STABILIZED JELLIUM MODEL-DERIVED SURFACE STRESS OF METALS

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Abstract

A model for calculating the surface stress of metals based on the stabilized jellium model was fully developed. The model was used to calculate the surface and face dependent surface stress of metals (Mo, Pb, Ni, Cu, Rh, Pd, Ag, Ir, Pt, Al, Y, Au, Zr, and Ru). The surface stress of metals calculated using the stabilized jellium model was compared with surface stress of metals calculated using other methods and available experimental values. The result obtained revealed that tensile stress is present on the surfaces of the metals. Metals in the high-density limit have high strain derivative and high values of surface stress while metals in the low-density limit have low strain derivatives and low values of surface stress. The results obtained in this work compares very well with results obtained using other methods and compares well with available experimental values. The stabilized jellium model predicts poorly the face dependence of surface stress of metals.

Keywords: *Metals, surface, stress, stabilized jellium model and strain derivative.*

Introduction

Surface stress is the solid state analogue of surface tension. Surface stress is essential where dynamical, structural and morphological issues are studied (Sander, 2003). The surface stress is the reversible work per unit area needed to elastically stretch a pre-existing surface (Cammarata,1994).

Surface stress originates from the nature of chemical bonding of atoms at the surface. The atoms in the surface are bonded differently from the atoms in the interior. Consequently, the atoms at the surface would have an equilibrium interatomic distance different from that of the interior atoms if the surface atoms were not constrained to remain structurally coherent with the underlying lattice (Cammarata, 1994). Surface atoms have lower co-ordination number than atoms in the bulk. Consequently, surface bonds may contract to increase the effective co-ordination number towards the bulk value (Needs and Godfrey, 1990).

The sign of surface stress is positive if the surface would contract under its own stress. Surface stress is called "tensile" when the stress is positive and "compressive" when the stress is negative. Surface stress is positive for clean surfaces (Ibach, 1997). Surface stress is negative or compressive when the surface layer tends to expand and positive or tensile when a smaller lattice constant is preferred.

Surface stress and surface energy are of different nature. For a solid, the surface energy is positive; else the solid would gain energy by fragmentation. The surface stress can be either positive or negative (Kollar et al., 2003). Surface stress depends on

the surface and direction of strain and is given in general a rank two symmetric tensor of three components; For symmetrical surfaces such as cubic (001) or (111) surface stress is just one component (Marcus *et al.,* 2000). Surface stress affects surface stability, dynamical properties such as surface vibration (Needs and Godfrey, 1990). Surface stress play very vital roles in surface construction and reconstruction, shape transition in nanoscale particles, surface alloying, surface diffusion epitaxial growth, and self-assembled domain patterns (Sanders, 2003). Surface stress also influences surface stability, defect formations, deformations and dynamics of metal surfaces. Surface stress plays basic roles in understanding and modelling phenomena taking place on solid surface.

Surface stress can be measured experimentally using atomic force microscope (Raiteri *et al.*, 1998) and Cantilever balancing method (Ibach, 1997). It has been proposed that absolute surface stress could be determined by measuring the detailed curvature of a thin membrane of the material as it bends by gravitation through its own weight. Unfortunately, up to now there is no practical method to determine the absolute surface stress (Ibach, 1997, Sander, 2003).

Surface stress has been a subject of study theoretically using different theories and techniques. Needs (1987), Needs and Godfrey (1990) performed first principle calculations of the surface stress tensor of aluminium (111) and (110) surfaces. Their calculation showed that tensile stress is present in the aluminium (111) and (110) faces, which causes the face to contract in the plane of the surface.

Gumbsch and Daw (1991) used the embedded-atom method to calculate the surface stress and interface stress for some fcc metals. The surface stress for the metals was positive and in many cases, the interface stress was negative.

Marcus (2000) used the composite elastic model to calculate the surface stress for the (001) face of Mo. The surface stress obtained for the (001) face of Mo was tensile. Marcus *et al.*, (2000) estimated some surface region parameters such as in-plane lattice constant and epitaxial elastic constant. Kollar *et al.*, (2003) used the density functional theory within the framework of the exact muffin-tin orbitals to calculate the surface stress for the (111) face for Rh, Pd, Ag, Ir, Pt and Au. The stress of the metals was tensile and the stress they calculated for Pd, Ir and Au was in good agreement with *ab initio* data.

Kada *et al.*, (2006) used the density functional theory formulated within the framework of the exact muffin-tin orbitals method to calculate the surface stress of 4d transition metals. Their calculations showed that the 4d transition metals have tensile stress along the (111), (110) and (100) faces. The surface stress of the 4d metals is in reasonable agreement with full-potential data.

