

## Calculations of Surface Energy for a Free-Electron Metal

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The surface energy of a free-electron metal is calculated using a square-cut barrier placed so that there is no net charge on the surface. The result is nearly independent of barrier height but leads to a value for surface tension less than half that observed for most molten metals. For sodium a self-consistent surface barrier, first developed by Bardeen, is also used in numerical computation of surface energy. The value so obtained is about half that resulting from the use of the square-cut barrier. Previous theoretical treatments of this problem have generally predicted surface energies larger than observed. The opposite result in this case appears to result from the requirement that the surface be maintained electrically neutral.

### I. INTRODUCTION

THERE have been several previous treatments<sup>1</sup> of the surface energy for a metal using the free-electron model. Of particular interest is the work of Brager and Schuchowitzky<sup>2</sup> who used a free-electron model with infinite potential barrier at the geometrical surface of the metal. (By geometrical surface is meant that surface which just contains the last layer of atomic cells.) They found a contribution to the energy proportional to the surface which they identified with the surface energy. When compared with the experimentally measured values for the surface energies of molten metals, this term was too large by a factor of two or three but varied proportionally in going from one metal to the next.

A good critical review of the preceding literature on this subject has been contributed by Skapski.<sup>3</sup> He criticizes in particular the notion that free electrons give metals a higher surface energy than is found for other solids or liquids. In fact, in terms of the free energy per surface atom the values for the monovalent metals are lower in comparison with their cohesive energy than those usually found in other materials. On the basis that the same forces which give rise to volume cohesion are also responsible for surface energy, Skapski shows that a very simple semi-empirical calculation can predict the surface energy quite satisfactorily.

Recently Huang and Wyllie<sup>4</sup> have used a free-electron model with barrier of finite height at the geometrical surface of the metal. This method gives results in better agreement with experiment than those of Brager and Schuchowitzky, as they turn out to be only about  $\frac{2}{3}$  the experimental values. The height of the barrier is in each case dictated by the known cohesive energy, and this choice serves to interrelate directly volume and

surface forces. Their treatment has the following defect, that by fixing the position and height of the square barrier simultaneously, one cannot be certain that charge will be conserved; i.e., that the negative charge outside the geometrical surface will equal the electronic charge missing inside the surface. In fact it can be seen from Eq. (2) that to conserve charge with a square-cut barrier at the geometrical surface would require that the height of the barrier be just at the Fermi level. This would be equivalent to postulating a zero work function. As we shall see, the requirement that charge be conserved greatly decreases the surface energy.

### II. SQUARE-CUT BARRIER POTENTIAL

In order to express the electron wave functions in a simple analytic form in the region of the surface one chooses a square-potential barrier<sup>5</sup> of height  $(\hbar p)^2/2m$  at  $x=a$ . The geometrical surface of the metal is taken to be the plane  $x=0$ . Negative values of  $x$  refer to the metal interior. For rectangular specimens with dimensions  $L_1, L_2, L_3$  the electronic wave functions can be written in the form of standing waves,

$$\psi = 2/(L_2 L_3)^{\frac{1}{2}} \sin k_y y \sin k_z z \phi(x) \quad (1)$$

where, for

$$\begin{aligned} x \leq a, & \quad \phi(x) = -(2/L)^{\frac{1}{2}} \sin(k_x \xi - \gamma) \\ x \geq a, & \quad \phi(x) = (2/L)^{\frac{1}{2}} \sin \gamma \exp\{-(p^2 - k_x^2)^{\frac{1}{2}} \xi\}. \end{aligned}$$

with  $\xi = x - a$  and  $\sin \gamma = k_x/p$ . The allowed values for  $k_y$  and  $k_z$  are positive multiples of  $\pi/L_2$  and  $\pi/L_3$  respectively. By virtue of the phase shift at the surface under consideration  $k_x = (n_x \pi - \gamma)/(L_1 + a)$ .

The requirement that charge be conserved prevents the independent choice of  $a$  and  $p$ . Their interrelationship can be expressed analytically:

$$\frac{2}{3} k_m^3 a = \frac{1}{4} \pi k_m^2 + (\frac{1}{2} p^2 - k_m^2) \sin^{-1}(k_m/p) - \frac{1}{2} k_m (p^2 - k_m^2)^{\frac{1}{2}}, \quad (2)$$

where  $k_m$  refers to the electrons on the Fermi surface, so that  $k_m^3/3\pi^2 = n$ , the density of electronic charge. In Fig. 1 the barrier height is plotted in units of the Sommerfeld bandwidth against the displacement of the barrier in units of  $r_s$  with  $4\pi r_s^3/3 = 1/n$ .

