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Strong-coupling theory for the driving force in thermomigration

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The electronic contribution to the driving force for thermomigration in metals is considered within the linear-response formalism. Kubo response functions are evaluated for impurities in an electron gas subjected to a thermal gradient. A jellium model is assumed, and the electron-impurity coupling is allowed to be arbitrarily strong. In analogy to our earlier electromigration work, we find that driving-force contributions arise from on-shell and off-shell integrals over the T matrix. The on-shell integrals yield the force expression previously obtained by Fiks and Huntington from ballistic momentum-transfer considerations. The off-shell integrals yield a new contribution to the force which does not appear in calculations based upon the weak-scattering limit or upon the ballistic model. This contribution can be significant when the electromigration direct-force valence, Z_d, is appreciably different from the bare valence Z. The resulting contribution to the heat of transport is temperature independent and is roughly on the order of $\frac{1}{2}(Z_d - Z)\varepsilon_F$, where ε_F is the Fermi energy. Numerical values on the order of an electron volt are possible for strong electron-impurity scattering.

I. INTRODUCTION

Electromigration and thermomigration continue to occupy central points of interest in transport theory.[1–18] This is due, in part, to the complicated many-body interactions that must be incorporated in order to describe adequately the driving forces for these processes. The earliest theoretical expositions concerning the driving forces exerted upon ions within a metal that is subjected to a thermal gradient were those of Fiks,[1] Huntington,[2] and Gerl.[10] These workers relied upon a Boltzmann equation for electrons in calculating the electronic contribution to the driving force for thermomigration. Another approach based upon kinetic equations has been developed by Allnatt;[11] this treatment, however, is restricted to insulators since it ignores the conduction-electron contributions. Recently, Jones[15] has used general linear response theory to provide a set of correlation functions for determining the electronic contribution to the driving force on an ion in a thermal gradient. Correlation function approaches by Cicotti *et al.* and by Gillan[14,17] have brought additional insight into methods of calculating the transport coefficients and the heat of transport. Indeed, in a series of papers,[17] Gillan has used a molecular dynamics simulation to evaluate Green-Kubo relations for the thermomigration of hydrogen in palladium, obtaining qualitative agreement with experiment.

The object of this paper is to provide a strong-coupling formalism for the electronic contribution to the driving force in thermomigration, following the Green function techniques previously utilized to describe the driving force and effective charge in electromigration.[7] This formalism has the advantage of incorporating the electron-ion potential to all orders in perturbation theory, and also provides a useful framework for both analytical and numerical computation.[7,9] Since reference will be made to our previous paper on electromigration, considerable duplication will be avoided by referring to that work as RS.[7] Several important conclusions particularly relevant to this work include the notion that when the electron-ion interaction is taken to all orders in perturbation, the driving force can be written as an expansion in $(\tau\varepsilon_F)^{-1}$, where τ is the relaxation time for electrons and ε_F is the Fermi energy. That is,

$$F = a(\tau\varepsilon_F)^1 + b(\tau\varepsilon_F)^0 + c(\tau\varepsilon_F)^{-1} + \cdots \ . \tag{1.1}$$

Similar expansions are endemic to other transport coefficients[19–22] and the problems associated with a precise evaluation of the coefficients a and b in the high-density–strong-scattering regime ($\tau\varepsilon_F \sim 1$) are well documented.[21] Nonetheless, in RS it was possible to identify and segregate important contributions to the factors a and b that heretofore had not been evaluated in the electromigration problem. It was determined that the coefficient a was essentially the electron wind term previously found by Sham[5] in his strong-coupling calculation. The important new result was that the coefficient b was a consequence of the so-called direct force. An explicit evaluation of this term gave the effects of bound states, and virtual bound states arising from the polarization of the electron gas by the screened impurity on which the driving force is acting. In addition, the two important contributions, wind and direct forces, were the results of on-the-mass-shell and off-the-mass-shell integrations over the energy-dependent T matrix, respectively. As with the aforementioned thermotransport response functions, e.g., thermopower, however, there were identified additional on-shell terms that contributed to b, so that a precise separation was found to be rigorous only in the regime of low-scattering-center density (though strong coupling).

Two quantities of interest in the thermomigration problem are related to the mass flow in a thermal gradient.[2] The ionic current in a Soret experiment is given by

$$J=\frac{Dc_i}{k_B T}F \;, \tag{1.2}$$

where D is the diffusion constant and c_i the ionic concentration. F is the driving force on the impurity ion and is given by

$$\mathbf{F}=-Q\frac{\nabla T}{T} \tag{1.3}$$

with Q the heat of transport. In this paper we are concerned with those components of the force F that arise from the electron-ion interaction, and the corresponding heat of transport Q. The electron-phonon interaction can also be incorporated to all orders in the adiabatic approximation, as suggested by Sham[5] in his T-matrix formulation. However, the ion-phonon interaction will be neglected so as to isolate the purely electronic effects on thermomigration. In this paper a similar expansion to Eq. (1.1) will be found for the driving force in thermomigration. As with the electromigration problem, the formalism will provide a formally exact expression for the driving force for arbitrary electron-ion coupling, and impurity concentration. Again, important terms not previously obtained in perturbation theory will be obtained from on-and-off-shell integrations in the strong-coupling regime. However, there is one significant difference. It will be found that at low temperatures an off-shell term of order $(\tau\varepsilon_F)^0$, including bound states and polarization of the electron gas by the impurity may be dominant.

The paper is outlined as follows. Section II will provide the strong-coupling formalism for the thermomigration driving force on a single atomic species in a jellium-model electron gas. Both the force and the heat of transport will be expressed in terms of ensemble-averaged Matsubara-Green functions.[23] Section III will provide the Boltzmann equation solution to the formulation of Sec. II, but in a strong-coupling form. In addition, it will be seen that the Boltzmann equation result is purely a consequence of the on-shell integrations over the T matrix. In Sec. IV the contributions of the off-shell terms will be formally evaluated and shown to be related to the direct force in electromigration. Section V closes the paper with a discussion of our main results.

