

## ARTICLES

## Scaling lengths of elemental metals

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The average interstitial electron densities  $n$  of the elemental alkali, noble, and transition metals were computed as a function of the lattice spacing using a scalar-relativistic total-energy band-structure code. The calculations showed that the average interstitial electron density varied exponentially as  $\exp(-a/L_D)$ , where  $a$  measures the lattice spacing in terms of the equivalent Wigner-Seitz radius. In principle, the value of  $L_D$  could be considered to be a new characteristic length for the metals—a density length scale. However, we found that  $L_D$  is very nearly proportional to the energy length scale  $L_E$  that enters into the definition of the universal bonding energy relations, i.e.,  $L_E \sim 0.85L_D$ . Two consequences of this approximate equality are described. First, the normalized cohesive energy can be usefully approximated by a universal function of the normalized interstitial density. Second, the bulk moduli of the elemental metals can be approximately determined from the Wigner-Seitz radius, the bonding valence, and the density length scale. [S0163-1829(98)04244-1]

The average interstitial electron charge density  $n$  plays a ubiquitous and pivotal role in the theory of the bonding of molecules and solids. The empiricism of chemistry, in particular, emphasizes the “pile up” of the electrons between the ions and assigns a critical role to the bond charge and the valence. In the realm of condensed-matter physics, Miedema<sup>1</sup> has emphasized the average value of the *equilibrium* interstitial charge density  $n_0$  as one of two key inputs to his empirical theory of the energetics of metals and alloys. The same input  $n_0$  is also the key to the theory of ideal metals,<sup>2</sup> a uniform electron gas model that is, in some ways, a quantum extension of Miedema’s ideas. This uniform electron gas model reproduces the trends in the cohesive energy<sup>3</sup> and elastic moduli<sup>4,5</sup> of the transition, noble, and simple metals. Its inputs are  $n_0$  and the specific volume per atom  $\Omega$ , or, equivalently,  $n_0$  and the bonding valence  $Z_B$ , which is defined by

$$Z_B \equiv \Omega n_0. \quad (1)$$

Bonding valences are derived from the heuristic idea that the cohesive energy depends on the number of valence electrons in the region between the ion cores. The bonding valence crudely estimates the number of electrons that participate in the bond by multiplying the density of interstitial electrons by the volume of the atom. In this work, we estimate the average interstitial electron density  $n$  and its equilibrium value  $n_0$  from a density-functional augmented plane wave (APW) band-structure code that uses a “touching” muffin-tin approximation. We define the interstitial electron

density by dividing the number of electrons outside the muffin tin by the volume of the same region. This definition is chosen for computational simplicity. Values of the bonding valence are given in Ref. 5.

In this paper, we consider the bonding energy of single-crystal elemental metals that have been uniformly expanded or compressed with respect to the equilibrium state, which changes both the bonding energy and the interstitial electron density. In particular, we propose a universal scaling relation to relate the changed bonding energy to the changed average interstitial electron density. Previous work<sup>1-5</sup> has established that the *equilibrium* density of electrons at the cell boundary is the single most important parameter in determining the bonding properties of elemental metals. We seek to discover the second most important parameter for the energetics of elemental metals. We hypothesize that that parameter is a new length scale  $L_D$ , which describes the change in density at the cell boundary as the lattice is uniformly expanded. We support our hypothesis by showing that a knowledge of  $L_D$  allows us to predict the bulk moduli of the elemental simple, noble, and transition metals. Further, we will show that  $L_D$ , although obtained from the density, has nearly the same numerical values as a well-known experimental length scale for the bonding energy of metals that derives from the universal bonding energy relations.<sup>6,8</sup> Finally, we use  $L_D$  to simplify the universal bonding energy relations and predict that the normalized cohesive energy is very nearly a universal function of the normalized density at the cell boundary.

