Theory of Ideal Metals

Herbert B. Shore
Department of Physics, San Diego State University, San Diego, California 92182

James H. Rose
Ames Laboratory, Iowa State University, Ames, Iowa 50011

(Received 20 September 1990)

An improved electron-gas model is proposed; it predicts the trends in the chemical potentials, cohesive energies, surface energies, and work functions of the simple metals. The uniform electron gas is altered so that it is in mechanical equilibrium at the electron density characteristic of a given metal. This leads to a new rule for splitting the constant background charge when jellium is cleaved. The trends in the energetics of metals result.

PACS numbers: 71.10.+x, 71.45.Nt

Many important problems in metal physics require a simple starting point, such as the electron-gas model, in order to be computationally tractable. Examples include the computation of (1) the vibrational spectra of adsorbed gas atoms or (2) the electronic excitation spectra at bare metal surfaces (e.g., multimode plasmons). The tunneling of electrons (e.g., in scanning tunneling microscopy) is another such problem, as is the computation of the adhesive force between metal half spaces. The new version of the electron gas presented in this Letter is expected to substantially improve all these calculations without introducing additional computational complexity. It retains the simplicity of jellium while modeling the electron energy levels with respect to vacuum more realistically.

A substantially improved version of the electron gas is presented. As with the present jellium model, the only input parameter is the average electron density. Jellium qualitatively predicts the electronic excitations of metals (e.g., the particle-hole and plasmon energy spectra). However, jellium fails qualitatively if it is used to predict metallic bonding. This failure will be shown to arise because jellium is not in mechanical equilibrium. A new model of the electron gas (the ideal metal) is proposed. This model is as simple as jellium for most purposes (e.g., calculating electronic excitations). Further, it is constructed to satisfy the condition of mechanical equilibrium. The ideal metal allows one to model simultaneously the qualitative features of the electronic excitation spectra and the bonding property of metals. In this Letter, we will focus on showing that the ideal metal explains the bonding energetics of simple metals.

Jellium fails qualitatively in predicting the bonding of metals. For example, it predicts negative surface energies for $r_s < 2$ (where $4\pi r_s^3/3 = 1/n$, and n is the electron density). This pathology arises since the uniform electron gas is under external pressure. The electrons have their minimum energy at $r_s \sim 4$. At other densities the positive background, which is kept rigid by external forces, imposes a pressure on the electrons to keep them at the specified r_s. Nonphysical external forces are particularly problematic for bonding (e.g., surface) energies, which are integrals of the force with respect to separation.

Utreras-Diaz and Shore[1] have included the effects of the ion core in a uniform electron-gas model by modifying the interaction of the electrons and the positive background. They model the additional electron-ion interaction (not accounted for by jellium) by adding an electron potential that is a constant inside pseudojellium and zero outside. As in the present work, this additional potential can be thought of as incorporating the electron-ion interaction via a pseudopotential that is constant inside the unit cell and zero outside. Pseudojellium requires an adjustable parameter (fixed by the chemical potential) and gives reasonably good agreement for the surface properties and cohesive energies of the simple metals. However, external forces are still required to maintain equilibrium. The work presented in the present Letter is the result of understanding how these external forces may be removed. This understanding allows us to predict the extra electron-ion interaction in an average way, and thus to fix the additional potential. In contrast to pseudojellium, *no parameters beyond the average electron density are introduced.* Since the work presented in this Letter has been completed, Perdew, Tran, and Smith[2] have presented results that are similar in many ways. Their work started from an attempt to extend the pseudopotential point of view.

Below, we first introduce a new prescription for the energetics of the electron gas. The major change is a new rule for cleaving the electron gas; the need for external forces is removed. This prescription ensures that the *uniform* electron gas is in mechanical equilibrium at any specified electron density. We call our approach *the theory of the ideal metal,* in analogy with ideal-gas theory. In this Letter we focus on showing that the theory of ideal metals can explain metallic bonding qualitatively. One immediate consequence of the model is an analytical prediction for the chemical potential of metals, which we show is in good agreement with experiment. We show that the theory of ideal metals accurately predicts the trends in the cohesive energies, the surface energies, and the work functions of the simple metals.

A consistent picture for the cleavage of the ideal metal into pieces should satisfy the following conditions: (1) It should be possible to reassemble the pieces to yield the uniform electron gas; (2) the reassembled uniform system should be in mechanical equilibrium; and (3) only Coulomb interactions should be introduced in the model (that is, arbitrary external forces should not be invoked to explain the interactions between pieces of the background). These conditions can be satisfied in the following way. Imagine that the background (which has density n_0 in the equilibrium state) has been split into pieces. For each piece the positive charge density is chosen to be uniform and to have a value n_0 within the boundaries of the piece and zero outside. In addition, we require a *δ-function dipole barrier* at the surface of the piece of the background density. This surface dipole barrier is chosen to have the same value for all pieces and for all points on their surfaces.

