ON THE SURFACE ENERGY OF ELEMENTAL METALS USING THE STABILIZED JELLIUM MODEL

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Abstract

The surface energy of elemental metals was calculated using the stabilized jellium approach. The surface energy of the (111), (100) and (110) faces of the face centred cubic (fcc) and body centred cubic (bcc) metals was also calculated. The calculated surface energy of metals was compared with experimental values and the variation of the calculated and experimental surface energy of metals with electron gas parameter was studied. The surface energy of metals calculated based on the kinetic, electrostatic, exchange-correlation, and pseudopotential components were higher than experimental values. The surface energy calculated without taking the different components into consideration was in perfect agreement with experimental values in the low-density regim. But in the high-density limit, there were discrepancies between the calculated surface energies and experimental values. The discrepancies increased towards the high-density limit. The calculated face dependent surface energy of bcc metals reveal that the (111) face has the highest surface energy while the (110) face has the least surface energy. But for the fcc metals the (110) face has the highest surface energy while the (111) face has the least surface energy.

***Keywords**: Metals, surface energy, stabilized jellium model, electron density parameter*

1. Introduction

Surface energy of solids is one of the important electronic properties of solid surfaces and controls a wide range of phenomenon such as stress for brittle fracture, the rate of sintering and the growth rate during particle coarsening. Consequently, a lot of efforts have been made to study surface energy theoretically and experimentally. Early calculation of surface energy excluded the important contributions of correlation and exchange (Huntigton, 1951). Lang and Kohn (1970), introduced the exchange and correlation contributions using local density approximation. The surface energy is the sum of four terms: kinetic, electrostatic, exchange and correlation terms. Lang and Kohn (1970) showed that the surface energy of the jellium was negative at high-electron density. The surface energy was negative because of the large contribution of the kinetic surface energy. Harris and Jones (1974) used the infinite barrier model to calculate the surface energy of metals. The infinite barrier model gave positive surface kinetic energy for metals unlike the results of Kohn and Lang (1970). In the infinite barrier model, the sum of the surface, exchange and correlation energy is dominated by the large contribution from the surface kinetic energy. Mahan (1975) used variational calculation of the jellium model of a metal surface to obtain results that prove that the results of Lang and Kohn (1970) are better than those reported using the infinite barrier and Kohn (1970) by treating the ground state of the metal surface variationally and self-consistently. The results of Monnier and Perdew (1978) revealed that the surface energy of some metals is lower

than the values predicted by Lang and Kohn (1970). Zhang et al. (1990) used the self-consistent Langreth-Mehl calculations for metal surfaces to calculate the surface energy of most densely closed packed faces of face centred cubic metals. The results of the self-consistent Langreth –Mehl calculations were close to experimental values for some of the metals. Skriver and Rosengaard (1992) used the *ab initio* method to calculate the surface energy for face centred cubic (fcc), body centred cubic (bcc) and hexagonal closed packed (hcp) metals. There were discrepancies between the *ab initio* calculated surface energy of metals and experimental values. Shore and Rose (1991) proposed the theory of idea metals and used the theory to predict the trend in surface energies among other properties. Kaijna (1993) calculated the surface energy of Li, Na, K, Rb,Cs, Al, Pb, Zn, and Mg using the structureless pseudopotential method. The results of this calculation were close to experimental values. Zang et al., (2006) calculated the surface energy of bcc transition metals using the second nearest neighbour modified embedded atoms method for 24 different faces of bcc metals. Their results for the bcc metals were consistent with experimental values for the (110), (100) and (111) faces and they proposed that for model. Monnier and Perdew (1978) improved the work of Lang the bcc metals, the (110) texture should be favourable for thin film formation.

In this work, the surface energy of elemental metals consisting of body centred cubic (bcc), face centred cubic (fcc) and hexagonal closed packed (hcp) metals was calculated using the stabilized jellium model. The results obtained using the stabilized jellium model will be compared with experimental values and the variation of the calculated surface energy of metals with electron gas parameter will be investigated.

The stabilized jellium model requires less computer resources unlike the self-consistent method of Monnier and Perdew (1978) and the *ab initio* surface calculation of Skriver and Rosengaard (1992). Also, the stabilized jellium model is used in conjunction with the density functional theory.

