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Interionic interactions in simple metals

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Second-order pseudopotential theory is combined with the Fermi-Thomas dielectric response to derive an analytic form for a purely repulsive screened Coulomb interaction between ions balanced by a volume-dependent energy which has no direct influence on the detailed structural properties. The interaction is evaluated for the empty-core pseudopotential and used to give direct predictions of the bulk modulus, the Cauchy ratio c_{12}/c_{44}, the Poisson ratio, and the Grüneisen constant for the simple metals, which are compared with experimental values. The interaction is also used to obtain phonon spectra and densities of modes for aluminum, and these are compared to experiment. Finally a simple expression for the principal volume-dependent energy is obtained.

I. INTRODUCTION

Simple metals were the first system for which it was possible to calculate the entire range of bonding and structural properties from first principles. This was accomplished using pseudopotential perturbation theory,[1] treating the weak influence of the ionic potentials in perturbation theory. The leading term in the energy which depended upon the detailed arrangement of the ions came in second order. It could be combined with the Coulomb interaction between ions to obtain a two-body central-force interaction between ions, plus a volume-dependent term; use of these was mathematically equivalent to the direct perturbation theory in wave-number space. In fact the calculation in wave-number space turned out ordinarily to be more practical, and the effective interaction between ions, with its Friedel oscillations and structure which proved very sensitive to the details of the treatment of the electron-electron interaction, was of little use.

This structure in the effective interaction is intimately associated with the logarithmic singularity at $q = 2k_F$ in wave-number space and the calculations in wave-number space have indicated that this singularity has very limited impact on the interesting properties; while it does give Kohn anomalies in the vibration spectrum, the general form and scale of the spectrum does not depend on the singularity. This explains why the effective interaction between ions can be so sensitive and uncertain while the mathematically equivalent calculations in wave-number space can be quite stable and insensitive. This also suggests that we might simplify the screening to obtain a stable and simple interionic interaction which still could give a good account of most properties of the metal.

The replacement of the Hartree dielectric function, with its logarithmic singularity, by the Fermi-Thomas dielectric function is the natural choice. The Fermi-Thomas function properly diverges as $1/q^2$ at small q and its use in calculations in wave-number space has proven quite successful,[2] which would seem to guarantee a degree of success.

A second reason to believe that this could be successful comes from the recent study of cohesion in simple metals by Chelikowsky.[3] He finds that the metal itself is a "Fermi-Thomas system" but that the atom is not. Combining this with Teller's finding[4] that the cohesion of the metal in the Fermi-Thomas approximation is negative and near zero, Chelikowsky is able to calculate the metallic cohesion in terms of the kinetic energy of the atom alone. This is, of course, interesting in its own right but, for our purposes, it is important in suggesting the use of the Fermi-Thomas method for the interatomic interaction even though it does not describe the cohesion itself.

In Sec. II we give a simple argument which leads to the form of the effective interaction between ions in the Fermi-Thomas approximation. We see that it is a simple screened Coulomb form

$e^{-\kappa r}/r$ for spacings great enough so that the cores do not overlap. The derivation is carried out in detail for local pseudopotentials in the Appendix and the leading constant coefficient is evaluated for the empty-core pseudopotential.

The view of the metal to which this leads is novel. The metal consists of ions interacting with purely repulsive interactions, but held to a finite volume by a volume-dependent energy which has no direct influence on most detailed properties. The exact form of this volume-dependent energy has been the center of recent discussion[5] and we shall obtain the principal contribution explicitly, but it does not affect the calculations performed here since they are carried out at constant volume. The exponentially decaying interaction leads to rapidly converging calculations. Meaningful, but not very accurate, results can even be obtained in many cases including only nearest neighbors; here we carry each calculation to convergence. Care must be taken in treating the volume dependence since most properties are measured at constant volume, but we see that even properties such as compressibility, Poisson's ratio, and thermal expansion can be suitably treated entirely in terms of the simple repulsions.

In Sec. III we report in detail the results of calculations of a wide variety of properties in terms of the simple interionic interaction. Note that all of these properties are determined by only two independent parameters for each metal: (1) the strength of the interaction, which depends upon the empty-core radius r_c, the valence Z, and the screening length $1/\kappa$, and (2) the ratio of the screening length $1/\kappa$, to the interatomic distance characterized by r_0 where the volume per atom is written as $4\pi r_0^3/3$. The strength of the repulsive interaction sets the scale of all interaction energies, and is tested for the empty-core pseudopotential by treating the bulk modulus. Most of the other properties we consider are ratios for which the strength of the repulsion cancels out. In this case, for a given structure, all variations from material-to-material are trends in κr_0, a parameter that increases with valence (to the right in the Periodic Table, with the alkalis and the alkaline earths having κr_0 greater than the trivalent metals) and with increasing atomic number.

