Screened polarization waves and the energies of simple metals: Formulation

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We investigate the effect that core polarization has on the energy of a simple metal. To do this we establish an approximate Hamiltonian based on the standard result for nearly-free-electron metals but generalized to include interactions between localized core electrons. An application of perturbation theory then leads to expressions for various contributions to the total energy and a reformulation of the one-electron Hamiltonian for use in structural applications. The fluctuating dipole interactions between the ions are dynamically screened by the valence electrons. In the crystalline context the corresponding excitations are screened polarization waves and are manifested as screened van der Waals forces between ions. The core electrons also participate in the screening of other interactions in the metal.

I. INTRODUCTION

In the structural expansion method[1] for determining the thermodynamic functions of a crystalline simple metal, the ions are considered to be immersed in a compensating system of valence electrons usually taken to be in one-electron Bloch levels. In this approach the ions themselves are regarded as inert spherically symmetric objects and the effects of their core electrons are assumed to be fully incorporated in the definitions of the single-particle electron-ion potentials (or pseudopotentials). The relaxation of the *static* (in the electronic sense) ion approximation is manifested mainly in two ways: first, there will be collective excitations of the ions. These can be expected to result in dispersion forces, the most prominent of which are the van der Waals interactions.[2-6] In metallic systems these interactions are dynamically screened by the conduction electrons[2,6]; the collective core-core excitations giving rise to such interactions are screened polarization waves, as we shall see below. Second, polarization of the ions can also lead to screening of the various static interactions between ions and electrons. We shall also see that if the ions are sufficiently tightly bound, an adiabatic principle will permit the mutual valence-electron interactions to be screened statically. The simplest physical picture of such effects is normally realized[7-10] by imagining nonpolarizable ions and interacting valence electrons to be placed in dielectric continuum with a dielectric constant ϵ_d representing all polarization effects not originating with the electron gas. In such a model, all microscopic fields will be reduced irrespective of the physical length scales of importance.

The aim of the present paper is to treat the problem of interacting dipoles and electrons in more detail.[10] We shall arrive at a model Hamil-

tonian for use in the calculation of thermodynamic and structural properties of simple metals. Because the problem we consider *a priori* lacks translational invariance we resort to approximations which account for the dominant effects. In Sec. II of the paper we write the fundamental starting Hamiltonian in terms of an unperturbed part (free electrons and independent ions) and a perturbation arising from Coulomb interactions. Following Mon *et al.*[6] we introduce a local pseudopotential to describe the interaction between itinerant valence electrons and localized core electrons. This standard procedure permits us to treat the valence-electron systems as a quasi-homogeneous system for the purpose of calculating its response in both the static and dynamic contexts. Screening of all the interactions is dealt with in Sec. III, and the energy of the screened polarization waves is reduced to pair terms between ions. The model Hamiltonian is discussed in Sec. IV.

II. THE TOTAL HAMILTONIAN

The system under consideration (a simple metal of nominal valence Z) consists of N-fixed ions,[11] positions $\{\vec{R}\}$, and NZ valence electrons, mass m, all in a volume Ω. The ions are to be regarded as compact objects on a scale of nearest-neighbor separations. They are composites of nuclei (charge $Z_A e$) and $Z_i = Z_A - Z$ *localized* core electrons with relative coordinates $\{\vec{r}_l^c(\vec{R})$, $l = 1, \ldots, Z_i\}$. We denote the positions of the valence electrons by $\{\vec{r}_i^v$, $i = 1, \ldots, NZ\}$. Implicit in this notation is an assertion of implied distinguishability by site of the core electrons on each ion and a further notion of distinguishability between core and valence electrons. As discussed in Ref. 6, the corresponding states ignore certain exchange corrections and these are assumed to be incorporated by local approximation into the relevant poten-

tials. We associate with each ion a Z_i-electron Hamiltonian $H_{\vec{R}}$ and corresponding states $\Phi_{\vec{R}}^i$:

$$H_{\vec{R}}\Phi_{\vec{R}}^i = \varepsilon^i \Phi_{\vec{R}}^i .\tag{1}$$

We then take as the unperturbed Hamiltonian for the system the quantity

$$H^{(0)} = \sum_i \frac{p_i^2}{2m} + \sum_{\vec{R}}' H_{\vec{R}} ,\tag{2}$$

where the first term in (2) is the kinetic energy of the valence-electron system. The total Hamiltonian is now written

$$H = H^{(0)} + H^{(1)} ,$$

where $H^{(1)}$ reflects all Coulomb interactions other than those already incorporated in the $\{H_{\vec{R}}\}$. We may therefore write

$$H^{(1)} = H_{ii}' + H_{iv} + H_{vv} ,\tag{3}$$

where H_{ii}' is the total interaction Hamiltonian between *different* ions, H_{vv} the mutual Coulomb interaction between valence electrons, and H_{iv} the coupling between both.

