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Kunio Takahashi and Tadao Onzawa
Mechanical Engineering for Production, Tokyo Institute of Technology, Meguro-ku Tokyo 152, Japan

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Simple formula for the surface energy by a shifted-step-potential approximation

Kunio Takahashi and Tadao Onzawa
Mechanical Engineering for Production, Tokyo Institute of Technology, Meguro-ku Tokyo 152, Japan
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The jelliumlike free-electron model is used, and the effective one-electron potential $v_{\rm eff}$ is approximated to be the step-function which is shifted to satisfy the neutrality of the charge. The eigenfunctions can be obtained in analytic form. Although not self-consistent, the calculated distribution of the electron density is very similar to the self-consistent field (SCF) jellium results by Lang and Kohn. A simple formula for the surface energy is obtained. The surface energy is given as a function of the Fermi energy and the work function. The formula suggests that the surface energy is sensitive to the Fermi energy and is not sensitive to the work function, i.e., the surface energy is approximately in proportion to the ~~fourth~~ 2nd power of the Fermi energy. The calculated surface energy approaches the SCF jellium results by Lang *et al.* and the structureless pseudopotential results by Perdew for small electron density.

I. INTRODUCTION

Simple *sp*-bonded metals are nearly-free-electron systems. The metals are often described theoretically by the jellium model, for a systematic understanding of material properties at the low-electron-density limit, although some corrections are required to obtain realistic results at higher density ($r_s \leq 4$).[1] Perdew, Tran, and Smith[2] propose perhaps the simplest model viable for all r_s by using a structureless pseudopotential model.

This paper is based on the general theory of the inhomogeneous electron gas. Consider the case with semi-infinite positive background. The total energy per valence electron in the bulk is written as

$$H = H_k + H_{\rm xc} + H_{\rm other}, \tag{1}$$

where H_k is the kinetic energy of the electron and $H_{\rm xc}$ is the exchange and correlation contributions. $H_{\rm other}$ includes the external potential and the electrostatic potential energy in the theory by Kohn and Sham.[3] In the theory by Perdew, Tran, and Smith,[2] the $H_{\rm other}$ includes the average Madelung energy, the band-structure energy, and the non-Coulombic contribution of the pseudopotential. In any approximation, an effective one-electron potential is defined and the barrier height of the potential can be obtained as a function of the interaction energies stated above.

In turn, if the work function Φ is given as an empirical parameter, the effective potential height can be given by $\Phi + \varepsilon_F$, where ε_F is the Fermi energy. Furthermore, assuming that the effective potential can be approximated to a step function, the electronic wave functions are written in simple analytic form. In Sec. III, we present a comparison between the results and the self-consistent field (SCF) results by Lang and Kohn.[1] The results are not self-consistent. However, one can obtain the more simplified formula on the trend of the surface energy.

The simplicity of this approximation proposes a rough understanding of the relation between the surface energy γ_s, the Fermi energy ε_F, and the work function Φ.

II. A SHIFTED STEP-POTENTIAL APPROXIMATION

The jelliumlike free-electron model with shifted step potential is used. If the approximation of Lang and Kohn[1] would be used (also see Ref. 4), the effective one-electron potential energy for a state would be defined self-consistently from the electron number density.

In order to simplify and obtain the analytic form of the electronic eigenfunctions, the effective potential $v_{\rm eff}$ is approximated to be the step function as shown in Fig. 1. The α is defined so that the electronic distribution obeys the neutrality condition. The potential energy is

$$v_{\rm eff}(x) = \begin{cases} 0 & (x < \alpha) \\ V & (\alpha \leq x) \end{cases}, \tag{2a}$$

$$V = \varepsilon_F + \Phi\ , \tag{2b}$$

where V is the total barrier height, assuming that the Fermi energy ε_F and the work function Φ are known.

Now, it is not necessary that the one-electron potential be written as the functional of the electron density. We take the assumption that the effective one-electron potential can be written as Eq. (2) on the basis of one-electron approximation. The exchange, correlation, and other contributions are included in the $v_{\rm eff}$.

