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Theoretical study on adsorbate-induced surface stress of iodide monolayer on Au(111) electrode

RONG XIE[*]
School of Materials Science and Chemical Engineering, Anhui Institute of Architecture and Industry,
Hefei 230022, PR China

The statistical thermodynamic theory of adsorbate-induced surface stress of anion adsorption monolayer on Au(111) has been established by using the lattice gas model and considering various components of the adsorbate-adsorbate interaction energies in the adlayer. The adsorbate-induced surface stress and its components due to various intermolecule forces of iodide adions on the Au(111) electrode surface have been calculated. The calculated surface stress of iodide adions on Au(111) approximates the experiment results. Among various components of the adsorbate-adsorbate interaction energies in the adlayer, the substrate –mediated interaction is significant for the adsorbate-induced surface stress, which shows that indirect contribution of the adsorption energy of iodide adions through the substrate-mediated interaction is very important.

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1. Introduction

Surface stress links the microscopic bonding configuration at an interfacial region with its macroscopic properties. It plays a central role in the thermodynamics of solid surfaces [1]. During the last decade increasing interest has been paid to processes which are strongly influenced by surface stress effects. In surface physics, the adsorbate induced modification in the surface stress is thought to play an important role in reconstruction process [2,3]. In thin films, the influence of the adlayer on surface stress is significant in epitaxial growth, nucleation, and dislocation etc. [4,5]. In biochemistry, the self-assembled molecular and biomolecular monolayers and biomolecular recognition have been investigated by means of the modulation of surface stress [6-8]. Relatively recently, it has been recognized that surface stress is a quantity which is important for a qualitative and sometimes even quantitative understanding of these microscopic and mesoscopic surface processes. New experimental methods have been developed which allow the study of surface stresses induced by sub-monolayer quantities of adsorbates on well defined metal [9, 10] and semiconductor [11] surfaces in ultrahigh vacuum, and it has been shown that the real-time monitoring of surface stress can be used to study surface reactions [12] even under elevated pressures. Increased knowledge about the surface stress of clean and adsorbate-covered metals has also been established by the development of new theoretical methods. The importance of surface stress for technological applications is demonstrated by the development of microcantilever sensors, which allow the detection of extremely small amounts of substances in gases or liquids [6].

Recently Evans et al [13] have measured the surface stress changes due to iodide adsorption on Au(111) of $-0.75\pm0.08 \mathrm{N\cdot m^{-1}}$. The surface stress measured compares well with the reported values for iodine adsorbed from solution onto a Au(111) electrode (0.1-$3.0\ \mathrm{N\cdot m^{-1}}$). However, the interpretation of the experiment results gave rise to some controversies [14,15]. For the electrocompression behavior of halide adlayers on Au(111), we have established a statistical thermodynamic theory and reasonably explained the relative experiment results [16]. In this paper, by using the similar method and taking iodide as an example, we attempt to establish the statistical thermodynamic theory of surface stress of anion adsorption monolayer on Au(111) and understand theoretically Evans et al’s experiment results.

2. Theory

2.1 Statistical thermodynamic theory

In order to apply our established statistical thermodynamic theory to iodide on Au(111), here we quote briefly the main formulas and necessary explanations from reference 16.

2.1.1 Physical model and partition function

Our physical model for iodide on Au(111) electrode assumes that the adsorbate monolayer consists of a regular two-dimensional lattice of adsorbates and constitutes a canonical ensemble. By using the Bragg-Williams approximation which is generally accepted and widely used in a system of adsorbates at a metal surface, the partition function (PF) to describe the halide adsorbate monolayer can been written as

$$(PF) = \frac{N_S!}{N_A!(N_S - N_A)!} j^{(s)}(T)^{N_A} \exp[-\frac{N_A(U+V)}{kT}], \quad (1)$$

where N_S and N_A are the number of substrate sites and adsorbates respectively. $j^{(s)}(T)$ is the partition function of a three-dimensional harmonic oscillator with the vibrational frequencies ν_x, ν_y and ν_z [16]. U is the potential energy at the minimum in an adsorbate-substrate interaction energy U(xyz).V is an average adsorbate-adsorbate interaction energy (the lateral interaction energy) per adsorbate

$$V = \frac{1}{2} Z\theta W \quad (2)$$

where Z is the nearest-neighbor coordinate number of an adsorbate. $\theta = N_A/N_S$ is the coverage of adsorbate relative to the substrate. W is an effective pair interaction energy between adsorbates

$$W = \frac{\sum_j V_{ij}}{Z}, \quad (3)$$

where V_{ij} is a pair interaction energy between the adsorbates i and j in the adlayer. The sum in eq 3 is over all sites in the adlayer except the adsorbate i.