Define an operator $\rho_{\vec{R}}^i(\vec{r})$ for the ion at $\vec{R}$ by

$$\rho_{\vec{R}}^i(\vec{r}) = Z_A \delta(\vec{r} - \vec{R}) - \sum_{i=1}^{z_i} \delta(\vec{r} - \vec{R} - \vec{r}_i^c(\vec{R}))$$

or

$$\rho_{\vec{R}}^i(\vec{q}) = e^{i\vec{q}\cdot\vec{R}}\left(Z + \sum_{i=1}^{z_i}(1 - e^{-i\vec{q}\cdot\vec{r}_i^c(\vec{R})})\right).\tag{4}$$

It follows that e times this quantity gives the charge-density fluctuations about Ze (the monopole charge on the ion at $\vec{R}$). Defining $v_c(q) = 4\pi e^2/q^2$ we have

$$H_{ii}' = \frac{1}{2}\sum_{\vec{q}}' \frac{v_c(q)}{\Omega} \sum_{\vec{R},\vec{R}'} \rho_{\vec{R}}^i(\vec{q})\rho_{\vec{R}'}^i(-\vec{q}) .\tag{5}$$

Since we have assumed the ions to be compact on a scale of the lattice constant, we shall rewrite (4) as

$$e\rho_{\vec{R}}^i(\vec{q}) = e^{i\vec{q}\cdot\vec{R}}(Ze + i\vec{q}\cdot\hat{d}_{\vec{R}} + \cdots) ,\tag{6}$$

where $\hat{d}_{\vec{R}}$ is the dipole operator for the ion at $\vec{R}$. The neglect of terms beyond those displayed in (6) amounts to the dipole approximation.

Next, let

$$\rho^v(\vec{r}) = \sum_i \delta(\vec{r} - \vec{r}_i^v)$$

be the density operator for the valence electrons. Then

$$H_{vv} = \frac{1}{2}\sum_{\vec{q}} \frac{v_c(q)}{\Omega}[\rho^v(\vec{q})\rho^v(-\vec{q}) - NZ] .\tag{7}$$

Finally we write

$$H_{iv} = \sum_{\vec{q}} \frac{v_{ps}(q)}{\Omega} \sum_{\vec{R}} \rho_{\vec{R}}^i(\vec{q})\rho^v(-\vec{q})\tag{8}$$

as the coupling between valence electrons and ions. Here $v_{ps}(q)$ is a pseudopotential which is taken as local.[12] Using (6) we rewrite (8) as

$$H_{iv} = \sum_{\vec{q}} \frac{v_c(q)}{\Omega}\rho^v(-\vec{q})[\rho^i(\vec{q})f(\vec{q}) + (i/e)\bar{f}(\vec{q})\vec{q}\cdot\hat{d}_{\vec{q}}]\tag{9}$$

where

$$\hat{d}_{\vec{q}} = \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}}\hat{d}_{\vec{R}}\tag{10}$$

and

$$\rho^i(\vec{q}) = \sum_{\vec{R}} e^{i\vec{q}\cdot\vec{R}} .$$

Here $v_c(q)f(q)$ is defined as the monopole (static) part of the pseudopotential $[f(q) = -Z\cos qr_c$ for an empty-core pseudopotential]. The quantity $\bar{f}(q)v_c$ is the pseudopotential representing the coupling of valence electrons and fluctuating dipoles. As discussed in Ref. 6 an empty-core model can also describe this term though it is not necessary that the corresponding core radius be exactly equal to the corresponding static pseudopotential value.

Before proceeding to the thermodynamic limit we accumulate the $q \to 0$ limit of all the terms in $H^{(1)}$ and refer to the result[13] as NZE_0. Then in the limit $N \to \infty$, $\Omega \to \infty$, $N/\Omega = \rho^i$, we have where

$$H - NZE_0 = H^{(0)} + \frac{1}{2}\sum_{\vec{q}\neq 0} \frac{v_c(q)}{\Omega} \sum_{\vec{R},\vec{R}'}' \rho_{\vec{R}}^i(\vec{q})\rho_{\vec{R}'}^i(-\vec{q}) + \sum_{\vec{q}\neq 0} \frac{v_{ps}(q)}{\Omega}\sum_{\vec{R}} \rho_{\vec{R}}^i(\vec{q})\rho^v(-\vec{q}) + \frac{1}{2}\sum_{\vec{q}\neq 0} \frac{v_c(q)}{\Omega}\rho^v(\vec{q})\rho^v(-\vec{q})\tag{11}$$