In the mid 1980’s Rose and co-workers<sup>6-8</sup> discovered the universal bonding energy relations that relate the bonding

energy of the elemental single-crystal metals to the spatial distance between atoms. These relations state, among other things, that the bonding energy of a metal can be accurately described by a universal function when plotted as a function of the scaled distance between atoms—supposing that the lattice is uniformly expanded or contracted. The scaling parameters are the equilibrium cohesive energy ( $\Delta E$ ) and a length scale ( $L_E$ ). The scaling of the energy is expressed by

$$E(a) = \Delta E E^*(a^*). \quad (2)$$

Here  $\Delta E$  denotes the equilibrium cohesive energy, and  $E^*(a^*)$  is a nearly universal function that can be well approximated by

$$E^*(a^*) = -(1 + a^*)e^{-a^*}. \quad (3)$$

The coordinate  $a^*$  is the scaled Wigner-Seitz radius

$$a^* = (a - a_0)/L_E, \quad (4)$$

where  $a_0$  denotes the radius of the equilibrium Wigner-Seitz sphere, while  $a$  denotes the Wigner-Seitz radius for an arbitrary state of uniform compression. The length scale is defined so that the second derivative of  $E^*$  with respect to  $a^*$  is equal to 1. Consequently,  $L_E$  can be determined from experimental measurement via

$$L_E = \sqrt{\Delta E / 12\pi a_0 B}. \quad (5)$$

That is,  $L_E$  can be calculated given the experimentally measured cohesive energy, the bulk modulus  $B$  and the Wigner-Seitz radius (or, equivalently, the volume per atom  $\Omega$ ).  $L_E$  was calculated in this way for a variety of elements and is tabulated in Ref. 7.

A heuristic and semiquantitative theory of the energetics of metals under uniform compression, including the equation of state, would follow from Eqs. (2)–(5)—if reliable estimates could be made for  $\Delta E$ ,  $\Omega$ , and  $B$ . Qualitatively useful estimates for  $\Delta E$  and  $\Omega$  are available. In this paper, we provide a means of estimating the bulk modulus. These estimates for  $\Delta E$ ,  $\Omega$ , and  $B$  provide a heuristic model for the energetics of metals that appears to be suitable for pedagogy.

The cohesive energy can be estimated from the theory of ideal metals, given  $n_0$  and  $Z_B$ .<sup>3</sup> However, this estimate requires the solution of the Kohn-Sham equations for electrons bound to a small sphere of uniform positive background. Fortunately, the same analysis leads to an empirical fit to the experimental cohesive energies of the transition and noble metals in terms of the bonding valence that was given in Ref. 9

$$\Delta E = 2.45Z_B - 3.47 \text{ eV}. \quad (6)$$

The equilibrium volume per atom can be roughly estimated as follows, after assuming that  $n_0$  and the electronic charge cloud of the isolated atoms are known. One “freezes” the charge density for the isolated atom and estimates the density by overlapping the electronic densities of these “frozen” atoms. The correct volume per atom is chosen to be the one that yields the known interstitial density.

Next, we provide a means of estimating the bulk modulus. In this paper, we bring together the lines of development based on (1) the theory of ideal metals, which focuses on the

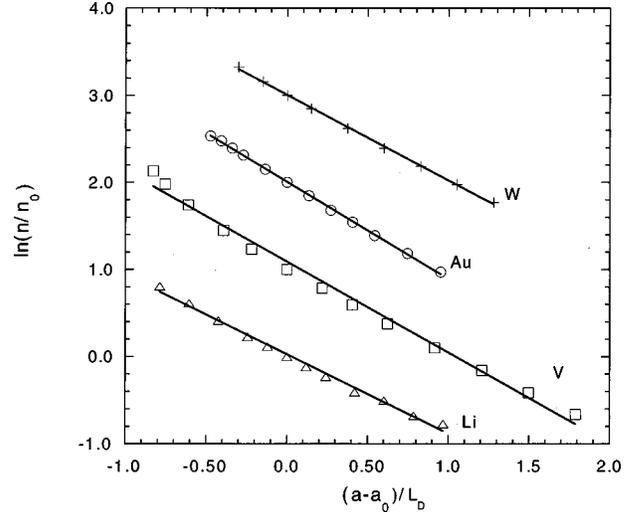


FIG. 1.  $\ln(n/n_0)$  is plotted vs  $(a - a_0)/L_D$  for Li, V, Au, and W (triangles, squares, circles, and crosses, respectively). In order to distinguish the curves we have added one to  $\ln(n/n_0)$  for V, two to the value for Au and 3 to the value for W.

interstitial electron density, and (2) the universal bonding energy relations. The result is a semiempirical formula for the bulk modulus that can, in principle, be entirely determined from the behavior of the interstitial electron density. This completes the task of estimating  $\Delta E$ ,  $\Omega$ , and  $B$ —the inputs to the universal bonding energy relations—from the observed electron density and the properties of the isolated atoms.