In this work, we apply the structureless pseudopotential formalism to calculate the surface stress of metals ((Mo, Pb, Ni, Cu, Rh, Pd, Ag, Ir, Pt, Al, Y, Au, Zr, and Ru). Unlike the *ab initio*, embedded atom, muffin-tin orbitals methods, the structureless pseudopotential model requires less computational resources, less input parameters and can be used in conjunction with the density functional theory.

Theoretical Consideration

The change of the total energy of a system during the change in the surface elastic strain tensor ij of the deformation tensor is given by (Kollar et al., 2003)

$$\int \sum_{ij} \sigma_{ij}(r)\delta\varepsilon_{ij}dr \qquad (1)$$

where ij(r) stands for the stress tensor at a point, r. Considering the geometry of the metal and assuming periodicity in x and y directions we have

$$\delta E = A \int_{-d/2}^{d/2} \sum_{ij} \tau_{ij}(z)\delta\varepsilon_{ij}dz \qquad (2)$$

where d is the thickness of the metal slab, and ij(z) are the components of the metal slab stress tensor introduced as

$$\tau_{ij}(z) = \frac{1}{A}\int\sigma_{ij}(r)dxdy \qquad (3)$$

where ij(z) is

$$\tau_{ij}(z) = \int\left[\tau_{ij}(z) - \tau_{ij}^{(b)}\right]dz \qquad (4)$$

where ij(b) is the stress tensor in the bulk region. For the surface stress tensor, equation (2) can be separated into two parts as

$$\delta E = 2\delta E^{(s)} + \delta E^{(b)} = 2A\sum_{ij}\tau_{ij}^{(s)} + Ad\sum_{ij}\tau_{ij}^{(b)}\delta\varepsilon_{ij} \qquad (5)$$

The factor of two comes from the two surfaces of the metal slab. From equation (5)

$$\delta E^{(s)} = \frac{1}{2}\left[\delta E - \delta E^{(b)}\right] = A\sum_{ij}\tau_{ij}^{(s)}\delta\varepsilon_{ij} \qquad (6)$$

and

$$\tau_{ij}^{(s)} = \frac{1}{A}\frac{\partial E^{(s)}}{\partial\varepsilon_{ij}} \qquad (7)$$

But, $E^{(s)} = A\gamma$ where is the surface energy and it is defined as the reversible work per unit area to create a surface, so we can write

$$\tau_{ij}^{(s)} = \frac{1}{A}\frac{\partial A\gamma}{\partial\varepsilon_{ij}} = \gamma\delta_{ij} + \frac{\partial\gamma}{\partial\varepsilon_{ij}} \qquad (8)$$

Where $\partial\gamma/\partial\varepsilon_{ij}$ is the residual stress. ij is the kronecker delta function, i,j denote the directions in the surface plane surface.

Based on the work of Needs and Godfrey, (1990), the surface stress can be written as

$$\tau(\bar{n}) = \gamma(\bar{n}) - \frac{\bar{n}\,d\gamma(\bar{n})}{d\,\bar{n}} \qquad (9)$$

where $\gamma(\bar{n})$ is the surface energy in the stabilized jellium of density $n = 3/4\pi r_s^3$ The second term in the right hand of equation (9) is the strain derivative of the surface energy, which in terms of r_s is given as (Needs and Godfrey, 1990)

$$-\bar{n}\frac{d\gamma}{d\bar{n}} = \frac{r_s}{3}\frac{d\gamma}{dr_s} \qquad (10)$$

Hence

$$\tau = \gamma + \frac{r_s}{3}\frac{d\gamma}{dr_s} \qquad (11)$$

$$\tau - \gamma = \frac{r_s}{3}\frac{d\gamma}{dr_s} \qquad (12)$$

Equation (12) shows that the difference between the surface stress and the surface energy is the strain derivative. The face dependent stress is calculated using the expression

$$\tau = \gamma + \frac{r_s}{3}\frac{d\gamma}{dr_s} + \frac{3z}{10r_0}\left[1 - \frac{5}{12}\left(\frac{d}{r_0}\right)^2\right] \qquad (13)$$

where z is valency, $r_0 = z^{1/3}r_s$, r_s is electron density parameter and d is the interplanar spacing for the face. In this work the parameterized expression of the surface energy of metals based on the jellium model of Brajczewska et al., (2001) was used.

In this work, we calculated the surface stress of metals using equation (11) and the face dependent surface stress using eqn. (13).

