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Comparison between phenomenological and pseudopotential force constants for the lattice dynamics of Al

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In this paper we present a critical comparison of calculations of phonon-dispersion curves for aluminum, based on pseudopotential and empirical force-constant methods. The former method is based on both perturbative and nonperturbative evaluations of the total energy of the crystal. In the perturbative approach the total energy is evaluated to second order in the electron-ion interaction with a local pseudopotential. In the nonperturbative approach the electron-ion interaction is treated exactly using a nonlocal *ab initio* pseudopotential. In the empirical force-constant method the total energy is represented by a sum of two-body and three-body terms, the latter being restricted to interactions among triplets of nearest neighbors and of nearest and next-nearest neighbors. All models include physical mechanisms for ensuring the breakdown of the Cauchy relation. We show that in each method convergence of the calculated phonon frequencies requires the inclusion of long-range interactions. The radial-force constants obtained by the empirical and perturbative pseudopotential methods are very similar for the first three shells of neighbors. On the other hand, the tangential force constants differ markedly, a reflection of the different physical mechanisms that come into play in the various models in the establishment of equilibrium.

I. INTRODUCTION

Lattice dynamics has been of great theoretical interest since the slow neutron-scattering technique was developed as a powerful tool for obtaining detailed information on the phonon-dispersion curves of single crystals.[1] Early analyses of the experimental results were based on the use of phenomenological force-constant models, usually of the general Born–Von Karman type with the possible requirement of axial symmetry.[2] The results so obtained have two features in common; namely, force constants connect atoms which are relatively widely separated in the crystal, and more than one model can give rise to similar phonon frequencies.

A significant development in the evaluation of the dispersion curves was achieved by the use of pseudopotential theory.[3] In this microscopic approach, the electron-ion system has been treated perturbatively by considering the effect of the electronic screening on the effective electron-ion interaction.[4] The conceptual advantage of this method is that the force constants are actually calculated rather than determined by fitting to experimental phonon-dispersion curves and elastic moduli. The pseudopotential approach is particularly useful for simple metals, for which the pseudopotential is weak.[5] For noble and transition metals, the presence of highly localized *d* electrons leads to a stronger pseudopotential, which rules out the use of perturbation theory.[6,7]

Total-energy methods, e.g., the frozen-phonon approach, have been developed which are able to produce accurate phonon frequencies for a variety of materials.[8] In this approach the interatomic-force constants, of central interest in the present paper, are not calculated directly. Rather, the method produces appropriate linear combinations of these force constants, viz., the elements of the dynamical matrix.

In the last few years, there has been a revival of interest in force-constant models in connection with the measurements of surface phonons.[9–11] These models provide a means of calculating phonon properties for bulk crystals and, with appropriate modifications, for crystals with surfaces. The computer power required is far less than that needed when the calculations are made using pseudopotential methods. However, this renewed interest in these parametrization schemes has reopened the question of the physical meaning that can be ascribed to the phenomenological force constants. In this paper we investigate this problem by a direct comparison of the force-constant tensor obtained in a phenomenological model built from the knowledge of both the experimental eigenvalues and eigenvectors and the force-constant tensor evaluated in the pseudopotential framework. As a

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test case, we will consider the simple metal aluminum. We will show that the pseudopotential calculations confirm the main predictions of the empirical model with regard to the range of the interactions and the values of the leading radial-force constants. It is noteworthy that the pseudopotential-based calculations have been performed both within a perturbative approach using a local pseudopotential[12] and with a nonperturbative approach which incorporates nonlocal *ab initio* pseudopotentials.[13] Both methods are based on the evaluation of the screening response of the conduction electrons to the ionic motion, which leads to an electronic contribution to the effective ion-ion interaction and thus to the interatomic-force constants. In the perturbative method, we use the response function for the electron-gas (jellium) model with the average density of Al. In the nonperturbative method, the response function is computed for the actual crystal including the ions, i.e., we use the full Bloch states of Al.

The paper is organized as follows. In Sec. II we introduce our empirical model. This model includes multi-ion interactions and is designed to violate the Cauchy relation $c_{12}=c_{44}$. We discuss the convergence of the force constants as the range of the interaction is increased. The total-energy functional evaluated perturbatively in the pseudopotential formalism[4] will be discussed in Sec. III. We consider second-order contributions of the electron-ion interaction, represented by a local pseudopotential, and derive a central force-pair potential which depends on the volume of the system. This volume dependence of the potential automatically ensures the violation of the Cauchy relation. Section IV describes a nonperturbative evaluation of the total energy in which the electron-ion interaction, represented by a nonlocal *ab initio* pseudopotential, is treated exactly. Section V is devoted to the comparison of the results obtained with the three approaches. In particular, we show that all approaches require long-range interactions extending up to the tenth shell of neighbors in order to describe accurately (to within 1%) the experimental phonon frequencies of aluminum.[14]

For the tangential-force constants, we show that a direct comparison between the empirical model and the pseudopotential procedure is difficult. In fact, because of the different descriptions of the noncentral potential, the violation of the Cauchy relation and the infinite crystal equilibrium condition give rise to different relationships between the values of the tangential-force constants in the various schemes. While in the phenomenological model the multi-ion potential affects only the violation of the Cauchy relation, in the pseudopotential approaches the volume-dependent potential enters into both the equilibrium condition and the violation of the Cauchy relation.

On the other hand, the radial-force constants do not enter the equations specifying the stress-free condition and the violation of the Cauchy relation, so that for these force constants it is possible to compare directly the results of the empirical and perturbative pseudopotential procedures. Furthermore, we show that the force-constant tensors, despite the differences between the empirical and screening approaches, compare very well for the first three shells of neighbors.

II. EMPIRICAL MODEL

In this section we consider an empirical model[15] in which the interatomic potential is a sum of a central-potential contribution $V^{c}(r_{ij})$, which depends on the distance r_{ij} between atom i located at $\mathbf{r}_i$ and atom j located at $\mathbf{r}_j$, and a noncentral contribution $V^{nc}(\cos\theta_{ijk})$ related to triplets of atoms,[15] where θ_{ijk} is the angle between the directions of the vectors $\mathbf{r}_i-\mathbf{r}_j$ and $\mathbf{r}_i-\mathbf{r}_k$. Since the angular forces turn out to be of a short-range nature, we will consider only triplets of atoms of the type illustrated in Fig. 1. These three-body interactions are sufficient to obtain the large violation of the Cauchy relation present in Al. The potential $V=V^{c}+V^{nc}$ gives rise to the following force constants.

(a) Tangential-force constants between the ith atom and the atom at the origin:

$$\alpha_i=\left|\frac{1}{r}\frac{\partial V^{c}}{\partial r}\right|_{r=r_i} . \tag{1a}$$

(b) Radial-force constants:

$$\beta_i=\frac{\partial^2 V^{c}}{\partial r^2}\bigg|_{r=r_i} . \tag{1b}$$

(c) Angular-force constants:

$$\delta_i=\frac{1}{3a_0^2}\frac{\partial^2 V^{nc}}{\partial\cos^2\theta}\bigg|_{\cos\theta=\cos\theta_i} , \tag{1c}$$

where, in the latter case, the subscript i refers to the angles depicted in Fig. 1 and a_0 is the lattice parameter.

