Interface modelling for \textit{ab initio} evaluation of contact angle on a metallic surface

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Controlling the contact angles of the wettability is an important issue especially in industrial applications. Establishing its \textit{ab initio} predictions is hence a topic of great interest. For the predictions, it is required to setup a model of the adsorption structure of liquid molecules on a surface. The appropriate setting is expected to depend on whether the surface is of insulating or metallic materials, the latter of which is the target of the present study while all preceding \textit{ab initio} studies have worked on the former. Since the feasibility of \textit{ab initio} evaluations relies on the approximation of the liquid-gas interface energy evaluated roughly by the crystal ice, it would be a natural choice to take the periodic honeycomb array of the water molecules as the adsorbing model of water on the surface. Although the periodic model have successfully been used for the preceding treatments of insulating surfaces, we found for the case with metallic surfaces that the periodic model gives worse predictions to reproduce experimental values. Rather than that, the models with isolated water multimers are found to give better predictions. The ambiguity of the models about the size of multimers and the coverage is found to be small ($\pm 10^{-3}$), and is averaged over to give a plausible value based on the Boltzmann weight with the adsorbing energies. The procedure we are providing can generally be applicable to any of wettability on the surfaces of metallic materials.

\section*{INTRODUCTION}

Controlling the wettability on surfaces is an important topic relevant to wider industrial applications. \cite{1–3} Wettability of on metal surfaces is of significant interest in relation with heterogeneous catalysis, corrosion and electrochemistry. \cite{1, 4, 5} The wettability is reported to show some relevance to the catalytic activity in electrochemical reactions, \cite{6} where the receding contact angle of water is correlated with the oxygen reduction reactions. This implies the possibility to enhance the efficiencies of electrochemical reactions by controlling the contact angle of water wetting on the surfaces.

The contact angle, $\theta$, is the primary measure of the wettability, with the larger ($\theta > 90^\circ$) indicating hydrophobic, while the smaller ($0^\circ < \theta < 90^\circ$) hydrophilic. Experimentally, it is measured directly by observing the angle captured by cameras. \cite{7, 8} The angle is determined by Young’s relation, \cite{9, 10}

$$\cos \theta = \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}},$$

(1)

where $\gamma_{SG}$, $\gamma_{LG}$, and $\gamma_{SL}$ denote the surface energies at solid-gas, liquid-gas, and solid-liquid interfaces, respectively. \textit{Ab initio} evaluations of the contact angle have recently been developed and applied to several surfaces of insulators. \cite{1, 11} An application to the water/Si case \cite{11} predicts 88$^\circ$, being closer to the experimental value (91$^\circ$). It is also applied to water/transition metal oxides \cite{1}, estimating 100$^\circ$ [103$^\circ$] compared with the experimental value 103$^\circ \pm 2^\circ$ [101$^\circ \pm 3^\circ$] for CeO$_2$(111) [Nd$_2$O$_3$(0001)] system, achieving fairly good coincidence. In these estimations, $\gamma_{LG}$ for water was substituted by that of the crystal ice. Experimental results show that these surface energies are closer each other, \cite{12} being a basis of this treatment.

We notice that all the preceding \textit{ab initio} evaluations of the contact angles treat the surface of insulator. When we estimate that of metal surfaces the structural modeling to describe the molecules adsorptions on the surface would be different from that of the surfaces of insulators. In the preceding works, \cite{1, 11} the modeling of the adsorbing structure is taken as the ‘ice-like bilayer model’ \cite{13, 14} [Fig.1 (a)] (periodic honeycomb structure of the ice), being a natural choice corresponding to the modeling of $\gamma_{LG} = \gamma_{CG}$. For the metallic surface, Cu for instance, it is reported however that there are isolated water hexamers observed by STM experiments, \cite{15, 16} and hence the ‘bilayer model’ seems inappropriate to be taken. Rather than that, the ‘isolated models’ without any bridging by hydrogen bondings on the neighboring unit cells would be more appropriate.

To construct the isolated model, we have to consider further freedom of the modelling choice, namely which $N$-mer/oligomer (monomer to hexamer) with how much coverage (how many $N$-mers within a unitcell) should be specified. We have to examine as well whether the prediction could not be so largely depending on the specific choice of the modeling, which is the central topic of the present study. We have confirmed that (i) the isolated modeling gives better prediction of the contact angle being closer to the experimental values than the periodic honey-comb modeling of the water molecules on the metal surfaces, and (ii) for the choice freedom of $[(N$-mer)$\otimes$coverage$]$], the averaging with the Boltzmann weight based on the adsorption energy seems working well.