2. Theoretical Consideration

The surface energy of a metal is the energy required to create a new unit area (Lang and Kohn 1970). The energy functional of a stabilized jellium model is (Kiejna, 1993)

$$E[n,n_+]=E_J[n,n_+]+(E_m+W_R)\int d^3r\, n_+(r)+\langle\delta v\rangle_{ws}\int d^3r\,\theta(r)[n(r)-n_+(r)] \quad (1)$$

where E_J is the jellium total energy functional given as

$$E_J = T_s[n]+E_{xc}[n]+\frac{1}{2}\int d^3r\,\phi([n,n_+],r)\left[n(r)-n_+(r)\right] \quad (2)$$

$T_s[n]$ and $E_{xc}[n]$ are the respective kinetic and exchange-correlation energies. $\phi([n,n_+],r)$ is the electrostatic potential of the jellium. E_m is the Madelung energy; W_R is the short range repulsive potential of the ionic potential and $\theta(r)$ is the unit function. For a metal surface, the second term in eqn. (1) does not contribute to the surface energy since it is purely a bulk property of the metal.

The surface energy is conventionally decomposed into the kinetic, electrostatic, exchange-correlation and the pseudopotential terms (Lang and Kohn, 1970) as

$$\sigma = \sigma_s + \sigma_{es} + \sigma_{xc} + \sigma_{ps} \quad (3)$$

where σ_s is the kinetic surface energy, σ_{es} is the surface electrostatic energy, σ_{xc} is the exchange-correlation surface energy and σ_{ps} is the pseudopotential surface energy term. The terms are expressed (Lang and Kohn, 1970) as

$$\sigma_s = \frac{1}{2\pi^2}\int_0^{k_f} dkk^3\left(n_k - \frac{\pi}{4}\right) - \int_{-\infty}^{\infty} dxn(x)\left[V_{eff}(x) - V_{eff}(-\infty)\right] \quad (4)$$

where n_k is the phase-shift and V_{eff} is the effective potential in the stabilized jellium model. For the electrostatic surface energy

$$\sigma_{es} = \frac{1}{2}\int_{-\infty}^{\infty} dx\phi(x)\left[n(x) - n_+(x)\right] \quad (5)$$

and the exchange-correlation components is

$$\sigma_{xc} = \int_{-\infty}^{\infty} dxn(x)\left\{\varepsilon_{xc}[n(x)] - \varepsilon_{xc}[\bar{n}]\right\} \quad (6)$$

In eqn. (8), ε_{xc} is the exchange-correlation energy in the local density approximation of the density functional theory, n(x) is the electron density and $n_+(x)$ is the density of the positively charged background. The jellium surface energy does not include the pseudopotential surface energy.

The pseudopotential surface energy is the surface energy arising from the stabilization of the jellium and it is

$$\sigma_{ps} = <\delta v>_{ws} \int_{-\infty}^{0} dx[n(x) - n_+(x)] \quad (7)$$

where $<\delta v>_{ws}$ is the stabilization potential given as (Perdew et al., 1990)

$$<\delta v>_{ws} = -\frac{d}{d\bar{n}}\left[t_s(\bar{n}) + \varepsilon_{xc}(\bar{n})\right] \quad (8)$$

where $t_s(n)$ is the kinetic energy in the density functional theory under the local density approximation.

Hence

$$\sigma = \sigma_{jellium} + \sigma_{ps} \quad (9)$$

For any exposed crystal face, the surface energy can be expressed as

$$\sigma = \sigma_{jellium} + \sigma_{ps} + \frac{3z}{10r_0}[1 - \frac{5}{12}\left(\frac{d}{r_0}\right)^2] \quad (10)$$

where $r_0 = z^{1/2}r_s$, r_s is electron gas parameter defined through the relation, $n_{ave} = 3/4\pi r_s^3$ $n_{ave} = 3/4\pi r_s^3$ and d is inter-planar spacing. The exchange and correlation energy used in this work is the exchange and correlation energy of Carpely and Alder as parameterized by Perdew and Zunger (1981).

Equations (4), (5), (6) and (7) for the different components of the surface energy of metals

were solved based on the stabilized jellium model in conjunction with the density functional theory under the local density approximation. The results obtained from eqn. (4), (5), (6), and (7) were used to calculate the surface energy of metals and its face dependence using equations. (9) and (10) respectively. Also, the surface energy of metals was calculated using the parameterised expression of Brajczewska et al. (2001). The parameterized expression of Brajcwska et al. (2001) does not take into account the different components of the surface energy of metals. The calculated surface energy of metals was compared with experimental values.