The solution of the wave equation,

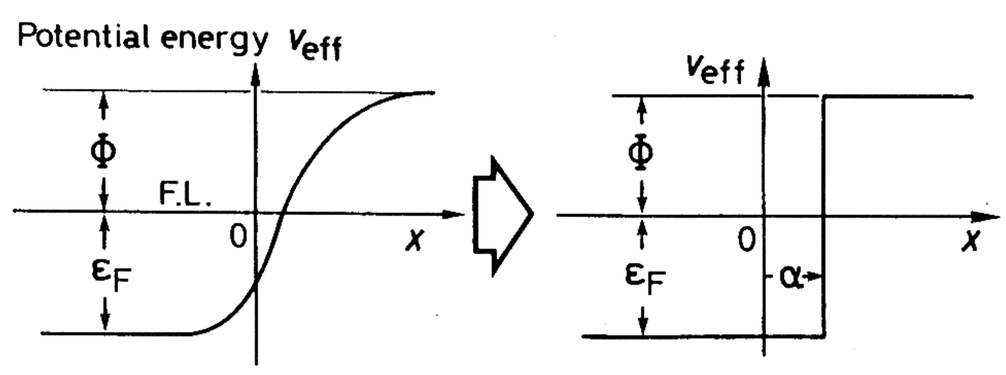

FIG. 1. Relation between the electron work function Φ, the Fermi energy ε_F, and the effective one-electron potential energy.

$$\mathcal{H}\Psi = \varepsilon\Psi \,, \tag{3a}$$

$$\mathcal{H} = -\frac{\hbar^2}{2m}\nabla^2 + v_{\text{eff}}(x) \,, \tag{3b}$$

can be written following Lang and Kohn:[1]

$$\Psi = A\Psi_x\Psi_y\Psi_z = A\Psi_x \exp(-ik_y y - ik_z z) \,, \tag{4}$$

$$\Psi_x = \begin{cases} \sin\left[k(x-\alpha)+\delta(k)\right] & (x<\alpha) \\ 0 & (x\to\infty) \,, \end{cases} \tag{5}$$

where the eigenfunction [Eq. (5)] and its differential should be continuous at the singularity $x=\alpha$, i.e.,

$$\Psi_x(\alpha-) = \Psi_x(\alpha+) \,, \tag{6a}$$

$$\frac{\partial\Psi_x}{\partial x}(\alpha-) = \frac{\partial\Psi_x}{\partial x}(\alpha+) \,. \tag{6b}$$

Now, the solution of Eq. (3a) can be written in analytic form,

$$A\Psi_x = \begin{cases} -\sqrt{\frac{2}{\Omega}}\sin(2\pi\kappa X+\delta) & (X<0) \\ \sqrt{\frac{2}{\Omega r}}\kappa\exp(-2\pi X\sqrt{r-\kappa^2}) & (0\le X) \,, \end{cases} \tag{7}$$

where

$$X = \frac{x-\alpha}{\lambda_F} \,,\ \kappa = \frac{k}{k_F} \,,\ r = \frac{V}{\varepsilon_F} \,, \tag{8}$$

and

$$\delta = \delta(r,\kappa) = \arctan\left(\frac{-\kappa}{\sqrt{r-\kappa^2}}\right) \,. \tag{9}$$

The coefficients of Eq. (7) are defined from the electron density of the bulk. The electron density is

$$n(x) = \frac{k_F^3}{3\pi^2}\mathcal{K}_1(X,r) \,, \tag{10}$$

where the $\frac{k_F^3}{3\pi^2}$ is the bulk density. The relative electron density $\mathcal{K}_1(X,r)$ is the function of X and r [see Eq. (8)],

$$\mathcal{K}_1(X,r) = \begin{cases} \frac{3}{2}\int_{-1}^{1}(1-\kappa^2)\sin^2(2\pi\kappa X+\delta)d\kappa & (X<0) \\ \frac{3}{2r}\int_{-1}^{1}(1-\kappa^2)\kappa^2\exp(-4\pi X\sqrt{r-\kappa^2})d\kappa & (0\le X) \,. \end{cases} \tag{11}$$

The surface energy γ_s of a crystal is the energy required, per unit area of new surface formed, to split the crystal in two along a plane. γ_s can be calculated from the total energy change in the splitting process.

The total energy per valence electron is the observable of the Hamiltonian. By using the Hamiltonian in Eq. (3a), the distribution of the energy density is written

$$\begin{aligned} \rho_{\text{energy}} &= \frac{2\Omega}{(2\pi)^3}\int_{\mathbf{k}_{\text{sphere}}}\Psi^*\mathcal{H}\Psi\, d^3k \\ &= \frac{\hbar^2 k_F^5}{10\pi^2 m}\mathcal{K}_2(X,r) \,, \end{aligned} \tag{12}$$

where

$$\mathcal{K}_2(X,r) = \begin{cases} \frac{5}{4}\int_{-1}^{1}(1-\kappa^4)\sin^2(2\pi\kappa X+\delta)d\kappa & (X<0) \\ \frac{5}{4r}\int_{-1}^{1}(1-\kappa^4)\kappa^2\exp(-4\pi X\sqrt{r-\kappa^2})d\kappa & (0\le X) \,. \end{cases} \tag{13}$$