II. STRONG-COUPLING FORMALISM

Following Fiks,[1] Huntington,[2] Gerl,[10] and others we express the driving force on the impurity in terms of the phenomenological Onsager transport coefficients.[24] However, whereas these authors (with the exception of Jones[15] and Gillan[17]) have used the Boltzmann equation to determine these coefficients, we formally extend their expression in terms of the exact quantum-mechanical correlation functions. As has been emphasized by Luttinger[24] and Jones,[15] such a procedure requires some care. The electron particle current, $\mathbf{J}_e$, and the electronic contribution to the driving force, $\mathbf{F}$, due to a thermal gradient and macroscopic electric field are given by

$$\mathbf{J}_e=L_{11}[-\beta\nabla(\mu+e\phi)]+L_{12}\nabla(\beta) \;, \tag{2.1a}$$

$$\mathbf{F}=F_{11}[-\beta\nabla(\mu+e\phi)]+F_{12}\nabla(\beta) \;, \tag{2.1b}$$

with $\beta=1/k_B T$. Here μ is the chemical potential for electrons, ϕ is the macroscopic electrostatic potential, and $e=-|e|$ is the electron charge. The Onsager coefficients are defined in terms of retarded current-current, and force-current correlation functions by[23]

$$L_{11}=\langle \mathbf{j}_e;\mathbf{j}_e\rangle \;, \tag{2.2a}$$

$$L_{12}=\langle \mathbf{j}_e;\mathbf{j}_Q\rangle \;, \tag{2.2b}$$

$$F_{11}=\left\langle\!\!\left\langle -\frac{\partial V}{\partial \mathbf{R}};\mathbf{j}_e\right\rangle\!\!\right\rangle \;, \tag{2.2c}$$

$$F_{12}=\left\langle\!\!\left\langle -\frac{\partial V}{\partial \mathbf{R}};\mathbf{j}_Q\right\rangle\!\!\right\rangle \;. \tag{2.2d}$$

$\mathbf{j}_e$ and $\mathbf{j}_Q$ represent the electron particle-current and heat-current operators, respectively, and $-\partial V/\partial\mathbf{R}$ is the electron-ion force operator. The angular brackets denoting averages for L_{11} and L_{12} designate thermal averages and configurational averages over a random distribution of impurities, whereas in Eqs. (2.2c) and (2.2d) the double brackets indicate that the configurational average for F_{11} and F_{12} is taken over all impurities *except* the one on which the force is being calculated.

In a Soret experiment,[2] the electronic current is zero so that the driving force on the atom can be written as

$$\begin{aligned}\mathbf{F}&=\beta\left[F_{11}\frac{L_{12}}{L_{11}}-F_{12}\right]\frac{\nabla T}{T}\\ &=-\left[Q_{12}-\frac{L_{12}}{L_{11}}Q_{11}\right]\frac{\nabla T}{T} \;,\end{aligned} \tag{2.3}$$

where $Q_{ij}=\beta F_{ij}$. The ratio L_{12}/L_{11} can be identified with the thermopower S by the relation $S=L_{12}/L_{11}eT$. Q_{11} is the electronic contribution to the effective valence Z^* in electromigration. These coefficients have been studied extensively;[5,7,19–22,25] however, for our purposes the formulation of Jonson and Mahan[25] is particularly useful. They have explicitly evaluated the L_{ij} coefficients taking into account the interaction between electrons and the static impurity and the electron-phonon interaction in the adiabatic approximation to all orders, thereby extending the Mott, and Wiedemann and Franz formulas to the strong-coupling domain.

The Hamiltonian for the electron-ion system is taken to be of the form

$$H=\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}c^\dagger_{\mathbf{k}}c_{\mathbf{k}}+\sum_{\mathbf{k},\mathbf{q}}U(\mathbf{q})c^\dagger_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}} \;, \tag{2.4}$$

where we formally retain the electron-phonon interaction in the effective electron-ion potential as follows:[25]

$$U(\mathbf{q})=V(\mathbf{q})\rho^{\mathrm{imp}}(\mathbf{q})+\sum_{\lambda} W_{\lambda}(\mathbf{q})Q_{\lambda}^{\mathrm{ad}}(\mathbf{q}) \ . \tag{2.5}$$

Here $V(\mathbf{q})$ is the electron interaction potential with a static impurity, $\rho^{\mathrm{imp}}(\mathbf{q})$ is the impurity density (Fourier transformed), W_{λ} is the electron-phonon interaction, and $Q_{\lambda}^{\mathrm{ad}}$ is the phonon displacement operator in the adiabatic approximation.[25] As shown by Sham,[5] the electron-phonon interaction can be formally included in the T matrix, and its presence will be implicit. Similarly, the electron-electron interaction can be included by inserting bubble diagrams (random-phase approximation) in the electron-ion interaction lines appearing in the Feynman diagrams for the correlation functions.[5,7] The net result is a screened potential for the electron-impurity interaction, so that following Sham[5] and RS one can effectively evaluate the response functions by taking V to be the screened self-consistent electron-impurity potential in Eqs. (2.2) and (2.5).

Given this Hamiltonian, the electron particle-current and heat-current operators are given, respectively, by[23]

$$\mathbf{j}_e=\frac{1}{m}\sum_{\mathbf{k}}\mathbf{k}c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}} \tag{2.6}$$

and

$$\mathbf{j}_Q=\frac{1}{m}\sum_{\mathbf{k}}\mathbf{k}\xi_{\mathbf{k}}c_{\mathbf{k}}^{\dagger}c_{\mathbf{k}}+\frac{1}{m}\sum_{\mathbf{k},\mathbf{q}}c_{\mathbf{k}+\mathbf{q}}^{\dagger}c_{\mathbf{k}}(\mathbf{k}+\tfrac{1}{2}\mathbf{q})U(\mathbf{q}) \ , \tag{2.7}$$

with $\xi_{\mathbf{k}}=\varepsilon_{\mathbf{k}}-\varepsilon_F$ and $\varepsilon_{\mathbf{k}}=k^2/2m$. We have chosen our system to be of unit volume, and have set $\hbar=1$.

Jonson and Mahan[25] evaluated L_{11} and L_{12} obtaining the expressions

$$L_{11}=\frac{T}{e^2}\int_{-\infty}^{\infty}\left[\frac{-\partial n_F(\varepsilon)}{\partial\varepsilon}\right]\sigma(\varepsilon)d\varepsilon \ , \tag{2.8a}$$

$$L_{12}=\frac{T}{e^2}\int_{-\infty}^{\infty}\left[\frac{-\partial n_F(\varepsilon)}{\partial\varepsilon}\right]\varepsilon\sigma(\varepsilon)d\varepsilon \ , \tag{2.8b}$$

where $n_F(\varepsilon)$ is the Fermi-Dirac distribution function, with energy origin $\varepsilon=0$ chosen to be at the Fermi level, and

$$\sigma(\varepsilon)=\frac{e^2}{2\pi m}\sum_{\mathbf{k}}\mathbf{k}\cdot\left[\frac{A(\mathbf{k},\varepsilon)}{2\Delta(\mathbf{k},\varepsilon)}\mathbf{\Gamma}(\mathbf{k},\varepsilon^-,\varepsilon^+)-\mathrm{Re}\{\mathcal{G}^0(\mathbf{k},\varepsilon^-)^2[\mathbf{k}+m\nabla_{\mathbf{k}}\Sigma(\mathbf{k},\varepsilon^-)]\}\right] \ . \tag{2.9}$$

