



FACE DEPENDENT SURFACE ENERGIES OF SIMPLE METALS

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Using a simple ansatz for the inhomogeneous screened linear electron gas susceptibility, we obtain the face dependent surface energies, σ , of the simple metals, through second order. In contrast to the results of the first-order Lang-Kohn method and the one-dimensional variational values of Monnier and Perdew, we obtain weakly face dependent σ values consistent with experiment. Our results hinge on two previously neglected considerations: (i) ion induced inhomogeneity of the bulk electron density prior to cleavage and (ii) ion induced electron density inhomogeneity in the surface region after cleavage.

The surfaces of the simple metals have come to serve as a theoretical laboratory for testing various models of the inhomogeneous electron gas. Of particular interest in this development was the introduction of density functional theory by Smith who used the gradient expansion for the kinetic energy.¹ This was followed by the striking success of the theory of Lang and Kohn.² They solved the self-consistent Kohn-Sham³ equations for a half space of jellium, and then included the ion cores via first order perturbation theory and via the classical cleavage energy. Later improvements in the calculations of the surface energy have followed two main paths. First, considerable effort has been expended in obtaining non-local corrections to the exchange-correlation^{4,5,6} energy. The second development was introduced by Monnier and Perdew who partially included the change in the conduction electron density induced by the discrete ion cores.

However, all of the theories mentioned above have made the approximation that the electron density varies only in the direction normal to the surface. This reduces the computations necessary to determine the wavefunction within the Kohn-Sham scheme and greatly eases the numerical labor. In this paper we use linear response theory about the non-uniform jellium solutions of Lang and Kohn to study the effects of the change in the conduction electron density induced by the ion cores in a fully three dimensional way. Thus we obtain an electron density which has the symmetry of the lattice parallel to the surface. We find that the inclusion of the resulting three dimensional density variation is crucial for understanding the surface energy of the simple metals. Very large effects are found in the surface energy of the higher index faces for Al and Pb. For example, the surface energy of the (1,1,0) face of Al is decreased by a factor of two when compared to the result obtained when the density variation is assumed to be one dimensional. For

Pb the changes are even more striking and we find that it is necessary to include fully the three dimensional density variation to obtain agreement with experiment even for the surface energy of the densest (1,1,1) face. If we restrict ourselves to a one dimensional density profile we find that the surface energy is too large by a factor of two. Our calculation introduces substantial corrections to the surface energies for the densest faces (the faces reported by Lang and Kohn) of Al, Zn, Mg, Pb, Li, Rb and Cs.

We should stress that up to the present time there has been no adequate microscopic theory of the face dependence of σ for the simple metals (see however, the next paragraph). Monnier and Perdew applied the technique of Lang and Kohn to the calculation of the surface energy of the three lowest index faces of the simple metals except for the hcp metals Mg and Zn, for which we, as they, calculated only the energy of the lowest (0,0,0,1) face. For Pb and Al they found very large changes in the surface energy from face to face. For example, they found that the surface energy of the (1,1,0) face of aluminum was a factor of four larger than the energy of the (1,1,1) face. Near the melting point the surface energy differences between various faces of the bcc transition elements are found experimentally to be no more than 10 to 20%.⁸ At lower temperatures and for the simple metals the differences may very well be larger. However, a factor of four is too large to be credible. Further, in ref. 7 the inclusion of electron relaxation in the one dimensional density profile made the differences between different faces even larger. For Pb, Monnier and Perdew found that the energy of the (1,1,0) face was a factor of 10 larger than the energy of the (1,1,1) face. Aside from the fact that the energy differences from face to face are expected to be small, there is no qualitatively satisfactory experimental determination of the face dependence of the surface energy, so a theory such as ours may provide useful guidelines. It should be pointed

out that the face dependence of the surface energy plays an important role in brittle fracture processes in metals. Even though brittle fracture is not the basic failure mechanism in simple metals we hope that a study of the surface energy anisotropy for these metals will shed some light on the corresponding quantities in the BCC transition metals where brittle fracture is an important technological problem.

Recently Bohnen and Ying⁹ have introduced a new technique which involves the variation of the total energy with respect to the one-particle density matrix. This technique naturally involves the three-dimensional density profile, and Bohnen and Ying have recently applied it to the study of the surface energy of the (1,1,0) and (1,0,0) face of Na, K, Rb and Cs.¹⁰ We received a copy of their results, ref. 10, in preprint form after our calculations were substantially complete. Comparison with their calculations, Table 1, show that for these metals our technique and theirs give rather similar answers both for the surface energy and for the energy differences between faces. We take this comparison as confirming both techniques.