<sup>5</sup> This treatment is based on that of J. Bardeen, Phys. Rev. 49, 653 (1936).

<sup>1</sup> D. V. Gogate and D. S. Kothari, Phil. Mag. 20, 1136 (1935); A. Samoilovich, Acta Physicochimica (U.S.S.R.) 20, 97 (1945); S. Dorfman, Compt. rend. 41, 386 (1943).

<sup>2</sup> A. Brager and A. Schuchowitzky, Acta Physicochimica 21, 13 (1946).

<sup>3</sup> A. S. Skapski, J. Chem. Phys. 16, 386, 389 (1948).

<sup>4</sup> K. Huang and G. Wyllie, Proc. Phys. Soc. (London) 62, 180 (1949).

\* Note added in proof:—In recent correspondence Mr. Wyllie has pointed out that charge is conserved by their method within the Fermi-Thomas approximation. The approximation, however, appears to be inadequate to treat a step-function potential.

To calculate the surface energy of this model one may find the energy required to split a block of dimensions  $(2L_1, L_2, L_3)$  in half. One half of this term then gives  $\Delta E$ , the energy associated with one newly formed surface. (The results are of course independent of where the break is made.) The total energy of the electrons in the unsplit block is given by the sum,

$$\frac{\hbar^2}{2m} \sum_{\text{spin}} \sum_{n_x} \sum_{n_y} \sum_{n_z} \left\{ \left( \frac{n_x \pi}{2L} \right)^2 + \left( \frac{n_y \pi}{L} \right)^2 + \left( \frac{n_z \pi}{L} \right)^2 \right\},$$

where the summations are over all positive values of the  $n$ 's for which the summand does not exceed  $k_m^2$ . After splitting, the energy is made up of two such expressions but only the terms involving  $k_x^2$  contribute to the change in energy. After summing over spins and integrating over  $k_y$  and  $k_z$  one obtains for total increase

$$2\Delta E = \frac{L_2 L_3 \hbar^2}{4\pi m} \left[ 2 \sum_{n_x=1}^{k_m L_1 / \pi} \left( \frac{n_x \pi}{L_1 + a} \right) \left\{ k_m^2 - \left( \frac{n_x \pi}{L_1} \right)^2 \right\} - \sum_{n_x=1}^{2k_m L_1 / \pi} \left( \frac{n_x \pi}{2L} \right)^2 \left\{ k_m^2 - \left( \frac{n_x \pi}{2L_1} \right)^2 \right\} \right] \quad (3)$$

$$= \frac{\hbar^2}{2m} \frac{L_1 L_2 L_3}{\pi^2} \int_0^{k_m} \frac{k_x}{L_1} \times \left( \frac{\pi}{2} - 2\gamma - 2k_x a \right) (k_m^2 - k_x^2) dk_x \quad (3a)$$

$$= \frac{3n\hbar^2 L_2 L_3}{2m} \left[ \frac{\pi k_m}{8} - \frac{4}{15} k_m^2 a - \frac{k_m}{2} \left\{ 1 - \left( \frac{p}{k_m} \right)^2 + \frac{3}{8} \left( \frac{p}{k_m} \right)^4 \right\} \sin^{-1} \frac{k_m}{p} - \frac{3}{8} k_m (p^2 - k_m^2)^{\frac{1}{2}} \left\{ \frac{1}{k_m} - \frac{p^2}{2k_m^3} \right\} \right]. \quad (3b)$$

The first term of (3b) inside the square brackets corresponds to that given by Brager and Schuchowitzky<sup>2</sup> using a slightly different approach. It would be the sole contribution for an infinite barrier at the geometrical surface. From Eq. (2) one can substitute for  $a$  and obtain for the energy per unit surface,

$$\frac{\Delta E}{L_2 L_3} = \frac{3n\hbar^2}{4m} \left[ \frac{\pi k_m}{40} - \frac{k_m}{10} \sin^{-1} \frac{k_m}{p} \left\{ 1 - 3 \left( \frac{p}{k_m} \right)^2 + \frac{15}{8} \left( \frac{p}{k_m} \right)^4 \right\} - \frac{k_m}{4} (p^2 - k_m^2)^{\frac{1}{2}} \left\{ \frac{7}{k_m} - \frac{15p^2}{2k_m^3} \right\} \right]. \quad (4)$$