The vertex function is given to all orders in the interaction and impurity concentration by[23]

$$\begin{aligned}\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})&=\mathbf{k}\Lambda(\mathbf{k},i\omega_n,i\omega_{n+l})\\&=\mathbf{k}+\sum_{\mathbf{k}'}W_{\mathbf{k}\mathbf{k}'}(i\omega_n,i\omega_{n+l})\mathcal{G}^0(\mathbf{k},i\omega_n)\mathcal{G}^0(\mathbf{k}',i\omega_{n+l})\mathbf{\Gamma}(\mathbf{k}',i\omega_n,i\omega_{n+l}) \ ,\end{aligned} \tag{2.10}$$

with $\mathcal{G}^0(\mathbf{k},i\omega_n)$ the configurational-averaged Matsubara-Green function [see Eq. (2.20)] and $W_{\mathbf{k}\mathbf{k}'}$ the generalized scattering function.[23] The spectral density and impurity scattering lifetime are defined by

$$A(\mathbf{k},\varepsilon)=-2\,\mathrm{Im}\mathcal{G}^0(\mathbf{k},\varepsilon^+) \ , \tag{2.11}$$

$$\Delta(\mathbf{k},\varepsilon)=-\mathrm{Im}\Sigma(\mathbf{k},\varepsilon^+) \ . \tag{2.12}$$

The driving-force coefficients F_{11} and F_{12} are given by the correlation functions

$$F_{11}=\lim_{\omega\to 0}\frac{\chi^E(\omega+i\delta)}{i\omega} \ , \tag{2.13a}$$

$$F_{12}=\lim_{\omega\to 0}\frac{\chi^T(\omega+i\delta)}{i\omega} \ , \tag{2.13b}$$

with

$$\chi^{E,T}(i\omega_l)=\frac{1}{3\beta}\int_0^{\beta}d\tau\left\langle T_{\tau}\left[-\frac{\partial V}{\partial\mathbf{R}}(\tau)\cdot\mathbf{j}_{e,Q}\right]\right\rangle e^{i\omega_l\tau} \tag{2.14}$$

in which $\mathbf{j}_e$ and $\mathbf{j}_Q$ are associated with χ^E and χ^T, respectively. δ is a positive infinitesimal and T_{τ} is the Wick time-ordering operator.[23]

Recalling that[5]

$$-\frac{\partial V}{\partial\mathbf{R}}=\sum_{\mathbf{k},\mathbf{q}}i\mathbf{q}V(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}c_{\mathbf{k}+\mathbf{q}}^{\dagger}c_{\mathbf{k}} \tag{2.15}$$

and inserting Eq. (2.15) into Eq. (2.14) we obtain[7,23]

$$\chi^E(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_{n}\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}V(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}\mathbf{q}\cdot\mathbf{k}G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)G(\mathbf{k}',\mathbf{k},i\omega_{n+l}) \ , \tag{2.16}$$

where G is the unaveraged Green's function. Upon averaging over all impurities except the one on which the force is acting, we have

$$\left\langle\!\left\langle V(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}\sum_{\mathbf{k}}\mathbf{k}G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)G(\mathbf{k}',\mathbf{k},i\omega_{nl})\right\rangle\!\right\rangle=V(\mathbf{q})\sum_{\mathbf{k}}\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_{n+l})\mathcal{G}(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})\ , \tag{2.17}$$

where $\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_n)$ is the off-diagonal, averaged Green function.[23] Setting $\mathbf{q}=\mathbf{k}''-\mathbf{k}'$ yields

$$\chi^E(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_n\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}V(\mathbf{k}''-\mathbf{k}')(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})\mathcal{G}(\mathbf{k},\mathbf{k}'',i\omega_n)\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_{n+l})\ . \tag{2.18}$$

We note in passing that in a previous calculation on averaging we retained nonlinear scattering in an effective potential [see RS Eq. (2.11)] $V_{\text{eff}}(\mathbf{k}',\mathbf{k}'',i\omega_n,i\omega_{n+l})$ and set V_{eff} to $V(\mathbf{k}''-\mathbf{k}')$ in order to evaluate the wave-vector summations. While this formal generalization can be made here, we ignore these higher-order scattering effects at the outset. Utilizing the Dyson equations[7]

$$\mathcal{G}(\mathbf{k},\mathbf{k}',i\omega_n)=\mathcal{G}^0(\mathbf{k},i\omega_n)\delta_{\mathbf{k}\mathbf{k}'}+\mathcal{G}^0(\mathbf{k},i\omega_n)\sum_{\mathbf{q}}V(\mathbf{q})\mathcal{G}(\mathbf{k}-\mathbf{q},\mathbf{k}',i\omega_n)\ , \tag{2.19a}$$

$$\mathcal{G}(\mathbf{k}'\mathbf{k},i\omega_n)=\mathcal{G}^0(\mathbf{k},i\omega_n)\delta_{\mathbf{k}\mathbf{k}'}+\mathcal{G}^0(\mathbf{k},i\omega_n)\sum_{\mathbf{q}}V(\mathbf{q})\mathcal{G}(\mathbf{k}',\mathbf{k}+\mathbf{q},i\omega_n)\ , \tag{2.19b}$$

with

$$\mathcal{G}^0(\mathbf{k},i\omega_n)=\frac{1}{i\omega_n-\xi_{\mathbf{k}}+\Sigma(\mathbf{k},i\omega_n)} \tag{2.20}$$

the averaged single-particle interacting Green function, χ^E can be written

$$\chi^E(i\omega_n)=-\frac{2i}{3m\beta^2}\sum_n\sum_{\mathbf{k},\mathbf{k}'}\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})\cdot\mathbf{k}'(\mathcal{G}(\mathbf{k},\mathbf{k}',i\omega_n)\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_{n+l})\{i\omega_l-[\Sigma(\mathbf{k}',i\omega_{n+l})-\Sigma(\mathbf{k}',i\omega_n)]\}$$
$$+\delta_{\mathbf{k}\mathbf{k}'}[\mathcal{G}(\mathbf{k},\mathbf{k},i\omega_{n+l})-\mathcal{G}(\mathbf{k},\mathbf{k},i\omega_n)]) \tag{2.21}$$

or

$$\chi^E(i\omega_l)=-\frac{2}{3m\beta}\frac{i}{\beta}\sum_n P(i\omega_n,i\omega_{n+l})\ . \tag{2.22}$$

Defining

$$\pi(i\omega_l)=\frac{i}{\beta}\sum_n P(i\omega_n,i\omega_{n+l})\ , \tag{2.23}$$

then[25,23]

$$\lim_{\omega\to 0}\frac{\pi(\omega+i\delta)}{i\omega}=\int_{-\infty}^{\infty}\frac{d\varepsilon}{2\pi i}\left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}[P(\varepsilon^-,\varepsilon^+)-\text{Re}P(\varepsilon^+,\varepsilon^+)]-2in_F(\varepsilon)\text{Im}\left[\frac{P(\varepsilon^+,\varepsilon^++\omega)}{\omega}\right]_{\omega\to 0}\right]\ . \tag{2.24}$$