The total energy is the integral of Eq. (12) over the space. So, the surface energy is given as

$$\gamma_s = \frac{\hbar^2 {k_F}^4}{5\pi m}\mathcal{K}_r(r) \,, \tag{14}$$

where

$$\mathcal{K}_r(r) = \int_{-\infty}^{-\alpha/\lambda_F}(\mathcal{K}_2-1)dX + \int_{-\alpha/\lambda_F}^{\infty}\mathcal{K}_2 dX \,. \tag{15}$$

As shown in Eq. (14) with Eqs. (8) and (2b), the surface energy γ_s is expressed as a function of Fermi energy ε_F and work function Φ. Exchange, correlation, and other contributions are obscurely enclosed in these material parameters.

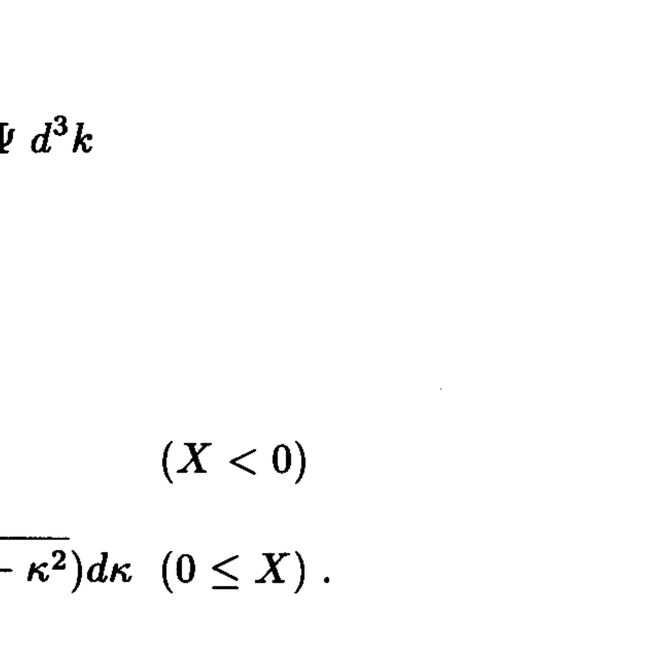

FIG. 2. Electron-density distribution near metal surface for $r_s = 5, r = 2.35$ (the solid line), which corresponds to SCF jellium result by Lang and Kohn (the broken line).

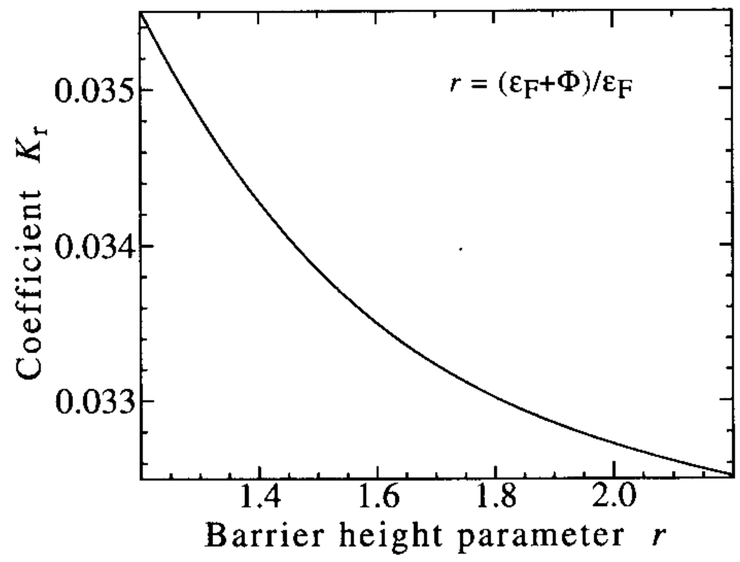

FIG. 3. The calculated result of the surface energy coefficient as a function of only $r(=\frac{\varepsilon_F+\Phi}{\varepsilon_F})$.

III. CALCULATED RESULTS AND DISCUSSION

Equation (11) gives the relative electron density as a function of X and r [see Eq. (8)]. A calculated result of the distribution of the relative electron density is plotted in Fig. 2 (the solid line). The SCF jellium result by Lang and Kohn also is plotted (the broken line). They are similar to each other, although the eigenfunction is not self-consistent. Friedel oscillations also can be represented. The surface energy is sensitive to the electron distribution. This similarity may give a good approximation for the surface energy.