II. THE EFFECTIVE INTERACTION BETWEEN IONS

The simple metal consists, to zero order in the pseudopotential, of metallic ions imbedded in a uniform free-electron gas(1); these ions interact with each other through their Coulomb replusion Z^2e^2/r for ions of valence Z. The ions interact with the electron gas through a weak pseudopotential, $w(\vec{r}-\vec{r}_i)$ for an ion at the position $\vec{r}_i$. The pseudopotential is taken to be independent of the relative positions of the ions so that to first order the shift in energy of each electronic state is a sum of terms $\langle \vec{k} \,|\, w \,|\, \vec{k}\rangle$, each independent of the relative positions of the ions. It is found[2] that the terms through first order, independent of ion position, give a fair description of the equilibrium energy and lattice spacing of the simple metals.

The leading position-dependent term in the energy of an electronic state is of second order. We display the equations necessary to show that this second-order term is equivalent to a two-body interaction, and we complete the derivation in the Appendix. The second-order term in the energy of the state $|\vec{k}\rangle$ may be written as follows:

$$E_k^{(2)}=\sum_q{}' \frac{\left\langle \vec{k}\,\middle|\, \sum_j w(\vec{r}-\vec{r}_j)\,\middle|\, \vec{k}+\vec{q}\right\rangle\left\langle \vec{k}+\vec{q}\,\middle|\, \sum_i w(\vec{r}-\vec{r}_i)\,\middle|\, \vec{k}\right\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}\,|^2)}$$

$$=\sum_{i,j}\sum_q{}' e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}\frac{\langle \vec{k}\,|\, w(\vec{r})\,|\, \vec{k}+\vec{q}\rangle\langle \vec{k}+\vec{q}\,|\, w(\vec{r})\,|\, \vec{k}\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}\,|^2)}\;. \tag{1}$$

The second form was obtained by changing the variable of integration in each matrix element from $\vec{r}$ to $\vec{r}-\vec{r}_i$ or $\vec{r}-\vec{r}_j$ and then reordering the summations. The only dependence upon the ionic positions is in the factor $e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}$. In evaluating the total energy we must sum over occupied states and since this contribution is already of second order in the pseudopotential we may perform the sum over states within the unperturbed Fermi surface $k<k_F$ to obtain a second-order result. Again interchanging sums, we obtain

$$\sum_{k<K_F} E_k^{(2)}=\sum_{i,j}\sum_q{}' e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}\sum_{k<k_F}\frac{\langle \vec{k}\,|\, w\,|\, \vec{k}+\vec{q}\rangle\langle \vec{k}+\vec{q}\,|\, w\,|\, \vec{k}\rangle}{(\hbar^2/2m)(k^2-|\vec{k}+\vec{q}\,|^2)}\;. \tag{2}$$

The final sum over $\vec{k}$ gives a simple function of the magnitude of $\vec{q}$ which we write as $F(q)$ (equal, except for screening corrections, to the energy-wave-number characteristic). Then the sum over $\vec{q}$, which is $\sum'_q e^{-i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)}F(q)$, is simply a Fourier transform giving a form which can be described as an effective interaction between ions $V(|\vec{r}_i-\vec{r}_j|)$ depending only upon internuclear distance. This point was apparently first made by Cohen.[6] Self-energy corrections do not modify this conclusion so that all of the terms, up to second order in the pseudopotential, depending upon the detailed positions of the ions, can be combined as a two-body central-force interaction and a volume-dependent term.

We may now seek a solution for this interaction using the Fermi-Thomas approximation; to obtain the energy to second-order in the pseudopotential we may in fact use the linearized Fermi-Thomas approximation. In this approximation the electron density (or the perturbing potential) arising from, and outside of, a spherically symmetric perturbation can be obtained from a second-order linear differential equation[7] and has the general form $(Ae^{-\kappa r}+Be^{\kappa r})/r$ and only the first term is allowed at large distance. κ is the Fermi-Thomas screening parameter,

$$\kappa=(4e^2k_Fm/\pi\hbar^2)^{1/2} \ . \tag{3}$$

Clearly, then, a second perturbation interacting with this field will, to lowest order, contribute a shift in energy also varying as $Ae^{-\kappa r}/r$ as a function of the separation.

A special case of this interaction is the well-known[7] screened Coulomb interaction between point charges Ze (or spherically-symmetric charges) given by $Z^2e^2e^{-\kappa r}/r$. We see here that all any localized pseudopotential operator can do in the Fermi-Thomas approximation is to change the leading coefficient.

In the Appendix we derive this result explicitly for local pseudopotentials and evaluate the result for the empty-core pseudopotential in which the unscreened pseudopotential is $-Ze^2/r$ for r greater than the core radius r_c and zero for r less than r_c. We obtain

$$V(r)=Z^2e^2\cosh^2(\kappa r_c)e^{-\kappa r}/r \ , \tag{4}$$

for r greater than $2r_c$. Note that it properly gives the usual screened Coulomb interaction as r_c approaches zero.

III. THE STRUCTURAL PROPERTIES

The picture of the metal which Eq. (4) provides is peculiar. This is a purely repulsive interaction, balanced by the volume-dependent energy which stabilizes the metal at the observed volume. Pseudopotential theory has always had this volume-dependent term but as long as the effective interaction between ions had an attractive part near the observed spacing we could, to some extent, put the volume-dependent term out of our minds; that is no longer possible. After the initial reaction we may see that this is a very fruitful view of the metal.