Below, we first briefly describe the computational method and show the results of the calculations. Second, we show that the calculated interstitial electron density can be fit to an exponential. Third, we define the density length scale  $L_D$ . Fourth, we show that the normalized cohesive energy is approximately a universal functional of the normalized interstitial electron density. Fifth, we give a semiempirical formula for the bulk modulus of the metals in terms of  $L_D$ ,  $\Omega$ , and  $Z_B$ .

The energies and densities of the alkali, noble, and transition metals were calculated using the scalar-relativistic APW method within the muffin-tin approximation.<sup>10–12</sup> The radius of the muffin-tin sphere was chosen to be half the nearest-neighbor distance (touching spheres). bcc, fcc, and hcp close-packed structures with lattice constants near equilibrium were computed. Details can be found in Refs. 10–12. The outputs from these calculations were the number of interstitial electrons and the total energy as a function of lattice spacing. The average interstitial electron density was found by dividing the number of electrons outside the muffin-tin by the volume of the same region.

The computed value of  $n$  was plotted as a function of the lattice spacing. We find that  $n$  can be fit by an exponential for all the metals considered and for a wide range of lattice constants about the equilibrium value. That is,

$$n = n_0 e^{-(a - a_0)L_D}, \quad (7)$$

which defines  $L_D$ . Figure 1 shows the natural logarithm of  $n/n_0$  plotted versus scaled lattice spacing,  $(a - a_0)/L_E$ , for Li, V, and W, calculated for a bcc lattice, and for Au, calcu-

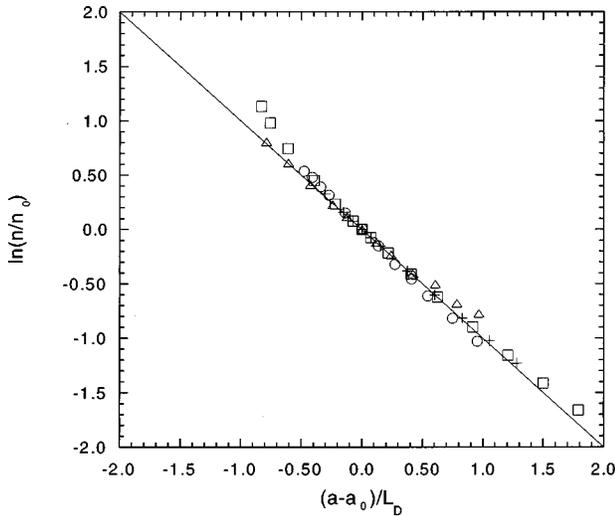


FIG. 2.  $\ln(n/n_0)$  is plotted vs  $(a-a_0)/L_D$  for Li, V, Au, and W. If the scaled calculations were perfectly exponential they would fall on a single line of slope minus 1.

lated for an fcc lattice (for clarity, we added 1 to the  $y$  value for V, 2 for W, and 3 for Au). The results can be fit to a line for each element—which supports the utility of the exponential ansatz given by Eq. (7). Figure 2 shows all of the curves plotted together and confirms the exponential nature of the density falloff. The calculation for gold differs from the line by the largest amount, but is still within 4% of it. It is worth pointing out that the ansatz of an exponential falloff of the interstitial electron density is valid for alkali, transition, and noble metals considered for a range of lattice constants for both bcc and fcc structures.