Then the free energy thermodynamic function of halide adlayer on mental electrode surface is obtained as

$$F = -kT\ln(PF) \quad (4)$$

from which thermodynamic properties of the adlayer can be decuced.

2.1.2 Statistical thermodynamic formulas of surface stress

From the definition of the surface stress Δg, the statistical thermodynamic expression of surface stress can be written as [16-18]

$$\Delta g = \left(\frac{\partial F}{\partial A}\right)_{N_A,T} = -\frac{kT}{a_S}\left(\frac{\partial \ln(PF)}{\partial N_S}\right)_{N_A,T}$$

$$= -\frac{ZW\theta^2}{2a_S} + \frac{kT}{a_S}\ln(1-\theta) - kTN_A\frac{d}{dA}\ln j^{(S)}(T) + N_A\frac{dU}{dA} + \frac{ZN_A\theta}{2}\frac{dW}{dA}$$

(5)

where a_S and a are the area of a single Au atom and a single adsorbate. For Au(111), $a_S = \frac{\sqrt{3}}{2} r_S^2$, r_S =2.885Å.

Based on the relative discussions and deductions in reference 16, $(d/da)\ln j^{(S)}(T) \approx 0$; with the change of adsorption site, the adsorption energy changes very little, $dU/da \approx 0$, and eq 5 becomes

$$\Delta g = -\frac{ZW\theta^2}{2a_S} - \frac{Z\theta^3}{2a_S}\frac{dW}{d\theta} + \frac{kT}{a_S}\ln(1-\theta) \quad (6)$$

which is the statistical thermodynamic formula for calculating the surface stress of halide adsorbate monolayers on metal electrode. It is evident that the surface stress is determined by two factors: adsorbate density and the adatom-adatom interaction energy with its derivative. The third term in eq 6 represents the contribution of configurational entropy.

Usually a pair interaction energy between the adsorbates can be written as a sum of the inverse power of their distance

$$W = \sum_n W_n \quad (7)$$

$$W_n = \frac{A_n}{Z}\frac{C_n}{r^n} = \frac{A_n}{Z}\frac{C_n}{r_S^n}\theta^{n/2} \quad (8)$$

where C_n is the coefficient of interaction energy. A_n is the lattice sum, whose value for hexagonal structure is calculated and shown in Table 1. r and r_S are the nearest–neighbor distance between the adsorbates in the adlayer and between the substrate sites respectively. Setting eq 8 into eq 6, we obtain a fundamental formula for calculating the surface stress in the hexagonal-structure halide adlayer,

$$\Delta g = -\frac{1}{4a_S}\sum_n (n+2)A_nC_n\frac{1}{r_S^n}\theta^{\frac{n+4}{2}} + \frac{kT}{a_S}\ln(1-\theta) \quad (9)$$

Table 1. Lattice sums of the hexagonal structure.

n	3	4	5	6	7	8	9	10	11	12
A_n	10.975	7.711	6.762	6.375	6.195	6.105	6.057	6.031	6.018	6.010

2.2 Adsorbate-adsorbate (Lateral) interaction energies

According to the theory of chemisorption,[19-21] the components of the lateral interaction energies in the halide adlayer on metal electrode like Au、Ag、Pt include: (1)The electrostatic energy among the adions; (2) Induction energy, i.e., induced dipole-induced dipole interaction energy due to the electrode potential; (3) Lennard-Jones potential including the van der Waals attraction and Pauli repulsion; (4) Many-body interaction within the adlayer, such as the triple-dipole energy, and so on; (5) The substrate-mediated interaction energy. We consider and evaluate each as follows.