The linear response formalism which we use provides a straightforward analytic method for addressing problems involving small changes in the positions of the ions. This allows the possibility of studying the static relaxation of the ions due to the surface as well as their dynamical properties. One major advantage of the linear response formalism is that it avoids, by analytic subtraction, the numerical evaluation of differences in large numbers which variational techniques typically encounter.

In the following paragraphs we will discuss briefly the formalism which we have used. After that we will present our results and conclude with a discussion. A discussion of the linear response formalism and its application to surface problems will be given in another publication. We use the Lang-Kohn solutions for a sea of electrons moving in the potential of a half space of uniform positive background as a zero order solution about which we do perturbation theory. The Lang-Kohn calculation introduced the effects of the ions via the classical cleavage energy (ion-ion term) and via first order perturbation theory for the electron-ion interaction, where the ions are modeled by the Ashcroft¹¹ pseudopotential. We go beyond the results of Lang and Kohn by using linear response theory to calculate the second-order energy contribution due to the electron-ion interaction, both in the initial bulk system and in the final cleaved system with two surfaces. For the latter system we need a linear response function calculated about a nonuniform zero-order state.

The surface energy, σ , is found by subtracting the energy, E_B , of the bulk metal from the energy $2E_S$, of the cleaved system, then dividing by the total surface area, $2A$. The second order contribution, which we add to the Lang-Kohn result σ^{LK} , is

$$\sigma(2) = \frac{1}{2A} \left(2E_S^{(2)} - E_B^{(2)} \right). \quad (1)$$

Here, the total energy contribution of 2nd order in the electron-ion interaction, for a semi-infinite lattice of pseudopotential ions is

Table 1

Surface Energy of the Alkali Metals (ergs/cm²)

- The calculated surface energies of the alkali metals is compared with those of Bohnen and Ying within the local density approximation. Note that our energies are lower than those of Bohnen and Ying except for Na where they used a slightly different pseudopotential radius. This is consistent with their use of a variational ansatz.

	Present Work			Bohnen-Ying		
	1,1,0	1,0,0	$\sigma_{100}/\sigma_{110}$	1,1,0	1,0,0	$\sigma_{100}/\sigma_{110}$
Li	341	413	1.21	—	—	—
Na	229	261	1.14	221	261	1.18
K	139	158	1.14	144	170	1.18
Rb	107	122	1.14	107	132	1.23
Cs	70	93	1.33	89	109	1.22

$$E_s^{(2)} = \frac{1}{2} \sum_{i \leq 0} \sum_{j \leq 0} \int d^3 r d^3 r' \Delta v_{ps}(\vec{r}-\vec{R}_i) \Delta v_{ps}(\vec{r}'-\vec{R}_j) \chi_s(|\vec{r}_\parallel - \vec{r}'_\parallel|, z, z') . \quad (2)$$

Δv_{ps} is the change in the potential due to adding a pseudopotential ion to the system and subtracting out a cuboid of jellium background with equal charge. The ions are centered about the crystal lattice sites denoted by \vec{R}_i , and for this expression are restricted to the left half space ($i, j \leq 0$). We use the Ashcroft pseudopotential and the Wigner form for the exchange and correlation energy¹² to maintain contact with previous calculations. The function χ_s represents the screened density-density linear response function of the jellium half space including the effects of the surface.

The bulk term in the second-order surface energy contribution (1) is given by

$$E_B^{(2)} = \frac{1}{2} \sum_{-\infty < i < \infty} \sum_{-\infty < j < \infty} \int d^3 r d^3 r' \Delta v_{ps}(\vec{r}-\vec{R}_i) \Delta v_{ps}(\vec{r}'-\vec{R}_j) \chi_B(|\vec{r}-\vec{r}'|) . \quad (3)$$

Here χ_B represents the screened density-density linear response function for the uniform electron gas.