In Fig. 1 there is also shown the dependence of surface energy on the barrier position,  $a$ , as found from Eqs. (2) and (4). It is rather encouraging to notice that the total variation of this quantity is little more than 10

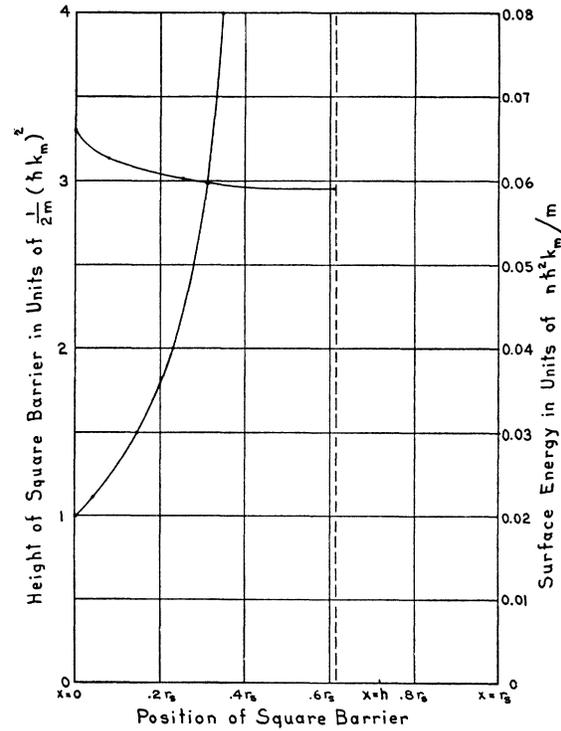


FIG. 1. The height of the square-cut barrier in units of  $(\hbar k_m)^2/2m$  is plotted against its position where  $x$  is measured in units of  $r_s$ . Vertical line is the asymptote for infinite barrier. The nearly horizontal curve is the plot of surface energy in units of  $n\hbar^2 k_m/m$  as a function of barrier position.

percent for the complete range of possible values for barrier height and barrier position. One might be tempted to argue from this that for the purpose of calculating surface energy all barriers which conserve charge give essentially the same result and it is unnecessary to seek a self-consistent solution. In the next section it will be shown to what extent this is borne out.

The surface energy term just evaluated amounts to nearly one-fourth the Brager and Schuchowitzky term. It has already been pointed out<sup>2</sup> that such a term, varying as  $\Omega^{-4/3}$ , where  $\Omega$  is the atomic volume, follows fairly well the variations of surface tension from one molten metal to another. As the original was too large by a factor between 2 and 3, the present result lies in the neighborhood of 60 percent of the experimental values. Unfortunately most of the considerations which have been omitted in this comparison tend to increase the discrepancy.

### III. SELF-CONSISTENT SOLUTION FOR SODIUM

The actual surface barrier is known to be of the image type rather than square-cut. For sodium there exist the self-consistent solutions developed by Bardeen<sup>5</sup> for his treatment of work functions and dipole layers. In this section the result is given of a calculation of surface energy based on these solutions.<sup>6</sup>

<sup>6</sup>H. B. Huntington, Phys. Rev. 75, 1627A (1949).

In Bardeen's work the variation of the exchange potential with the total momentum of the electron causes the form of the barrier potential to depend on the value of  $|k|$  of the electron. Besides the exchange potentials there is an electrostatic contribution to the barrier from the dipole layer which is the same for all electrons. Though the exchange curves could be read with sufficient accuracy from the figures of Bardeen's article, it was found necessary to obtain the electrostatic potential by integrating the Poisson equation using the final self-consistent charge distribution (see Fig. 2a). There was need to have this potential fairly well-defined since it had a shallow minimum in the region where the electronic density had nearly reached full value, and therefore influenced the wave functions critically. It was found on integrating these functions numerically that the phase shifts caused by the barrier depended mainly on  $k_x$  and barely at all on  $|k|$ . It can be shown that the different curves for the exchange potential can be approximately superimposed by vertical displacements for the region over which the wave functions have appreciable amplitude. In Fig. 2b is shown the complete potential used for  $|k|=0.8k_m$ , which is very nearly correct for any other value of  $|k|$ . As a result the integrations over  $k_y$  and  $k_z$  can be performed immediately in the calculation of the surface energy.