\section*{INTERFACE MODELLING}

Following the preceding studies, \cite{1, 11} we estimate

$$\gamma_{SG} - \gamma_{SL} = -E_{\text{ads}}^{\text{water}} / A,$$

(2)
The formula for the contact angle is then,
\[ \cos \theta = \frac{-E_{\text{ads}}}{A \cdot \gamma_{\text{ice}}} , \]  
being reduced to the \textit{ab initio} energy evaluations.

\[ E_{\text{ads}} = E_{\text{tot}} - E_{\text{water(onSurf)}} - E_{\text{CuSlab}} , \]

where \( E_{\text{CuSlab}}, E_{\text{water(onSurf)}}, \) and \( E_{\text{tot}} \) denote the energy of Cu-slab, the energy of water molecules under the adsorbed structure on the surface, and the total energy of the system with the molecules on the surface, respectively. The surface energy \( \gamma_{\text{ice}} \) is evaluated as
\[ \gamma_{\text{ice}} = \frac{E_{\text{ice}}(n; \text{Slab}) - E_{\text{ice}}(n; \text{Bulk})}{2A_{\text{ice}}} , \]

being a measure of the stabilization by making the surface of the ice, where \( E_{\text{ice}}(n; \text{Slab}) \) and \( E_{\text{ice}}(n; \text{Bulk}) \) denote the energies of the slab and the bulk of ice composed of \( n \) water molecules, respectively.

The contact angle is then estimated by the five quantities, \( E_{\text{ice}}(n; \text{Bulk}), E_{\text{ice}}(n; \text{Slab}), E_{\text{CuSlab}}, E_{\text{water(onSurf)}}, \) and \( E_{\text{tot}} \), which are all possible to be evaluated by \textit{ab initio} DFT (density functional theory) calculations. Taking the surface as Cu(111), we calculated the energies using a DFT package, CASTEP. [17] To make comparisons with preceding works, [1, 11] we used the same exchange-correlation functional, GGA-PBE, [18] as in the preceding studies. Normal-conserving pseudo potentials [19] are used to describe ionic cores. Detailed computational conditions for each calculation are summarized in Table I.

For the modeling geometries of adsorbing molecules, we provide the detailed information in the next section, Sec. ‘Computational Details’. The main comparison is made between the predictions by periodic honeycomb model (bilayer) [13, 14] [panel (a) in Fig. 1] and the isolated molecular models (buckled) [16, 20] [panel (b)], which are evaluated using the slab composed of nine atomic layers of Cu. To investigate whether the considerable bias on the choice of \( N \)-mer and the coverage exists or not, we further compared the predictions with \( N=1,2,3,4, \) and 6, but with reduced cost and complexity of the computation, namely with H-parallel model [21] (planar model) [panel (b’) in Fig. 1] and with reduced number of layers, four. The choice of \( N \), excluding five, is because we limited the possible geometry to satisfy the ‘on-top alignment’ which is supported by preceding studies [20, 21] [i.e., \( N=5 \) cannot accommodate the molecules within a unitcell so that they are located as ‘on-top’]. For the multimers, \( N > 2 \), there are the possibilities for them to take chain or circular form. For \( N=3 \) and 4, we took both possibilities, while for \( N=6 \) only the circular form is taken into account as supported by preceding studies. [16, 20] The dependence on the coverage (\textit{i.e.} on how many \( N \)-mers are put within a unitcell) was examined upto \( N=3 \).

**COMPUTATIONAL DETAILS**

For the energies required to evaluate the contact angles, we have to prepare the geometries of the Cu slab (for \( E_{\text{CuSlab}} \)), the ice bulk and the slab (for \( E_{\text{ice}}(n; \text{Bulk}) \) and \( E_{\text{ice}}(n; \text{Slab}) \)), and the water molecules adsorbing on the Cu slab (for \( E_{\text{water}(\text{onSurf})} \) and \( E_{\text{tot}} \)).

A Cu bulk with a initial lattice constant, 3.6147 Å, was prepared to generate the Cu slab structure. The constant was optimize under the bulk structure getting 3.728 Å, and then the
TABLE I. Computational conditions of DFT calculations for each energies required to evaluate contact angles. The k-mesh and the $E_{\text{CUT}}$ (given in [eV]) are the mesh size for the Brillouin zone [22] and the plane wave energy cutoff, respectively. These values were determined by the convergence of the total energies. 'Cu-struct-opt' and 'Cu-surf-relax' mean the optimized Cu bulk and Cu slab structures, respectively.

| k-mesh       | $E_{\text{CUT}}$ [eV] |
|--------------|-----------------------|
| $E_{\text{tot}}$ (Bulk) | 4x2x2 750 |
| $E_{\text{tot}}$ (Slab)  | 4x4x1 750 |
| $E_{\text{CuSlab}}$      | 1x1x1 700 |
| $E_{\text{water(onSurf)}}$ | 1x1x1 600 |
| $E_{\text{surf}}$        | 1x1x1 700 |
| Cu-struct-opt        | 8x8x8 800 |
| Cu-surf-relax   | 11x11x1 800 |

bulk was cleaved in the (111) plane, used as the initial structure of the slab. A nine (four) layered slab was located periodically with a 30 Å depth vacuum layer attached on, and the atomic positions within three (one) layers from the surface are relaxed by the geometry optimization to get the final structure of the Cu slab. For the ice bulk, we took the Ih structure with a lattice constant, 4.516Å. [23, 24] We cleaved the bulk to get four layers of H$_2$O being parallel to the basal plane of a Ih crystal. A slab is formed by attaching a vacuum layer with a 30 Å depth, without further relaxations.