The effect of the dipole barrier can be seen by considering the interaction of a single electron with one particular piece of background that is otherwise isolated in free space. The electron potential is given by

$$V_e(\mathbf{r}) = n_0 \int d^3r' \frac{\gamma(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} + V_0 \gamma(\mathbf{r}) . \tag{1}$$

Here, $\gamma(\mathbf{r})$ is the characteristic function, defined to be one within the piece and zero outside. The first term on the right-hand side represents the electron's interaction with the charge interior to the piece. The second term represents the extra electron-ion interaction, since the effect of the dipole barrier is to cause the electron to see an additional constant potential V_0 inside the piece and zero additional potential outside the piece.

Now imagine reassembling the system. When the pieces of background are brought into contact, their dipole barriers cancel and one is left with the background of the uniform electron gas. The effect of the dipole barriers on the dynamics of the electrons can be simply described. It causes the electrons to experience a constant added potential V_0 when they are inside the positive background and zero added potential when they are outside. As shown below, the value of the dipole barrier can be chosen, i.e., V_0 can be chosen, so that the reassembled system is in mechanical equilibrium for the uniform state.

We now imagine that we have many pieces of the positive background. The question arises: How do these pieces interact when they overlap? The positive background charges of the overlapped pieces add linearly, as do the potentials. Thus if the local positive background density is $2n_0$, then the additional local potential is $2V_0$.

The following example illustrates the rule, gives an idea of its origin, and sets the stage for the numerical results that follow. Consider cleaving the ideal metal into two half spaces of positive background, and separating the two pieces along a line that is normal to the half-space surface. In this case, the additional electron potential (by the definition just given) is V_0 inside the charged half spaces, but zero between them. The two half spaces may, also, be overlapped. In this case, the potential is equal to twice V_0 in the overlap region and V_0 elsewhere.

The additional potential clearly changes the force between the two half spaces. We *choose the value of the potential so that the force is zero when the separation is zero.* That is, the ideal metal is in mechanical equilibrium for the specified r_s. In the present example, this is the same as requiring that there be zero forces between the half spaces when they are aligned and have zero separation.

The fact that there is one value of V_0 that allows one to split the uniform metal into arbitrary pieces and to maintain mechanical stability may be somewhat surprising. Here, we analyze the stability of the ideal metal by dividing it into an arbitrary number of pieces and then shifting these pieces infinitesimally with respect to each other. The change in energy can be computed up to second order in perturbation theory given the linear-response function of the electron gas. The energy can be written as

$$\delta E = E_1 + E_2 , \tag{2}$$

where E_1 and E_2 denote the first- and second-order energies, respectively. However, the mechanical stability of the system only requires that the first-order term in the energy be zero. First-order perturbation theory evaluates the change in the energy due to the change in the potential while the electron density is kept uniform. We consider two states: (1) the uniform state at the equilibrium density and (2) the state with the background and potentials overlapped but with a constant electron density at the new average electron density $\bar{n}$. E_1 is the difference in energy between these two states and is given explicitly by

$$E_1 = N[e_{\text{jell}}(\bar{n}) - e_{\text{jell}}(n_0) + V_0(\bar{n} - n_0)/n_0] . \tag{3}$$

Here, n_0 is the average electron density at equilibrium while $\bar{n}$ is the average electron density after the various pieces are shifted. Finally, the energy per electron in the standard uniform electron gas is denoted by $e_{\text{jell}}(n)$.

Mechanical stability is obtained by requiring that E_1 be zero for infinitesimal shifts in the positions of the background pieces. Upon expanding $e_{\text{jell}}(\bar{n})$ about the equilibrium density and setting $E_1 = 0$, we find

$$V_0 = -n_0 (\partial e_{\text{jell}}/\partial n)_{n_0} . \tag{4}$$

Equation (4) establishes the additional potential required to keep the electron gas in mechanical equilibrium at the specified density n_0.

The ideal metal can be used to explain a variety of the bonding properties of metals. We will present results below for the chemical potentials, the cohesive energies, the surface energies, and the work functions of the ideal metal. The result for the chemical potentials is simple and analytic, while the surface energy and work functions were computed numerically. Generally, the results agree in a quantitatively reasonable way for the simple metals. This is much the same situation that one finds when the electron gas is used to explain electron excitations (such as plasmons) in metals.

