

Pseudojellium Model for Surface Properties of Simple Metals

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(Received 22 June 1984)

A new simple method is presented for calculating properties of nonuniform real metals, i.e., surfaces, vacancies, small clusters, etc. The bulk metal is represented by a jelliumlike homogeneous electron gas with an effective exchange-correlation energy that includes electron-ion correlations. As an example, the method is applied to calculate surface energies. One-dimensional calculations, with no further corrections for the lattice, give results in reasonable agreement with experiment.

PACS numbers: 73.20.Cw, 68.40.+e, 71.10.+x, 71.45.Jp

We wish to present a simple approximate method for studying the properties of nonuniform simple metals. The method is applicable to surface energies and work functions, small clusters, surface steps, vacancies, atoms on surfaces, etc. We will present the method and work out one application by way of example: the surface energy.

As used in this paper, the words *homogeneous* and *uniform* have different meanings. A homogeneous system has electronic and positive background density independent of position; i.e., jellium. A real bulk metal without imperfections is inhomogeneous but uniform, in that an appropriate *average* ionic density, n_i , is constant. The surface, vacancy, etc., result in a nonuniform metal.

The essence of the method is a separation of the nonuniform problem into two steps. Density-functional calculations are first performed for the total energy of the *uniform* bulk metal. One then extracts from the results an effective "exchange-correlation" energy. From this point, the positions and character of the ionic cores are no longer needed; the bulk will henceforth be replaced by a jelliumlike homogeneous background, but with exchange-correlation energy modified by the results of the (in principle exact) calculations of the bulk.

The result of step one is the production of a "pseudojellium" model with homogeneous positive background, but with cohesive energy, bulk modulus, and most importantly, internal chemical potential, given by the actual bulk values.¹ In step two the calculation of the nonuniform system, e.g., surface, vacancy, etc., is performed; this step is greatly simplified by use of the pseudojellium model to represent the bulk.

This approach is conceptually similar to the effective-mass theory for shallow impurities in sem-

iconductors, where the details of the lattice can be processed into two relevant quantities, the effective mass and the dielectric constant. In the present case, however, we cannot offer a rigorous justification for the accuracy of the method, since a comparison of the relevant length scales, the size of a unit cell as compared to the electron density decay length (e.g., surface width), does not yield a small parameter.

We begin the derivation of the model by defining n_e and n_i as the average electronic and ionic densities of the uniform bulk metal. In terms of these parameters, the volume of a unit cell is $\Omega = 1/n_i$. The total number of electrons in one cell is Ωn_e , distributed within the cell with density $n(r)$. The average charge density ρ is given by $\rho = n_i Z - n_e$, where Z is the valence. In the interior of the bulk metal, electrical neutrality requires that $\rho = 0$; however, for our purposes we will regard n_e and n_i as independent variables. The energy per unit volume $\epsilon(n_e, n_i)$ and the density profile within the unit cell $n(r)$ can then be calculated as a function of n_e and n_i with use of standard methods.^{2,3} For $\rho \neq 0$, a technical difficulty arises: ϵ becomes infinite as a result of the long-range interaction between non-neutral unit cells. The appropriate correction is to subtract off the intercell electrostatic energy of a homogeneous charge distribution of density ρ , producing an $\epsilon(n_e, n_i)$ that is finite and unique for all n_e, n_i .

The pseudojellium model is now introduced by considering the exact $\epsilon(n_e, n_i)$ to be broken up into three components:

$$\begin{aligned} \epsilon(n_e, n_i) \\ = n_e t_s(n_e) + U(n_e, n_i) + \epsilon'_{xc}(n_e, n_i). \end{aligned} \quad (1)$$

Here $n_e t_s(n_e)$ is the kinetic energy density of a

noninteracting electron gas,

$$t_s(n_e) = \frac{3}{10} (3\pi^2 n_e)^{2/3}, \quad (2)$$

and $U(n_e, n_i)$ is the intracell electrostatic energy of a uniform electron gas of density ρ . The exact expression for U depends slightly on the shape of the unit cell, but is given with good accuracy by the spherical cell value:

$$U(n_e, n_i) = (4\pi/5) R_W^2 \rho^2, \quad (3)$$

where $R_W = Z^{1/3} r_s$ is the Wigner sphere radius. Subtracting these jellium kinetic and Coulomb energies from the total energy of the real metal defines ϵ'_{xc} , the "exchange-correlation" energy density in the pseudojellium model. The difference in exchange-correlation energies between pseudojellium and jellium is then

$$\Delta\epsilon_{xc}(n_e, n_i) = \epsilon'_{xc}(n_e, n_i) - \epsilon_{xc}(n_e). \quad (4)$$

In applying the model to a nonuniform system such as a surface, the simplest approach assumes that $n_i = 0$ outside the metal and jumps discontinuously to $n_i = \bar{n}_i$, the bulk density at the surface. Then $\Delta\epsilon_{xc} = 0$ in the vacuum. Inside the metal, it is very useful¹ to express the n_e dependence of $\Delta\epsilon_{xc}$ to first order in ρ as

$$\Delta\epsilon_{xc}(n_e, \bar{n}_i) = \Delta\epsilon_{xc}(\bar{n}_e, \bar{n}_i) + \Delta\bar{\mu}(n_e - Z\bar{n}_i) + O(\rho^2). \quad (5)$$

This is our major result. Here $\Delta\bar{\mu} = \bar{\mu} - \bar{\mu}_j$ is the difference in internal chemical potential for the actual metal and for jellium.