In order to reproduce correctly the stress-free condition of the infinite crystal, our potential should produce zero pressure in the crystal.[16] A uniform virtual expansion of the crystal allows us to relate the pressure to the tangential-force constants α_i,

$$p=-\frac{1}{6\Omega_0}\sum_i \alpha_i r_i^2 , \tag{2}$$

where Ω_0 is the unit-cell volume. Therefore the stress-free condition becomes

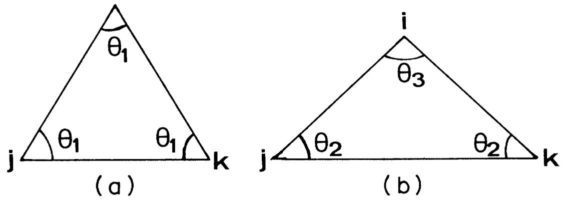

FIG. 1. Two types of triplets of atoms considered in the angular part of the potential. (a) Type I: all the atoms are first-nearest neighbors and form a $\theta_1=60°$ angle. (b) Type II: $i-j$ and $i-k$ are first-nearest neighbors and form a $\theta_3=90°$ angle, while $j-k$ is a second-nearest-neighbor distance forming a $\theta_2=45°$ angle both with $i-j$ and $i-k$.

TABLE I. Radial-force constants β_i vs the range of central interactions for the empirical model of Al. The models *n*C2A refer to central interactions extending up to *n* neighbors and second-nearest-neighbor angular interactions. The units are 10^3 dyn/cm.

Model	β_1	β_2	β_3	β_4	β_5
2C2A	23.820	1.419			
4C2A	24.609	2.483	−0.585	−0.094	
6C2A	24.694	2.544	−0.515	0.094	−0.026
8C2A	24.671	2.676	−0.566	0.168	0.170
10C2A	24.565	2.685	−0.640	0.253	0.002

$$\sum_i \alpha_i r_i^2 = 0 \ . \tag{3}$$

Note that the angular interactions do not contribute to this condition, because in a uniform expansion the angles θ_{ijk} are not changed. From the long-wavelength limit of the dynamical matrix, one can determine the elastic moduli. The violation of the Cauchy relation is embodied in the right-hand side of the equation

$$c_{12} - c_{44} = -18\frac{\delta_1}{a_0} - 8\frac{\delta_2}{a_0} \ , \tag{4}$$

being nonzero. We emphasize that it is the presence of the angle-bending terms in the empirical model that is responsible for this violation.

The values of the force constants are determined by fitting the experimental neutron data of Stedman and Nilsson[14] through a weighted least-squares procedure in which Eqs. (3) and (4) are included. The range of the central interactions has been chosen to minimize the standard deviation[17] χ^2 between the observed and evaluated photon frequencies, the elastic moduli, and the speeds of sound along the high-symmetry directions in the Brillouin zone. As illustrated in Fig. 2, the most accurate fit, with an overall precision better than 1%, is obtained by considering long-range forces extending over eight to ten shells of neighbors. We will present the results for the model with central interactions extending up to ten shells of neighbors and with the inclusion of the angular interactions δ_1 and δ_2 up to second neighbors. This model will be referred to as 10C2A.

In Table I we present the numerical values of the radial force constants for the first five shells of neighbors as functions of the range of the central interactions. As one can see, only the leading force constants involving interactions out to third neighbors are relatively unaffected as the range is increased. For this reason the comparison with the pseudopotential results becomes meaningful only for the first three shells. In Fig. 3 we present results for the elastic moduli versus the range of the interactions. Note that c_{44} is particularly affected by the variation of the range of the interactions and that all the elastic moduli require the inclusion of long-range interactions in order for them to reach their experimental values to within 1%.

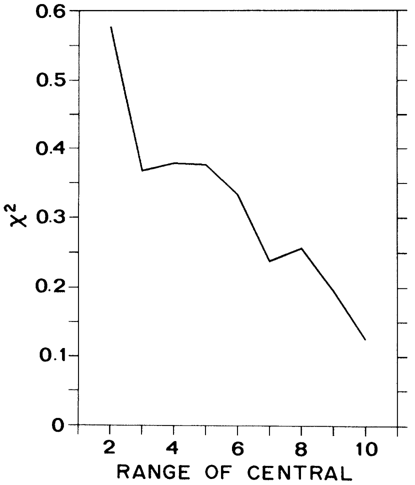

FIG. 2. χ^2 of calculated phonon frequencies of Al vs the range of the central interactions for the phenomenological model. The range of the angular interactions is kept fixed to second-nearest neighbors.

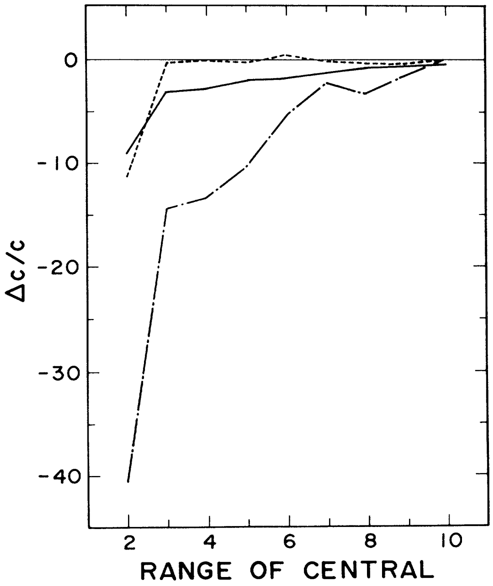

FIG. 3. Percent errors of the elastic moduli of Al as functions of the range of central interactions for the phenomenological model. Solid line, c_{11}; dashed line, c_{12}; dot-dashed line, c_{44}.

III. PERTURBATIVE PSEUDOPOTENTIAL APPROACH

The total energy of a simple metal[4] in the small core approximation can be written as

$$E = E_{ii} + E_{ei} \ , \tag{5}$$

where E_{ii} is the Coulombic energy of the ions treated as positive charges of valence Z ($Z = 3$ for Al) and E_{ei} is the energy of the electrons for a fixed configuration of the ions. The E_{ei} term is evaluated in the pseudopotential theory. Two versions of pseudopotential theory are employed. In the first version, discussed in this section, the electronic ground-state energy is expanded to second order in the electron-ion interaction expressed in terms of a local pseudopotential. In the second version, discussed in the next section, the electron-ion interaction is incorporated into the electronic ground-state energy to all orders in the pseudopotential, which, furthermore, is a nonlocal *ab initio* pseudopotential.

For the local pseudopotential, we employ the Heine-Abarenkov form[12]

$$V(r) = \begin{cases} -CZe^2 & \text{if } r < R_M \ , \\ -Z\dfrac{e^2}{r} & \text{if } r \geq R_M \ , \end{cases} \tag{6}$$

where the well depth C and the core radius R_M are parameters which were determined by requiring that (a) the total energy E given by Eq. (5) be a minimum for the experimental value a_0 of the lattice constant. This condition ensures the fulfillment of the stress-free condition given below in Eq. (22). (b) The average of the squares of the bulk phonon frequencies over the Brillouin zone agree with the value extracted from neutron-scattering data.

