of momentum

For impurities in a homogeneous electron gas, there is a momentum-conservation argument for obtaining the driving force in terms of the resistivities due to Das and Peierls[20] and due to Landauer.[21] We reproduce a simple version of the argument here in order to show that the result is consistent with the microscopic derivation in the previous sections.

Consider a pure homogeneous electron gas with density n_0 including the effects of electron-electron and electron-phonon interaction. A concentration n_1 of randomly distributed impurities of valence Z is added, contributing an additional density $n_1 Z$ to the conduction electrons. The total density of the electrons is

$$n = n_0 + n_1 Z . \tag{3.27}$$

The rate of the momentum given to the electrons by the electric field is $-neE$. The rate of momentum given to the electrons by the phonons is $-P/\tau_{ep}$, where P is the total electron momentum and τ_{ep} is the relaxation time due to the electron-phonon scatterings. In the steady state with a current E/ρ, ρ being the resistivity of the system including the impurities,

$$P = -mE/e\rho . \tag{3.28}$$

The sum of the rates of momentum given to the electrons by the electric field and by the phonons must be equal to the rate of momentum given by the electrons to the impurities, since in the steady state the total rate of the electron-momentum change must be zero. The average force on an impurity due to the electrons is, therefore,

$$(-neE - P/\tau_{ep})/n_1 = -(n - n_0\rho_0/\rho)eE/n_1 , \tag{3.29}$$

where $\rho_0 = m/n_0 e^2 \tau_{ep}$ is the resistivity of the pure system. Thus, the total force on the impurity is

$$F = ZeE - (n - n_0\rho_0/\rho)eE/n_1$$
$$= -eEn_0(\rho - \rho_0)/n_1\rho \ , \qquad (3.30)$$

when Eq. (3.27) is used for the total density n.

Equation (3.30) is consistent with the microscopic result Eq. (3.17) if Eq. (3.18) is used to give

$$n\rho - n_0\rho_0 = n_1 v_F S_1 m/e^2 \ . \qquad (3.31)$$

Huntington's expression[1,10] for the homogeneous gas case is

$$F = (Z - n\rho_d/n_1\rho)eE \ , \qquad (3.32)$$

which is consistent with Eq. (3.30) only if we take the defect resistivity ρ_d to mean

$$\rho_d = n_1 v_F S_1 m/ne^2 \ , \qquad (3.33)$$

which is not really the difference between the total resistivity of the pure system, $\rho - \rho_0$.

F. Use of the Boltzmann equation

From Eqs. (2.1) and (3.4), it is clear that we need the expectation value of the electron-density component $\langle n(\vec{q})\rangle$ to the first order in the electric field, not averaged over the position of the impurity ion whose driving force is being considered. Das and Peierls[22] used the Boltzmann equation to solve for the electron-density distribution in the presence of the electric field and the defect potential at $\vec{R}$ simultaneously. As was pointed out by these authors, the method treats the impurity potential in the semiclassical approximation, i.e., only the small momentum transfer of the impurity potential $v_1(q)$ is included. The method is not valid for the impurity potential which varies on the microscopic scale.

Nevertheless, the Boltzmann equation can be used for the current vertex part Λ in Fig. 1. The Bethe-Salpeter equation in Fig. 2, which may now include the electron-phonon scattering, can be shown to reduce to a Boltzmann equation or a Landau-Boltzmann equation[23,24] if one wishes to include the Fermi-liquid effect.[16] The linearized Boltzmann equation includes the effect of the impurities averaged over their distribution, and the impurity potential at $\vec{R}$ is not singled out as in Das and Peierls' treatment. Solution of the Boltzmann equation yields the deviation of the electron-distribution function $\delta f(k)$ from equilibrium. Then by the arguments in Sec. III A, the electron contribution to the driving force on an ion at $\vec{R}$ is

$$\lim_{\omega\to 0} \chi_{\alpha\beta}(\omega + i0)E_\beta/i\omega$$
$$= 4\int \frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3}(\vec{k}' - \vec{k})_\alpha \,|T_1(k, k', -i0)|^2$$
$$\times[\mathrm{Im}G(k', i0)]\delta f(k) \ . \qquad (3.34)$$

While $\delta f(k)$ contains the effect of all other impurities averaged over their distribution, the T matrix contains the effect of the impurity ion at $\vec{R}$ on its own driving force. This expression is useful in that we do not have to go back to microscopic arguments to solve for $\delta f(k)$ without sacrificing the rigor of the microscopic derivation.