The chemical potential is the energy required to remove an electron to infinity, neglecting the surface. From Eq. (3), the chemical potential μ_{ideal} of the ideal metal is shifted from the jellium value by V_0, i.e.,

$$\mu_{\text{ideal}} = [\partial n e_{\text{jell}}(n)/\partial n]_{n_0} + V_0 \,. \tag{5}$$

Using Eq. (4) for V_0, we get the remarkably simple result

$$\mu_{\text{ideal}}(n) = e_{\text{jell}}(n) \,. \tag{6}$$

Thus for any r_s, $V_0 = e_{\text{jell}} - \mu_{\text{jell}}$, where μ_{jell} is the chemical potential of the uniform electron gas. Equation (6) has been previously suggested by Hodges[3] based on a Wigner-Seitz model for the cohesion of metals and a gradient expansion of the kinetic energy. Note that for metals with $r_s \approx 4.0$, such as sodium, V_0 is close to zero and the jellium model is itself "ideal."

Figure 1 shows the predicted chemical potentials as given by Eq. (6) for the ideal-metal model. The parametrization of Gunnarson and Lundqvist[4] was used to estimate the exchange-correlation energy here and in the density-functional calculations that follow. Weinert and Watson[5] have estimated the chemical potentials for most of the metallic elements based on a combination of first-principles band-structure calculations, model estimates of the dipole barrier, and experimental evaluations of the work functions. These values are compared with the ideal metal in the figure. As can be seen, Eq. (6) accurately explains the trends in the chemical potentials for the simple metals.

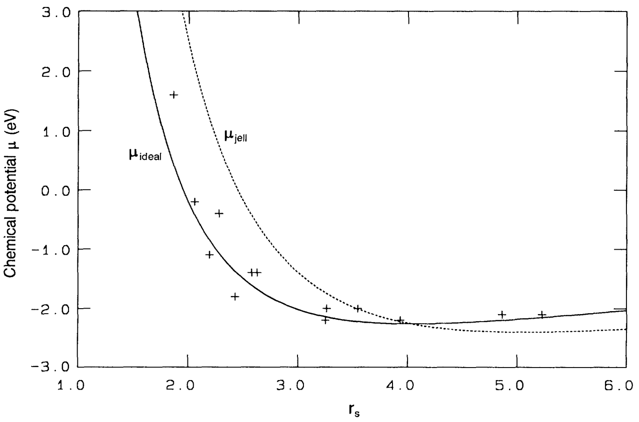

FIG. 1. Chemical potentials predicted for the ideal metal and jellium. The crosses show the estimates of Weinert and Watson. The particular simple metals can be identified by noting the r_s's in Table I.

The cohesive energy is the difference in energy between the metal (the ideal metal in this case) and the isolated neutral atoms. We estimate the binding energy of the atoms, using the theory of ideal metals, in the following simple way. Namely, we cut a ball of positive background charge out of the ideal metal. This ball serves as our model of the atom.[6] The ball's total positive charge corresponds to the nominal valence of the metal; as before, we associate the potential V_0 with the background. We then solved for the energy of electrons in the resulting potential using local-density-functional theory and computed the binding energy of the neutral "atoms." The resulting cohesive energies are shown in Table I. As can be seen, our model allows a good understanding of the trends in the cohesive energies of the simple metals. That is, the size of the cohesive energies of the simple metals can be understood in terms of the uniform electron gas and the condition of mechanical equilibrium.

The surface properties of the ideal metal have, also, been calculated using the local-density approximation (LDA) to density-functional theory. The calculation follows along the lines of the work of Lang and Kohn.[7] We imagine a uniform half space of the ideal metal filling all

TABLE I. The cohesive energies of the simple metals both for experiment and for the ideal metal.

			Cohesive energy per atom (eV)	
Material	Valence	r_s	Calculated	Experiment
Li	1	3.25	1.54	1.65
Na		3.93	1.22	1.13
K		4.86	0.923	0.941
Rb		5.23	0.835	0.858
Cs		5.63	0.754	0.827
Be	2	1.87	1.13	3.33
Mg		2.62	1.23	1.53
Ca		3.26	1.09	1.83
Sr		3.55	1.02	1.70
Ba		3.69	0.989	1.86
Zn	2	2.28	1.26	1.35
Cd		2.57	1.24	1.16
Hg		2.66	1.22	0.694
Al	3	2.06	4.10	3.34
Ga		2.19	3.92	2.78
In		2.43	3.61	2.6
Pb	4	2.30	5.21	2.04