If indeed there were no volume-dependent term, so that the ions were in equilibrium under two-body central forces alone, the Cauchy relations among the elastic constants would obtain[8] $c_{12}=c_{44}$ for cubic metals. We shall soon see that experimentally these are generally violated for simple metals by a factor of about 2 so that the traditional view of two-body interactions is not even approximately valid; this is rectified quantitatively by the new view. We shall see how the new view makes other phenomena in metals immediately apparent, as well as providing a method for very elementary estimates of any of the atomic properties of the simple metals.

Of course, there cannot be a truly volume-dependent term in the energy. It would, for example, modify the bulk modulus associated with uniform dilatations but would not modify the bulk modulus entering the speed of longitudinal sound (waves propagating in the system at constant total volume). This violates the well-known validity of the method of long waves.[8] The resolution of this contradiction comes in recognizing that the volume-dependent energy is really a multi-ion interaction of sufficiently long range and sufficiently weak structure, so that it does not have an important influence on detailed atomic properties. We shall see in the Appendix that the principal contribution to the volume-dependent energy is the self term $i=j$ in Eq. (2), but there are others.

It might at first seem unreasonable that a property such as the bulk modulus could be calculated either at constant volume, on the basis of the second-order terms, or independently from the volume dependence, neglecting the second-order terms. The reason is that the sum of all second-order terms, including the $i=j$ term in Eq. (2), is rather insensitive to volume. In fact, to the extent that k^2 is negligible in comparison to the $q^2(\neq 0)$

TABLE I. Pseudopotential core radii fit to the observed bulk modulus. Also given are the radius r_0 of the atomic volume and the ratio κr_0 of r_0 to the screening length.

	r_c (Å)	r_0 (Å)[a]	κr_0		r_c (Å)	r_0 (Å)[a]	κr_0
Cu	0.80	1.41	2.55	Sn	0.68	1.87	3.70
Ag	0.99	1.59	2.71	Pb	0.45	1.93	3.76
Au	1.15	1.59	2.71	Ca	0.75	2.17	3.56
Mg	0.49	1.76	3.20	Sr	0.90	2.37	3.72
Zn	0.30	1.52	2.97	Li	0.38	1.73	2.83
Cd	0.53	1.71	3.16	Na	0.76	2.11	3.12
Hg	0.55	1.78	3.22	K	1.12	2.62	3.48
Al	0.23	1.58	3.24	Rb	1.33	2.80	3.59
Ga	0.31	1.67	3.33	Cs	1.42	3.03	3.74
In	0.46	1.84	3.50	Ba	0.96	2.46	3.78
Tl	0.48	1.89	3.55				

[a] See Ref. 19.

entering Eq. (2) the sum is completely independent of volume.

The method by which we predict properties then, is by calculating vibrational frequencies, holding the volume of the system fixed. This is, of course, done by imposing displacements proportional to $\exp(i\vec{k}\cdot\vec{r}_j)$, calculating the forces on an individual ion using the interatomic interactions of Eq. (4), and solving the Newton's-law equations for the three components of the force and acceleration. From these we can extract the elastic constants and from the changes in the elastic constants with volume we can obtain the Grüneissen constant.

A. The bulk modulus and the values of r_c

Given the pseudopotential core radii, obtained from the pseudopotential or from the atomic term values,[2] we thus can directly predict the elastic constants by standard lattice-dynamic techniques.[8] It is more convenient for our purposes to turn this process around and estimate the core radius from the observed bulk modulus and then compare it with the previously given core radius. We did this for the observed structure, but assuming face-centered-cubic structures for both hexagonal and cubic close-packed metals. The values obtained from a fit to the observed bulk modulus at the observed spacing are listed in Table I and plotted in Fig. 1 against the core radii listed in Ref. 2. The agreement with respect to both trends and general magnitudes gives strong support to the use of the simple Fermi-Thomas approximation to the dielectric constant for this elastic property. One of the evaluations came from the bulk modulus and the other from electronic structure considerations which are unrelated to the elastic properties.

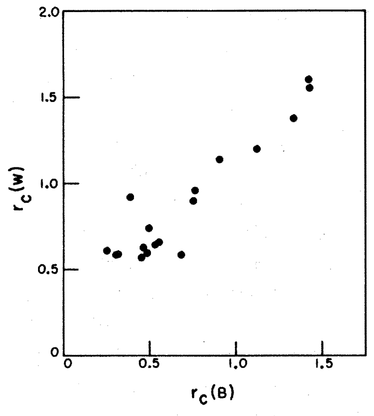

FIG. 1. Empty-core pseudopotential core radii $r_c(w)$ obtained by fitting to known pseudopotentials w plotted against radii $r_c(B)$ fitted to the observed bulk modulus.

This agreement does not, of course, mean that other interpretations of the elastic properties are incorrect; as we have indicated, simple predictions of the bulk modulus based upon the volume-dependent energy by itself but with the same pseudopotential gave comparable agreement with experiment.[9] However, the treatment in terms of interionic interactions is of more interest since it allows a treatment of a much wider range of properties.