IV. EFFECTIVE FORCE IN A CRYSTAL

In a regular crystal lattice, the electron's wave function is a Bloch wave $\phi_{\nu k}$ for band ν and wave vector $\vec{k}$ with energy $\mathcal{E}_{\nu k}$. The force operator on the impurity ion at $\vec{R}$ is

$$-\partial V/\partial R_\alpha$$
$$= \sum_{\nu k \nu' k'} \langle \nu' k' | -\partial v_1(r - R)/\partial R_\alpha | \nu k\rangle c^\dagger_{\nu' k'} c_{\nu k} \ , \qquad (4.1)$$

where $c_{\nu k}$ is the annihilation operator for the Bloch state νk and $\langle \nu' k' | A | \nu k\rangle$ denotes the matrix element

$$\langle \nu' k' | A | \nu k\rangle = \int d^3r \, \phi^*_{\nu' k'}(\vec{r}) A(\vec{r}) \phi_{\nu k}(\vec{r}) \ . \qquad (4.2)$$

Alternatively,

$$-\partial V/\partial R_\alpha = \Omega^{-1} \sum_{\nu k \nu' k' G} i(\vec{k}' - \vec{k} + G)_\alpha$$
$$\times v_1(\vec{k}' - \vec{k} + \vec{G})\, e^{-i(\vec{k}' - \vec{k} + \vec{G})\cdot\vec{R}}$$
$$\times\langle \nu' k' | e^{i(\vec{k}' - \vec{k} + \vec{G})\cdot\vec{r}} | \nu k\rangle c^\dagger_{\nu' k'} c_{\nu k} \ . \qquad (4.3)$$

When an electron is scattered by the impurity from the state νk to $\nu' k'$, the momentum transfer to the impurity is a weighted sum of all crystal-momentum changes $\vec{k}' - \vec{k} + \vec{G}$ for all reciprocal-lattice vectors $\vec{G}$. The current density operator is

$$J_\alpha = (-e/m) \sum_{\nu\nu' k} \langle \nu' k | p_\alpha | \nu k\rangle c^\dagger_{\nu' k} c_{\nu k} \ , \qquad (4.4)$$

where p_α is the electron momentum, and[25]

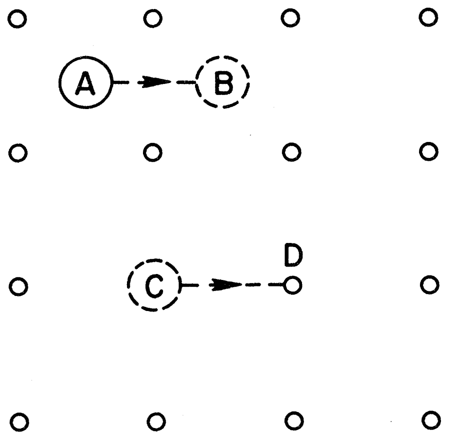

FIG. 5. Diffusion paths in a crystal: *AB* for an interstitial and *CD* for a vacancy.

$$m^{-1}\langle\nu k|p_\alpha|\nu k\rangle = \partial\mathcal{E}_{\nu k}/\partial k_\alpha = v_\alpha(\nu k)\ , \tag{4.5}$$

the velocity of the Bloch electron.

The driving force on the impurity ion given by Eqs. (2.3) and (2.4) is a function of the ion position $\vec{\mathrm{R}}$. The effective force for the ion diffusion is an average over the migration path.[10] To be specific, we may consider the average over the path *AB* in Fig. 5 for the interstatial impurity or the path *CD* for the vacancy along a principal crystal axis. We are neglecting the important effect of crystal-lattice relaxation around the defect which affects its potential.

Evaluation of the force-current response function in the crystal follows the same lines as in Sec. III A. The term of first order in the impurity potential is shown in Fig. 1(a). The impurity position dependence is in the factor $\langle\nu k| - \partial v_1(r-R)/\partial R_\alpha|\nu' k\rangle$ whose path average is

$$\begin{aligned} L^{-1}\int dR_\alpha\langle\nu k| &- \partial v_1(r-R)/\partial R_\alpha|\nu' k\rangle \\ &= L^{-1}\int dR_\alpha \sum_G \langle\nu k|e^{i\vec{\mathrm{G}}\cdot\vec{\mathrm{r}}}|\nu' k\rangle e^{-i\vec{\mathrm{G}}\cdot\vec{\mathrm{R}}}\, iG_\alpha v_1(G)\Omega^{-1} \\ &= 0\ , \end{aligned} \tag{4.6}$$

where L is the path length.