$$= H^{(0)} + \frac{1}{2}\sum_{\vec{q}\neq 0} \frac{v_c(q)}{\Omega} \sum_{\vec{R},\vec{R}'}' e^{i\vec{q}\cdot(\vec{R}-\vec{R}')}\left(Z + \frac{i}{e}\vec{q}\cdot\hat{d}_{\vec{R}}\right)\left(Z - \frac{i}{e}\vec{q}\cdot\hat{d}_{\vec{R}'}\right)$$

$$+ \sum_{\vec{q}\neq 0} \frac{v_c(q)}{\Omega}\rho^v(-\vec{q})[\rho^i(\vec{q})f(\vec{q}) + (i/e)\bar{f}(q)\vec{q}\cdot\hat{d}_{\vec{R}}] + \cdots + \frac{1}{2}\sum_{\vec{q}\neq 0} \frac{v_c(q)}{\Omega}\rho^v(\vec{q})\rho^v(-\vec{q}) ,\tag{12}$$

which we take as a model Hamiltonian. Setting $\{\hat{d}_{\vec{R}}\} \equiv 0$ and $\{H_{\vec{R}}\} \equiv 0$ recovers the starting point of the pseudopotential approach to the energetics of simple metals. The theory of dispersion forces

(neglecting retardation effects) for insulating systems follows from (12) by taking $Z = 0$ [or $\rho^v(\vec{q}) = 0$]. In the next section we wish to combine both cases.

III. SCREENING AND PERTURBATION THEORY

As noted earlier we shall assume the system is such that the dipole approximation is valid: The ions must be sufficiently compact that even microscopic local fields do not vary appreciably over an ionic dimension. To obtain the ground-state energy of the system, we follow Rehr *et al.*[2] and apply standard many-body perturbation theory to (12). If we write

$$H = H^{(0)} + H^{(1)}(\lambda), \quad 0 \leqslant \lambda \leqslant 1$$

where

$$H^{(1)}(\lambda) = \lambda H^{(1)},$$

then

$$E = E_u + \int_0^1 \frac{d\lambda}{\lambda} \langle \Psi_\lambda | H^{(1)}(\lambda) | \Psi_\lambda \rangle$$

$$= E_u + \sum_n E^{(n)},$$

where E_u is the unperturbed energy and $E^{(n)}$ is the contribution nth order in $H^{(1)}$. It is given by

$$E^{(n)} = \left(\frac{-i}{\hbar}\right)^{n-1} \frac{1}{n!} \int_{-\infty}^{\infty} dt_1 \cdots \int_{-\infty}^{\infty} dt_{n-1} \langle \Psi_0 | T H^{(1)} H^{(1)}(t_1) \cdots H^{(1)}(t_{n-1}) | \Psi_0 \rangle_c , \tag{13}$$

where T is the time-ordering operator and c restricts the diagrammatic representation of $E^{(n)}$ only to connected diagrams. In (13) $H^{(1)}(t_j) = H'_{ii}(t_j) + H_{iv}(t_j) + H_{vv}(t_j)$; note that in the absence of H_{ii} and H_{iv} the retention of H_{vv} to all orders leads to the familiar diagrammatic expansion for the ground-state energy E_{EG} of interacting electron gas. On the other hand, if we set $\{\hat{d}_{\vec{R}}\} = 0$ but retain all the other terms, we recover the structural expansion[1] for the thermodynamic functions of simple metals. An important example is the case where H_{iv} is kept to second order, but H_{vv} is taken to all orders. We then find the linear-response result

$$E = E_{EG} + E_0 + E_M$$
$$+ \sum_{\vec{q} \neq 0} \rho^i(\vec{q}) \rho^i(-\vec{q}) \frac{4\pi Z^2 e^2}{q^2} f^2(q) \left(\frac{1}{\epsilon(q)} - 1\right), \tag{14}$$

where E_M is the Madelung Hamiltonian

$$E_M = \frac{1}{2Z\Omega} \sum_{\vec{q} \neq 0} Z^2 v_c(q) \left(\frac{1}{N} \rho^i(\vec{q}) \rho^i(-\vec{q}) - 1\right), \tag{15}$$

which includes the direct Coulomb interaction between point ions. If instead this is combined with the last term of (14) we may obtain a (linear-response) pair potential between the ions as

$$\phi_{ps}(r) = \int d\vec{q} (2\pi)^{-3} \left(\frac{4\pi Z^2 e^2}{q^2}\right) \left[1 + f^2(q)\left(\frac{1}{\epsilon(q)} - 1\right)\right] e^{i\vec{q} \cdot \vec{r}}, \tag{16}$$