In the nonuniform system, n_e varies with position. The electron effective potential $V_{\text{eff}}(\vec{r})$ is altered by $\Delta\epsilon_{xc}$. If we keep only terms to order ρ in $\Delta\epsilon_{xc}$, $\Delta V_{\text{eff}} = \partial\Delta\epsilon_{xc}/\partial n_e$ is simply the constant value $\Delta\bar{\mu}$ inside the metal and 0 outside. Thus, V_{eff} has a discontinuous step of amplitude $\Delta\bar{\mu}$ at the surface

of the metal. The zeroth-order term $\Delta\epsilon_{xc}(\bar{n}_e, \bar{n}_i)$ gives a constant correction independent of local electron density. While ensuring that the bulk has the correct cohesive energy, this term does not alter V_{eff} or the surface energy.

To use the method, we need to obtain values of ϵ'_{xc} and $\bar{\mu}$ for real metals. To do this as simply as possible, we performed a variational extended Thomas-Fermi calculation to obtain $\epsilon(n_e, n_i)$ and $n(r)$ in a spherical unit cell, with the electron-ion interaction represented by the Ashcroft-Langreth pseudopotential.⁴ Recently, Wienert and Watson⁵ have obtained values of $\bar{\mu}$ that are probably more accurate than ours, since they use the self-consistent values of the Fermi energy of Moruzzi, Janek, and Williams² and shift these by a correction to the muffin-tin zero. In Table I, we list values of $\bar{\mu}$ calculated by several workers. Also listed are the jellium values, using the Wigner interpolation expression for the jellium ϵ_{xc} . Our values are in remarkable agreement with those of Ref. 5 for the high-density metals, and are about 0.6 eV more negative for the low-density cases. From Table I, it can be seen that the correction $\Delta\bar{\mu}$ is quite small for the dilute alkali metals and is large and negative for the multivalent metals.

We turn now to the surface energy of real metals. It is worthwhile to recall the results for uncorrected jellium, as calculated by Lang and Kohn.^{7,8} For the dilute alkali metals the surface energies are in reasonable agreement with experiment; but for the high-density multivalent metals, the jellium calculation fails completely, giving a negative surface energy.

To correct for this deficiency of the jellium model, Lang and Kohn include the effect of the ionic lattice by adding two terms to the surface energy: a classical cleavage term, representing the change in lattice electrostatic energy, and a term

TABLE I. Calculated values of the internal chemical potential $\bar{\mu}$ (in electronvolts).

Metals	r_s	Jellium	WW ^a	HH ^b	This Work
Al	2.07	2.37	-0.2	-0.8	-0.20
Pb	2.30	0.97	...	-3.7	-0.28
Zn	2.30	0.97	-0.4	-1.4	-0.34
Mg	2.65	-0.38	-1.4	-1.7	-1.68
Li	3.28	-1.59	-2.2	-1.9	-2.66
Na	3.99	-2.15	-2.2	-2.0	-2.73
K	4.96	-2.37	-2.1	-2.2	-2.80
Rb	5.23	-2.39	-2.1	-2.1	-2.67

^aWienert and Watson, Ref. 5.

^bHeine and Hodges, Ref. 6.

describing the first-order perturbation energy of the electron-ion interaction. Inclusion of these terms results in positive surface energies; however, a new problem arises. As shown by Monnier and Perdew,⁹ the first-order results display a much larger *face dependence* in surface energies and work functions than is observed experimentally. Rose and Dobson¹⁰ included the effect of the ionic cores by using an approximate linear response method, thus allowing the electron density to relax to second order around the cores. They found two interesting results: First, the second-order contribution to the cleavage energy almost cancels the first-order term. Second, the surface energy becomes only weakly face dependent.

We now seek to interpret the above results in a way that motivates the pseudojellium surface calculation. High-density jellium has $\bar{\mu} > 0$; therefore electrons try to spill out, leading to a negative surface energy. The ions must be included, to provide the additional cohesion required to hold a high-density metal together. However, there is a much smaller dependence of surface properties on the specific *location* of the fully screened ions than is obtained from first-order perturbation theory. In particular, the three-dimensional screened charged density has very small electric fields extending beyond the surface, leading to a greatly reduced cleavage energy.

