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# Phase Transitions A Multinational Journal

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713647403

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Online Publication Date: 01 April 2007 To cite this Article: Stampfl, Catherine , (2007) 'Predicting surface phase transitions from **ab initio** based statistical mechanics and thermodynamics', Phase Transitions, 80:4, 311 - 332 To link to this article: DOI: 10.1080/01411590701228596 URL: <u>http://dx.doi.org/10.1080/01411590701228596</u>

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# Predicting surface phase transitions from *ab initio* based statistical mechanics and thermodynamics

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(Received 13 November 2006; in final form 19 January 2007)

The atomic structure and stoichiometry of a solid surface dictates its physical and chemical properties, and hence plays a crucial role in the performance of a material in technological applications. Indeed, in the field of surface science, a significant proportion of studies address the determination of surface atomic geometries and associated phase transitions. From the theoretical side, the desire is to obtain a first-principles based description that can accurately predict arbitrary surface structures and phase transitions under various conditions, such as temperature, partial pressure, and adparticle coverage. In the present paper, we discuss recent theoretical approaches through various examples, which address this goal. In particular, *ab initio* atomistic thermodynamics, which affords determination of the surface free energy as a function of relevant atom chemical potentials, and varying pressure and temperature conditions, as well as more powerful schemes that combine first-principles quantum mechanical calculations with statistical mechanics, namely, the lattice-gas or cluster-expansion approach in combination with Monte Carlo simulations.

Keywords: Density-functional theory; Surface oxides; Surface phase transition; Chemisorption

# 1. Introduction

A main goal of theoretical surface science is to achieve an accurate description of solids and their surfaces that can predict the detailed atomic structure and associated phase transitions as a function of, for example, temperature, gas-phase environment, and adsorbate concentration or coverage. Clearly, only with such knowledge can one understand the physical and chemical properties of material surfaces which dictate their behavior in technological applications such as heterogeneous catalysis, corrosion resistance, sensors, and fuel cells. Recent approaches and results have been discussed in Refs. [1–5]. The present Chapter will describe, through various examples, recent first-principles based approaches for predicting the structure of solid surfaces and associated surface phase transitions. In particular, we describe the method of "*ab initio* atomistic thermodynamics" which affords determination of the relative stability of surface structures as a function of relevant atom chemical potentials and varying gas-pressure and temperature conditions.

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Here we largely focus on oxygen/transition-metal systems as the examples. We then illustrate how this approach can be extended to a surface in contact with a two (or more) component gas-phase through consideration of a so-called "constrained" or "restricted" thermodynamic equilibrium. This is followed by a description of the more involved, but more powerful, approach of combining an *ab initio* based Latticegas Hamiltonian (LGH) or a Cluster-expansion (CE), with statistical mechanical schemes such as Monte Carlo (MC) simulations. This methodology is capable of accurately predicting unanticipated stable phases, and phase transitions, as well as various associated thermodynamic functions. Here we describe the application of the theory to determine the surface phase-diagram of oxygen adsorbed on the Ru(0001) surface and the study of oxygen-induced segregation and ordering of PtRu alloy surfaces. Finally, we describe how this methodology can be used to study orderdisorder phase transitions, where instead of the usual Metropolis MC scheme [6], the approach of Wang and Landau [7] is employed in which the (configurational) density of states (CDOS) are explicitly obtained. From the CDOS, the all the major thermodynamic functions can be straightforwardly determined. Finally, in section 4 the conclusion is given.

# 2. Ab initio atomistic thermodynamics

The *ab initio* atomistic thermodynamics approach applies to systems in equilibrium; however, for not too low temperatures, a surface is likely to rapidly attain thermodynamic equilibrium with the ambient atmosphere. The goal of this method is to use the results from first-principles electronic structure theory, i.e., the information on the potential energy surface, to calculate appropriate thermodynamic potential functions like the Gibbs free energy [8–15]. With this approach, various structures can be "screened" to determine which is most stable under what values of the atom chemical potentials, which, for gas-phase species, can be translated into pressure and temperature conditions. This is an indirect approach in the sense that its reliability is restricted to the structural configurations that are explicitly considered. Also, the structures are restricted to being ordered geometries due to the periodic boundary conditions employed in the supercell approach of most modern density-functional theory (DFT) codes.