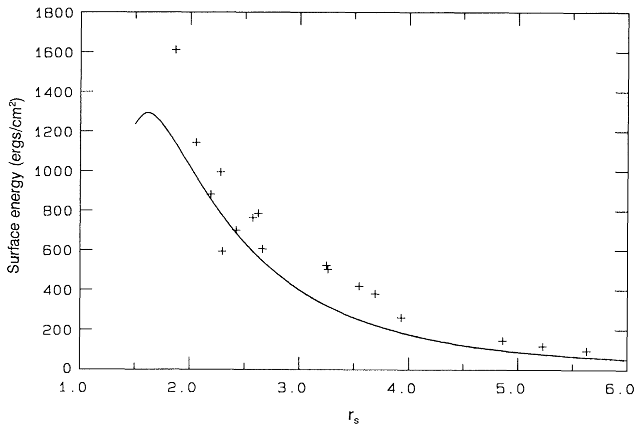

FIG. 2. Surface energies predicted for the ideal metal and compared with the experimental estimates of Tyson and Miller. The particular simple metals can be identified by noting the r_s's in Table I.

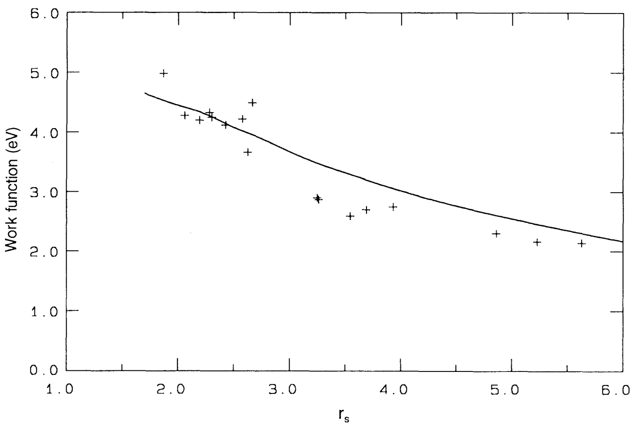

FIG. 3. Work functions predicted for the ideal metal and compared with the experimental values. The particular simple metals can be identified by noting the r_s's in Table I.

space for $z < 0$; the rest of space, $z > 0$, is imagined to be vacuum. The additional potential is chosen to be V_0 in the ideal metal and zero otherwise. A similar calculation was reported in Ref. 1, except that V_0 was fitted to the experimental chemical potential rather than being determined by Eq. (4). (In a different context, Monnier and Perdew have calculated the surface energy by, in part, adding an additional constant potential inside the metal.[8]) The surface energy and work function depend only on r_s in our approximation, and are plotted as the solid lines in Figs. 2 and 3. The general shape of the curve for the surface energy seems physically reasonable for $r_s > 2$. However, the predicted surface energies are systematically too small by about 25%, which is consistent with other density-functional calculations. For $r_s < 2$ the surface energy reaches a maximum of 1300 ergs/cm^2 at $r_s \sim 1.6$. This maximum is an artifact of the model. In fact, the transition metals with $r_s < 2$ have surface energies much greater than 1300 ergs/cm^2.

The ideal-metal model does a rather satisfactory job of predicting the trends in the surface energies of the simple metals. Figure 2 shows the theoretical results and the surface energies of the simple metals as estimated from experiment by Tyson and Miller.[9] The value of r_s is estimated from the nominal valence of a given metal. The agreement between theory and experiment might be considered startling since the only input to the theory is the average valence electron density of the given metal. There is no detailed information of any kind and there is no attempt to model the atomic core at all. The surface energy of a simple metal is determined by the theory of the electron gas, once it has been modified to be in mechanical equilibrium at the density of that metal.

The work functions predicted by the theory of ideal metals is shown by the solid curve in Fig. 3. The work functions of the simple metals are denoted by crosses. As can be seen, the agreement of experiment with the theory is good.

In summary, a simple model has been constructed for the energetics of the simple metals. The only ideas used are those of the electron gas and mechanical equilibrium. The trend for the chemical potential of the metals is given analytically in this simple model and is in good agreement with experiment. Further, the method predicts the cohesive and surface energies of the simple metals, as well as their work functions.

Ames Laboratory is operated for the U.S. DOE by Iowa State University under Contract No. W-7405-ENG-82. This work is supported by the Director, Office of Basic Energy Sciences.

---

[1] C. A. Utreras-Diaz and H. B. Shore, Phys. Rev. Lett. **53**, 2335 (1984).

[2] J. P. Perdew, H. Q. Tran, and E. D. Smith (to be published).

[3] C. H. Hodges, J. Phys. F **4**, 1961 (1974).

[4] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[5] M. Weinert and R. E. Watson, Phys. Rev. B **29**, 3001 (1984).

[6] A. R. Miedema, Phillips Tech. Rev. **38**, 257 (1978/79).

[7] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).

[8] R. Monnier and J. P. Perdew, Phys. Rev. B **17**, 2595 (1978).

[9] W. R. Tyson and W. A. Miller, Surf. Sci. **62**, 267 (1977).