3. Results and Discussion

The variation of the calculated kinetic, exchange and correlation, pseudopotential and electrostatic surface energies, with electron gas parameter is shown in Fig. 1. Also in Fig. 1 is the variation of surface energy calculated using eqn. (9) and experimental values of surface energy of metals taken from Skriver and Rosengaard, (1992) with electron gas parameter. Figure 1 revealed that the pseudopotential, exchange-correlation and electrostatic components of the surface energy decreases with an increase in the electron gas parameter. In the low-density region, the values of these surface energy components are close. As shown in the Fig. 1, the surface kinetic energy component is negative and increases with increase in the electron gas parameter. The trend exhibited by the kinetic, electrostatic and exchange-correlation surface energy components are in agreement with the trend predicted theoretically using the local density functional theory (Lang, 1983). As shown in Fig. 1, the surface energy calculated using eqn. (9) and experimental values decreases with an increase in the electron gas parameter, suggesting that surface energy of metals depends directly on the electronic concentration of the metal surfaces. The calculated surface energy values are not in good agreement with experimental values except in the low-density limit, where the calculated surface energy values are close to experimental values. The discrepancies between the calculated surface energy and the experimental values increase with a decrease in the electron gas parameter. Towards the high-density limit, the calculated surface energies are more than three times the experimental values. The large difference between the calculated and experimental surface energies may be due to the over estimation of the kinetic, exhange-correlation, electrostatic, and pseudopotential components of the surface energy as these components cannot be measured experimentally.

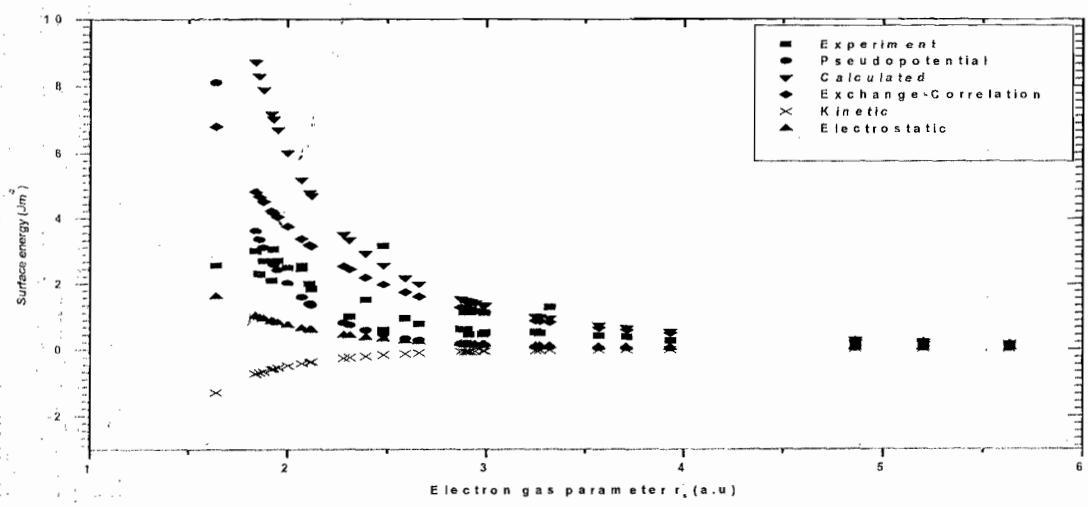

Fig. 1: Variation of kinetic, exchange-correlation, electrostatic and pseudopotential components of surface energy, experimental and calculated surface energies of metals with electron density parameter.

The variation of the surface energy calculated using the parameterized expression of Brajczewska et al., (2001) and experimental values is shown in figure 2. Figure 2 revealed that both the calculated and experimental surface energies decreases with increase in the electron gas parameter as metals in the high-density region has high surface energies while metals in the low-density has lower surface energies. As shown in figure 2, for r_s > 3a.u, (low density region) there is a good agreement between calculated surface energies of metals and experimental values. The agreement between the calculated surface energies and experimental values for metals in the low-density region may be due to the sp-bonds possessed by metals in this region. Metals possessing sp-bonds such as the alkali metals and the earth-alkaline metals are found in this density region. The alkaline metals approximate the free electron model on which the stabilized jellium model is based. In the high-density limit, r_s < 2.5a.u, there is disagreement between calculated and experimental values, although there are some metals in this density region whose surface energy agree quite well with experimental values. The disagreement between calculated and experimental values increases as r_s tend to the high-density limit. The disagreement between calculated and experimental values of the surface energies of metals in the high-density region may be due to their high bond strengths. Metals in the high-density region are characterized by d-bonds. The surface energy of the metals in the high-density region is affected by other properties such as the bond strength, crystal strength, and band energy. These were not put into consideration by the stabilized jellium model. In general, the surface energy of metals calculated using the stabilized jelium model is positive in the whole density range unlike the jellium model that gave negative surface energies for metals in the high-density region (Lang, 1983). This is because in the stabilized jellium model, the kinetic surface energy does not dominate at the high-density limit. If it does, the calculated surface energy of metals would have been negative in the high-density region.