The Fourier transform of the above pseudopotential is such that in the small wave-vector limit

$$V_{q\to 0} = -\frac{4\pi Ze^2}{q^2\Omega_0} + \frac{b}{\Omega_0} \ , \tag{7}$$

where

$$b = 4\pi Ze^2 R_M^2 \left[\frac{1}{2} - \frac{CR_M}{3} \right] . \tag{8}$$

Imposing the condition of charge neutrality amounts to setting the $\mathbf{q}=0$ component of the Coulomb interaction equal to zero.[18,19] Thus we set

$$V_{q=0} = \frac{b}{\Omega_0} \ . \tag{9}$$

The total energy of the crystal can be represented by a power-series expansion in the pseudopotential,[18]

$$E_{ei} = E_0 + E_1 + E_2 + E_3 + E_4 + \cdots \ . \tag{10}$$

The leading terms E_0 and E_1 in this expansion are independent of the atomic structure; they depend only on the electronic density $n_0 = Z/\Omega_0$. E_0 is the energy of a uniform interacting electron gas; it contains the average kinetic energy per electron ($\frac{3}{5}\hbar^2 K_F^2/2m$, where K_F is the Fermi wave vector) and exchange and correlation terms.[20] The explicit form for E_1 is[18]

$$E_1 = \frac{NbZ}{\Omega_0} \ . \tag{11}$$

The term E_2 arises from pairwise interactions, while E_3 is related to triplets of atoms, etc. It is important to note that the latter two terms are volume-dependent quantities. The two-body contribution is of particular interest in the present work. It is given by[4]

$$E_2 = -\frac{N\Omega_0}{2} \sum_{\mathbf{q}\neq 0} |V_{\mathbf{q}}|^2 \chi(\mathbf{q}) S^*(\mathbf{q}) S(\mathbf{q}) \ , \tag{12}$$

where

$$S(\mathbf{q}) = (1/N) \sum_i \exp(-i\mathbf{q}\cdot\mathbf{r}_i)$$

is the structure factor and $\chi(\mathbf{q})$ is the Fourier transform of the density-response function for interacting electrons, defined in terms of the irreducible polarizability $\tilde{\chi}(\mathbf{q})$ by the exact equation[20]

$$\chi(\mathbf{q}) = \frac{\tilde{\chi}(\mathbf{q})}{1 + (4\pi e^2/q^2)\tilde{\chi}(\mathbf{q})} \ . \tag{13}$$

In the random-phase approximation (RPA) one has that $\tilde{\chi} = \chi^{(0)}$, where $\chi^{(0)}$ is the well-known Lindhard function, or density-response function for noninteracting electrons. A simple way to introduce the effects of exchange and correlation is via the approximation[19,20]

$$\tilde{\chi}(\mathbf{q}) = \frac{\chi^{(0)}(\mathbf{q})}{1 + F_{\text{xc}}(\mathbf{q})\chi^{(0)}(\mathbf{q})} \ , \tag{14}$$

where $F_{\text{xc}}(\mathbf{q})$ is termed a vertex function. In the response schemes based on density-functional theory in the local-density approximation (LDA),[20] we have that $F_{\text{xc}}(\mathbf{q})$ becomes the $\mathbf{q}$-independent quantity $d^2(n_0\varepsilon_{\text{xc}}/d^2n_0$, ε_{xc} being the exchange-correlation energy per electron at the density n_0. Our numerical calculations, and the discussion given below, assume the validity of Eq. (14).

In the determination of the total energy, in the interest of simplicity, we disregard the E_3, E_4, and higher terms because the volume dependence of E_2 is already sufficient to produce a violation of the Cauchy relation. All higher-order terms are taken into account automatically in the next section.

By considering the ionic and electronic contributions, the dynamical matrix to second order in the pseudopotential is

$$D_{\alpha\beta} = \frac{1}{M} \sum_{\mathbf{G}} (\mathbf{q}+\mathbf{G})_\alpha (\mathbf{q}+\mathbf{G})_\beta \varphi(\mathbf{q}+\mathbf{G}) - \sum_{\mathbf{G}\neq 0} G_\alpha G_\beta \varphi(\mathbf{G}) \ , \tag{15}$$

where the $\mathbf{G}$ are the reciprocal-lattice vectors and the effective pair potential φ is given by[18]

$$\varphi(\mathbf{q}) = \frac{4\pi Z^2 e^2}{q^2 \Omega_0} - \Omega_0 |V_{\mathbf{q}}|^2 \chi(\mathbf{q}) \ . \tag{16}$$

It is to be emphasized that the computation of the dynamical matrix based on Eq. (15) takes into account interactions arising from all the neighbors in real space.

At this point we note that a formulation of the problem in real (configuration) space is also possible. In it the effective pair potential for two ions located at lattice site i and at the origin is given by the equation[19]

$$\varphi(\mathbf{r}_i)=v(\mathbf{r}_i)+\int d^3x \int d^3x' V(\mathbf{x}-\mathbf{r}_i)\chi(\mathbf{x},\mathbf{x}')V(\mathbf{x}') \ . \tag{17}$$

It is possible to show that for a central pseudopotential [such as that of Eq. (6)] and with the use of the electron-gas response function, the pair potential given by Eq. (17) is central if Eq. (10) is terminated at second order. Thus the interatomic-force-constant tensor $\Phi_{\alpha\beta}^{(i)}$ can be written as

$$\Phi_{\alpha\beta}^{(i)}=-\left[\alpha_i\delta_{\alpha\beta}+(\beta_i-\alpha_i)\frac{r_{i\alpha}r_{i\beta}}{r_i^2}\right] , \tag{18}$$

where the radial- and tangential-force constants are directly obtained from the pair potential according to the equations

$$\alpha_i=\left[\frac{1}{r}\frac{d\varphi(r)}{dr}\right]_{r=r_i} \tag{19a}$$

and

$$\beta_i=\left[\frac{d^2\varphi(r)}{dr^2}\right]_{r=r_i} . \tag{19b}$$

It is to be noted that the derivatives required in Eqs. (19) are taken at constant volume.

From the knowledge of the response function χ, we compute the pair potential φ and the radial- and tangential-force constants for any pair of ions. We thus construct the force-constant tensor $\Phi_{\alpha\beta}^{(i)}$, and from it we evaluate the dynamical matrix $D_{\alpha\beta}(\mathbf{q})$ given by the equation

$$D_{\alpha\beta}(\mathbf{q})=\sum_i e^{-i\mathbf{q}\cdot\mathbf{r}_i}\Phi_{\alpha\beta}^{(i)} . \tag{20}$$

The computation of the dynamical matrix according to Eq. (20) is done by summing over shells of neighbors in real space. The number of shells is increased until the phonon frequencies agree with those obtained from the all-neighbor formulation [Eq. (15)] to within 0.1%. Typically, this requires the inclusion of eight to ten shells of neighbors.