It is easily shown that the term $\text{Re}P(\varepsilon^+,\varepsilon^+)$ vanishes identically for both χ^E and χ^T so that we need

$$\lim_{\omega\to 0}\frac{\pi(\omega+i\delta)}{i\omega}=\int_{-\infty}^{\infty}\frac{d\varepsilon}{2\pi}\left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\frac{P(\varepsilon^-,\varepsilon^+)}{i}-2n_F(\varepsilon)\text{Im}\left[\frac{P(\varepsilon^+,\varepsilon^++\omega)}{\omega}\right]_{\omega\to 0}\right]\ . \tag{2.25}$$

Q_{11} is found to be[7]

$$Q_{11}=-\frac{2}{3m}\int_{-\infty}^{\infty}\frac{d\varepsilon}{\pi}f(\varepsilon)=-\Delta Z^*\ , \tag{2.26}$$

where

$$f(\varepsilon)=-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\sum_{\mathbf{k},\mathbf{k}'}\mathbf{\Gamma}(\mathbf{k},\varepsilon^-,\varepsilon^+)\cdot\mathbf{k}'[\Delta(\mathbf{k}',\varepsilon)\,|\,\mathcal{G}(\mathbf{k}',\mathbf{k},\varepsilon^+)\,|^2+\delta_{\mathbf{k}\mathbf{k}'}\text{Im}\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)]$$
$$-n_F(\varepsilon)\sum_{\mathbf{k},\mathbf{k}'}\text{Im}\left[[\mathbf{k}+m\nabla_{\mathbf{k}}\Sigma(\mathbf{k},\varepsilon^+)]\cdot\mathbf{k}'\left[\mathcal{G}(\mathbf{k},\mathbf{k}',\varepsilon^+)\mathcal{G}(\mathbf{k}',\mathbf{k},\varepsilon^+)Z^{-1}(\mathbf{k}',\varepsilon)+\delta_{\mathbf{k}\mathbf{k}'}\frac{\partial\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)}{\partial\varepsilon}\right]\right] \tag{2.27}$$

or

$$f(\varepsilon)=-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}g(\varepsilon)-n_F(\varepsilon)h(\varepsilon)\ . \tag{2.28}$$

To obtain this form we have used the Ward identity, $\mathbf{\Gamma}(\mathbf{k},\varepsilon^+,\varepsilon^+)=\mathbf{k}+m\nabla_k\Sigma(\mathbf{k},\varepsilon^+)$ and the renormalization factor $Z^{-1}(\mathbf{k},\varepsilon)=[1-\partial\Sigma(\mathbf{k},\varepsilon^+)/\partial\varepsilon]$ in the off-shell term.[23] Our ΔZ^* is the electronic contribution to the effective valence coefficient, Z^*, in electromigration previously found in RS; that is $Z^*=\Delta Z^*+Z$, where Z is the bare valence. Our result is somewhat more general than in RS in that additional terms in the $\tau\varepsilon_F$ expansion have been identified. As before, however, the force naturally separates into on-and-off-shell factors.

The calculation of Q_{12} is slightly more intricate in that additional terms from the heat-current operator appear that must be dealt with. From Eq. (2.14) we have

$$\chi^T(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_n\sum_{\mathbf{k},\mathbf{q},\mathbf{k}'}V(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}\mathbf{q}\cdot\left[\mathbf{k}\xi_k G(\mathbf{k}',\mathbf{k},i\omega_{n+l})G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)\right.$$
$$\left.+\sum_{\mathbf{q}'}U(\mathbf{q}')\left[\mathbf{k}+\frac{\mathbf{q}'}{2}\right]G(\mathbf{k}',\mathbf{k}+\mathbf{q}',i\omega_{n+l})G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)\right]\ . \tag{2.29}$$

In the last term write

$$\mathbf{S}=\sum_{\mathbf{k},\mathbf{q}'}U(\mathbf{q}')\tfrac{1}{2}(\mathbf{k}+\mathbf{k}+\mathbf{q}')G(\mathbf{k}',\mathbf{k}+\mathbf{q}',i\omega_{n+l})G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n) \tag{2.30}$$

and replace $\mathbf{k}$ by $\mathbf{k}-\mathbf{q}'$. Now substitute the analogous equations to Eqs. (2.19a) and (2.19b) but with unaveraged Green functions, i.e.,[25]

$$G(\mathbf{k},\mathbf{k}',i\omega_n)=G^0(\mathbf{k},i\omega_n)\delta_{\mathbf{k},\mathbf{k}'}+G^0(\mathbf{k},i\omega_n)\sum_{\mathbf{q}}U(\mathbf{q})G(\mathbf{k}-\mathbf{q},\mathbf{k}',i\omega_n)\ , \tag{2.31a}$$

$$G(\mathbf{k}',\mathbf{k},i\omega_n)=G^0(\mathbf{k},i\omega_n)\delta_{\mathbf{k},\mathbf{k}'}+G^0(\mathbf{k},i\omega_n)\sum_{\mathbf{q}}U(\mathbf{q})G(\mathbf{k}',\mathbf{k}+\mathbf{q},i\omega_n)\ , \tag{2.31b}$$

with

$$G^0(\mathbf{k},i\omega_n)=\frac{1}{i\omega_n-\xi_{\mathbf{k}}}\ . \tag{2.32}$$

Then $\mathbf{S}$ can be written

$$\mathbf{S}=\tfrac{1}{2}\sum_{\mathbf{k}}\mathbf{k}\{G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)G^{0^{-1}}(\mathbf{k},i\omega_n)[G(\mathbf{k}',\mathbf{k},i\omega_{n+l})-G^0(\mathbf{k},i\omega_{n+l})\delta_{\mathbf{k},\mathbf{k}'}]$$
$$+G(\mathbf{k}',\mathbf{k},i\omega_{n+l})G^{0^{-1}}(\mathbf{k},i\omega_n)[G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)-G^0(\mathbf{k},i\omega_n)\delta_{\mathbf{k},\mathbf{k}'+\mathbf{q}}]\}\ .$$

Giving for χ^T

$$\chi^T(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_n\left[\sum_{\mathbf{k},\mathbf{k}',\mathbf{q}}V(\mathbf{q})e^{-i\mathbf{q}\cdot\mathbf{R}}\left[\frac{\mathbf{k}\cdot\mathbf{q}}{2}\right][(i\omega_n+i\omega_{n+l})G(\mathbf{k},\mathbf{k}'+\mathbf{q},i\omega_n)G(\mathbf{k}',\mathbf{k},i\omega_{n+l})\right.$$
$$\left.-\delta_{\mathbf{k}\mathbf{k}'}(G(\mathbf{k},\mathbf{k}+\mathbf{q},i\omega_n)+G(\mathbf{k}-\mathbf{q},\mathbf{k},i\omega_{n+l}))]\right]\ . \tag{2.33}$$