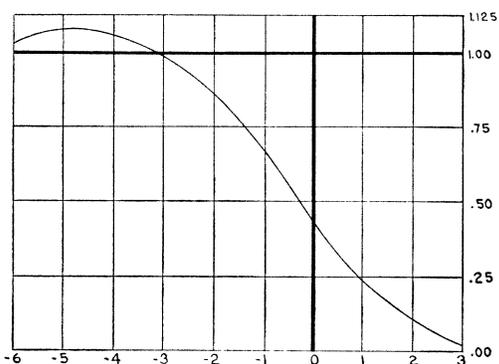


FIG. 2 (a). Charge density distribution at surface. Charge density is normalized to unity at interior of metal. Position  $x$  is measured in Bohr units. (From Bardeen.)

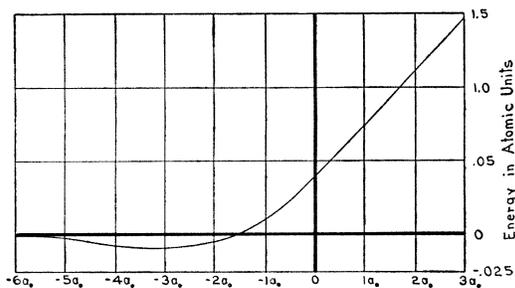


FIG. 2 (b). Typical potential curve. Potential is in atomic units and includes both electrostatic and exchange contributions. Former is cause of shallow trough inside metal. Exchange contribution ( $k=0.8k_m$ ) is magnified slightly to include correlation effect.

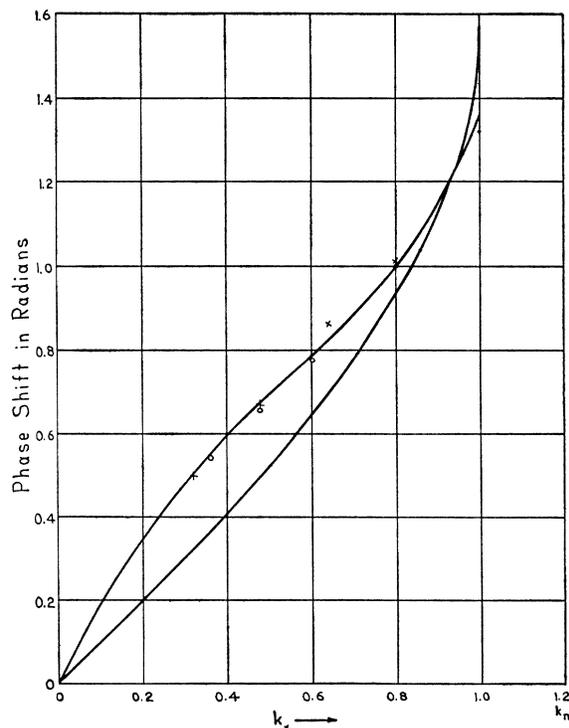


FIG. 3. Phase shifts in radians as function of  $k_x$ .  $\bullet$  for  $k/k_m=1.0$ ,  $\times$  for  $k/k_m=0.8$ ,  $\circ$  for  $k/k_m=0.6$ . Curve through points is graph of Eq. (6). Lower curve gives phase shift for square barrier at geometrical surface.

In an equation analogous to Eq. (3a) one obtains:

$$\Delta E = (\hbar^2 L_2 L_3 / 2m) \int_0^{k_m} (\frac{1}{4}\pi - \gamma)(k_m^2 - k_x^2) k_x dk_x, \quad (5)$$

where the  $\gamma$  are phase shifts in the standing electron waves as caused by the average barrier ( $|k|=0.8k_m$ ). The dependence of  $\gamma$  on  $k_x$  is shown by the points plotted on Fig. 3. Different symbols indicate results obtained from curves for different values of  $|k|$ . It can be seen that  $\gamma$  depends principally on  $k_x$ . This dependence can be fitted by the analytic expression,

$$\gamma = k_x r_s [0.66 + 0.7\{0.8 - (k_x/k_m)\}^2] \quad (6)$$

and the curved line through these points is the plot of this expression. The other line in Fig. 3 gives for comparison the phase shifts for the case of the square barrier placed at the geometrical surface. Though the two curves do not differ too markedly, the surface energy term obtained by evaluating Eq. (5) with the help of expression (6) is 0.023 in units of  $n\hbar^2 k_m/m$ , or about 40 percent of the result previously given for the square barrier (see Fig. 1). This comes about because the surface energy term is obtained by subtracting two quantities of nearly equal magnitudes.