Using Eqs. (2) and (3) in (1) and regrouping terms to avoid numerical subtraction of comparable large quantities, we find that the total second order contribution to the surface energy is

$$\sigma^{(2)} = \sigma_{\frac{1}{2}, \frac{1}{2}} + \sigma_{\delta\chi} . \quad (4)$$

The first term in (4) is

$$\sigma_{\frac{1}{2}, \frac{1}{2}} = \frac{1}{2} \sum_{i \leq 0} \sum_{j > 0} \int d^3 r d^3 r' \Delta v_{ps}(\vec{r}-\vec{R}_i) \Delta v_{ps}(\vec{r}'-\vec{R}_j) \chi_b(|\vec{r}-\vec{r}'|) . \quad (5)$$

It depends only on bulk properties of the metal and is independent of the zero-order electronic surface profile. Surprisingly, this term is dominant in the corrections to the face dependence of the surface energy in Al and Pb. The second term, which is sensitive to changes in electron density at the surface, is given by

$$\sigma_{\delta\chi} = \frac{1}{2} \sum_{i \leq 0} \sum_{j \leq 0} \int d^3 r d^3 r' \Delta v_{ps}(\vec{r}-\vec{R}_i) \Delta v_{ps}(\vec{r}'-\vec{R}_j) [\chi_s(|\vec{r}_\parallel - \vec{r}'_\parallel|, z, z') - \chi_B(|\vec{r}_\parallel - \vec{r}'_\parallel|, z-z')] . \quad (6)$$

In performing the numerical evaluation of Eqs. (5) and (6) we took advantage of the translational invariance parallel to the surface and Fourier transformed the variable $\vec{r}_\parallel - \vec{r}'_\parallel$ in terms of the two dimensional surface reciprocal lattice vectors \vec{G}_\parallel . In order to evaluate the second order contributions it is necessary to know both χ_B and χ_s . For the bulk the answer is straightforward within the Kohn-Sham formalism:¹³

$$\chi_B(|\vec{q}|) = \frac{\chi^o(|\vec{q}|)}{1 - \left(\frac{4\pi e^2}{q} + \frac{d^2(\pi\epsilon_{xc})}{dn^2} \right) \chi^o(|\vec{q}|)} . \quad (7)$$

Here χ^o is the Lindhard response function and ϵ_{xc} is a local approximation for the exchange and correlation energy per particle. The determination of the screened density-density response function for non-uniform systems within the framework of the Kohn-Sham equations is considerably more difficult (see for example the work of Zaremba and Stott¹⁴). We avoid this difficulty by making the following ansatz

$$\chi_s(\vec{r}, \vec{r}') = \chi_B \left(\vec{r}-\vec{r}' ; \frac{n(\vec{r})+n(\vec{r}')}{2} \right) . \quad (8)$$

Here χ_B is evaluated at the average value of the densities $n(\vec{r})$ and $n(\vec{r}')$. This ansatz has been used quite successfully to study the ground state properties of molecular hydrogen.¹⁵ In that case the perturbation theory contributed about 10% to the total energy of the hydrogen molecule. In the very low density limit of an isolated H₂ molecule it was found that the interproton spacing, the molecular binding energy and the vibrational energy of the molecule agreed with experiment to within 1/2%. Beyond

this demonstration of a successful use for the ansatz, we base our use of the ansatz a posteriori on the results which we obtain. The detailed evaluation of Eqs. (5) and (6) will be made in a latter publication for which the present work is intended to serve as a brief report.

Table 2 shows our results for the surface energy of the simple metals. They are to be compared with zero temperature extrapolation of the 'average' surface energy performed by Tyson and Miller¹⁶ from measurements made at and near the melting point. A second comparison is provided by the results of Wawra¹⁷ who extrapolated the surface energies to low temperatures on the basis of an empirical relation between the surface energy and the measured elastic constants. We have added to our results the wavevector correction to the exchange-correlation energy proposed by Langreth and Perdew.⁴ This contribution to the surface energy is relatively independent of the surface density profile and we have simply used the results quoted in ref. 7. We find agreement between our results and experiment to within the experimental uncertainty with the possible exception of Zn for which our results seem somewhat too low. We should add, though, that the experimental value of the surface energy for Zn has been the subject of some controversy with

Table 2
Surface Energy of Simple Metals (erg/cm²)

2. The calculated values of the surface energy are compared with experimental extrapolation of the surface energies to zero temperature. The extrapolation of the experimental surface energy is quite difficult and the experimental results quoted here are rather uncertain.