The term of second order in the impurity potential at $\vec{\mathrm{R}}$ is given by Figs. 1(b) and 1(c). The path average of the $\vec{\mathrm{R}}$ dependent factors in Fig. 1(b) is given by

$$\begin{aligned} P_\alpha(0k,\nu'k') &= \Omega^2 L^{-1}\int dR_\alpha\langle 0k|i\partial v_1/\partial R_\alpha|\nu'k'\rangle\langle\nu'k'|v_1|0k\rangle \\ &= \sum_{GG'}\langle 0k|e^{i(\vec{\mathrm{k}}-\vec{\mathrm{k}}'+\vec{\mathrm{G}})\cdot\vec{\mathrm{r}}}|\nu'k'\rangle\langle\nu'k'|e^{i(\vec{\mathrm{k}}'-\vec{\mathrm{k}}-\vec{\mathrm{G}})\cdot\vec{\mathrm{r}}}|0k\rangle \\ &\qquad\times v_1(\vec{\mathrm{k}}'-\vec{\mathrm{k}}-\vec{\mathrm{G}})v_1(\vec{\mathrm{k}}-\vec{\mathrm{k}}'+\vec{\mathrm{G}}')(\vec{\mathrm{k}}-\vec{\mathrm{k}}'+\vec{\mathrm{G}}')_\alpha\delta_{G_\alpha,G'_\alpha}\, e^{i(\vec{\mathrm{G}}-\vec{\mathrm{G}}')_\perp\cdot\vec{\mathrm{R}}_\perp}\ , \end{aligned} \tag{4.7}$$

where $\nu=0$ is taken to be the conduction band and $\vec{\mathrm{R}}_\perp$, etc., are the vectors perpendicular to the diffusion path. Similarly, for the $\vec{\mathrm{R}}$ dependent factors in Fig. 1(c),

$$\begin{aligned} \Omega^2 L^{-1}\int dR_\alpha&\langle 0k|v_1|\nu'k'\rangle\langle\nu'k'|i\partial v_1/\partial R_\alpha|0k\rangle \\ &= -P_\alpha(0k,\nu'k')\ . \end{aligned} \tag{4.8}$$

Now the two diagrams can be evaluated as before, giving the average driving force,

$$\begin{aligned} F_\alpha = ZeE_\alpha - 4\sum_{\nu'}\int\frac{d^3k}{(2\pi)^3}\int\frac{d^3k'}{(2\pi)^3} \\ \times P_\alpha(0k,\nu'k')[\mathrm{Im}G(\nu'k',i0)]\delta f(0k)\ , \end{aligned} \tag{4.9}$$

where $\delta f(0k)$ is the deviation from equilibrium of the electron-distribution function obtained from solving the usual Boltzmann equation.

With the relaxation-time solution,[14]

$$\delta f(0k) = -e\tau(0k)\vec{\mathrm{v}}(0k)\cdot\vec{\mathrm{E}}\delta(\mathcal{E}_{0k})\ , \tag{4.10}$$

the driving force is

$$\begin{aligned} F_\alpha = eE_\beta\bigg(Z\delta_{\alpha\beta} - 4\pi\int\frac{dS_k}{(2\pi)^3 v(0k)} \\ \times\int\frac{dS_{k'}}{(2\pi)^3 v(0k')}P_\alpha(0k,0k')v_\beta(0k)\tau(0k)\bigg)\ , \end{aligned} \tag{4.11}$$

where $\tau(0k)$ is the relaxation time at $\vec{\mathrm{k}}$ on the Fermi surface, and $\vec{\mathrm{k}}$ and $\vec{\mathrm{k}}'$ are integrated over the Fermi surface.