We note that the volume dependence, implicit in the effective interaction $\varphi(\mathbf{r})$, prevents the fulfillment of the Cauchy relation. To prove this, we expand the dynamical matrix [Eq. (15)] in the long-wavelength limit to relate this quantity to the elastic moduli. By following Born and Huang,[16] a lengthy calculation gives

$$c_{12}-c_{44}=\frac{1}{\Omega_0}\sum_i [\Phi_{xx}^{(i)}r_{ix}^2-\Phi_{xy}^{(i)}r_{ix}r_{iy}] . \tag{21}$$

This relation is valid in general for cubic crystals. For the case of central potentials, we can use Eqs. (18) and (19) to transform Eq. (21) into the form

$$c_{12}-c_{44}=-\frac{1}{3\Omega_0}\sum_i \alpha_i r_i^2 . \tag{22}$$

In the case of the empirical model, the stress-free condition given by Eq. (3) requires the right-hand side of Eq. (22) to be zero, and hence Cauchy's relation is satisfied. The pseudopotential approach, however, leads to a more complicated stress-free condition and to a violation of Cauchy's relations, to which we turn next.

We now discuss the stress-free condition which should be imposed on the infinite crystal. It can be written as

$$p=-\left.\frac{\partial E}{\partial \Omega}\right|_{\Omega=N\Omega_0}=0 . \tag{23}$$

It is convenient to write p, as we have done for E in Eq. (10), as a power-series expansion in the pseudopotential,

$$p=p_0+p_1+p_2+\cdots . \tag{24}$$

Here we have included in the structure-dependent term p_2 the ion-ion interaction,

$$p_2=-\left.\frac{d}{d\Omega}(E_{ii}+E_2)\right|_{\Omega=N\Omega_0} . \tag{25}$$

Now in the study of the interacting electron gas it has been proved[18] that the term p_0 related to the electronic ground-state energy E_0 can be written as

$$\begin{aligned} p_0&=-\left.\frac{\partial E_0}{\partial\Omega}\right|_{\Omega=N\Omega_0} \\ &=\frac{1}{2}\frac{n_0^2}{\tilde{\chi}(0)}-\frac{1}{2}\int_0^{n_0} n_0^2\frac{\partial}{\partial n_0}\left[\frac{1}{\tilde{\chi}(0)}\right]dn_0 , \end{aligned} \tag{26}$$

where the effects of exchange and correlation are built into the irreducible polarizability $\tilde{\chi}$ introduced in Eq. (13) and modeled in the present work by Eq. (14).

The term p_1 is easily evaluated and is given by

$$p_1=\frac{bZ}{\Omega_0^2} . \tag{27}$$

To determine p_2 we write $E_{ii}+E_2$ in terms of an effective ion-ion interaction in real space. We substitute Eqs. (11) and (12) into Eq. (10) and exploit the condition of electroneutrality. As is shown in the Appendix, various terms cancel and the $E_{ii}+E_2$ energy can be written as[18]

$$\begin{aligned} E_{ii}+E_2=&-\frac{\Omega_0}{2}\sum_{\mathbf{q}}|V_{\mathbf{q}}|^2\chi(\mathbf{q})+\frac{1}{2}\sum_i\sum_{j\neq i}\varphi(\mathbf{r}_i-\mathbf{r}_j) \\ &-\frac{NZ^2}{2\Omega_0\chi^{(0)}(0)}-\frac{NZb}{\Omega_0}-\frac{NZ^2F_{\mathrm{xc}}(0)}{2\Omega_0} . \end{aligned} \tag{28}$$

In order to perform the total volume derivative of $E_{ii}+E_2$, we note that E_2 depends explicitly on the volume ($V_{\mathbf{q}}\simeq 1/\Omega_0$) and implicitly through the lattice vectors r_i as well as through the electron density n_0. We have then

$$\frac{d}{d\Omega}=\left.\frac{\partial}{\partial\Omega}\right|_{r_i,n_0}+\left.\frac{r_i}{3\Omega}\frac{\partial}{\partial r_i}\right|_{\Omega,n_0}-\left.\frac{n_0}{\Omega}\frac{\partial}{\partial n_0}\right|_{r_i,\Omega} . \tag{29}$$

We perform the first two derivatives of $E_{ii}+E_2$ appearing on the right-hand side of Eq. (29) by using Eq. (28). We note that the term $(\Omega_0/2)\sum_{\mathbf{q}}|V_{\mathbf{q}}|^2\chi(\mathbf{q})$ does not depend on the volume because $V_{\mathbf{q}}\simeq 1/\Omega_0$ and $\sum_{\mathbf{q}}$, when transformed into an integral, gives $(\Omega/8\pi^3)\int d\mathbf{q}$. The result of this derivation, taking into account Eq. (19a) and Eq. (14), is

$$\frac{1}{6\Omega_0}\sum_{i\neq 0}\alpha_i r_i^2+\frac{Z^2}{2\Omega_0^2\chi^{(0)}}+\frac{bZ}{\Omega_0^2}+\frac{Z^2F_{\mathrm{xc}}(0)}{2\Omega_0^2}$$
$$=\frac{1}{6\Omega_0}\sum_{i\neq 0}\alpha_i r_i^2+\frac{bZ}{\Omega_0^2}+\frac{Z^2}{2\Omega_0^2\tilde{\chi}(0)} . \tag{30}$$

To perform the derivative with respect to n_0, it is more convenient to write E_2 in the form

$$E_2=-\frac{N\Omega_0}{2}\sum_{\mathbf{G}\neq 0}|V_{\mathbf{G}}|^2\chi(\mathbf{G}) . \tag{31}$$

We note that E_{ii} does not depend on the electron density n_0, and so the term in p_2 involving the derivative with respect to n_0 can be written in the form

$$-\frac{n_0}{2}\sum_{\mathbf{G}\neq 0}|V_{\mathbf{G}}|^2\frac{\partial\chi(\mathbf{G})}{\partial n_0} . \tag{32}$$

Collecting all the above terms, we finally obtain

$$p=-\frac{1}{6\Omega_0}\sum_i\alpha_i r_i^2-\frac{1}{2}\int_0^{n_0}n_0^2\frac{\partial}{\partial n_0}\left[\frac{1}{\chi^{(0)}(0)}\right]dn_0$$
$$-\frac{n_0}{2}\sum_{\mathbf{G}\neq 0}|V_{\mathbf{G}}|^2\frac{\partial}{\partial n_0}[\chi(\mathbf{G})] . \tag{33}$$

The choice of the pseudopotential parameters according to criterion (a) following Eq. (6) ensures that $p=0$. We emphasize that the presence of the last two terms in Eq. (33) leads to the violation of the Cauchy relations in metals as indicated by Eq. (22). Physically, the second and third terms originate in the density dependence of both $\chi^{(0)}(\mathbf{q})$ and the local field correction $F_{\mathrm{xc}}(\mathbf{q})$, which is the origin of the density dependence of the effective pair potential defined in Eq. (17).

We would like to note that in an exact treatment of the interacting electron-gas response function according to Eq. (13), Eq. (33) would be exact. In that case the last term on the left-hand side of Eq. (30) would be absent and all the exchange and correlation effects would be directly built into $\tilde{\chi}$ as in the case with Eq. (26).