	Present Work			Wawra	Tyson & Miller
FCC	(1,1,1)	(1,0,0)	(1,1,0)		
Al	1065	1160	1700	1170	1143
Pb	720	930	1575	690	593
HCP	(0,0,0,1)				
Mg	670	—	—	—	785
Zn	670	—	—	1040	913
BCC	(1,1,0)	(1,0,0)			
Li	380	450	—	—	522
Na	250	280	—	275	261
K	150	170	—	135	145
Rb	115	130	—	—	117
Cs	80	100	—	—	95

much lower values quoted⁷ than those given by Tyson and Miller and Wawra. It is of some interest to display the two second order contributions to the surface energy. For Al (1,1,1), $\sigma_{\frac{1}{2},\frac{1}{2}} = -373$ erg/cm² and $\sigma_{\Delta\chi} = 555$ erg/cm². These terms include the effects of the three dimensional density profile. The large size of $\sigma_{\frac{1}{2},\frac{1}{2}}$ indicates the necessity of including the change in electron density induced by the ion cores in the bulk solid in order to obtain reliable surface energies. The effect of a one dimensional density profile can be obtained by taking only the $\vec{G}_{\parallel} = \vec{0}$ contributions to the second order energy. In that case we find $\sigma_{\frac{1}{2},\frac{1}{2}} = -137$ erg/cm² and $\sigma_{\Delta\chi} = 31$ erg/cm². Thus the total second order contribution is $\Delta\sigma = -105$ erg/cm² for the $\vec{G}_{\parallel} = \vec{0}$ term compared to $\Delta\sigma = +180$ erg/cm² when all \vec{G}_{\parallel} 's are included. This demonstrates the importance of including the three dimensional nature of the electron density profile in evaluating the surface energy.

The face dependence of the surface energy is much smaller for Al and Pb in our calculations than in the work of Monnier and Perdew as can be seen in table 3. For the two densest faces we find $\sigma(1,0,0)/\sigma(1,1,1) = 1.09$ for Al and 1.30 for Pb. The values for $\sigma(1,1,0)/\sigma(1,1,1)$ were 1.6 for Al and 2.1 for Pb. The face dependence for the alkali metals is given in table 1. An interesting point for the alkalis is that the first order calculation of Monnier and Perdew

finds that the (1,0,0) face of Rb and Cs have a lower surface energy than the denser (1,1,0) face. This is somewhat surprising since we expect from bond-breaking arguments that the denser face will have the lower energy.^{8,18} Our calculation reverses this anomaly and shows that the denser (1,1,0) face has the lower surface energy. One final comment on the anisotropy, between the energy of the densest face and the next densest face is in order. We find that the ratio of these energies is between 1.1 and 1.3 for the metals we have considered. Lacking any other guide we feel that taking this ratio to be 1.2 for the transition metals at $T = 0^{\circ}\text{K}$ would be reasonable.

Our results have consequences for several other calculations beyond the surface energy. For example, the determination of the static relaxation of the lattice at the surface of a metal depends on the screening of the ions by the electrons. Hence we would expect that the determination of this quantity would depend quite sensitively on the exact form of the three dimensional density profile. A similar consideration is involved in the determination of the phonon contribution to the temperature dependence of the surface energy. We have adapted our formalism to these calculations also. Details will be published shortly.

A final comment is in order concerning the calculation of Monnier and Perdew. As we

Table 3
Surface Energy (erg/cm²)

3. The face dependence of the surface energy is given for Al and Pb. For comparison we give the results of Monnier and Perdew for their "perturbational self-consistent calculation" (the method of Lang-Kohn) to which we have added the wavevector corrections quoted in the same paper.

	This Work	Monnier & Perdew
Al		
(1,1,1)	1065	885
(1,0,0)	1160	1640
(1,1,0)	1700	3385
Pb		
(1,1,1)	720	1250
(1,0,0)	930	2390
(1,1,0)	1575	5050

remarked they include the relaxation of the conduction electrons by the ion cores within the constraint of a one dimensional variation of the density and found that the face dependence of the surface energy became more pronounced rather than less. We attribute this result to two approximations made in their calculation. First was the approximation of a one dimensional density variation. The second approximation involved the assumption that the relaxation of the electrons to the ions was unimportant in the bulk. Within our procedure these approximations are found to be inadmissible by detailed calculation.

In summary, we have calculated the surface energy of the simple metals to second order in the electron-ion interaction. The result is a systematic improvement of the surface energies in comparison with experiment except possibly for Li. The face dependence of the surface energy has been calculated and we have found that the ratio of the surface energies for the two densest

faces ranges between 1.1 and 1.3. We have also adduced some consequences of our work for other possible calculations. We close with the thought that the time has come when it should be possible to obtain accurate reliable numbers for the surface energies of the simple metals by a careful choice of the pseudopotential and the exchange-correlation energy functional.

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