For the prediction of atomic properties of metals the fitted values of the core radius r_c given in Table I are preferable to the values obtained earlier. However, we wish to avoid the use of adjusted parameters here since our goal is to learn about the validity of this approach. This can be accomplished by evaluating ratios of observables for

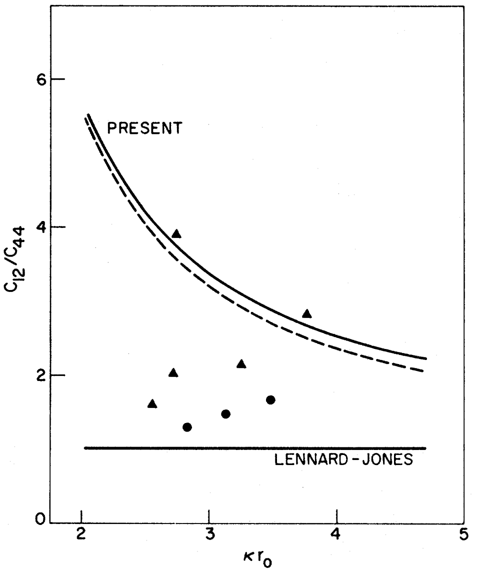

FIG. 2. Cauchy ratio c_{12}/c_{44} plotted as a function of the ratio κr_0 of the radius of the atomic volume to the screening length. The solid curve is for the face-centered-cubic structure, the broken curve for the body-centered-cubic structure. Experimental points are from Table II, with triangles for the face-centered-cubic structure and solid dots for the body-centered-cubic structure. The solid line $c_{12}/c_{44}=1$ is for a Lennard-Jones type potential for which the structure is stable under the interionic interactions alone.

which the value of the core radius cancels out. The calculated results obtained in Secs. II B – II E did not entail any adjustment of the core radii; they are from first principles. (The Grüneissen constant actually has a weak dependence upon r_c, but it is unimportant on the scale of the comparison with experiment.)

B. Deviations from the Cauchy relations

The lattice-dynamics calculations which give the bulk modulus as described above also give the three independent elastic constants for the cubic structures. Of particular interest are the deviations from the Cauchy relation, $c_{12}=c_{44}$. Every term in the elastic energy is seen from Eq. (4) to be proportional to $\cosh^2\kappa r_c$ and to have no other dependence upon r_c. Thus, the "Cauchy ratio", defined by c_{12}/c_{44}, is directly predictable and is a function only of κd (with d the nearest-neighbor distance) for any structure. It is predicted and compared with experiment for some of the cubic metals in Table II and plotted against κr_0 in Fig. 2. Again there is reasonable accord with experiment, particularly in comparison to a model of two-body central-force interactions alone which yields a universal value of unity. Although we tend to overestimate the magnitude of the deviation, we note that both the direction and structural dependence of the deviation from unity are correctly given.

TABLE II. The Cauchy ratio c_{12}/c_{44} predicted for the cubic metals and compared with observed values.

	κr_0	c_{12}/c_{44} Predicted	Observed[a]
Cu	2.55	4.07	1.61
Ag	2.71	3.78	2.03
Au	2.71	3.78	3.88
Al	3.24	3.10	2.15
Pb	3.76	2.68	2.84
K	3.48	2.72	1.67
Na	3.12	3.05	1.48
Li	2.83	3.43	1.30

[a] See Ref. 20.

C. Poisson's ratio

Poission's ratio is a second independent elastic parameter which can be predicted and compared with experiment. It is the decrease in the cross-section diameter for a specimen with free lateral surfaces under a uniaxial stress. It is remarkable that this can even be evaluated in our framework, which requires volume-dependent energy and thus, in some sense, surface stresses. However, elasticity theory gives the Poisson ratio in terms of the elastic constants of cubic crystals as

$$\sigma=c_{12}/(c_{11}+c_{12}) . \tag{5}$$

Again the dependence of the energy upon r_c cancels out. The predicted ratios are compared with experiment in Table III. The Poisson ratio is observed to be relatively constant for a given structure, in agreement with our calculation. Agreement with observed values is typically within 30%; as in the Cauchy ratio, we tend to overestimate the relative magnitude of c_{12}.

The prediction of the bulk modulus, the Cauchy ratio, and the Poisson ratio provides three independent tests of the approximate theory. Further independent tests can be obtained from prediction of the volume dependence of the elastic constants. We consider only the volume-dependence of the

TABLE III. The Poisson ratio defined as the ratio of lateral contraction to longitudinal expansion for uniaxial stress. Experimental values are given for comparison.

	σ Predicted	σ Observed[a]		σ Predicted	σ Observed[a]
Cu	0.48	0.36	Al	0.47	0.33
Ag	0.48	0.37	Tl	0.47	0.35
Au	0.48	0.36	Sn	0.46	0.33
Mg	0.47	0.35	Pb	0.46	0.40–0.45
Zn	0.47	0.25	Na	0.49	0.43
			K	0.49	0.44

[a] See Ref. 21.

bulk modulus, which can be related approximately to the thermal expansion.