IV. NONPERTURBATIVE PSEUDOPOTENTIAL APPROACH

In the nonperturbative approach,[13] the effects of the ions are included in the calculation of the ground-state energy to all orders in perturbation theory. The total energy is found by self-consistently solving the Kohn-Sham equations[21] of density-functional theory,

$$\left[-\nabla^2+\sum_l V_{\mathrm{ion}}[\mathbf{r}-\mathbf{R}(l)]\right.$$
$$\left.+\int d^3r'\frac{2n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\mu_{\mathrm{xc}}(\mathbf{r})\right]\psi_\nu=\varepsilon_\nu\psi_\nu , \tag{34}$$

with the electron-number density $n(\mathbf{r})$ given by

$$n(\mathbf{r})=\sum_\nu f_\nu|\psi_\nu|^2 , \tag{35}$$

where f_ν are the electron occupation numbers which are determined by the condition

$$Z=\sum_\nu f_\nu . \tag{36}$$

In the above, V_{ion} is the bare electron-ion interaction, l labels the atomic sites, ν labels both the band and wave vector in the Brillouin zone, and in the LDA $\mu_{\mathrm{xc}}(\mathbf{r})$ is the derivative of $n\varepsilon_{\mathrm{xc}}$ with respect to the electron density n. Using the Kohn-Sham eigenvalues and eigenfunctions, the energy of the interacting electrons is given by[22]

$$E_{ei}=\sum_\nu f_\nu\varepsilon_\nu-\frac{1}{2}\int d^3r'\int d^3r\frac{2n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$
$$-\int d^3r\, n(\mathbf{r})[\mu_{\mathrm{xc}}(\mathbf{r})-\varepsilon_{\mathrm{xc}}(\mathbf{r})] . \tag{37}$$

The above equations give the electronic contribution to the total energy for a fixed set of ionic coordinates. To determine the interatomic forces, we need an expression for the change in energy as the ions vibrate about their equilibrium positions. The interatomic-force-constant tensor $\Phi_{\alpha\beta}(l,l')$ is related to the second-order change in the total energy of the solid by

$$E_2=\frac{1}{2}\sum_{ll'}\Phi_{\alpha\beta}(l,l')u_\alpha(l)u_\beta(l') , \tag{38}$$

where $u_\alpha(l)$ is the α component of the displacement of the lth atom. If the change in energy is known for all displacements of the atoms, then $\Phi_{\alpha\beta}(l,l')$ can be determined. The method we use for the determination of the change in energy is based upon linear-response theory. The second-order change in the energy is written[23]

$$E_2=\sum_\nu f_\nu\langle\nu|V_2|\nu\rangle$$
$$+\frac{1}{2}\sum_{\nu,\nu'}\frac{f_\nu-f_{\nu'}}{\varepsilon_\nu-\varepsilon_{\nu'}}\langle\nu'|H_1|\nu\rangle\langle\nu|V_1|\nu'\rangle , \tag{39}$$

where H_1 is the first-order change in the Hamiltonian, and V_1 and V_2 are the first- and second-order changes, respectively, in the bare electron-ion interaction. H_1 is the sum of V_1 and the change in the electron-electron interaction due to screening. The screening has contributions from both the direct Coulomb interaction and from exchange and correlation.

From linear-response theory, we can write the change in the electron density as[23]

$$n_1(\mathbf{r})=\sum_{v,v'}\frac{f_v-f_{v'}}{\varepsilon_v-\varepsilon_{v'}}\langle v'|H_1|v\rangle\psi_v^*(\mathbf{r})\psi_{v'}(\mathbf{r}) \ . \tag{40}$$

By linearizing the Hamiltonian in Eq. (34), we obtain the first-order change in the Hamiltonian,

$$H_1(\mathbf{r})= V_1(\mathbf{r})+\int d^3r'\frac{n_1(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+n_1(\mathbf{r})\frac{d}{dn}F_{\rm xc}[n(\mathbf{r})] \ . \tag{41}$$

The first-order change in the electron-ion interaction is given by

$$V_1(\mathbf{r})=\sum_l\frac{d}{dR_\alpha(l)}V_{\rm ion}[\mathbf{r}-\mathbf{R}(l)]u_\alpha(l) \ . \tag{42}$$

These two equations are combined to form an integral equation for n_1,

$$n_1(\mathbf{r})=n_p(\mathbf{r})+\int d^3r'K(\mathbf{r},\mathbf{r}')n_1(\mathbf{r}') \ , \tag{43}$$

with the kernel of the integral equation given by

$$K(\mathbf{r},\mathbf{r}')=\sum_{v,v'}\frac{f_v-f_{v'}}{\varepsilon_v-\varepsilon_{v'}}\psi_v^*(\mathbf{r})\psi_{v'}(\mathbf{r}')\langle v'|V_{ee}|v\rangle \ , \tag{44}$$

and n_p is the induced electron density from V_1 only. Consistent with Eq. (14), V_{ee} is the electron-electron interaction given by

$$V_{ee}(\mathbf{r},\mathbf{r}')=\frac{1}{|\mathbf{r}-\mathbf{r}'|}+\delta(\mathbf{r}-\mathbf{r}')\frac{d}{dn}F_{\rm xc}[n(\mathbf{r})] \ . \tag{45}$$

After solving for n_1, the second-order change in the energy is obtained, from which the force constants can be extracted,

$$\begin{aligned}\Phi_{\alpha\beta}(l,l')=&\sum_v f_v\left\langle v\left|\frac{d^2}{dr_\alpha dr_\beta}V_{\rm ion}[\mathbf{r}-\mathbf{R}(l')]\right|v\right\rangle\delta_{ll'}\\&+\sum_{v,v'}\frac{f_v-f_{v'}}{\varepsilon_v-\varepsilon_{v'}}\langle v'|H_1(l\alpha)|v\rangle\\&\times\left\langle v\left|\frac{d}{dr_\beta}V_{\rm ion}[\mathbf{r}-\mathbf{R}(l')]\right|v'\right\rangle \ ,\end{aligned} \tag{46}$$

where $H_1(l\alpha)$, is the first-order coefficient of the expansion of the change in energy in atomic displacements.

For the present study, the electron-ion interaction is taken as a nonlocal *ab initio* pseudopotential generated by the method of Troullier and Martins.[24] For the exchange and correlation, the Wigner interpolation formula[25] is used. The wave functions are expanded in plane waves with a cutoff of 12 Ry. Sixty points in the irreducible element of the Brillouin zone were used to perform the sums over the Brillouin zone. The static properties obtained are 4.01 Å for the equilibrium lattice constant and 74 GPa for the bulk modulus, both of which are in excellent agreement with experiment.

There are two sources for the violation of the Cauchy relations in the nonperturbative approach. The first is through the density-dependent terms in the expression for the pressure, just as in the perturbative approach. The second is through the contributions of three-, four- and higher-body interactions that are included in the nonperturbative approach, but not in the perturbative approach. The physics of the density-dependent terms has been discussed at length in the previous section, and the numerical consequences of the inclusion of interactions beyond pairs of atoms are contained in the results presented in the following section. We have found that the $\Phi_{\alpha\beta}(l,l')$ calculated by the nonperturbative approach do not correspond to central potentials and cannot be presented by Eqs. (18) and (19).