2.2.1 Substrate-mediated interaction

Atoms adsorbated on the surface of a solid interact with each other directly as well as indirectly through the substrate. The interaction between adsorbates on solid surfaces due to direct mechanisms is usually short-ranged (the repulsive due to the overlap of electronic orbitals) or weak (electric dipole-dipole interaction), [22] and therefore the indirect or through-the-substrate mechanism (substrate-mediated interaction) are of considerable interest. For most chemisorption systems, it is well-known [19, 23-25] that the substrate-mediated interaction is dominant among the components in the lateral interaction energy, especially for most atoms and small molecules even at monolayer coverage [26,27]. In physisorption adlayer, Sinanoglu, Pitzer [28] and Mclachlan [29] put forward and developed the substrate-effected dispersion energy. The simplest expression of Sinanoglu-Pitzer-McLachlan energy is [20,30]

$$S(r) = \frac{9}{16}\alpha\frac{1}{r^3}\left(\frac{S_3}{L^3}\right) \tag{10}$$

where α is the adatom polarizability, S_3/L^3 is the negative one-adatom holding potential, S_3 is the strength coefficient of adatom-substrate interactions, L is the perpendicular distance of the adatom from the substrate, and $9/16$ is an empirical parameter. The halide adatom on Au(111) is weakly chemisorbed because their chemisorption energies are quite smaller than the typical value of chemisorption energy of an adatom 1-7eV [24,21,32]. Hence for simplicity, we attempt to use a simplification form of the Sinanoglu-Pitzer-McLachlan energy, such as eq 10, to express the indirect interaction energy of halide adsorbates on Au(111). After considering the lattice sum of halide adlayer, [16] we have

$$W_{sub} = \frac{A_3}{Z}\alpha\frac{1}{r^3}\left(\frac{S_3}{L^3}\right) \tag{11}$$

where the units are W_{sub} in eV, r, L in Å ,and α in Å^3. It is noteworthy that eq 11 is an empirical expression of the substrate-medicated interaction.

2.2.2 Electrostatic interaction

Many experimental results indicate that the halide ions (aq) undergo spontaneous oxidation and transfer charge to Au electrode upon chemisorption and form almost a zero valent halide adlayer; the halide adsorbate on $Au(111)$ can carry a rather small charge, $(-1-\gamma)e$, where γ is the electrosorption valency. Similar to Langmuir's treatment of Cs on W, [33] after derivation, the electrostatic interaction energy between adions is [16]

$$W_{el} = \frac{14.4(1+\gamma)^2}{Z\varepsilon}\left(\frac{2A_3L^2}{r^3} - \frac{6A_5L^4}{r^5} + \frac{20A_7L^6}{r^7} - \frac{70A_9L^8}{r^9}\right) \tag{12}$$

where ε is the dielectric constant and the units are W_{el} in eV, r and L in Å .

2.2.3 Induction interaction energy

The induced dipole-induced dipole interaction energy is [16]

$$W_{ind} = 0.624\frac{A_3\mu_0^2}{Zr^3} = 0.624\frac{A_3}{Z}\frac{1}{r^3}\left(\mu_0^0 + \frac{1}{3}\frac{\alpha E'}{L}\right)^2 \tag{13}$$

where μ_0^0 is the dipole moment when the electrode potential E' is 0. α is the polarizability of an adatom. The units are W_{ind} in eV, μ_0, μ_0^0 in $Debye$, E'

in V, L and r in Å, α in $Å^3$.

2.2.4 Lennard-Jones potential

We combine Pauli repulsion between adatoms from the wave function overlap of the closed shell and van der Waals attraction between adatoms into the Lennard-Jones potential, [16]

$$W_{L-J} = 8.625\times10^{-5}\frac{\in}{Z}\left[A_{12}\left(\frac{r_0}{r}\right)^{12} - 2A_6\left(\frac{r_0}{r}\right)^{6}\right] \quad (14)$$

where $\in$ is the depth of the potential energy minimum, r_0 is the van der Waals diameter of the adsorbae atoms. The units are W_{L-J} in eV, r_0 in Å, $\in$ in K.