In any energy calculation involving self-consistent wave functions one must avoid counting electron interactions twice by subtracting one-half of the change in

TABLE I. Comparison of calculation with measured surface tension values (units of dyne/cm).

	Surface energy			Surface tension (calc.)	Surface tension (exp.)	
	Square-cut barrier	Self-consistent barrier	$-TS_A^4$		Liquid	Solid (reference 9)
Copper	860	—	-360	500	1100	1370
Sodium	170	—	-34	136	290	—
Sodium	—	88	-34	54	290	—

the self-energy of the electrons which amounts to a contribution,

$$\frac{1}{2} \int \rho_i \phi(\rho_i) d\tau - \frac{1}{2} \int \rho_f \phi(\rho_f) d\tau$$

$$= \frac{1}{2} \int (\rho_i - \rho_f) \phi(\rho_i) d\tau - \int \rho_f [\phi(\rho_f) - \phi(\rho_i)] d\tau, \quad (7)$$

where  $\rho_i$  and  $\rho_f$  are respectively the initial and final electron distributions and  $\phi(\rho)$  in each case the appropriate self-potential. (Because of the crude nature of the square barrier model there was no consistent way to include a term such as Eq. (7) in that calculation.) Here the  $\phi$ 's include, beside electrostatic, also exchange and correlation contributions. Since the initial situation refers to a uniform value for  $\rho_i$  and  $\phi$ , i.e., no surface, it follows the first term on the right of Eq. (7) vanishes as a result of the conservation of charge.

It is not correct, however, to take  $\phi(\rho_f) - \phi(\rho_i)$  to be just the barrier potential at the surface,  $\phi_b$ . As formulated here the barrier potential arises only from mutual interactions of the electrons, namely the surface dipole layer and the changes in the exchange and correlation potential caused by the introduction of the surface. It does not include, however, the change in the electronic coulomb interaction. In the Wigner-Seitz method<sup>7</sup> the coulomb interaction potential arises from the electronic distribution in the same atomic polyhedron as the field point. The charge outside of this polyhedron is neutralized by the coulomb potentials of the outside ions. In the approximation of uniform electronic distribution the coulomb interaction potential can be written:

$$V_e(r) = 3e/2r_s - er^2/2r_s^3,$$

where  $r$  is measured from the center of the atomic polyhedron. The average value of this potential is  $1.2e/r_s$ . It follows that

$$\phi(\rho_f) - \phi(\rho_i) = \phi_b + \Delta V_e, \quad (8)$$

where  $\Delta V_e$  is the change in the coulomb potential caused by the surface.

A fundamental difficulty in treating  $V_e$  in a unique manner arises because this potential is developed from

<sup>7</sup> F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chapter X.

the concept of the atomic polyhedron, whereas our present model has dispensed with the polyhedra in the postulation of a geometrically plane surface. Some arbitrariness is, therefore, involved in the following procedure for establishing  $\Delta V_e$ . This procedure was to assume that  $V_e(x)$  remains unchanged at its average value,  $1.2e/r_s$ , in the region inside the geometrical surface ( $x \leq 0$ ). Outside the surface,  $x > 0$ , it is assumed that the electrostatic interaction potential is that arising from a uniform charge distribution in the atomic polyhedron nearest to the field point. By appropriate averaging, this potential is expressed as a function of  $x$  only. Accordingly the resulting function becomes

$$V_e(x) = (2/s_0^2) \int_0^{s_0} V_e(r) s ds,$$

where  $r^2 = (x + \frac{1}{2}d)^2 + s^2$ ,  $d$  is the distance between atomic planes parallel to the surface and  $s_0^2 d$  equals the volume of the atomic polyhedron. For  $r < r_s$ ,  $V_e(r) = 3e/2r_s - er^2/2r_s^3$  and for  $r > r_s$ ,  $V_e(r) = e/r$ .