where $f(q)$ reflects the presence of the (static) electron ion pseudopotential. Equation (16) (or its generalization beyond linear response) neglects contributions to ion pair energies from fluctuating dipole interactions. These are readily obtained from (13) as follows: Suppose we take $Z = 0$ (i.e., $\rho^v \equiv 0$), then to second order in H_{ii} we have

$$E^{(2)} = \frac{1}{2} \sum_{\vec{R},\vec{R}'}' \frac{1}{\Omega^2} \sum_{\vec{q},\vec{q}'} v_c(q) v_c(q') e^{i(\vec{q}-\vec{q}') \cdot (\vec{R}-\vec{R}')} \left(\frac{-i}{\hbar}\right) \int_{-\infty}^{\infty} dt \langle \Phi_{\vec{R}} | T\vec{q} \cdot \hat{d}_{\vec{R}} \vec{q}' \cdot \hat{d}_{\vec{R}'}(t) | \Phi_{\vec{R}} \rangle + \langle \Phi_{\vec{R}'} | T\vec{q} \cdot \hat{d}_{\vec{R}} \vec{q}' \cdot \hat{d}_{\vec{R}'}(t) | \Phi_{\vec{R}'} \rangle \tag{17}$$

and since the ions are spherically symmetric we may write this as

$$E^{(2)} = \frac{1}{2} \sum_{\vec{R},\vec{R}'} \left(\frac{1}{\Omega}\right)^2 \sum_{\vec{q},\vec{q}'} v_c(q) v_c(q') e^{i(\vec{q}-\vec{q}') \cdot (\vec{R}-\vec{R}')} (\vec{q} \cdot \vec{q}')^2 \left(\frac{-i}{\hbar}\right) + \int_{-\infty}^{\infty} dt \langle \Phi_{\vec{R}} | T\hat{d}_{\vec{R}} \hat{d}_{\vec{R}}(t) | \Phi_R \rangle \langle \Phi_{R'} | T\hat{d}_{\vec{R}'} \hat{d}_{\vec{R}'}(t) | \Phi_{\vec{R}'} \rangle. \tag{18}$$

Using the identity

$$\frac{1}{2} \sum_{\vec{q},\vec{q}'} W(q) W(q') e^{i(\vec{q}-\vec{q}') \cdot \vec{r}} (\vec{q} \cdot \vec{q}')^2$$

$$= \left(\frac{\partial^2 W(r)}{\partial r^2}\right)^2 + \frac{2}{r^2} \left(\frac{\partial W}{\partial r}\right)^2, \tag{19}$$

we may rewrite (18) as

$$E^{(2)} = \frac{1}{2} \sum_{\vec{R},\vec{R}'} \phi_L(\vec{R} - \vec{R}'), \tag{20}$$

where

$$\phi_L(r) = -\left[\left(\frac{\partial^2 v_c}{\partial r^2}\right)^2 + \frac{2}{r^2}\left(\frac{\partial v_c}{\partial r}\right)^2\right] \int_0^{\infty} \frac{du}{2\pi} \alpha_0^2(iu). \tag{21}$$

The quantity $\alpha_0(\omega)$ is the frequency-dependent polarizability of the isolated ion, i.e.,

$$\alpha_0(\omega) = \int_0^\infty dt\, e^{i\omega t}(i/\hbar)\langle[\hat{d}(t), \hat{d}(0)]\rangle,$$

and is a scalar. For the Coulomb interaction v_c $\sim r^{-1}$ and (21) gives the London or van der Waals interaction between ions. These dispersion forces follow from consideration of a Hamiltonian of the form

$$H_{DF} = \sum_{\vec{R}} H_{\vec{R}} + \tfrac{1}{2}\sum_{\vec{R},\vec{R}'}{}' \hat{d}_{\vec{R}}\vec{T}(\vec{R}-\vec{R}')\hat{d}_{\vec{R}'}, \qquad (22)$$

where $\vec{T}$ is the dipolar coupling

$$\vec{T}(\vec{R}) = \vec{\nabla}\vec{\nabla}\frac{1}{R} = \frac{1}{R^3}(I - 3\hat{R}\hat{R}). \qquad (23)$$