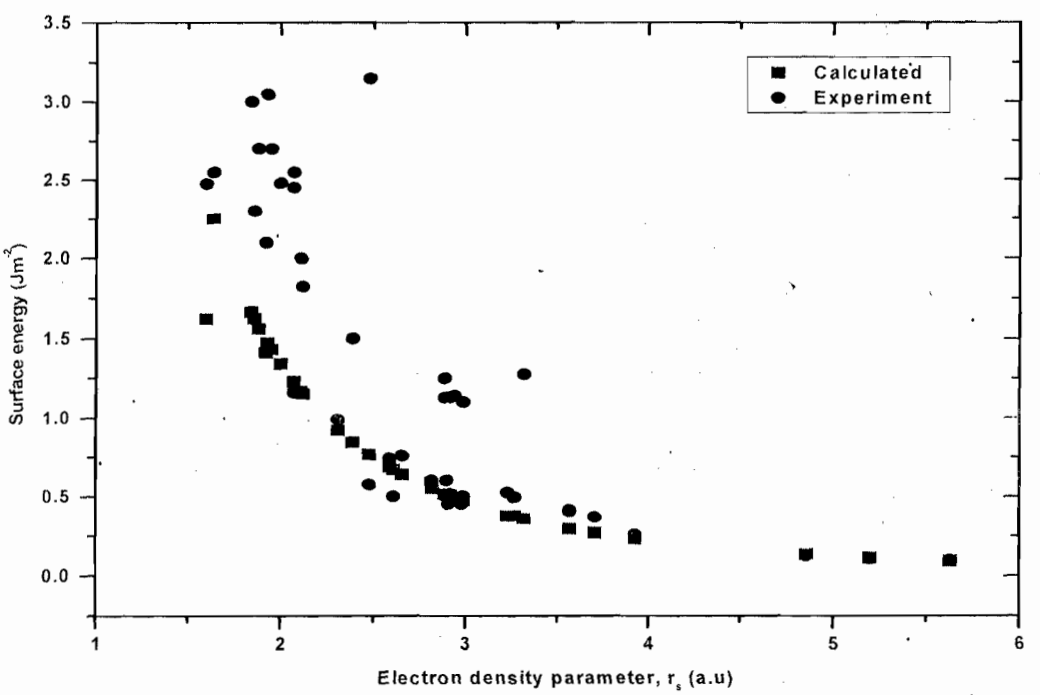

Fig. 2: Variation of calculated and experimental surface energies of metals with electron density parameter.

Figure 3 revealed that for the body centred cubic metals, the (111) face has the highest surface energy followed by the (100) face while the (110) face has the least surface energy. But in Fig. 4, for the face centred cubic (fcc) metals, the (110) face has the highest surface energy followed by the (100) face while the (111) face has the least surface energy. These are in agreement with the predictions of Lang and Kohn (1970) and prove that there is a direct relationship between work function of metals and their surface energies.