The coefficient of the surface energy [Eq. (15)] is a function of only r which means the barrier height normalized by the Fermi energy [see Eq. (8)]. The coefficient $\mathcal{K}_r$ is plotted in Fig. 3 as a function of r. As for common metals, the barrier height parameter r takes the value from 1.35 to 2.2. The coefficient of the surface energy is, therefore, $3.35 \times 10^{-2} \pm 3\%$, i.e.,

$$\gamma_s = \frac{\hbar^2 {k_F}^4}{5\pi m} 3.35 \times 10^{-2} \pm 3\% \,. \tag{16}$$

The surface energy calculated from Eq. (16) is plotted in Fig. 4. It is compared with the experimental values[2] extrapolated to 0 K, the SCF jellium result by Lang and Kohn,[1] and the structureless pseudopotential result by Perdew, Tran, and Smith.[2] The result of Eq. (16) approaches the results by Perdew, Tran, and Smith and Lang and Kohn for large r_s. This suggests that the shifted step potential is one of the good approximations at the low electron density limit. The $\pm 3\%$ may explain the fact that the surface energy is sensitive to ε_F and it is not sensitive to Φ. This would mean that the surface

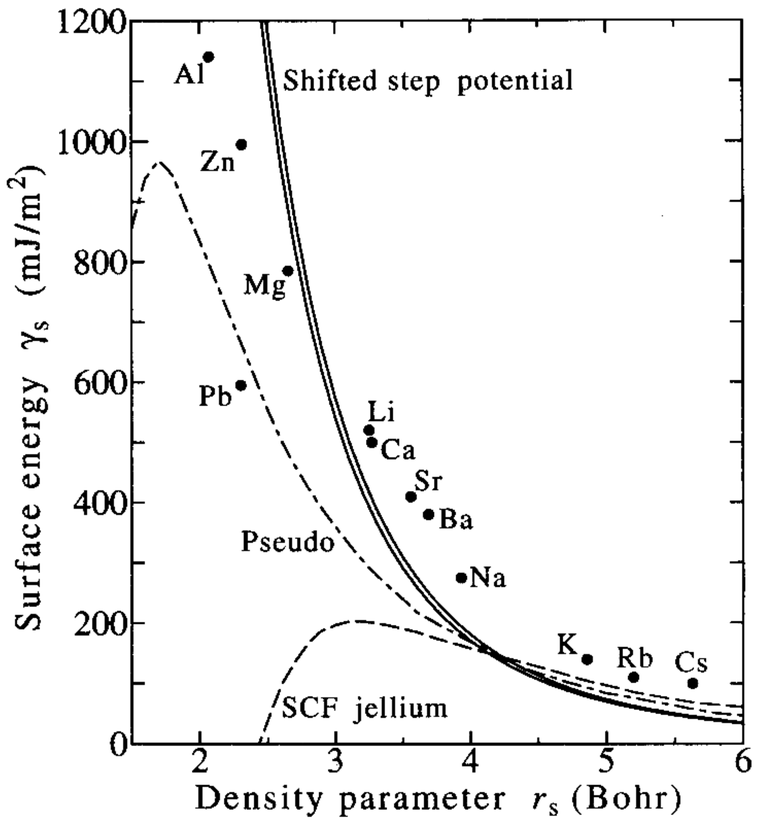

FIG. 4. Surface energy calculated here by using the shifted step potential compared with experimental value extrapolated to 0 K, the SCF jellium result by Lang and Kohn, and the structureless pseudopotential result by Perdew, Tran, and Smith.

energy is in proportion to the fourth power of the Fermi ~~energy~~. wave vector k_F

Exchange, correlation, and other contributions are obscurely enclosed in ε_F and Φ, and the eigenfunctions obtained [Eq. (7)] are not self-consistent. However, the electron density is very similar to the SCF jellium result by Lang and Kohn. This approximation can propose a rough understanding of the relation between the surface energy γ_s, the Fermi energy ε_F, and the work function Φ.

IV. CONCLUSION

This paper is based on a simple approach to the electronic structure of semi-infinite jellium. The effective potential v_{eff} is approximated to be the step function which is shifted to give the charge neutrality. The eigenfunctions can be obtained in analytic form. They are not self-consistent. However, the electron density distribution calculated is very similar to that of the SCF jellium result. The calculated surface energy approaches the result by Perdew, Tran, and Smith and Lang and Kohn for the small electron density. The simplicity of this approximation proposes a rough understanding of the relationship between the surface energy and the material parameters at the low electron-density limit.

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