As is known[4,14-16] this Hamiltonian can be solved for crystalline symmetry; its excited states are collective excitations of all the ions in the system. For crystals, the collective states are polarization waves with frequencies $\omega_\lambda(q)$ given by solutions to

$$\det[I + \alpha_0(\omega)\vec{T}(\vec{q})] = 0. \qquad (24)$$

Here

$$\vec{T}(\vec{q}) = \sum_{\vec{R}}{}' e^{i\vec{q}\cdot\vec{R}}\vec{T}(\vec{R})$$

and for a cubic solid

$$\lim_{q\to 0}\vec{T}(\vec{q}) = 4\pi\frac{N}{\Omega}(\hat{q}\hat{q} - \tfrac{1}{3}I).$$

In terms of the determinant in (24) whose vanishing gives the mode frequencies, the ground-state energy can be written

$$E_{DF} = \frac{1}{4\pi}\sum_{\vec{q}}\int_{-\infty}^\infty du\, \log\{\det[I + \alpha_0(iu)\vec{T}(\vec{q})]\} \qquad (25)$$

as shown by Mahan.[4] A straightforward expansion of the integrand then leads to (20).

In the presence of conduction electrons (25) has a natural extension. A simple one-electron mean-field argument gives an indication of the general result to be obtained from perturbation theory. Let $\hat{\nu}_i$ be the single-particle density matrix for the system of ions. The single-particle levels are $\{|\alpha\rangle\}$ and f_α their occupancy. The system is subjected to an external field $\vec{E}_{ext}(\vec{r})$ with time dependence $e^{i\omega t}$. The corresponding potential is V_{ext}, and that of any induced electron charge is V_{ind}. If $\hat{\nu}_i^{(1)}$ is the first-order change in $\hat{\nu}_i$ then we have

$$\langle\alpha|\hat{\nu}_i^{(1)}|\beta\rangle = \frac{f_\alpha - f_\beta}{\varepsilon_{\alpha\beta} - \hbar\omega}\langle\alpha|(-e)(V_{ext} + V_{ind})|\beta\rangle, \qquad (26)$$

where $\varepsilon_{\alpha\beta} = \varepsilon_\alpha - \varepsilon_\beta$.

In the vicinity of the ion at $\vec{R}$ we have

$$V_{ind} = \vec{r}_{\vec{R}}\cdot\sum_{\vec{R}'}\vec{T}(\vec{R}-\vec{R}')\langle\hat{d}_{\vec{R}'}\rangle, \qquad (27)$$

where $\langle\hat{d}_{\vec{R}'}\rangle$ is the induced dipole moment at site $\vec{R}'$. We also require the contribution to V_{ind} from the valence electrons. The Fourier transform of this quantity is $v_c(q)\rho_{ind}(\vec{q}, \omega)$. We can obtain $\rho_{ind}(\vec{q}, \omega)$ as follows: Let $\hat{\nu}_{el}$ be the single-particle density matrix for the system of valence electrons in the absence of interactions. The levels of the system are labeled by $\vec{k}$ and the energies are $\varepsilon_{\vec{k}}$. Then

$$\rho_{ind} = \text{Tr}[\hat{\nu}_{el}^{(1)}\delta(\vec{r}_{el} - \vec{r})],$$

where $\hat{\nu}_{el}^{(1)}$ is the first-order shift in $\hat{\nu}_{el}$. From the equation corresponding to (26) we have

$$\rho_{ind}(q, \omega) = \sum_{\vec{k},\vec{k}'}\frac{f_{\vec{k}} - f_{\vec{k}'}}{\varepsilon_{\vec{k}\vec{k}'} - \hbar\omega}\frac{(-e)}{\Omega}[V_{ext}(\vec{k}' - \vec{k}, \omega)$$

$$+ V_{ind}(\vec{k}' - \vec{k}, \omega)]\delta_{\vec{q}, \vec{k}'-\vec{k}}. \qquad (28)$$

If $\epsilon_{el}(q, \omega)$ is the wave-number- and frequency-dependent dielectric function of the valence-electron system we may rewrite (28) as

$$\rho_{ind}(q, \omega) = \frac{1}{v_c(q)}[\epsilon_{el}(q, \omega) - 1]$$

$$\times [V_{ext}(q) + i\vec{p}(q, \omega)\cdot\vec{q}v_c(q)] \qquad (29)$$

and hence that

$$V_{ext}(q, \omega) + V_{ind}(q, \omega) = \frac{V_{ext}(q, \omega)}{\epsilon_{el}(q, \omega)} + \frac{i\vec{p}(q, \omega)\cdot\vec{q}v_c(q)}{\epsilon_{el}(q, \omega)}. \qquad (30)$$

Here we have defined the induced polarization $\vec{p}$ by

$$\vec{p}(q, \omega) = \sum_{\vec{R}}e^{i\vec{q}\cdot\vec{R}}\langle\hat{d}_{\vec{R}}(\omega)\rangle. \qquad (31)$$