Performing the ensemble averages as above we have

$$\chi^T(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_n\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}\tfrac{1}{2}\{V(\mathbf{k}''-\mathbf{k}')(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})(i\omega_n+i\omega_{n+l})\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_{n+l})\mathcal{G}(\mathbf{k},\mathbf{k}'',i\omega_n)$$
$$-[(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{k}\delta_{\mathbf{k}\mathbf{k}'}(V(\mathbf{k}''-\mathbf{k}')\mathcal{G}(\mathbf{k},\mathbf{k}'',i\omega_n)-V(\mathbf{k}'-\mathbf{k}'')\mathcal{G}(\mathbf{k}'',\mathbf{k},i\omega_{n+l}))]\}\ . \tag{2.34}$$

The Matsubara sum now will be evaluated. It can be shown after some algebraic manipulations that the final term multiplying the Kronecker delta vanishes identically so we are left with

$$\chi^T(i\omega_l)=-\frac{2i}{3m\beta^2}\sum_n\sum_{\mathbf{k},\mathbf{k}',\mathbf{k}''}[V(\mathbf{k}''-\mathbf{k}')\tfrac{1}{2}(i\omega_n+i\omega_{n+l})(\mathbf{k}''-\mathbf{k}')\cdot\mathbf{\Gamma}(\mathbf{k},i\omega_n,i\omega_{n+l})\mathcal{G}(\mathbf{k}',\mathbf{k},i\omega_{n+l})\mathcal{G}(\mathbf{k},\mathbf{k}'',i\omega_n)]\ . \tag{2.35}$$

Using Eq. (2.25) we write

$$Q_{12}=-\frac{2}{3m}\int_{-\infty}^{\infty}\frac{d\varepsilon}{\pi}\varepsilon f(\varepsilon)\ . \tag{2.36}$$

Combining Eqs. (2.3), (2.26), and (2.36) we obtain the force expression

$$\mathbf{F}=Q_{11}\left[\frac{\int_{-\infty}^{\infty}\left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\right]\varepsilon\sigma(\varepsilon)d\varepsilon}{\int_{-\infty}^{\infty}\left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\right]\sigma(\varepsilon)d\varepsilon}-\frac{\int_{-\infty}^{\infty}\varepsilon f(\varepsilon)d\varepsilon}{\int_{-\infty}^{\infty}f(\varepsilon)d\varepsilon}\right]\frac{\nabla T}{T}\ , \tag{2.37}$$

which exhibits a structural similarity to the Mott formula for the thermopower [see Ref. 25, Eq. (1)]. This expression will prove particularly useful in the next section, in which the Boltzmann equation result will be reproduced.

III. REDUCTION TO BOLTZMANN EQUATION RESULT

As previously mentioned, most calculations[1,2,10–12,18] to date have provided a Boltzmann equation solution for the driving force, albeit in a weak scattering, perturbation formulation. It is our desire here to derive a strong-coupling Boltzmann approximation and, in addition, demonstrate those factors due to the electron-ion interaction neglected in such a description. We will find that the Boltzmann equation is reproduced in the low-density, strong-coupling regime, neglecting all off-shell contributions to the force correlation functions.

Recognizing that the low-density limit implies $n_i\rightarrow 0$, we obtain the following approximations[23]

$$W_{\mathbf{kk}'}(i\omega_n,i\omega_{n+l})\sim n_i T(\mathbf{k},\mathbf{k}',i\omega_n)T(\mathbf{k}',\mathbf{k},i\omega_{n+l})\ , \tag{3.1}$$

$$\begin{aligned}\mathcal{G}(\mathbf{k},\mathbf{k}',\varepsilon^+)&\sim\mathcal{G}^0(\mathbf{k},\varepsilon^+)\delta_{\mathbf{k},\mathbf{k}'}\\&\quad+\mathcal{G}^0(\mathbf{k},\varepsilon^+)T(\mathbf{k},\mathbf{k}',\varepsilon^+)\mathcal{G}^0(\mathbf{k}',\varepsilon^+)\ ,\end{aligned} \tag{3.2}$$

$$\begin{aligned}A(\mathbf{k},\varepsilon)&\sim 2\pi\delta[\varepsilon-\xi_k+\mathrm{Re}\Sigma(\mathbf{k},\varepsilon^+)]\\&\approx 2\pi\delta(\varepsilon-\xi_k)+O((\tau\varepsilon_F)^{-1})\ ,\end{aligned} \tag{3.3}$$

and

$$\mathcal{G}^0(\mathbf{k},\varepsilon)\rightarrow G^0(\mathbf{k},\varepsilon^+)\ .$$

Identify

$$\frac{\boldsymbol{\Gamma}(\mathbf{k},\varepsilon^-,\varepsilon^+)}{\Delta(\mathbf{k},\varepsilon)}=\frac{\mathbf{k}\Lambda(\mathbf{k},\varepsilon^-,\varepsilon^+)}{\Delta(\mathbf{k},\varepsilon)} \tag{3.4}$$

and define the transport lifetime by[26]

$$\tau_T(\mathbf{k},\varepsilon)=\frac{\Lambda(\mathbf{k},\varepsilon^-,\varepsilon^+)}{\Delta(\mathbf{k},\varepsilon)}\ . \tag{3.5}$$

Observing that terms such as

$$\mathrm{Re}[\mathcal{G}^{0^2}(\mathbf{k},\varepsilon^+)(\mathbf{k}+m\nabla_{\mathbf{k}}\Sigma(\mathbf{k},\varepsilon^+)]$$

are higher order in $(\tau\varepsilon_F)^{-1}$, we may write

$$\begin{aligned}\sigma(\varepsilon)&=\frac{e^2}{2\pi m}\sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}A(\mathbf{k},\varepsilon)\frac{\tau_T(\mathbf{k},\varepsilon)}{2}\\&=\frac{e^2}{m}N(\varepsilon+\varepsilon_F)(\varepsilon+\varepsilon_F)\tau_T(\varepsilon+\varepsilon_F,\varepsilon)\ .\end{aligned} \tag{3.6}$$