2.2.5 Nonadditive three body potential

The contribution of the nonadditive three body potential is present in the adlayer, [16]

$$W_{thr} = \frac{A_9}{Z}\frac{\upsilon}{3r^9} \quad (15)$$

where υ is strength of the three body interaction. The units are W_{thr} in eV, υ in $\mathrm{eV}\cdot Å^9$.

For the iodide adlayer the parameters in the forgoing formulas have been listed in Table 2. Their explanation and the parameters for the other halide anions refer to reference 16.

Table 2. Parameters used in the calculation of the iodide Adlayer on Au(111) surface.

Parameter	$S_3(eV\ Å^3)$	$\alpha(Å^3)$	$2L(Å)$	ε	γ
I^-	3.794	5.29	$2.40(hex)$	4.00	$-1.0(hex)$
Parameter	$E'_{Ag/AgCl}(V)$	$\mu_0^0(Debye)$	$r_0(Å)$	$\in(K)$	$\upsilon(eV\ Å^9)$
I^-	$0.21(hex)$	0.2	4.24	281.0	4.62

3. Results and discussion

Evans et al have measured the surface stress changes due to iodide adsorption on Au(111) of -0.75±0.08N·m^{-1}. In order to comprehend these experiment results, we have calculated the adsorbate-induced surface stress of the iodide adions on Au(111) electrode. In the first we should consider the adsorption of iodide on Au(111). Iodide is the largest, most polarizable, and strongest adsorbing of the halides and exhibits ordered phases over the widest potential region. Incommensurate, hexagonal monolayers are observed for iodide on the Au(111) electrode prior to bulk electrooxidation [34]. In the incommensurate hexagonal phase, with increasing potentials the separation decrease. The iodide adlayer coverage increases from 0.415 to 0.445 with increasing potential. With eq 9, the fundamental formula for calculating the surface stress in the hexagonal-structure halide adlayer, we calculated the contribution of iodide adions on Au(111) electrode to the surface stress and the different contributions to the surface stress from various components of the lateral interaction energies.

3.1 The different contributions to the surface stress from various components of the lateral interaction energies

From the formulas for calculating the surface stress eq 6, the surface stress is mainly constitute by two parts: the contribution of the interaction energies in the adlayer with their derivatives and the configuration entropy. The interaction energies consists five terms: (1) The substrate-mediated interaction energy; (2) The electrostatic energy among the adions; (3) Induction energy; (4) Lennard-Jones potential including the van der Waals attraction and Pauli repulsion between two adatoms; (5) Many-body interaction in the adlayer. In order to discuss the physical origin of the surface stress, we have calculated the contribution of each term of the interaction energies and configuration entropy, which is shown in Table 3 and Fig. 1.

Table 3. The contribution to the surface stress Δg *from each term of the interaction energies and configuration entropy (unit: in N·m*$^{-1}$*).*

θ	Δg_{sub}	Δg_{el}	Δg_{ind}	Δg_{L-J}	Δg_{thr}	Δg_{com}
0.415	-0.6791	0	-0.0094	0.0692	-0.0014	-0.0306
0.420	-0.7082	0	-0.0098	0.0695	-0.0015	-0.0311
0.425	-0.7381	0	-0.0103	0.0695	-0.0016	-0.0316
0.430	-0.7689	0	-0.0107	0.0690	-0.0017	-0.0321
0.435	-0.8007	0	-0.0111	0.0681	-0.0018	-0.0326
0.440	-0.8334	0	-0.0116	0.0667	-0.0020	-0.0331
0.445	-0.8670	0	-0.0120	0.0647	-0.0021	-0.0336