In principle,  $L_D$  might be taken to be a new length scale for metals—used to describe the variation of the density with the separation of the atoms and thus related to the screening length. However, Fig. 3 plots the values of  $L_D$  taken from our calculations and compares them to the energy length scale  $L_E$  taken from the universal bonding energy relations, Ref. 8. One sees that  $L_D$  and  $L_E$  are nearly the same aside from a constant of proportionality of order 1. That is,

$$L_E \approx 0.85L_D. \quad (8)$$

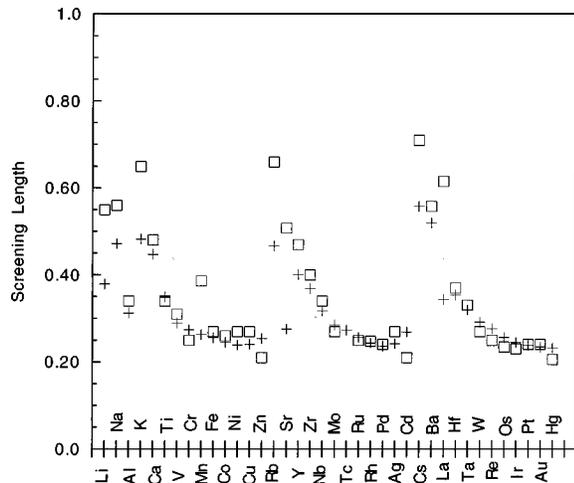


FIG. 3. The energy length scale  $L_E$  (squares) is compared with  $0.85L_D$  (crosses) for alkali, transition, and noble metals.

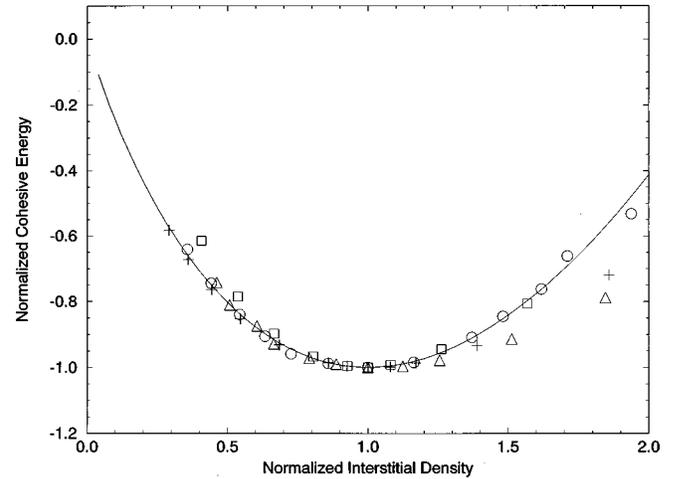


FIG. 4. The normalized cohesive energy,  $E/\Delta E$  is plotted vs the normalized electron density  $n/n_0$  for Li (squares), V (circles), and Au (triangles). The solid line corresponds to Eq. (11).

The largest disagreements are for the alkali metals. The best agreement is for the transition metals. This is consistent with the fact that the local-density-approximation error in the determination of the equilibrium lattice constant is very small for the transition metals and larger for the alkalis. Equation (8) is one of our most important results and has some interesting consequences that we discuss next.

Up to the present, the universal features of the scaled bonding energy have been investigated as a function of the separation. Here, we will show that the scaled bonding energy can be approximated by a universal function of the normalized average interstitial density  $n/n_0$ . On the one hand, the universal scaling function for the energy is  $E^* = (1 + a^*)\exp(-a^*)$ , where  $a^*$  is the scaled separation coordinate. On the other hand, Eqs. (4) and (7) imply that the density behaves as  $n = n_0 \exp(-a^*L_D/L_E)$ . Upon eliminating  $a^*$  from these equations

$$E^* \approx -y(1 - \ln(y)), \quad (9)$$

where  $y$  is defined by

$$y = (n/n_0)^{L_D/L_E}. \quad (10)$$

The content of Eq. (9) is that the scaled energy can be approximated by a universal function of  $y$ , which depends on the normalized density and the ratio  $L_D/L_E$ . One can go a little further by using Eq. (8) to approximate  $L_D/L_E$  and thus find  $E^*$ ,

$$E^* \approx -(n/n_0)^{1.18} [1 - 1.18 \ln(n/n_0)]. \quad (11)$$

Equation (11) implies that the scaled energy depends only on the scaled interstitial density  $n/n_0$ .