$N(\varepsilon)$ is the electronic density of states. This expression will be used to evaluate L_{11} and L_{12}. Ignore the off-shell terms in the force correlation functions as they are of order $(\tau\varepsilon_F)^0$ and write

$$f(\varepsilon)\approx-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}g(\varepsilon)\ , \tag{3.7}$$

with

$$\begin{aligned}g(\varepsilon)=\sum_{\mathbf{k},\mathbf{k}'}\mathbf{k}'\cdot\mathbf{k}\Lambda(\mathbf{k},\varepsilon^-,\varepsilon^+)[\Delta(\mathbf{k}',\varepsilon)\,|\,\mathcal{G}(\mathbf{k}',\mathbf{k},\varepsilon^+)\,|^2\\+\delta_{\mathbf{k},\mathbf{k}'}\mathrm{Im}\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)]\ .\end{aligned} \tag{3.8}$$

Substitute Eq. (3.2) into Eq. (3.8) and use the identity[23]

$$\begin{aligned}\Delta(\mathbf{k}',\varepsilon)\,|\,\mathcal{G}^0(\mathbf{k}',\varepsilon^+)\,|^2&=-\mathrm{Im}\mathcal{G}^0(\mathbf{k}',\varepsilon^+)\\&=\tfrac{1}{2}A(\mathbf{k}',\varepsilon)\end{aligned} \tag{3.9}$$

and the generalized optical theorem

$$\mathrm{Im}T(\mathbf{k},\mathbf{k},\varepsilon^+)=-\tfrac{1}{2}\sum_{\mathbf{k}'}|\,T(\mathbf{k}',\mathbf{k},\varepsilon^+)\,|^2A(\mathbf{k}',\xi_k)\ . \tag{3.10}$$

$g(\varepsilon)$ then can be written

$$g(\varepsilon)=-\tfrac{1}{4}\sum_{\mathbf{k}}\tau_T(\mathbf{k},\varepsilon)A(\mathbf{k},\varepsilon)k^2v_{\mathbf{k}}\sigma_T(\mathbf{k},\varepsilon)\ , \tag{3.11}$$

where $v_{\mathbf{k}}=v(\varepsilon_{\mathbf{k}})$ is the magnitude of the electron velocity and σ_T is the transport (or resistive) cross section due to electron-ion scattering. The latter is given by

$$v_{\mathbf{k}}\sigma_T(\mathbf{k},\varepsilon)=\sum_{\mathbf{k}'}|\,T(\mathbf{k}',\mathbf{k},\varepsilon^+)\,|^2A(\mathbf{k}',\xi_k)(1-\hat{\mathbf{k}}\cdot\hat{\mathbf{k}}')\ . \tag{3.12}$$

As with $\sigma(\varepsilon)$ in Eq. (3.6), $g(\varepsilon)$ can be written

$$\begin{aligned}g(\varepsilon)&=-m\pi N(\varepsilon+\varepsilon_F)(\varepsilon+\varepsilon_F)\tau_T(\varepsilon+\varepsilon_F,\varepsilon)\\&\quad\times v(\varepsilon+\varepsilon_F)\sigma_T(\varepsilon+\varepsilon_F,\varepsilon)\\&=-\frac{m^2\pi}{e^2}\sigma(\varepsilon)v(\varepsilon+\varepsilon_F)\sigma_T(\varepsilon+\varepsilon_F,\varepsilon)\ .\end{aligned} \tag{3.13}$$

The following identity[25] facilitates evaluation of L_{12} and Q_{12}:

$$\int_{-\infty}^{\infty}\left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\right]\varepsilon^n\sigma(\varepsilon)d\varepsilon=\sigma(0)\delta_{n,0}+\frac{\pi^2}{6}(k_BT)^2[n(n-1)\varepsilon^{n-2}\sigma(\varepsilon)+2n\varepsilon^{n-1}\sigma'(\varepsilon)+\varepsilon^n\sigma''(\varepsilon)]_{\varepsilon=0}\ . \tag{3.14}$$

From Eq. (2.37) the driving force for thermomigration can now be written

$$\mathbf{F}=\frac{2\pi^2}{9}[N(\varepsilon_F)\varepsilon_F\tau_T(\varepsilon_F)v(\varepsilon_F)\sigma_T(\varepsilon_F)](k_BT)^2 \times\left\{\frac{d\ln\sigma(\varepsilon)}{d\varepsilon}-\frac{d\ln[\sigma(\varepsilon)v(\varepsilon+\varepsilon_F)\sigma_T(\varepsilon+\varepsilon_F,\varepsilon)]}{d\varepsilon}\right|_{\varepsilon=0}\frac{\nabla T}{T}\ . \tag{3.15}$$

This simplifies somewhat for free electrons for which $\frac{2}{3}N\varepsilon_F=n$, the electron concentration. Equation (3.15) then reduces to the form determined by Fiks,[1] Huntington,[2] and Gerl:[10]

$$\mathbf{F}=-\frac{\pi^2}{3}(k_BT)^2\tau_T(\varepsilon_F)n\frac{d}{d\varepsilon}[v(\varepsilon)\sigma_T(\varepsilon)]\bigg|_{\varepsilon=\varepsilon_F}\frac{\nabla T}{T}\ , \tag{3.16}$$

where we have redefined the energy zero to be at the bottom of the conduction band, so that the Fermi level is now at $\varepsilon=\varepsilon_F$ rather than at $\varepsilon=0$. Alternatively, defining the effective valence for the wind force in electromigration in the strong-coupling regime following Sham (Ref. 5) and RS (Ref. 7) as

$$Z^*_{\rm wind}=-Q_{11}^{\rm on}=-n\tau_T(\varepsilon_F)v(\varepsilon_F)\sigma_T(\varepsilon_F)\ , \tag{3.17}$$

we have

$$\mathbf{F}=\frac{\pi^2}{3}(k_BT)^2Z^*_{\rm wind}\frac{d\ln[v(\varepsilon)\sigma_T(\varepsilon)]}{d\varepsilon}\bigg|_{\varepsilon=\varepsilon_F}\frac{\nabla T}{T}\ . \tag{3.18}$$

Equation (3.18) represents the strong-coupling result exactly to order $(\tau\varepsilon_F)^1$. It is important to recognize the fact that this on-shell term contains the factor $(k_BT)^2$. It will be shown below that there are off-shell terms, although of order $(\tau\varepsilon_F)^0$, which do not have this factor at least in first order in the expansion Eq. (3.15). We therefore can write the force in the form

$$\mathbf{F}=-[Q'(k_BT)^2+Q_{12}^{\rm off}]\frac{\nabla T}{T}\ , \tag{3.19}$$

where Q' contains all the on-shell terms and the off-shell term from the electromigration coefficient. The second function $Q_{12}^{\rm off}$, which may superficially be considered a higher-order term, is best analyzed by examining the heat of transport, which we do in the following section.