It remains, therefore, to calculate $\langle\hat{d}_{\vec{R}}\rangle = \text{Tr}[\nu_i^{(1)}(-e r_{\vec{R}})]$. Using (26) and (31) we find after a little algebra that

$$\vec{p}(\vec{q}, \omega) = \alpha_0[I + \alpha_0(\omega)\vec{T}^{sc}(\vec{q}, \omega)]^{-1}\vec{E}^{sc}(\vec{q}, \omega). \qquad (32)$$

Here $\vec{E}^{sc}(\vec{q}, \omega)$ is just $\sum_{\vec{R}}e^{i\vec{q}\cdot\vec{R}}\vec{E}^s(\vec{r}, \omega)$, where $\vec{E}^s(\vec{r}, \omega)$ is a screened external field whose potential is $V_{ext}(\vec{q}, \omega)/\epsilon_{el}(q, \omega)$. In a similar way, the static Coulomb interaction used in the definition of $\vec{T}(\vec{R})$ or $\vec{T}(\vec{q})$ [see Eq. (23)] is also screened by $\epsilon_{el}(q, \omega)$. It is apparent from (32) that the collective excitations of the *dipolar* system are now *screened polarization waves*, and are given by the solutions to

$$\det[I + \alpha_0(\omega)\vec{T}^{sc}(\vec{q}, \omega)] = 0. \qquad (33)$$

Correspondingly, the ground-state energy of the screened polarization waves is [see (25)]

$$E_{DF}^{sc} = \sum_q \int_{-\infty}^{\infty} du \log\{\det[I + \alpha_0(iu)\overline{T}^{sc}(\vec{q}, iu)]\}$$
(34)

and the lowest-order expansion of this quantity leads again to pair potentials, in this case [see Eq. (21)]

$$\phi_L^{sc}(r) = \int_{-\infty}^{\infty} \frac{du}{2\pi} \alpha_0^2(iu)\left[\left(\frac{\partial^2 v(r, iu)}{\partial r^2}\right)^2 + \frac{2}{r^2}\left(\frac{\partial v(r, iu)}{\partial r}\right)^2\right],$$
(35)

where

$$v(r, iu) = \int \frac{d\vec{q}}{(2\pi)^3} \frac{\overline{v}_{ps}(q)}{\epsilon_{el}(q, iu)} e^{i\vec{q}\cdot\vec{r}}.$$
(36)

Here $\overline{v}_{ps}$ is taken for convenience as an empty core pseudopotential (see Ref. 6). It is important to note that (34) is only the contribution to the pair potential arising from screened fluctuating dipole interactions. The total potential requires the addition of the statically screened pseudopotential contribution. Part of this is given by (16); there is, however, a modification arising from the static screening of the ions. We return to this point in a moment.

Equation (35) can also be obtained from perturbation theory starting from (13) as shown by Rehr et al.[2] The necessary modifications to (18) are those that result from including the valence electron-dipole part of the coupling H_{iv} to finite order and H_{vv} to all orders. As discussed in Refs. 2 and

6, the four lowest-order diagrams that emerge after inserting the polarization of the electron gas are equivalent to a single diagram represented by a term with a structure identical with that of (18) but with the interaction v_c replaced by $v_c(q)/\epsilon_{el}(q, \omega)$. It then follows that lowest-order dispersion forces are the screened van der Waals interactions given by (35).

This accounts for physical processes involving collective excitations and dynamic screening. It remains to consider those interactions that are statically screened by the polarizable ions. This system constitutes an inhomogeneous dielectric for which we may define an inverse static dielectric constant $\epsilon_d^{-1}(\vec{q}, \vec{q}')$ by relating a static external scalar potential $V_{ext}(\vec{q})$ to a total potential $V(\vec{q}) = V_{ext}(\vec{q}) + V_{ind}(\vec{q})$. The defining relation is[17]

$$V(\vec{q}) = \frac{1}{\Omega} \sum_{\vec{q}'} \epsilon_d^{-1}(\vec{q}, \vec{q}') V_{ext}(-\vec{q}').$$
(37)

Then

$$\rho_{ind}(\vec{q}) = \frac{1}{\Omega} \sum_{q'} [\epsilon_d^{-1}(\vec{q}, \vec{q}') - \delta_{\vec{q},\vec{q}'}]\frac{q^2}{4\pi} V_{ext}(-\vec{q}').$$
(38)