3. Results and Discussion

The calculated stress, strain derivative

for the metals are positive showing that tensile stress is present on the metals surfaces. This is in agreement with results obtained using other models (Cammarata, 1994, Kadas et al., 2006). Both the strain derivative and the surface stress of metals decreased with an increase in the electron gas parameter as shown in figure 1. In the high-density, $r_s \leq 2.50$a.u the main contribution to the stress comes from the strain limit $r_s \geq 3.0$, the surface stress is small and the strain is also small. In the low-density limit, the difference between the calculated stress and strain derivative is small and this increases towards the low-density limit. In the high-density limit, the stress is more than twice the strain derivative. Table 1 shows the stabilized jellium
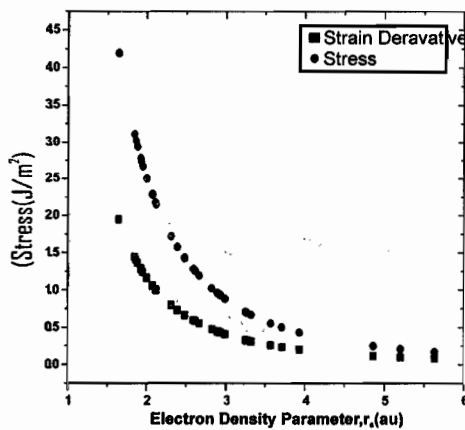

Fig. 1: Variation of surface stress and strain derivative of metals with electron density parameter.

model calculation of the surface stress of body centred cubic (bcc), face centred cubic (fcc) and hexagonal close packed (hcp) metals. Also shown in Table 1 is the surface stress of some metals calculated using other models and few available experimental values. As shown in table 1, the surface stress of the (111), (100) and (110) faces are positive. Table 1 shows that the stabilized jellium model produced poor surface dependence of the surface stress of metals. The stabilized jellium model results of the surface stress of Au, Pb, Rh, Ag (100) and Pb are close

to the results obtained for the metals by Kadas et al., 2006, Gumbsch and Daw (1991). But the calculated surface stress calculated for Ni, Cu, Mo, Ru, Zr and Y were not in close to the results of Kadas et al. (2006). The observed discrepancy seems to suggest that the electronic configurations of these metals may be a major contributory factor affecting the surface stress of these metals. For example, Kadas et al. (2006) used a slap of N layers embedded in vacuum to calculate the surface stress for 4d transition metals. Our stabilized jellium model results were close to experimental values for Pt, Ag, and Au. But for Al, the calculated surface stress differed from the experimental value. The discrepancy between the calculated surface and experimental values may be due to poor vacuum conditions and it is not yet possible to determine the absolute value of the surface stress experimentally with acceptable accuracy (Kollar et al., 2003).

Table 1: Calculated and experimental values of surface stress of metals.

Metal	structure	Face	Surface stress (Jm⁻²)		
			Stabilized jellium	other calculations	Expt
Mo	bcc	flat	3.1106		
			3.1120		
		100	1.1108	3.27[a]	
		110	3.1115	4.15[a]	
Pb	fcc	flat	0.9531		
		111	0.9532	0.82[c], 0.95[a]	
		110	0.9540		
Ni	fcc	flat	2.2901		
		111	2.2902	0.43[c]	
		100	2.2904	1.27[c]	
		110	2.2907		
Cu	fcc	flat	2.1523		
		111	2.1524	0.86[c]	
		100	2.1527	1.38[c]	
		110	2.1531	0.86[c]	
Rh	fcc	flat	2.6747		
		111	2.6749	2.11[a]	
		100	2.6752	2.14[a]	
		110	2.6760	0.93[a]	
Ag	fcc	flat	0.9617		
		111	0.9618	0.75[a], 0.64[b]	
		100	0.9620	0.88[b],0.82[b],1.14[a]	
		110	0.9623	0.43[a], 1.415[c]	
Pt	fcc	flat	2.5043		
		111	2.5045	2.86[b] 2.574[c]	
		100	2.5042	2.69[a]	
		110	2.5053		
Pd	fcc	flat	1.7813		
		111	1.7814	2.15[a]	
		100	1.7818	1.69[a]	
		110	1.7824	0.68[a]	
Au	fcc	flat	1.5759		
		111	1.5760	1.51[b] 1.175[c]	
		100	1.5761	1.79[b]	
		110	1.5764		
Al	fcc	flat	2.2901		
		111	2.2902	1.25[c]	
		100	2.2904		
		110	2.2909		
Y	hcp	flat	1.2534		
		0001	1.2535	0.60[a]	
Zr	hcp	flat	2.1789		
		0001	2.1790	1.57[a]	
Ru	hcp	flat	2.7474		
		0001	2.7475	4.75[a]	

KEY
[a]Kada et al (2006)
[b]Gumbsch and Daw (1991)
[c]Cammarata (1994)

Conclusion

In this work, we have calculated the surface stress of metals of different crystal structures. The stress present in the metal surfaces is tensile stress. In the high-density limit, the strain derivative is high just like the surface stress while it is small in the low-density limit. The surface stress of metals exhibits a trend that suggests that there is a direct relation between surface stress and electron concentration of the metal surface. The stabilized jellium model surface stress was in good agreement with some available experimental results and surface stress calculated by other workers. But the stabilized jellium model produced poor face dependence of the surface stress of metals.

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