A water molecule was prepared with the initial geometry, $l_{\text{O-H}} = 0.96$ Å and $\theta_{\text{H-O-H}} = 104.5^\circ$. For the periodic honeycomb model [panel(a) in Fig. 1], we took the 'bilayer model' used in preceding studies. [13, 14] The structure is generated starting from 'H-parallel' structure, [21] where all the H$_2$O molecular planes being parallel to the slab surface. Positions of oxygen atoms are then adjusted so that their heights from the slab surface get alternating in every molecule to form the buckled structure. [16, 20] For 4-layer slab models to evaluate contact angles (as shown later in Fig. 2), we put the water molecules with the initial geometry explained above as the 'on-top' locations [20, 21] with the H-parallel orientation, [21] where the vertical height is optimized by DFT.

RESULTS AND DISCUSSION

As shown in Table II, the periodic honeycomb model (bilayer) [1, 11] gives worse coincidence with experiments. [25, 26] The isolated molecular models (buckled and planar) [14, 16] seem more appropriate modelling for the absorption even for the evaluation of the contact angles. The difference in their predictions would be attributed to whether the hydrogen bonding bridges over neighboring unitcells or not. The lattice mismatching between the Cu surface and the honeycomb network seems difficult to be attributed to the reason, because it amounts just to $-2.1\%$. [13]

As mentioned in Sec. 'Introduction', a range of the choice freedom about [(N-mer)$\otimes$(coverage)] is introduced for the isolated molecular model. We examined the dependence of the predictions on the variety of the modeling, as shown in Fig. 2 but with reduced cost (4-layered) and complexity (planar structure) of the calculations. In this reduction, the contact angle changes from 78.41° (buckled/9-layers) → 77.13° (buckled/4-layers) → 77.29° (planar/4-layers), being small enough to justify the simplification. Fig. 2 shows the dependence of the predictions on the variety of the modeling with 4-layers. The dependence ranges within ±10° around their average. It is, then, reasonable to put the significance on the average value to some extent, taking over the possible choices with the Boltzmann weight based on the adsorption energy, $E_{\text{ads}}$, as a measure of the stability. The average, 78.47°, gets to be closer slightly to the experimental values [25, 26] caused by the higher contact angles predicted for smaller Nmers (monomer and dimer).

FIG. 2. Dependence of the predicted contact angles on the variety of the modeling of adsorbing water molecules.

We can further examine the justification via comparisons of intermediate values appeared in Eq. (4), $\gamma_{\text{ice}}$ and $E_{\text{ads}}$, with other preceding studies. For the surface energy, our value,
and 187 meV/kJ, water molecules evaporate, then leading to the more stabilized value. For the adsorption energy, our estimation amounts to \( E_{\text{water}}^{\text{ads}} = 238 \text{ meV}/\text{H}_2\text{O} \) (monomer), which can be compared with an experimental value [TPD (Temperature programmed desorption evaluation) applied to Cu(111)], 352 meV/H\(_2\)O(34 kJ/mol). \([21]\) The apparent underestimation of our value can be attributed to the fact that, in experiments, the value includes the energy cost to break the hydrogen bonding when water molecules evaporate, then leading to the more stabilized value. The same explanation would be applicable to the preceding DFT values (for monomer), 145-157 meV \(/\text{H}_2\text{O}\) \([20]\) and 187 meV/H\(_2\)O(18 kJ/mol), \([21]\) which are smaller than the experimental value as well. The previous studies also provide the values for dimers, being 321-332 meV/H\(_2\)O \([20]\) and 352 meV/H\(_2\)O(34 kJ/mol). \([21]\) The reason for the large increase in values for the dimer is because their definitions are different from ours. In their definition, the hydrogen bonding interactions between water molecules are included in \( E_{\text{water}}^{\text{ads}} \), and hence it increases as the size of \( N \)-mer gets larger.

**CONCLUSIONS**

An ab initio evaluation of the contact angle is performed for the water wetting on the Cu(111) surface. The evaluation is feasible under the approximation for the water surface energy, \( \gamma_{\text{LG}} \), evaluated by that of the ice crystal, which has widely been used in preceding studies. \([1, 11]\) The periodic honeycomb lattice of ice crystals hence seems to be a natural candidate for the adsorbing model for the water on the surface, which has been accepted for the contact angles on the surfaces of insulating materials. \([1, 11]\) We found that such a model with the periodic array of water molecules gives worse coincidence of the contact angle with experimental values than the models with isolated water multimers, which are supported by several experimental observations. \([14, 16, 21]\) For the freedom of the model choice, namely the size of the multimers and the coverage, we showed the averaging over the possible choices with the Boltzmann weight based on the adsorption energies gives a fairly reasonable comparison with the experimental values.

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