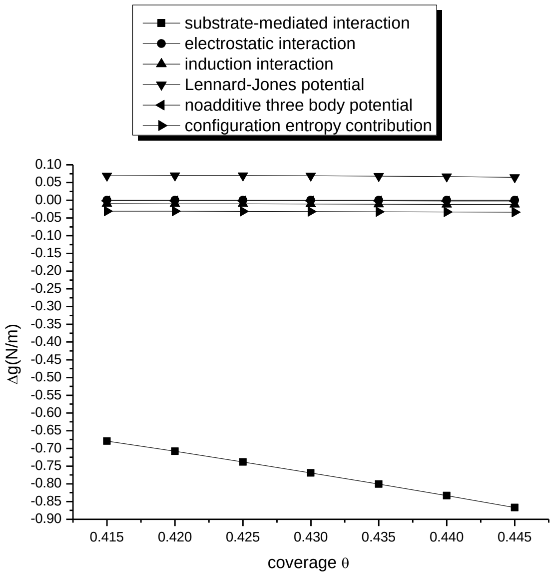

Fig. 1. The contribution of each term of the interaction energies and configuration entropy to the surface stress from iodide adions on Au(111) electrode: ■ substrate-mediated interaction; ●electrostatic interaction;▲ induction interaction; ▼ Lennard-Jones potential; ◀ noadditive three body potential; ▶configuration entropy contribution.

Table 3 and Fig. 1 reveal that, among various terms in the surface stress, except the positive contribution of Lennard-Jones potential, all the other terms are negative. Among them, the contribution of substrate-mediated interaction energy is determinant.

3.2 The contribution of iodide adions on Au(111) electrode to the surface stress

Summing Δg_{sub} , Δg_{el} , Δg_{ind} , Δg_{L-J} , Δg_{thr} and Δg_{com} in Table 3, we can get the contribution of iodide adions on Au(111) electrode to the surface stress Δg_{tol}. The calculated result is shown in Table 4 and Fig. 2.

Table 4. Contribution Δg_{tal} *of iodide adions on Au(111) to the surface stress.*

θ	0.415	0.420	0.425	0.430	0.435	0.440	0.445
Δg_{tol}	-0.6513	-0.6810	-0.7120	-0.7444	-0.7781	-0.8134	-0.8501

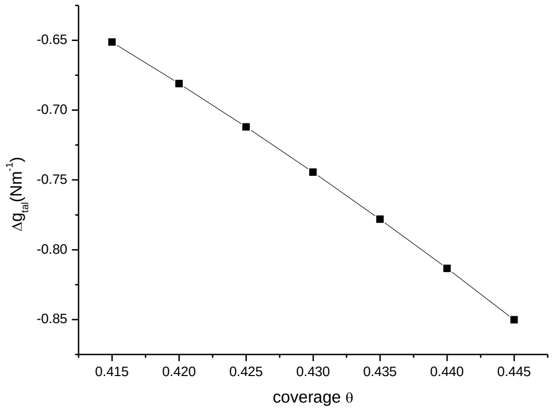

Fig. 2. Contribution Δg_{tal} *of iodide adions on Au(111) to the surface stress.*

Table 3 and Fig. 2 reveal two important results: (1) The contribution of iodide adions on Au(111) to the surface stress approximately to Evans et al's measurement; (2) The change of surface stress is approximately linearly correlated with coverage. In our model, the Bragg-Williams approximation is used, which is generally accepted and widely used in a system of adsorbates at a metal electrode [35]. Prince and Venables [30] pointed out at high coverage, the Bragg-Williams approximation becomes equivalent to assuming a random distribution of a small number of noninteracting vacancies. This approximation is good and much better than the normal application to regions of low coverage. With this approximation, we achieve satisfactory results in the iodide adlayers on Au(111).

4. Conclusion

The statistical thermodynamic theory of the adsorbate-induced surface stress of adion monolayer on Au(111) has been established by using the lattice gas model. The surface stress and its components due to various intermolecule forces of iodide adlayer on the Au(111) electrode surface have been calculated. The calculational result of surface stress of iodide adlayer is associated with the experiment. About the physical origin of the adsorbate-induced surface stress in iodide adlayer on Au(111) electrode, the analysis for various components of intermolecular forces indicates that the substrate-medicated interaction energies makes dominant contribution to the adsorbate-induced surface stress, through them the adsorption energy of adions on Au(111) plays indirectly a very important role.

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*Corresponding author: xr@aiai.edu.cn