If we have a system of point charges (the monopole part of the ions, for example)

$$V_{ext}(\vec{q}) = Zv_c(q)\rho^i(\vec{q}),$$

so that from a simple coupling-constant integration the total energy of the system in linear response is

$$\frac{1}{2}\sum_{\vec{q}} V_{ext}(\vec{q})\rho_{ind}(\vec{q}) = \frac{1}{2\Omega^2} \sum_{\vec{q}} \sum_{\vec{q}'} Z^2 v_c(q)v_c(q')\rho^i(\vec{q})\rho^i(-\vec{q}')\left(\frac{q^2}{4\pi}\epsilon_d^{-1}(\vec{q}, \vec{q}') - \delta_{\vec{q},\vec{q}'}\right).$$
(39)

For the *homogeneous* dielectric ϵ_d^{-1} is diagonal and (39) reduces to the expected

$$\frac{1}{2\Omega^2} \sum_q v_c^2(q)\rho_i(\vec{q})\rho^i(-\vec{q})\frac{q^2}{4\pi}[\epsilon_d^{-1}(q) - 1].$$
(40)

We may compare (39) with the result for $E^{(2)}$ obtained from (13) by taking the monopole-dipole interaction to second order, i.e.,

$$\frac{1}{2\Omega^2} \sum_{\vec{q}} \sum_{\vec{q}'} Z^2 v_c(q)v_c(q')\rho^i(\vec{q})\rho^i(-\vec{q}')\left(\frac{-i}{\hbar}\right) \int_{-\infty}^{\infty} dt \langle\Psi_0 | T\vec{q}\cdot\hat{d}_{-\vec{q}}\vec{q}'\cdot\hat{d}_{-\vec{q}'}(t)|\Psi_0\rangle,$$

which involves single-ion polarizabilities. Going beyond second order can only be carried out approximately. We first assume, as in (40), that the major contributions to the energy can be calculated by taking ϵ_d^{-1} to be diagonal. For long-range interactions in systems of high symmetry this approximation, though neglecting certain local-field effects, is not unreasonable. Second, dipole-dipole interactions will be included by an

appeal to the standard random-phase approximation. Then

$$\epsilon_d^{-1}(q) - 1 \cong -4\pi n\alpha_0/[1 + \alpha_0\overline{T}(\vec{q})],$$
(41)

where $\overline{T}(q)$ is a cubic average of $-\sum' e^{i\vec{q}\cdot\vec{R}}\nabla\nabla(1/R)$. In the long-wavelength limit (41) reduces to the Clausius-Mossotti result.[18]

The background dielectric, described by $\epsilon_d(q)$, leads to a modification of the Madelung Hamilton-

ian to give

$$\frac{1}{2Z\Omega}\sum_{\vec{q}\neq0}Z^2\frac{v_c(q)}{\epsilon_d(q)}\left(\frac{1}{N}\rho^i(\vec{q})\rho^i(-\vec{q})-1\right)$$

$$+\frac{1}{2Z\Omega}\sum_{\vec{q}\neq0}Z^2v_c(q)\left(\frac{1}{\epsilon_d(q)}-1\right),\qquad(42)$$

where the first term describes screened point-ion interaction and the second a one-body self-energy that can be combined with E_0. The magnitude of the Madelung energy will be reduced by the screening action of the ions.

In arriving at (42) all static interactions have been screened by $\epsilon_d(q)$. A similar principle clearly holds for the band-structure energy term [the last term of (14)]. Per electron, this becomes

$$\frac{1}{2\Omega}\sum_{\vec{q}\neq0}\rho^i(\vec{q})\rho^i(-\vec{q})\frac{4\pi Z^2e^2}{q^2}\left(\frac{f(q)}{\epsilon_d(q)}\right)^2\left(\frac{1}{\epsilon_{el}(q)}-1\right).\qquad(43)$$

The replacement of the (static) pseudopotential by

$v_{ps}(q)/\epsilon_d(q)$ evidently holds to all orders in the structural expansion so that we may replace the electron (static) ion interaction of Eq. (12) by

$$\sum_{\vec{q}\neq0}\frac{v_c(q)}{\Omega\epsilon_d(q)}\rho^i(\vec{q})\rho^v(-\vec{q})f(q).\qquad(44)$$

A similar argument can be advanced in support of the replacement of the mutual valence-electron interactions by

$$\frac{1}{2}\sum_{\vec{q}\neq0}\frac{v_c(q)}{\Omega\epsilon_d(q)}\rho^v(\vec{q})\rho^v(-\vec{q}).\qquad(45)$$