Summing over the terms of all powers in the impurity potential at $\vec{\mathrm{R}}$, the driving force on that impurity is still given by Eq. (4.9) or Eq. (4.11) with, however, the path-averaged transition probability given by

$$\begin{aligned} P_\alpha(0k,0k') = \Omega^2 L^{-1}\int dR_\alpha \\ \times\langle 0k|i\partial T(-i0)/\partial R_\alpha|0k'\rangle\langle 0k'|T(i0)|0k\rangle\ . \end{aligned} \tag{4.12}$$

These formulas are similar to the one given by Fiks[12] and by Feit.[26] What Fiks calls the transition probability with momentum transfer $\vec{\mathrm{k}}-\vec{\mathrm{k}}'+\vec{\mathrm{G}}'$

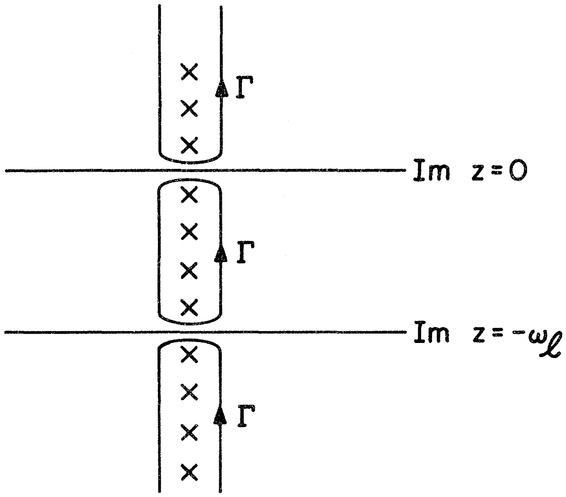

FIG. 6. Contours in the z plane for the integral in Eq. (A2). × denotes a pole of $\tanh(z/2T)$.

is given by Eq. (4.7) within the Born approximation. The T-matrix modification is rather more complicated but can be deduced from Eq. (4.12).

If the Fermi surface is a hole surface, the electron-wind force on the ion is opposite in sign to the one for an electron Fermi surface.[12] For a small Fermi surface near a band extremum, such as in a degenerate semiconductor, this result follows from Eq. (4.11). For then by the effective-mass approximation,[27]

$$\Omega\langle k|\,i\partial v_1/\partial R_\alpha\,|k'\rangle \simeq (\vec{\mathrm{k}}-\vec{\mathrm{k}}')_\alpha v_1(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\,e^{-i(\vec{\mathrm{k}}-\vec{\mathrm{k}}')\cdot\vec{\mathrm{R}}}\ . \tag{4.13}$$

For a crystal with cubic symmetry, the electron-wind term in Eq. (4.11) has the same sign as $(\vec{\mathrm{k}}'-\vec{\mathrm{k}})\cdot\vec{\mathrm{v}}(k)$ on the Fermi surface—negative for an electron surface and positive for a hole surface.

APPENDIX

In the evaluation of the Feynman diagrams for the impurity force and current response function, the electron frequency sum of the following form is frequently encountered:

$$X(i\omega_l) = T\sum_n F(iE_n, iE_{n+l})\ . \tag{A1}$$

Let $\omega_l > 0$. The sum is transferred[7] into a contour integral along Γ shown in Fig. 6,

$$X(i\omega_l) = \int_\Gamma \frac{dz}{4\pi i}\tanh\left(\frac{z}{2T}\right)F(z, z+i\omega_l)\ . \tag{A2}$$

Usually, the function F is analytic everywhere except for the cuts along the lines $\mathrm{Im}z = 0$ and $\mathrm{Im}z = -\omega_l$. The contour Γ can be deformed into lines just above and below these cuts. On continuing $i\omega_l$ into $\omega + i0$ where ω is real,

$$\begin{aligned} X(\omega+i0) = {} & \int_{-\infty}^{\infty}\frac{dx}{4\pi i}\tanh\left(\frac{x}{2T}\right)[F(x+i0, x+\omega+i0) \\ & - F(x-\omega-i0, x-i0)] + \int_{-\infty}^{\infty}\frac{dx}{4\pi i} \\ & \times\left[\tanh\left(\frac{x+\omega}{2T}\right) - \tanh\left(\frac{x}{2T}\right)\right]F(x-i0, x+\omega+i0)\ . \end{aligned} \tag{A3}$$

In the zero-temperature and low-frequency limit,

$$\begin{aligned} X(\omega+i0) = {} & \int_{-\infty}^{\infty}\frac{dx}{4\pi i}(\mathrm{sgn}x)[F(x+i0, x+\omega+i0) \\ & - F(x-\omega-i0, x-i0)] + \omega F(-i0, i0)/2\pi i\ . \end{aligned} \tag{A4}$$

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