V. NUMERICAL CALCULATIONS AND DISCUSSION OF THE RESULTS

In this section we present and compare the results of the calculations based on the methods outlined in Secs. II–IV. Comparison of the predictions of these methods with experiment and with each other reveals that the lattice dynamics of Al involves forces of relatively long-range character. This feature is consistent with the long-range nature of the Friedel oscillations present in the simple metals. For this reason we present results with interactions extending up to ten shells of neighbors. In the phenomenological force-constant model, we include the angular interactions δ_1 and δ_2 up to second-nearest neighbors.

In the perturbative pseudopotential calculation, the elements of the force-constant matrices $\Phi_{\alpha\beta}(l,l')$ are consistent with central potentials of interaction; i.e., one can express all $\Phi_{\alpha\beta}(l,l')$ in the form of Eq. (18). Thus, for a given pair of interacting atoms, the nonzero $\Phi_{\alpha\beta}(l,l')$ can be expressed in terms of just two parameters α_i and β_i. In order to facilitate comparison with the empirically determined force constants, we therefore express the perturbative pseudopotential results in terms of the α_i and β_i.

In the nonperturbative pseudopotential calculation, the elements of the force-constant matrices do not correspond to central potentials of interaction. In other words, more than two nonzero parameters are generally required to represent the $\Phi_{\alpha\beta}(l,l')$ for a given pair of interacting atoms and one cannot characterize the $\Phi_{\alpha\beta}(l,l')$ by α_i and β_i alone. The values of the nonperturbative $\Phi_{\alpha\beta}(l,l')$ are compared directly with those obtained by the other two methods. (The latter comparison is presented later in connection with the discussion of Table III.)

The force constants obtained with the 10C2A model by means of the best-fit procedure outlined in Sec. II, together with the perturbative pseudopotential results, are listed in Table II. With regard to the radial-force constants β_i, there is a good deal of agreement between the values obtained with the perturbative and empirical methods, which, in particular, yield very similar values for the leading force constants β_1, β_2, and β_3. For the distant shells of neighbors, the comparison becomes difficult, even though there is good agreement between the three values of β_6, β_7, and β_8 in Table II. In fact, in the empirical model the assumed finite range of the interactions in-

TABLE II. Theoretical force constants for Al out to tenth-nearest neighbors. The units are 10^3 dyn/cm.

	α		β	
n	Perturbative screening method	Empirical model	Perturbative screening method	Empirical model
1	−1.26	0.27	21.7	24.6
2	−0.16	0.20	2.60	2.68
3	0.047	0.008	−0.86	−0.64
4	−0.031	0.054	0.24	0.25
5	0.015	0.071	0.58	0.003
6	0.0013	0.047	−0.31	−0.36
7	−0.0087	0.003	0.09	0.12
8	0.0032	0.022	0.16	0.20
9	0.0043	−0.070	−0.12	0.12
	0.0043	−0.070	−0.10	0.12
10	−0.0025	0.004	−0.10	−0.38

hibits the convergence of the radial-force constants beyond third neighbors, as one can see in Table I. With regard to the tangential-force constants, the different physics behind the satisfaction of the stress-free condition in the two models renders a precise comparison impossible. In the phenomenological model, the α_i satisfy Eq. (3), while in the perturbative pseudopotential scheme they satisfy Eq. (22). As an example of the comparison of the quantitative predictions of both methods, we note that in the phenomenological 10C2A model our fitting procedure gives $c_{12}-c_{44}=0.330\times10^{12}$ dyn/cm^2. The experimental value taken from Ref. 26 is 0.325×10^{12} dyn/cm^2. With the perturbative pseudopotential method, using the data of Table II and Eq. (22) we obtain $c_{12}-c_{44}=0.251\times10^{12}$ dyn/cm^2. We stress again that the difference between c_{12} and c_{44} in the latter case is entirely due to the volume dependence of the pairwise interaction. The discrepancy between theory and experiment, in this case, is not very serious because it can be imputed to the neglect of the three- and four-body contributions to the total energy, which, for the sake of simplicity, we have not included in the perturbative scheme.

A more general comparison can be made by considering the force produced on the reference atom 0 when we displace the *i*th atom. For this purpose we discuss the force-constant tensor $\Phi^{(i)}_{\alpha,\beta}$ for the first three shells of neighbors in the 10C2A model. Concerning the first shell of neighboring atoms, we choose $\mathbf{r}_i=(1,1,0)a_0/2$. In the phenomenological method, we get

$$\Phi^{(1)}_{\alpha\beta}=\begin{bmatrix} -\frac{1}{2}(\beta_1+\alpha_1)-3\delta_1-2\delta_2 & -\frac{1}{2}(\beta_1-\alpha_1)-\frac{3}{2}\delta_1 & 0 \\ -\frac{1}{2}(\beta_1-\alpha_1)-\frac{3}{2}\delta_1 & -\frac{1}{2}(\beta_1+\alpha_1)-3\delta_1-2\delta_2 & 0 \\ 0 & 0 & -\alpha_1-3\delta_1 \end{bmatrix}. \tag{47}$$

The force-constant tensor in the perturbative pseudopotential framework is given by the same expression upon setting $\delta_1=\delta_2=0$.

For the second shell of neighbors, we obtain, with $r_i=(1,0,0)a_0$,

$$\Phi^{(2)}_{\alpha\beta}=\begin{bmatrix} -\beta_2 & 0 & 0 \\ 0 & -\alpha_2 & 0 \\ 0 & 0 & -\alpha_2 \end{bmatrix}, \tag{48}$$

while for the third shell of neighbors, with $r_i=(2,1,1)a_0/2$, we have

$$\Phi^{(3)}_{\alpha\beta}=\begin{bmatrix} -\frac{1}{3}(2\beta_3+\alpha_3) & -\frac{1}{3}(\beta_3-\alpha_3) & -\frac{1}{3}(\beta_2-\alpha_3) \\ -\frac{1}{3}(\beta_3-\alpha_3) & -\frac{1}{6}(\beta_3+5\alpha_3) & -\frac{1}{6}(\beta_3-\alpha_3) \\ -\frac{1}{3}(\beta_3-\alpha_3) & -\frac{1}{6}(\beta_3-\alpha_3) & -\frac{1}{6}(\beta_3+5\alpha_3) \end{bmatrix}. \tag{49}$$

Note that in $\Phi^{(2)}_{\alpha\beta}$ for the 10C2A model the term containing δ_2 cancels out, so that $\Phi^{(2)}_{\alpha\beta}$ is the same as for central potentials. Both in the phenomenological and perturbative pseudopotential approaches, $\Phi^{(3)}_{\alpha\beta}$ is related to central potentials only. In the nonperturbative pseudopotential approach, the $\Phi^{(3)}_{\alpha\beta}$ cannot be expressed solely in terms of central potentials.