IV. OFF-SHELL CONTRIBUTIONS TO THE HEAT OF TRANSPORT

The importance of the off-shell term is evident when one considers the heat of transport.[2,15–17] It is easily seen that the on-shell contributions to Q multiply a factor of $(k_BT)^2$, but in addition, because of the thermopower coefficients, the off-shell terms of the electromigration coefficient also multiply such a factor. As will be explicitly shown below, the off-energy shell contribution from Q_{12} is a temperature independent quantity in the degenerate and/or zero-T limit. This allows Q to be written to lowest order in T as an expansion of the form

$$Q=[a(\tau\varepsilon_F)^1+b+c(\tau\varepsilon_F)^{-1}+\cdots](k_BT)^2+Q_{12}^{\rm off}\ . \tag{4.1}$$

We now determine $Q_{12}^{\rm off}$. Previously we disregarded the following terms as being of order $(\tau\varepsilon_F)^0$:

$$Q'_{12}=\frac{2}{3\pi m}\int d\varepsilon\, n_F(\varepsilon)\varepsilon \times{\rm Im}\left[\sum_{\mathbf{k},\mathbf{k}'}\mathbf{k}\cdot\mathbf{k}'\mathcal{G}(\mathbf{k},\mathbf{k}',\varepsilon^+)\mathcal{G}(\mathbf{k}',\mathbf{k},\varepsilon^+)+\sum_{\mathbf{k}}k^2\frac{\partial}{\partial\varepsilon}\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)\right]\ . \tag{4.2}$$

Sorbello[9] has shown that the sum

$$\frac{1}{3}{\rm Im}\sum_{\mathbf{k},\mathbf{k}'}\mathbf{k}\cdot\mathbf{k}'\mathcal{G}(\mathbf{k},\mathbf{k}',\varepsilon^+)\mathcal{G}(\mathbf{k}',\mathbf{k},\varepsilon^+) =-m\sum_{\mathbf{k}}{\rm Im}\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)\ . \tag{4.3}$$

This allows Eq. (4.2) to be rewritten as

$$Q'_{12}=-\frac{2}{\pi}\int d\varepsilon\, n_F(\varepsilon)\sum_{\mathbf{k}}{\rm Im}\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) +\frac{2}{3\pi m}\int d\varepsilon\,\varepsilon n_F(\varepsilon)\sum_{\mathbf{k}}k^2{\rm Im}\frac{\partial\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+)}{\partial\varepsilon}\ . \tag{4.4}$$

A convenient formal expression will be determined below by substituting into Eq. (4.4) the following identity,

$$\frac{2}{\pi}\int d\varepsilon\, n_F(\varepsilon)\varepsilon\sum_{\mathbf{k}}{\rm Im}G^0(\mathbf{k},\varepsilon^+) =\frac{2}{3\pi m}\int d\varepsilon\, n_F(\varepsilon)\varepsilon\sum_{\mathbf{k}}k^2\frac{\partial G^0(\mathbf{k},\varepsilon^+)}{\partial\varepsilon}\ , \tag{4.5}$$

to obtain

$$Q'_{12} = -\frac{2}{\pi}\int d\varepsilon\, n_F(\varepsilon)\varepsilon \sum_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] + \frac{2}{3\pi m}\int d\varepsilon\, n_F(\varepsilon)\varepsilon \sum_{\mathbf{k}} k^2 \mathrm{Im}\frac{\partial}{\partial\varepsilon}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \; . \tag{4.6}$$

Integrating the last term by parts gives

$$\begin{aligned} Q'_{12} = &-\frac{2}{\pi}\int d\varepsilon\, \varepsilon n_F(\varepsilon) \sum_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \\ &- \frac{4}{3\pi}\int d\varepsilon\, n_F(\varepsilon) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \\ &+ \frac{4}{3\pi}\int d\varepsilon\, \varepsilon \left[-\frac{\partial n_F(\varepsilon)}{\partial\varepsilon}\right] \\ &\times \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \; . \end{aligned} \tag{4.7}$$

The last term in this expression is an additional on-shell term of order $(k_B T)^2$ that can be added to the constant b in Eq. (4.1) which is a small correction to Q^{on} so that we can take

$$Q_{12}^{\mathrm{off}} = -\frac{2}{\pi}\int d\varepsilon\, \varepsilon n_F(\varepsilon) \sum_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] - \frac{4}{3\pi}\int d\varepsilon\, n_F(\varepsilon) \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \; , \tag{4.8}$$

which does not vanish in the $T \to 0$ limit.

In Ref. 9, Eq. (12), Sorbello has demonstrated that the effective valence for the direct force, Z_d, equals the following quantity evaluated at the Fermi level:

$$Z_d(\varepsilon) = -\frac{4}{3\pi}\sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] \; . \tag{4.9}$$

Fumi's theorem[23] allows us to write for the first sum in Eq. (4.8)

$$\begin{aligned} -\frac{2}{\pi}\int_{-\infty}^{\infty} d\varepsilon\, n_F(\varepsilon)\varepsilon \sum_{\mathbf{k}} \mathrm{Im}[\mathcal{G}(\mathbf{k},\mathbf{k},\varepsilon^+) - G^0(\mathbf{k},\varepsilon^+)] &= -\frac{2}{\pi}\int_{-\infty}^{\infty} d\varepsilon\, n_F(\varepsilon - \varepsilon_F) \sum_{l} (2l+1)\delta_l(\varepsilon) \\ &= -\int_{-\infty}^{\infty} d\varepsilon\, Z(\varepsilon) n_F(\varepsilon - \varepsilon_F) \; , \end{aligned} \tag{4.10}$$

where $Z(\varepsilon)$ is the energy-dependent bare valence, which is related to the impurity scattering phase shifts $\delta_l(\varepsilon)$ by the usual Friedel sum. [We have ignored corrections of order $(k_B T/\varepsilon_F)^2$.] With these definitions, it is appropriate to write Eq. (4.8) as

$$Q_{12}^{\mathrm{off}} = \int_{-\infty}^{\infty} d\varepsilon\, n_F(\varepsilon - \varepsilon_F)[Z_d(\varepsilon) - Z(\varepsilon)] \; . \tag{4.11}$$

For all energies below the band bottom, i.e., in the bound-state energy range, one finds that $Z_d(\varepsilon) = Z(\varepsilon)$,[9] so that we are left with

$$Q_{12}^{\mathrm{off}} = \int_0^{\varepsilon_F} d\varepsilon [Z_d(\varepsilon) - Z(\varepsilon)] \; , \tag{4.12}$$

where we have replaced the Fermi-Dirac function by its zero-temperature limit, which is appropriate for a degenerate electron gas.