In the pseudojellium approach, the screening of the cores is in principle done exactly, as part of the bulk energy calculation. However, in going over to a one-dimensional model for the surface, the cleavage energy becomes zero and there is no face dependence. The above discussion suggests that this liquidlike picture of the surface may be more realistic than the first-order (i.e., unscreened) inclusion of the lattice.

The numerical procedure for the calculation of the surface electronic density is quite similar to that of Monnier and Perdew⁹ and Monnier *et al.*,¹¹ in that there is a step in the effective potential at the surface. In the present case, however, the step is a direct consequence of the energy functional Eq. (5); the calculated density exactly minimizes our energy functional and is therefore fully self-consistent. We use Eq. (5) for the correction to ϵ_{xc} inside the metal, with our values for $\Delta\bar{\mu}$.

The results for the surface energies are shown in Table II. The quoted experimental values are the "recommended" values of Miedema.¹² The surface energies are positive in all cases, and compare favorably with experimental values and with the first-order-perturbation-corrected values of Lang and Kohn.⁷ In Fig. 1 we show the total effective potential V_{eff} and the electrostatic contribution ϕ to V_{eff} in both the jellium and pseudojellium models, for Al ($r_s = 2.07$). The key points are the step in V_{eff} and the reduced dipole layer $\Delta\phi$ for the pseudojellium case. The work function Φ is also shown in Fig. 1. The increase of 0.5 eV in Φ over the jellium value brings our calculated pseudojellium value (4.36 eV) into very close agreement with the experiment. Additional results for work functions will be reported elsewhere.

Concluding the discussion of the surface energy calculation, we see that by including the pseudojellium correction $\Delta\epsilon_{xc}$, one obtains good results for surface energies and work functions from a purely one-dimensional calculation, with no further correction for the lattice.

The functional E_{xc} used in this paper is local in both electron and ion densities. Nonlocal corrections, e.g., ∇n_i , could in principle be significant, since the calculated electronic density at the surface varies on the same scale as the interatomic spacing.

TABLE II. Surface energies (in ergs per square centimeter).

Metal	Jellium	First-order perturbation ^a	This work	Expt. ^b
Al	-730	730	840	1200
Pb	-130	1400	600	610
Zn	-130	440	460	1020
Mg	110	640	600	790
Li	210	380	390	530
Na	160	210	220	260
K	100	140	120	150
Rb	85	110	100	120

^aRef. 7.

^bRef. 12.

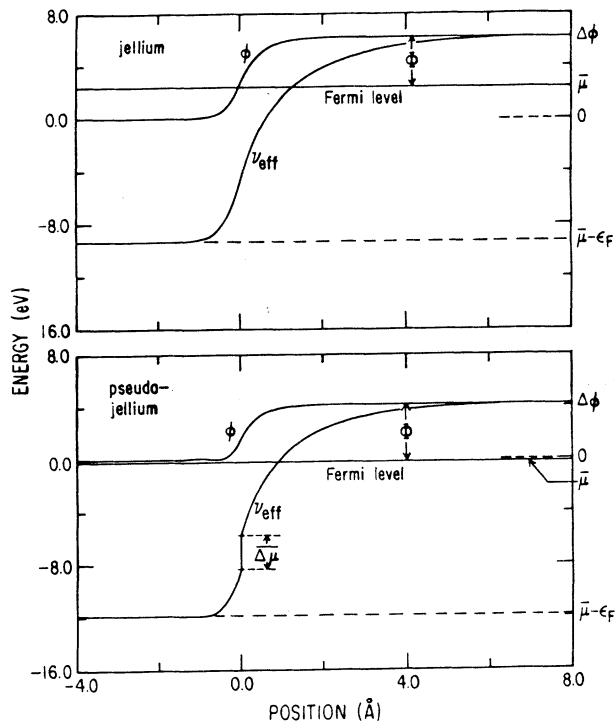


FIG. 1. Contributions to the effective potential for aluminum ($r_s = 2.07$) in the jellium and pseudojellium models. Note the positive values of $\bar{\mu}$ in the jellium model.

One reason for suggesting that the local approximation is useful is that nonlocal corrections for pure electronic E_{xc} are fairly small, even though electron-electron screening lengths are also on the same scale as surface widths. Further, the calculated surface energy changes very little if the location of the discontinuity in V_{eff} is shifted slightly from the jellium edge; what counts is the magnitude $\Delta\bar{\mu}$ of the discontinuity.

One can use the model to solve self-consistently

for n_i as well as n_e near the surface to obtain estimates of ionic relaxation, surface acoustic phonons, etc.

The authors wish to acknowledge many helpful discussions with J. H. Rose. This work was supported in part by the National Science Foundation under Grant No. DMR 82-17708 and by the Universidad de Chile and ODEPLAN.

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