D. The Coefficient of Thermal Expansion

A Grüneisen constant can be defined in terms of the vibrational frequency ω_K for any vibrational mode of a solid by[10]

$$\gamma_K = -\frac{\Omega}{\omega_K}\frac{d\omega_K}{d\Omega} = -\frac{\partial \ln \omega_k}{\partial \ln \Omega} . \tag{6}$$

ω_K is proportional to the square root of the elastic ridigity against the mode K. The Grüneisen constant does depend upon which mode is considered but we take a value determined in terms of the bulk modulus B as representative,

$$\gamma = -\frac{\Omega}{2B}\frac{dB}{d\Omega} . \tag{7}$$

The coefficient of linear thermal expansion is related to the Grüneisen constant by the formula[10]

$$\alpha = \gamma C_V / 3B\Omega , \tag{8}$$

where C_V is the heat capacity at constant volume. We may thus estimate the Grüneisen constant from the thermal expansion coefficient measured at high temperatures where the heat capacity is $3kT$ per mode.

We calculate the Grüneisen constant by varying the total volume, as opposed to the local variations from which we derived the bulk modulus, and hence the value depends on the core radius through the volume dependence of the screening length in the coefficient $\cosh^2 \kappa r_c$. The Grüneisen constant and the bulk modulus are the two properties we treat that depend on the core radius. For this application, it is appropriate to use core radii obtained from fitting the bulk modulus as in Sec. III A to obtain values for γ; the values obtained with this fitted core radius are listed in Table IV. Using core radii obtained from known pseudopotentials as in Sec. III A results in values from 2% to 9% larger than these. We also list for comparison, experimental values derived from the coefficient of linear expansion as in Eq. (8). Slater[11] derived an expression for γ based on the compressibility and its pressure derivative and subsequently Dugdale and MacDonald[12] have given a necessary correction to that expression. The values in Table IV are obtained from the corrected expression.

E. The vibration spectrum

The entire spectrum of lattice vibrations and density of phonon modes in the simple metals can

TABLE IV. The Grüneisen constant γ, defined by Eq. (7). The observed values are deduced from the linear expansion coefficient at room temperature.

	Predicted	Observed[a]	Slater[b]
Cu	1.19	1.96	1.63
Ag	1.26	2.40	2.2
Au	1.31	2.94	
Mg	1.16	1.48	
Zn	1.08	2.19	
Cd	1.17	2.18	
Al	1.10	2.17	0.94
Tl	1.20	2.21	
Pb	1.23	2.70	
Na	1.19	1.25	1.50
K	1.31	1.34	2.32
Ca	1.27	1.07	
Sn	1.31	4.34	

[a] See Ref. 19.

[b] See Refs. 10, 11, and 12.

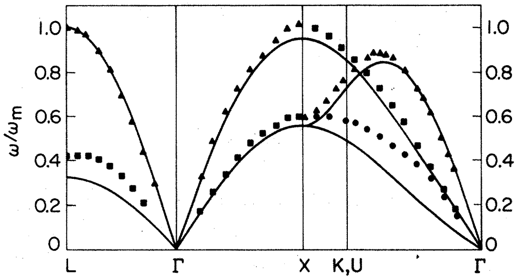

FIG. 3. Phonon spectra in aluminum for wave numbers in the [111], [100], and [110] directions. The frequencies are normalized to the high-frequency mode ω_m at L in the Brillouin zone. Experimental points are from Ref. 22.

be obtained from the same approach that led to the long-wavelength results given above. As in most of the other properties we consider, the coefficient of the effective interaction, which contains the core-radius dependence, sets the scale of the spectrum; its shape is a function only of κd and of structure. In the spectra and densities below, which are for the fcc structure, the phonon frequencies are normalized to the longitudinal mode at L in the Brillouin zone; hence, the results depend only on κd, where d is the nearest-neighbor distance, and structure.

In Fig. 3 the phonon spectra for three symmetry lines in aluminum are given and compared to experimental results. Note that, with the exception of the lower transverse mode, the spectra in the [100] and [110] directions agree, within an overall scale factor, very well with the experimental points; in the [111] direction we again reproduce the shapes of the experimental curves but overestimate the relative scale of the longitudinal and transverse modes.

The density of phonon modes in aluminum was obtained using the Gilat-Raubenheimer scheme with tetrahedral decomposition as carried out by Ren,[13] and plotted as a function of ω/ω_m in Fig. 4, with ω_m the high-frequency mode at L. Comparison with the experimental results indicates that our simple model reproduces the shape of the experimental curve quite well. The shift in position of the Van Hove singularities is apparent from a comparison of Figs. 3 and 4.

With the normalization of the phonon modes to a particular point in the Brillouin zone, the density of states $D(\omega)$ is independent of the core radius. When normalized $D(\omega)$ depends only upon structure and κd. Hence, for a particular structure we obtain a one-parameter family of curves for different metals.