Our heat of transport contribution (4.12) arises entirely from the polarization of the electron gas by the impurity in the presence of a thermal gradient. It is associated with, but not equal to, the difference between the direct force and the bare valence in electromigration, since these are given by $Z_d(\varepsilon_F)$ and $Z(\varepsilon_F)$, respectively. We have performed model calculations of Q_{12}^{off} using a Koster-Slater model similar to that used by RS for the electromigration problem. We find that Q_{12}^{off} values on the order of tenths of ε_F are possible.[27]

V. DISCUSSION

We have presented a strong-coupling theory of the electronic contributions to the driving force for thermomigration based upon the model of an impurity in jellium. This driving force arises from the coupling of the electronic carriers to gradients in the electrochemical potential and in the temperature, as is clear from Eqs. (2.1b), (2.2c), and (2.2d). This force arises within the framework of the Born-Oppenheimer adiabatic approximation. Hence, it should be visualized as a steady push on slowly moving, massive ions, which assists them to surmount the potential energy maximum (equal to the activation energy) along the jump path. The result is a tendency for migration in the direction parallel to the force, leading to the current contribution given by Eq. (1.2).

In addition to the force calculated here, there is a small contribution arising from the force exerted by the electric field which is present in the Soret experiment, and which acts on the impurity ion. Thus, a term equal to $Ze\nabla\phi$ should be added to Eq. (2.1b) if one wishes to include the effects of the electric field. Generally, however, this is a small correction.[2]

To put the electronic contribution to the driving force in perspective, especially as far as making contact with experiment, we note that there are two additional contributions to thermomigration which are not treated here. One of these is the phonon contribution,[2,18,28,29] which arises from the stream of phonons that is generated by the thermal gradient and is subsequently scattered by the impurity. There is also the so-called intrinsic contribution,[2,3,18] which arises from the effects of a thermal gradient on the diffusion dynamics rather than on the electronic carriers. The intrinsic contribution is more properly regarded as a contribution to the heat of transport, Q_{int}, rather than as a driving force. Q_{int} can be numerically calculated, with great effort, from a molecular dynamics simulation.[17] In the simplest theory of interstitial diffusion, one regards Q_{int} as the activation energy.[30] In more sophisticated treatments,[2] there are corrections to this, but Q_{int} still turns out to be essentially temperature independent. Despite the presence of the phonon and intrinsic contributions to the heat of transport, there are a number of systems for which the electronic contribution is inferred to be the dominant one.[2,10,18] Furthermore, the temperature dependence of the latter should distinguish it from the temperature-independent quantity Q_{int}, or so it has been assumed prior to this work.

We have found that the electronic contribution to the thermomigration driving force has the form given in Eq. (2.37), and that it contains the usual Fiks-Huntington-Gerl (FHG) ballistic term given by Eq. (3.16) or Eq. (3.18). We have shown that the FHG term derives from on-shell contributions to the correlation functions and is valid for a dilute concentration of impurities to all orders in the electron-impurity scattering potential. This part of our work represents the first microscopic derivation of the FHG expression for the strong-coupling regime (beyond the Born approximation and the Boltzmann equation). The FHG driving force corresponds to the term of order $\tau\varepsilon_F(k_BT)^2$ in the heat of transport expression (4.1). The other terms having $(k_BT)^2$ dependence in that expression are corrections that are higher order in $(\tau\varepsilon_F)^{-1}$. The new term that we have found in the heat of transport is the temperature-independent off-shell term Q_{12}^{off} appearing in expression (4.1), and which can be put into the form given in Eq. (4.12). The Q_{12}^{off} term is formally higher order in $(\tau\varepsilon_F)^{-1}$ compared to the FHG contribution, but because of the differing temperature factors, Q_{12}^{off} may be on the order of, or larger than, the FHG contribution.

The Q_{12}^{off} term arises from the dynamic polarization effects of a thermal gradient on the electron screening cloud surrounding the impurity ion. As can be seen from Eqs. (2.1) and (2.3), the force associated with the Q_{12}^{off} term would also exist in a *Gedankenexperiment* for which the electrochemical field $-\nabla(\mu+e\phi)$ vanishes while a thermal gradient ∇T were maintained. In such an experiment there would be no appreciable electric field to complicate the discussion, and only an electron current and thermal gradient would be present. Thus, the dynamic nature of the polarization response giving rise to Q_{12}^{off} is apparent. This is also consistent with the fact that the direct force in electromigration is a dynamic polarization effect[9] and that Q_{12}^{off} is related to the direct-force valence Z_d. More precisely, Q_{12}^{off} is related to the integral of the energy-resolved direct force by Eq. (4.12). In the most naive theory, or in weak-coupling theory, Z_d equals the bare valence Z, so that one would expect no Q_{12}^{off} contribution from Eq. (4.12). In reality Z_d and Z differ,[9] and as a consequence Q_{12}^{off} may be significant. An estimate of Q_{12}^{off} based on model calculations[27] suggests that Q_{12}^{off} may be on the order of tenths of ε_F. More realistic calculations of Q_{12}^{off} can be performed using Sorbello's expression (14) in Ref. 9, which relates $Z_d(\varepsilon)$ to the diagonal elements (in coordinate space) of the Green's function for the problem of a single screened impurity in an electron gas. Such calculations await the procurement of accurate Green's functions based on realistic impurity potentials. Lacking these, we can conclude from Eq. (4.12) that a relatively large magnitude of Q_{12}^{off} is expected for systems in which the direct-force valence in electromigration, Z_d, differs appreciably from the bare valence Z. As a crude estimate, let us assume a linear energy dependence for $Z_d(\varepsilon)$ and $Z(\varepsilon)$. We then find that $Q_{12}^{\text{off}} \sim \frac{1}{2}(Z_d-Z)\varepsilon_F$, where the relevant electromigration quantities Z_d and Z are equal to $Z_d(\varepsilon_F)$ and $Z(\varepsilon_F)$, respectively.

We would encourage experimentalists to look for such a correlation between the direct force in electromigration and the temperature-independent part of the heat of transport. Unfortunately, accurate experimental determinations of Z_d have been lacking, except for recent measurements of Z_d for hydrogen in the transition metals V, Ta, and Nb.[31] The experiments on these systems reveal that there is a substantial difference between Z_d and Z only for the Nb system; however, our suggested theoretical correlation between (Z_d-Z) and the heat of transport is not reflected in the hydrogen in Nb thermomigration data.[32] This may be due to the markedly non-free-electron-like nature of Nb, thereby rendering our jellium model unreliable. Also as we have pointed out earlier, there are phonon and intrinsic contributions to Q which may mask the electronic contribution.

In any case, the existence of our new Q_{12}^{off} term means that the usual procedure of identifying the temperature-independent part of the heat of transport with Q_{int} is, in general, incorrect. We also emphasize that despite some encouraging results from molecular dynamics simulations for the nonelectronic contribution to Q,[17] one does need to consider both the FHG term and the Q_{12}^{off} term for any quantitative comparison with experiment. The Q_{12}^{off} contribution may in fact be the dominant one, especially at lower temperatures where the FHG term is diminished.

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the equals sign in Eqs. (A4) and (A8). In Eq. (A11) ∂E should read $\partial \epsilon$.

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