By this somewhat arbitrary procedure, one can express as a function of  $x$ ,

$$\phi(\rho_f) - \phi(\rho_i) = \phi_b + V_e(x) - 1.2e/r_s,$$

where  $\phi_b$  stands for the barrier potential. Direct evaluation gives

$$-\frac{1}{2} \int \rho_f \phi_b d\tau - \frac{1}{2} \int \rho_f (V_e - 1.2e/r_s) d\tau$$

$$= (-0.034 + 0.043) n \hbar^2 k_m / m.$$

The final value for the surface energy of sodium turns out to be 0.032 in  $n \hbar^2 k_m / m$ , or 88 ergs per cm<sup>2</sup>, on the basis of the self-consistent solution.

#### IV. CONCLUSION

The results of these calculations are summarized for the cases of copper and sodium, together with experimental data for comparison, in Table I. The result of the square barrier calculation can be applied directly to any metal since it varies as the 4/3 power of the electronic density. The self-consistent barrier is specialized for the electronic density of sodium. In the fifth column are given experimentally determined values for the surface tension of the molten metals near the melting point.<sup>8</sup> The surface tension, or free energy per unit surface, can be obtained from the surface energy (more strictly speaking the surface enthalpy) by subtracting the product of the absolute temperature times the surface entropy. This latter quantity has been evaluated by Huang and Wylie<sup>4</sup> using the calculation of Brager and Schuchowitzky<sup>9</sup> of the part of the specific heat of a solid which is proportional to the surface.

<sup>8</sup> For more extensive listings of this quantity see references 2 or 4.

<sup>9</sup> A. Brager and A. Schuchowitzky, *Acta Physicochemica* **21**, 1001 (1946).

Their results are given in column 3 and combined with the tabulations in the preceding columns in column 4 for comparison with the data from the molten metals. Reliable measurements of surface tension for solids are difficult to find but recently Udin, Shaler, and Wulff<sup>10</sup> have employed the technique of observing the elongation and contraction of fine wires under small loads at high temperatures to obtain an apparently quite reliable value for the surface tension of copper. Their value for this quantity just above the melting point is given in column 6 of Table I.

It is evident from a comparison of columns 4 and 5 in Table I that in all cases the calculations give values considerably smaller than the experiments. Of the quantities which a more complete theory might have included there does not appear to be any which would readily remove the discrepancy. (a) A consideration of the short range repulsive forces between ions would lower still more the calculated values, though this term is not large. (b) The calculations are strictly for a solid metal and the experimental evidence is for the most part taken on molten metals but the evidence of the measurements on copper indicate that surface tension is larger in the solid than in the liquid phase (as seems rather sensible intuitively). (c) Surface energy calculated here applies to the freshly cleaved surface. Surface tension measurements refer to equilibrated, or partially equilibrated, surfaces where the density of the surface layer has been reduced. Since the lowered surface density corresponds to a more thermodynamically stable state, this also has the effect of decreasing the surface energy. (d) In this calculation the surface has been assumed to be geometrically plane, which is a valid approximation for the close-packed surfaces. Smoluchowski<sup>11</sup> has shown for tungsten that the energy

<sup>10</sup> Udin, Schaler, and Wulff, *Met. Trans. A. I. M. E.* 186 (February, 1949).

<sup>11</sup> R. Smoluchowski, *Phys. Rev.* 60, 661 (1944).

differences between crystal surfaces should be quite appreciable. The inclusion of surface planes, other than closest packed, would alter results in the right direction but it appears unlikely the correction would be large since for the equilibrated specimen surfaces of low energy would predominate.

To summarize the results of this investigation. It would appear that surface tensions for metals as calculated on a free-electron model for surfaces of closest packing are less than half those found experimentally for molten metals. This discrepancy is in the opposite direction from that reported by the more recent treatments of this problem, where the investigators did not insist on the conservation of charge. The replacement of the usual square barrier by one shown to be self-consistent had the effect of still further increasing the discrepancy. It is difficult to surmise what may be the cause of the present disagreement. It should be remembered that these values for surface energy are obtained from the rather close cancellation of two large terms. Small errors in evaluation or uncertain assumptions, usually physically satisfactory, may play a part. It may be that the free-electron model is simply too crude for this problem and to improve the results one must take into account the periodicity of the metallic potential field. The presence of the surface disturbs the charge distribution as far back as the position of the centers of the first layer of atoms. The interaction of this modulation of wave functions in the neighborhood of the ionic core, which one overlooks in the free-electron model, could possibly be important in determining the surface energy.

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