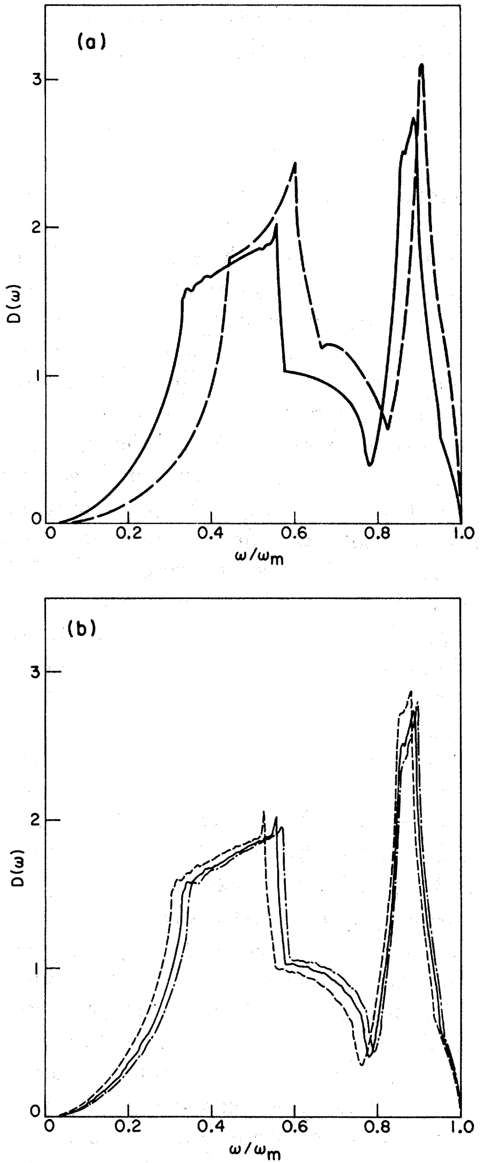

FIG. 4. (a) Density of phonon modes in aluminum as a function of ω/ω_m with ω_m the high-frequency mode at L. The solid line is the prediction of the Thomas-Fermi empty-core model; the dashed line is the experimental density (see Ref. 23). Both curves integrate to 1. (b) The density of phonon modes for copper (dashed line), aluminum (solid line), and lead (broken line) predicted by the Fermi-Thomas empty-core model. Copper ($\kappa d = 4.62$) and lead ($\kappa d = 6.80$) represent the extremes of the face-centered-cubic simple metals, while aluminum ($\kappa d = 5.86$) is midrange. The curves are plotted as a function of ω/ω_m, with ω_m as in (a); each curve integrates to 1.

In Fig. 4(b) we show three curves corresponding to extreme and middle values of κd in the fcc simple metals: $\kappa d = 4.62$ (Cu), $\kappa d = 5.86$ (Al), and

$\kappa=6.80$ (Pb). We find that in this simple model $D(\omega)$ is relatively insensitive to material.

F. Other properties

A number of other applications come immediately to mind, some of which we have explored. First is a comparison of the energies of different crystal structures. Again for the ratios of the energies, the dependence upon r_c cancels out if the comparisons are made at equal density. Then stability depends only upon κr_0 and we found the face-centered-cubic structure stable over most of the range of κr_0 which occurs in the simple metals. This lack of success is not surprising since it seems unlikely that the structure is really determined even by the most accurate second-order pseudopotential theory.[18] Corrections were also made for comparison at constant pressure using the bulk modulus discussed earlier and a change in pressure at constant volume, computed using the interaction given in Eq. (4) but this had only small effects on the results.

The study of defects might be a particularly interesting application. One could, for example, compute the formation energy for a vacancy. The first such analysis in terms of pseudopotential theory was carried out by Harrison[19] for zinc. It was carried out at constant volume by first removing a single ion from the crystal and then decreasing the lattice distance to make room for an additional site for that ion at the surface, conserving the number of ions and the volume. One could then make a correction to obtain the value at constant pressure as suggested above for structure determination. The result, however, is not directly comparable to experiment since in the real crystal there will be local deformations of the lattice. These also could be calculated using our interionic interactions, and that should be done before allowing the volume to relax. This calculation would give the atomic positions, the energy of formation, and the activation volume. It has not yet been undertaken.

We initially thought that simple formulas for the elastic constants derived using only nearest-neighbor interactions could be useful. This turned out not to be the case. Under nearest-neighbor interactions alone, even the face-centered-cubic structure turned out to be unstable under some distortions for small values of κr_0, though the three elastic constants themselves were positive. In the context of our calculation the more distant neighbors are not only quantitatively significant, but are necessary for stability.

IV. SUMMARY

Use of the Fermi-Thomas approximation has eliminated the complexity and slow convergence of the two-body interaction obtained using the Hartree dielectric function. Little in the way of essential physics is lost, though as a first-principles method for calculating bonding properties it is of limited accuracy; it also cannot produce the same accuracy as empirical models with sufficient numbers of adjustable parameters. Its principal virtue is its simplicity, universality, and ease of application. In addition it is a considerable improvement over other two-body interactions such as the Lennard-Jones potential which led to elastic constants satisfying the Cauchy relations. The purely repulsive interaction also gives immediate intuitive conclusions, such as the direction of relaxations of the neighbors to a vacancy, which are not easy to obtain from the more complete theory. With use of the core radii listed in Table I, this approach immediately provides an interaction in terms of which the entire range of elastic properties of simple metals and their alloys may be treated.