Figure 4 shows the scaled energy versus the scaled interstitial density of Li, V, Au, and W. All the results follow the formula given in Eq. (11) (solid line in Fig. 4) for scaled densities less than 1.5. For even higher densities there are important discrepancies. These discrepancies may be due to the idealization of the core states as atomically sharp levels in our calculations, since for sufficient compression the core levels develop significant linewidths and must be treated on a

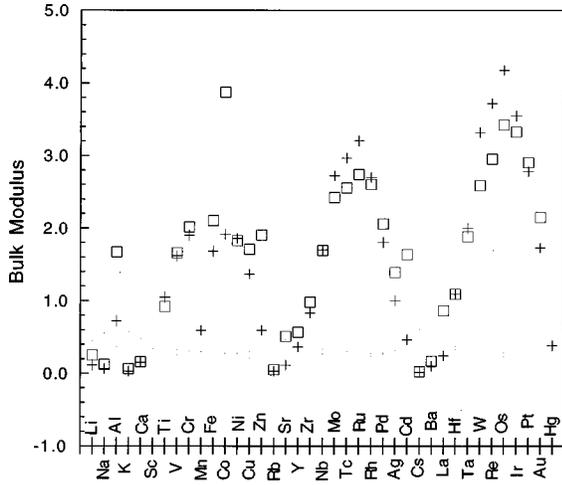


FIG. 5. The semiempirical formula (squares) for the bulk modulus, Eq. (12), is compared with experimental values (crosses) for the alkali, transition, and noble metals.

par with the valence electrons. However, the discrepancies may also represent a limit on the universal behavior of metals. Hopefully, more sophisticated calculations will clarify the origin of these discrepancies and further test the utility of Eq. (11) at high densities.

Next, we test the hypothesis that the bulk modulus is determined by the behavior of the average equilibrium interstitial density. We expect that the bulk modulus will depend strongly on the density scaling length via Eq. (8), since  $B$  is directly related to the energy length scale via Eq. (5). Combining Eqs. (5), (6), and (8) yields a semiempirical formula for the bulk modulus,

$$B \approx \frac{5.30Z_B - 7.50}{12\pi a_0 L_D^2} 10^{-12} \text{ erg/cm}^3. \quad (12)$$

Figure 5 plots  $B$  as estimated from Eq. (12), for most of the noble and transition metals, and compares the estimates with experiment. We see that, with a few exceptions, the bulk modulus can be estimated from the equilibrium interstitial density and its change under compression.

Two parenthetical remarks are in order. First, the utility of the bonding valence for describing the energies of metals is confirmed, since  $Z_B$  plays a key role in the successful de-

scription of the bulk modulus. Second, solids will burst if subjected to a large uniform expansive force. Imagine expanding a crystal uniformly. For small expansions the change in cohesive energy results in a restoring force that is linear with expansion. For somewhat larger expansions the force continues to increase but more slowly. At some expansion, the restoring force reaches a maximum and then declines for further expansion. If the external force is greater than this maximum restoring force, the crystal will burst. The universal bonding energy relations give the cohesive energy and consequently the restoring force as a function of lattice expansion. A simple calculation (see Ref. 7) based on the universal bonding energy relations predicts that the brittle fracture limit for a single crystal occurs at  $a^* = 1$ . Combining this fact with Eqs. (7) and (8) leads to the following prediction. Perfect crystals of the alkali, noble, and transition metals can be expected to burst when the interstitial electron density has been reduced to  $\approx 40\%$  of its equilibrium value.

In conclusion, we have calculated the average interstitial electron density  $n(a)$  as a function of the lattice spacing for the alkali, noble, and transition metals using a first-principles, density-functional code. We found that the interstitial densities varied approximately as  $\exp[-(a-a_0)/L_D]$  for all the metals considered. This led us to the conclusion that  $L_D$  is an important length scale for metals. We combined these results with the universal bonding energy relations and found that  $L_D \propto L_E$ , with a constant of proportionality nearly equal to one. This implies a connection between the universal bonding energy relations and the theory of ideal metals. This connection resulted in two discoveries. First, the scaled energy is nearly a universal function of the normalized interstitial density. Second, the bulk modulus of the metals can be predicted from the  $L_D$ ,  $\Omega$ , and  $Z_B$ . We opened this paper with the question:—What other features of the interstitial charge density will be useful in describing the energetics of metals? Our conclusion is that the density length scale, which characterizes the exponential falloff of the interstitial electron density with expansion or compression, will be proven useful for understanding the energies of metals.

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