However, here it is also necessary to invoke an adiabatic approximation in comparing valence-electron and core-electron motions. The relevant physical requirement is that core-excitation energies be considerably in excess of the characteristic valence-electron energies (say ε_F). If this condition is satisfied the pseudopotential part of the Hamiltonian can now be rewritten as

$$\sum_i\frac{p_i^2}{2m}+\frac{1}{2}\sum_{\vec{q}\neq0}\frac{v_c(q)}{\Omega\epsilon_d(q)}\rho^v(q)\rho^v(-\vec{q})+\sum_{q\neq0}\frac{\bar{v}_{ps}(q)}{\Omega\epsilon_d(q)}\rho^i(\vec{q})\rho^v(-\vec{q})+\frac{1}{2}\sum_{q\neq0}Z^2\frac{v_c(q)}{\Omega\epsilon_d(q)}[\rho^i(\vec{q})\rho^i(-\vec{q})-N]+NZE_0\qquad(46)$$

where, as noted earlier, E_0 is the sum of all $q\to0$ terms in the starting Hamiltonian. In (46) $\bar{v}_{ps}$ is the assumed local pseudopotential [previously written as $v_c(q)f(q)$]. For systems in which the adiabatic approximation is satisfactory, we may therefore write the total Hamiltonian for a crystal as

$$H=NZE_0+T_i+E_m+\frac{1}{2}\sum_{\vec{R},\vec{R}'}{}'\phi_L^{SC}(\vec{R}-\vec{R}')+\sum_i\frac{p_i^2}{2m}+\frac{1}{2}\sum_{\vec{q}\neq0}\frac{v_c(q)}{\Omega\epsilon_d(q)}\rho^v(\vec{q})\rho^v(-\vec{q})$$

$$+\sum_{\vec{q}\neq0}\frac{\bar{v}_{ps}(q)}{\Omega\epsilon_d(q)}\rho^i(\vec{q})\rho^v(-\vec{q})+\frac{1}{2}\sum_{\vec{q}\neq0}\frac{Z^2v_c(q)}{\Omega\epsilon_d(q)}[\rho^i(\vec{q})\rho^i(-\vec{q})-N],\qquad(47)$$

where T_i is the kinetic energy of the ionic system.

IV. COMMENTARY AND CONCLUSIONS

In simple metals the ions are tightly bound, the core excitation energies are large, and the macroscopic background dielectric constants $\epsilon_d(q\to0)$ are typically quite close to unity. We might reasonably expect, therefore, that the numerical consequences of including ϵ_d in (47) will be relatively minor, at least so far as the thermodynamic functions of the metal are concerned. It would appear plausible, for example, that in calculating the Madelung energy, a scaling procedure involving the replacement of e^2 by $e^2/\epsilon_d(q\to0)$ will be adequate. Similarly, such a replacement may seem sufficient for a reformulation of the electron gas problem in the presence of a polarizable background of ions.[19] A simple argument shows otherwise: Suppose we estimate the Madelung energy by the familiar ion sphere method. Each point ion of charge Ze is surrounded by a uniform sphere of valence electrons, radius $r_sZ^{1/3}$. To within *very small* multipole corrections, the ener-

gy, per electron, of the entire system is then Z^{-1} times the electrostatic energy of a *single neutral sphere*. This is, per electron, $-1.8Z^{2/3}/r_s$ (Ry/electron). But since the energy is determined so closely by a region of essentially atomic dimensions, it is quite apparent that the effect of polarizable dipoles must be small. This is merely a restatement of the fact that one expects $\epsilon_d(q\gtrsim r_s^{-1})$ to rapidly approach unity. Accordingly, for problems in which the physically important length scales are r_s (or k_F^{-1}) the scaling behavior assumed to follow from the replacement $e^2\to e^2/\epsilon_d$ will lead to error.

Notice that although core-polarization effects in the simple metals may contribute little to the internal energy compared with the large direct Coulomb interactions and volume-dependent terms, they may nevertheless have important structural consequences. This point was emphasized in Ref. 6 and also more recently in the context of the structure of the alkali metals by Upadhyaya *et al.*[20] In the analysis above, core polarization has

been included for structural purposes only to the extent that it modifies the pair interaction between ions. Thus (47) is proposed as a Hamiltonian for use in lattice statics, lattice dynamics, statistical mechanics, and so on. It is clear, however, that it is still approximate. In particular three-body (and higher-body) dispersion forces are neglected. These are contained implicitly in the formulation in terms of screened polarization waves and will arise systematically from the expansion of (34). Two physical points may be made: (a) Providing the polarizability of α_0 of the ions is not large, these multicenter potentials are expected to be smaller than the standard fluctuating-dipole (pair) terms, even in the absence of the valence electrons; (b) dynamic screening by the valence electrons will reduce the higher-order contributions still further relative to screened van de Waals interactions. The restriction to pair terms is thus reasonable.

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