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APPENDIX: DETAILED DERIVATION OF INTERACTION

In the pseudopotential theory of metals, the energy of each electronic state is calculated to second order in the pseudopotential,[1]

$$E_k=\frac{\hbar^2k^2}{2m}+\langle\vec{k}\,|\,W\,|\,\vec{k}\rangle+\sum_q{}'\frac{\langle\vec{k}\,|\,W\,|\,\vec{k}+\vec{q}\rangle\langle\vec{k}+\vec{q}\,|\,W\,|\,\vec{k}\rangle}{(\hbar^2/2m)(k^2-|\,\vec{k}+\vec{q}\,|^2)}\,, \tag{A1}$$

where the pseudopotenetial enters in matrix elements between plane waves. The prime indicates the omission of the term $q=0$. This theory can be carried out for a full nonlocal pseudopotential,[1] but the notation is simpler if the pseudopotential is taken as local. We summarize that analysis[2] here. From the argument given in Sec. II it is clear that the form of the result is the same. We write W as a sum of local pseudopotentials $w(\vec{r}-\vec{r}_j)$ centered on the ion positions $\vec{r}_j$. Then the matrix elements become

$$\langle \vec{k}+\vec{q} \mid W \mid \vec{k} \rangle = S(\vec{q}) w_q \ , \tag{A2}$$

with the structure factor a sum over the N_a ions

$$S(\vec{q}) = \frac{1}{N_a} \sum_j e^{-i\vec{q}\cdot\vec{r}_j} \tag{A3}$$

and the form factor

$$w_q = \frac{1}{\Omega_0} \int e^{-i\vec{q}\cdot\vec{r}} w(\vec{r}) d^3r \ . \tag{A4}$$

Ω_0 is the atomic volume Ω/N_a.

In particular $\langle \vec{k} \mid W \mid \vec{k} \rangle$ becomes w_0, independent of the ion positions as long as the total volume Ω and the number of ions N_a remain fixed. Thus, at fixed volume the first two terms of Eq. (A1) are independent of the ion positions. When we sum over occupied states in the evaluation of the total energy, these two terms are incorporated in the volume-dependent "free-electron energy." It can readily be shown[14] that to second order in the pseudopotential this sum over states may be taken as a sum over $k < k_F$ rather than within the true nonspherical Fermi surface. Thus, the leading term from Eq. (A1), which depends upon the ion positions, is

$$\sum = \sum_q{}' S^*(\vec{q}) S(\vec{q}) w_q^2 \times \sum_{k<k_F} (2m/\hbar^2)(k^2 - |\vec{k}+\vec{q}|^2)^{-1} \ . \tag{A5}$$

We have substituted the form for the matrix elements, Eq. (A2), and interchanged the sums over $\vec{q}$ and $\vec{k}$. The sum on k implies a sum over spin as well as over wave number.

The pseudopotential which enters is a screened pseudopotential; that is, for a local pseudopotential, w_q can be written as an unscreened pseudopotential w_q^0 divided by a dielectric constant,

$$\epsilon(q) = 1 - \left[\frac{8\pi e^2}{q^2\Omega}\right] \times \sum_{k<k_F} \left[\frac{2m}{\hbar^2}\right] (k^2 - |\vec{k}+\vec{q}|^2)^{-1} \ . \tag{A6}$$

Note that the sum performed in Eq. (A6) is exactly that appearing in Eq. (A5) so that the sum in Eq. (A5) may be written

$$\sum = \sum_q{}' S^*(\vec{q}) S(\vec{q}) \frac{q^2\Omega(w_q^{0^2})[1-\epsilon(q)]}{8\pi e^2 \epsilon(q)^2} \ . \tag{A7}$$

Obtaining the total energy to this order requires two more steps. First we must substract electron-electron interactions which are counted twice in the one-electron approximation used here. One effect of this is to replace the $\epsilon(q)^2$ in the denominator of Eq. (A7) by $\epsilon(q)$; then $\sum$ becomes the "band-structure energy" E_{bs}. Second, we must add the interactions between ions. For atoms with Z_i valence electrons per atom, this energy is

$$E_{es} = \tfrac{1}{2} \sum_{i,j}{}' Z_i Z_j e^2 \Big/ |\vec{r}_i - \vec{r}_j| \ . \tag{A8}$$

It was first noted by Cohen[6] that the sum of electronic energies, Eq. (A7), can also be written as a similar sum over indirect interionic interactions. We write out the structure factors in Eq. (A7),

$$S^*(q)S(q) = N_a^{-2} \sum_{i,j} e^{i\vec{q}\cdot(\vec{r}_i - \vec{r}_j)} \ . \tag{A9}$$

We interchange the sum over q with those over i and j to obtain

$$N_a E_{\text{bs}} = \tfrac{1}{2} \sum_{i,j}{}' V_{\text{ind}}(\vec{r}_i - \vec{r}_j) + \sum_q{}' \frac{\Omega_0 q^2 (w_q^0)^2}{8\pi e^2} \left[\frac{1-\epsilon(q)}{\epsilon(q)}\right] . \tag{A10}$$

The first sum contains only the terms with $i \neq j$. In that sum

$$V_{\text{ind}}(\vec{r}) = \frac{1}{N_a} \sum_q{}' \frac{\Omega_0 q^2 (w_q^0)^2 [1-\epsilon(q)] e^{-i\vec{q}\cdot\vec{r}}}{4\pi e^2 \epsilon(q)} \ . \tag{A11}$$

The second sum in Eq. (A10) comes from the terms with $i=j$ and does not depend upon the detailed structure. We treat the $i \neq j$ sum first.