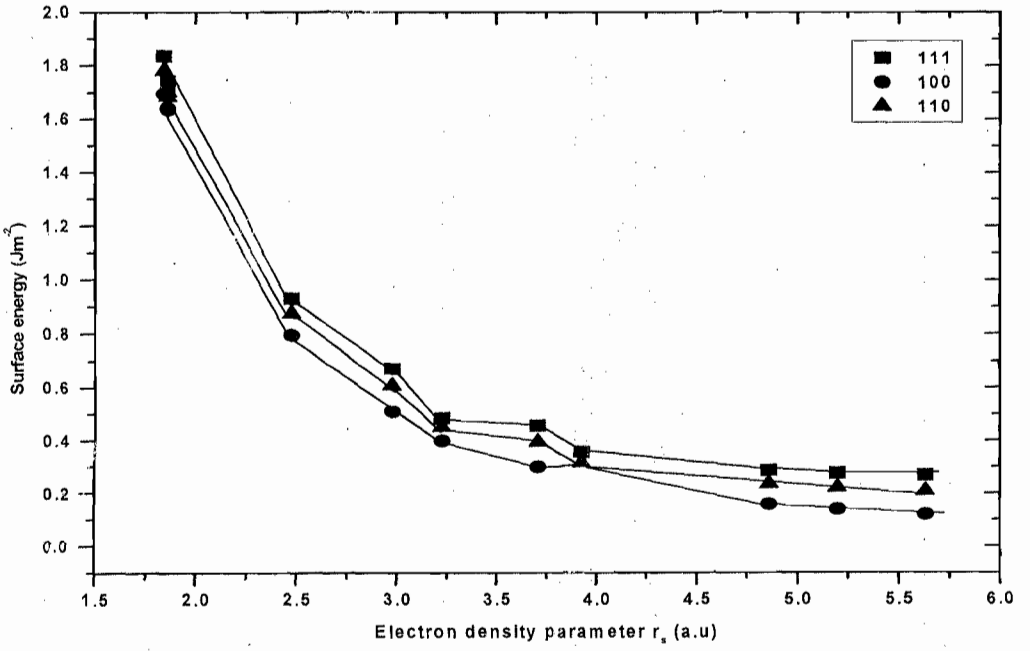

Fig. 3: Variation of surface energy for the (111), (100) and (110) faces for body centred cubic (bcc) metals with electron density parameter

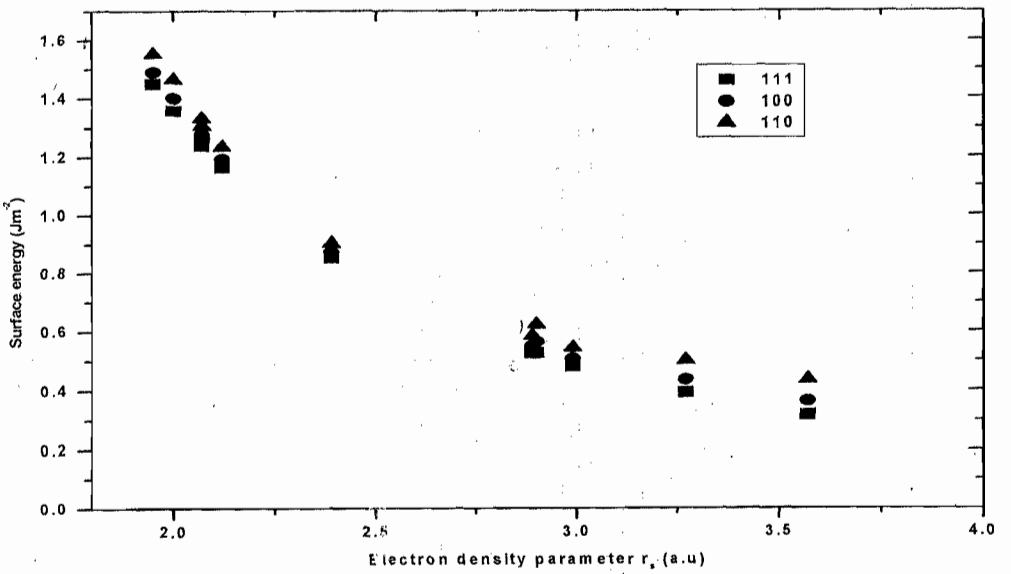

Fig. 4: Variation of surface energy for the (111), (100) and (110) faces of face centred cubic (fcc) metals with electron density parameter.

The results obtained in this work are in better agreement with experiment results than the results of Kaijna (1993). Also the results obtained in this work is in better agreement with experimental values than the work of Takahashi and Onzawa (1993) that used a shifted-step-potential approximation to obtain a simple formula for calculating surface energy. In the low-density limit, the results of Takahashi and Onzawa (1993) were lower than experimental values while they were higher than the experimental values in the high-density limit. The results obtained in this work are lower than the *ab initio* results for the (110) and (111) faces for the metals in the high-density region (Skriver and Rosengaard, 1992).

4. Conclusion

The surface energy of metals was successfully calculated using the stabilized jellium model. Calculating the surface energy of metals through the kinetic, exchange-correlation, electrostatic, and pseudopotential components does not give results that are in good agreement with experimental values. The parameterized expression of Brajczewska et al. (2001) gives surface energy of metals that are in good agreement with experimental values. The surface energy of metals depends directly on the concentration of electrons on the metal surface. The surface energy of sp-bonded metals in the low-density limit is good agreement with experimental values. But the surface energy of the d and f bonded metals in the high-density region are not in good agreement with experimental values because the surface energy of the d and f-bonded metals are affected not only by the electronic concentration of the metals. The surface energy of the body centred cubic (bcc) and face centred cubic (fcc) metals for the (111), (110) and (100) faces follows a trend which suggests a direct relationship between surface energy and work function of metals.

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