The numerical values of the nonzero elements of the force-constant tensor (given in units of 10^3 dyn/cm) for the first three shells of neighbors are presented in Table III. The agreement between the three sets of matrix elements is very good for the first shell of neighbors. The angular interactions δ_1 and δ_2 practically compensate the difference in sign of the α_1 between the empirical and perturbative pseudopotential methods. For the second shell of neighbors given in Table III, there is a difference in the sign of the small *yy* and *zz* components of the perturbative results compared to the nonperturbative and phenomenological results. For the third shell of neighbors, there is reasonably good agreement between the empirical model and perturbative approaches. The nonperturbative scheme, however, gives a value of $\Phi^{(3)}_{22}$ that differs by more than a factor of 2 from the values given by the other two schemes.

We comment next on the previously mentioned noncentral character of the dynamical matrix obtained by the nonperturbative pseudopotential method. The number of nonzero, independent $\Phi_{\alpha\beta}(l,l')$ for a given pair of interacting neighbors depends on the particular pair. If the number is greater than 2, one can calculate more than one value of α using Eq. (18). Only in the case of second, sixth, and eighth neighbors does one obtain a unique value of α. In all other cases (first, third, fourth, fifth, seventh, ninth, and tenth neighbors), one obtains multiple

TABLE III. Nonzero elements of the force-constant tensors in 10^2 dyn/cm for the first three shells of neighbors according to the three methods described in the text.

Force-constant tensor element	Perturbative pseudopotential	Nonperturbative pseudopotential	Phenomenological
$\Phi_{11}^{(1)}=\Phi_{22}^{(1)}$	−10.220	−9.930	−10.379
$\Phi_{12}^{(1)}=\Phi_{21}^{(1)}$	−11.480	−10.948	−10.886
$\Phi_{33}^{(1)}$	1.260	1.510	2.247
$\Phi_{11}^{(2)}$	−2.600	−2.141	−2.686
$\Phi_{22}^{(2)}=\Phi_{33}^{(2)}$	0.160	−0.168	−0.198
$\Phi_{11}^{(3)}$	0.558	0.330	0.424
$\Phi_{12}^{(3)}=\Phi_{21}^{(3)}$	0.302	0.347	0.216
$\Phi_{13}^{(3)}=\Phi_{31}^{(3)}$	0.302	0.347	0.216
$\Phi_{22}^{(3)}=\Phi_{33}^{(3)}$	0.104	0.252	0.100
$\Phi_{23}^{(3)}=\Phi_{32}^{(3)}$	0.151	0.121	0.108

values of α that can differ in magnitude and even in sign. For example, for third neighbors one obtains three values of α_3: $\alpha_3'=+0.365\times10^3$ dyn/cm, $\alpha_3''=-0.226\times10^3$ dyn/cm, and $\alpha_3'''=-0.132\times10^3$ dyn/cm. These results demonstrate that the inclusion of three-, four-, and higher-body interactions in the nonperturbative method leads to a dynamical matrix which cannot be described solely by central potentials.

We have attempted to calculate $c_{12}-c_{44}$ from the $\Phi_{\alpha\beta}(l,l')$ obtained by the nonperturbative approach. Using the general relations for the elastic moduli given by Born and Huang,[16] one must take differences of large quantities involving the $\Phi_{\alpha\beta}(l,l')$ to yield small quantities. So far, we have been unable to calculate the $\Phi_{\alpha\beta}(l,l')$ with sufficient accuracy by the nonperturbative approach to yield convergent results for $c_{12}-c_{44}$.

Finally, we present the results of calculations of the phonon-dispersion curves obtained with the force constants of the three methods. Figure 4(a) corresponds to the 10C2A model, and Figs. 4(b) and 4(c) correspond to the perturbative and nonperturbative pseudopotential schemes, respectively. In all cases the agreement with the experimental neutron data is excellent over the entire Brillouin zone. This type of agreement, particularly in the case of the transverse phonon branches along the ΓK direction which are nearly degenerate in the first third of that direction, is due to the inclusion of long-range forces. A nearest-neighbor model would produce a large splitting between these two branches.

In conclusion, the pseudopotential second-order perturbative approach allows us to construct an effective pairwise volume-dependent potential. The results of the nonperturbative pseudopotential approach, however, cannot be described by central potentials. The singularity of the dielectric function produces an oscillating tail in the potential which cannot be neglected if one wants to reproduce accurately both the elastic and dynamical properties. Our calculations show that the range of the interactions in real space extends up to eight to ten neighbors. These results justify the introduction of relatively long-range forces in the phenomenological force-constant models in order to minimize the χ^2 of the calculated pho-

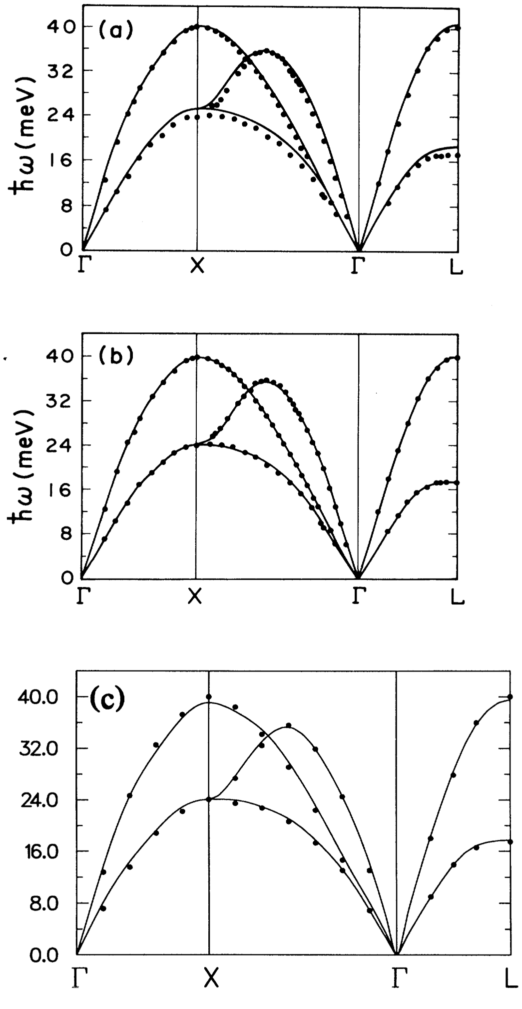

FIG. 4. (a) Bulk phonon-dispersion curves for Al evaluated with the 10C2A empirical model. The dots represent the experimental neutron data of Ref. 14. (b) Perturbative pseudopotential calculations of the phonon frequencies from Ref. 12. The dots as in (a). (c) Nonperturbative pseudopotential calculations of the phonon frequencies from Ref. 13. The dots as in (a).

non frequencies. Furthermore, the short-range angular forces of the phenomenological model mimic very closely the effects derived from the volume dependence of the pseudopotential as shown by the analysis of the forces acting between atoms in the crystal. Finally, we have shown that for aluminum the principal radial-force constants derived from the phenomenological model are in good overall agreement with those derived from the pseudopotential calculations.