The sum over q in Eq. (A11) may be replaced by an integral $(\Omega/8\pi^3)\int d^3q$ and performed if w_q^0 is known. The result may be added to Eq. (A8) to give the effective interaction between ions. If all ions are of the same element,

$$V(r) = V_{\text{ind}}(r) + Z^2 e^2 / r \ . \tag{A12}$$

If it is an alloy, Z^2 is replaced by $Z_i Z_j$ and $(w_q^0)^2$ is replaced by the product of the form factors for the two ions in question.

This result is quite familiar. The dielectric constant is ordinarily taken as the Hartree dielectric function[15] and the asymptotic form of Eq. (A12) for large distances varies as $r^{-3}\cos 2k_F r$, with the familiar Friedel oscillations arising from the logarithmic singularity in $\epsilon(q)$ at $q=2k_F$.[15] These oscillations are intimately related to the Kohn anomalies in the vibration spectrum, but they are best treated directly in terms of the wave-number sum of Eq. (A7). Surprisingly, few other properties have turned out to be sensitive to the oscillations. It becomes interesting to consider the very much simpler theory obtained by using the Fermi-Thomas dielectric function,[20] $\epsilon(q)=1+\kappa^2/q^2$, with the Fermi-Thomas screening parameter given in Eq. (3). Then the indirect interaction of Eq. (A11) becomes

$$V_{\text{ind}}(r)=-\frac{\kappa^2\Omega_0^2}{8\pi^3 e^2 r} \times \int_0^\infty dq \frac{q^3(w_q^0)^2 \sin qr}{q^2+\kappa^2} \;. \tag{A13}$$

We have used the spherical symmetry of the problem to write $e^{-i\vec{q}\cdot\vec{r}}$ as $(qr)^{-1}\sin qr$. The integrand is even in q so we may extend the integration from $-\infty$ to ∞ and divide by 2; then $\sin qr$ may be replaced by e^{iqr}/i. Such a form is useful since it allows us to evaluate the integral by closing the contour in the upper half plane. The contribution from the pole at $q=i\kappa$ gives an interaction proportional to $e^{-\kappa r}/r$ and to $(w_q^0)^2$, evaluated in the plane of complex q. To obtain an explicit value for the leading coefficient, it is necessary to have an analytic form for w_q^0. A very convenient one is the Ashcroft empty-core pseudopotential,[17] used extensively in Ref. 2, though similar results can be obtained with the point-ion model.[1] The unscreened empty-core pseudopotential is $-Ze^2/r$ for r greater than the core radius r_c and zero for r less than r_c. The corresponding form factor,

$$w_q^0=-4\pi Ze^2\cos qr_c/(q^2\Omega_0) \;, \tag{A14}$$

may be substituted in Eq. (A13). The integration over the closing contour only goes to zero if $r>2r_c$ but in that case the integration is simple. The contribution from a pole at $q=0$ just cancels the Z^2e^2/r of Eq. (A11) and that at $q=i\kappa$ gives

$$V(r)=\frac{Z^2e^2}{r}\cosh^2\kappa r_c e^{-\kappa r} \;. \tag{A15}$$

If the two ions in question are different, $Z^2\cosh^2\kappa r_c$ becomes, of course, $Z_iZ_j\cosh\kappa r_{c_i} \times\cosh\kappa r_{c_j}$ with κ evaluated for the alloy. This simple result is very plausible. It is also plausible that it only obtains for $r>2r_c$ such that the cores do not overlap.

A similar treatment of the second term on the right-hand side of Eq. (A10) gives the second-order volume-dependent term in the Fermi-Thomas approximation. For the empty-core pseudopotential, we obtain

$$\frac{\Omega}{(2\pi)^3}\int d^3q \frac{\Omega_0 q^2(w_q^0)^2}{8\pi e^2}\left[\frac{1-\epsilon(q)}{\epsilon(q)}\right] = -\tfrac{1}{2}N_a Z^2 e^2\kappa\cosh(\kappa r_c)e^{-\kappa r_c} \;. \tag{A16}$$

In Sec. II of this paper just above Eq. (1) it was noted that terms in the total energy through first order give a fair description of the equilibrium lattice spacing in the simple metals. This could be calculated from the energy as a sum over independent atomic spheres. This implies that the sum of electrostatic and second-order terms in the total energy [Eqs. (A8) and (A10)] should also achieve their minimum near the equilibrium lattice spacing. Minimization of the sum of the contributions in Eqs. (A15) and (A16) shows this to indeed be the case. This minimization contains contributions from the volume-dependence of κ in Eq. (A15). Note that this consistency condition is independent of the consistency condition on the second-order terms alone, discussed at the beginning of Sec. III.

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