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APPENDIX

In this appendix we indicate the steps involved in passing from Eq. (5) to Eq. (27). The total energy of a simple metal in the small core approximation can be written as

$$E=E_{ii}+E_{ei} , \tag{A1}$$

where E_{ii} is the Coulombic energy of the ions treated as positive charges of valence Z ($Z=3$ for Al) and E_{ei} is the energy of the electrons for a fixed configuration of the ions. The ion-ion interaction energy can be expressed as

$$E_{ii}=\frac{N}{2}\sum_{\mathbf{q}\neq 0}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0}S^*(\mathbf{q})S(\mathbf{q})-\frac{1}{2}\sum_{\mathbf{q}\neq 0}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0} , \tag{A2}$$

where $S(\mathbf{q})=1/N\sum_j \exp(-i\mathbf{q}\cdot\mathbf{r}_j)$ is the structure factor. For an *sp*-bonded metal such as Al, it is appropriate to expand the electron-ion interaction energy to second order in terms of the pseudopotential, as

$$E_{ei}=E_0+E_1+E_2 . \tag{A3}$$

The zero-order term E_0, the energy of the interacting electron gas, and the first-order term E_1 are independent of the atomic structure and depend on the electronic density $n_0=Z/\Omega_0$. The second-order term E_2 is given by

$$E_2=-\frac{N\Omega_0}{2}\sum_{\mathbf{q}\neq 0}|V_{\mathbf{q}}|^2\chi(\mathbf{q})S^*(\mathbf{q})S(\mathbf{q}) , \tag{A4}$$

where, in the RPA LDA [see the discussion below Eq. (13)],

$$\chi(\mathbf{q})=\chi^{(0)}(\mathbf{q})/\{1+[(4\pi e^2/q^2)+F_{\mathrm{xc}}(\mathbf{q})]\chi^{(0)}(\mathbf{q})\}$$

is the negative of the Fourier transform of the density-response function for interacting electrons embedded in a uniform background, $V_{\mathbf{q}}$ is the Fourier transform of the pseudopotential, and $F_{\mathrm{xc}}(\mathbf{q})$ is the Fourier transform of the exchange and correlation terms.

We now write

$$\begin{aligned}E_{ii}+E_2&=\frac{N}{2}\sum_{\mathbf{q}\neq 0}S^*(\mathbf{q})S(\mathbf{q})\left[\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0}-\Omega_0|V_{\mathbf{q}}|^2\chi(\mathbf{q})\right]\\&\quad-\frac{1}{2}\sum_{\mathbf{q}\neq 0}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0}\\&=\frac{N}{2}\sum_{\mathbf{q}\neq 0}S^*(\mathbf{q})S(\mathbf{q})\varphi(\mathbf{q})-\frac{1}{2}\sum_{\mathbf{q}\neq 0}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0} ,\end{aligned} \tag{A5}$$

where

$$\varphi(\mathbf{q})=\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0}-\Omega_0|V_{\mathbf{q}}|^2\chi(\mathbf{q}) . \tag{A6}$$

To evaluate Eq. (A5) we add and subtract the $q=0$ term:

$$\begin{aligned}E_{ii}+E_2&=\frac{N}{2}\sum_{\mathbf{q}}S^*(\mathbf{q})S(\mathbf{q})\varphi(\mathbf{q})-\frac{N}{2}\varphi(0)\\&\quad-\frac{1}{2}\sum_{\mathbf{q}}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0} .\end{aligned} \tag{A7}$$

Note that the last sum can be unrestricted since the zeroth Fourier component of the Coulombic potential is zero for charge neutrality. Using the above definition of the structure factor, we get

$$\begin{aligned}E_{ii}+E_2&=\frac{N}{2}\sum_{\mathbf{q}}\sum_{j,k}\frac{1}{N^2}\varphi(\mathbf{q})e^{-i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)}\\&\quad-\frac{N}{2}\varphi(\mathbf{0})-\frac{1}{2}\sum_{\mathbf{q}}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0} .\end{aligned} \tag{A8}$$

On defining the interaction between pairs of atoms as

$$\varphi(\mathbf{r}_j-\mathbf{r}_k)=\frac{1}{N}\sum_{\mathbf{q}}\varphi(\mathbf{q})e^{-i\mathbf{q}\cdot(\mathbf{r}_j-\mathbf{r}_k)} , \tag{A9}$$

we write

$$\begin{aligned}E_{ii}+E_2&=\frac{1}{2}\sum_{j}\sum_{k\neq j}\varphi(\mathbf{r}_j-\mathbf{r}_k)+\frac{1}{2}\sum_{\mathbf{q}}\varphi(\mathbf{q})\\&\quad-\frac{N}{2}\varphi(\mathbf{0})-\frac{1}{2}\sum_{\mathbf{q}}\frac{4\pi Z^2e^2}{\mathbf{q}^2\Omega_0}\\&=\frac{1}{2}\sum_{j}\sum_{k\neq j}\varphi(\mathbf{r}_j-\mathbf{r}_k)\\&\quad-\frac{\Omega_0}{2}\sum_{\mathbf{q}}|V_{\mathbf{q}}|^2\chi(\mathbf{q})-\frac{N}{2}\varphi(\mathbf{0}) .\end{aligned} \tag{A10}$$

To evaluate the $\varphi(\mathbf{0})$ contribution, we use Eqs. (7), (13), and (14) to perform the limit

$$\lim_{\mathbf{q}\to 0}\varphi(\mathbf{q})=\lim_{\mathbf{q}\to 0}\left[\frac{4\pi Z^2e^2}{q^2\Omega_0}-\Omega_0\left[-\frac{4\pi Ze^2}{q^2\Omega_0}+\frac{b}{\Omega_0}\right]^2 \times\frac{\chi^{(0)}(\mathbf{q})}{1+[(4\pi e^2/q^2)+F_{\mathrm{xc}}(\mathbf{q})]\chi^{(0)}(\mathbf{q})}\right]. \tag{A11}$$

Care must be exercised in the second term, which leads us to the expression

$$\lim_{q\to 0}\left[\frac{4\pi Z^2e^2}{q^2\Omega_0}-\frac{1}{\Omega_0}\left[\frac{4\pi Z^2e^2}{q^2}-2Zb+\frac{q^2b^2}{4\pi e^2}\right]\times\left[1-\frac{q^2F_{\mathrm{xc}}(\mathbf{q})}{4\pi e^2}-\frac{q^2}{4\pi e^2\chi^{(0)}(\mathbf{q})}\right]\right]. \tag{A12}$$

The result of this limit is

$$\frac{Z^2}{\Omega_0\chi^{(0)}(0)}+\frac{2Zb}{\Omega_0}+\frac{Z^2F_{\mathrm{xc}}(0)}{\Omega_0}. \tag{A13}$$

The energy $E_{ii}+E_2$ of the crystal is then given by

$$E_{ii}+E_2=-\frac{NZ^2}{2\Omega_0\chi^{(0)}(0)}-\frac{NZb}{\Omega_0}-\frac{NZ^2F_{\mathrm{xc}}(0)}{2\Omega_0} -\frac{\Omega_0}{2}\sum_{\mathbf{q}}|V_{\mathbf{q}}|^2\chi(\mathbf{q})+\frac{1}{2}\sum_i\sum_{j\neq i}\varphi(\mathbf{r}_i-\mathbf{r}_j). \tag{A14}$$

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