We will illustrate this approach through consideration of a transition metal (TM) surface in contact with a gas phase of oxygen. The surface free energy of adsorption is calculated as,

$$\Delta G(\mu_{\rm O}) = -\frac{1}{A} \left( G_{\rm O/Surf.} - G_{\rm Surf.} - N_{\rm O}\mu_{\rm O} - N_{\rm M}\mu_{\rm M} \right),\tag{1}$$

where A is the area of the surface unit cell, and  $G_{O/Surf.}$  and  $G_{Surf.}$  are the Gibbs free energies of the oxygen/TM system and clean surface, respectively.  $\mu_O$  and  $\mu_M$ are the atom chemical potentials of the oxygen and metal atoms, and  $N_O$  is the number of oxygen atoms contained in the surface structure.  $N_M$  is the *difference* in the number of metal atoms between the clean surface and the O/TM system.

In the difference between the two Gibbs free energies, the vibrational contributions typically exhibit some cancellation [12]. However, when there are additional atomic or molecular species which are not present in the reference system, the situation may be different [16], as there will be no effective cancellation of the contributions of such species between surface and reference systems and this has to be carefully checked. For a number of systems (e.g., O/Ag(111) [15], O/Cu(111) [17]), it has nevertheless been found that these effects are sufficiently small as not to play an important role in the conclusions. In this case, the Gibbs free energy difference can be approximated by the difference of the total energy terms as obtained by first-principles electronic structure calculations, e.g., DFT. The temperature (T) and pressure (p) dependence is mainly given by  $\mu_O$ , i.e., by the O<sub>2</sub> gas phase atmosphere, where,

$$\mu_{\rm O}(T,p) = 1/2 \bigg[ E_{\rm O_2^{total}} + \tilde{\mu}_{\rm O_2}(T,p^0) + k_B T \ln\bigg(\frac{p_{\rm O_2}}{p^0}\bigg) \bigg].$$
(2)

Here  $p^0$  represents atmospheric pressure and  $\tilde{\mu}_{O_2}(T, p^0)$  includes contributions from rotations and vibrations of the molecule, as well as the ideal-gas entropy at 1 atmosphere. It can, for example, be taken from experimental values listed in thermodynamic tables [18]. The metal atom chemical potential,  $\mu_M$  is taken to be the bulk metal for the systems discussed in section 2.1, with which the surface is assumed to be in equilibrium. For a given atomic configuration,  $\Delta G(\mu_O)$  can then be plotted as a (linear) function of the oxygen chemical potential, where the more oxygen that is accommodated in the surface structure, the steeper the slope of the line. In the limiting case of the bulk oxide, the line will become vertical at a value of the oxygen chemical potential that equals the bulk oxide heat of formation per O atom. From consideration of many conceivably relevant surface atomic configurations, those with the lowest surface free energy of adsorption, for a given value of the oxygen chemical potential, can be identified.

#### 2.1. Surface-oxides on transition metals

To demonstrate the power and limitations of *ab initio* thermodynamics, we discuss several recent studies of the interaction of oxygen with hexagonal close-packed transition metal (TM) surfaces. From comparison of the particular systems, it also allows identification of general trends regarding relative stability of various surface structures, and onset of surface-oxide formation. Clearly, TMs are of high importance for oxidation catalysis [19–21] and this has motivated large numbers of studies on oxygen-metal interactions [22-24]. Recently, many advances in understanding have been made, which include the finding that for the carbon monoxide oxidation reaction over Ru(0001) and Pt(110), oxide patches on the surface exist which may be the active centers, in contrast to the hitherto believed pure metal. Furthermore, formation of two-dimensional surface oxides, which may or may not bear a resemblance to the corresponding bulk oxides have been identified, e.g., for O/Ag(111) [25–32], O/Pd(111) [33], O/Pd(100) [34, 35], O/Rh(100) [36], O/Rh(110) [37], and O/Pt(110) [38], and which may not necessarily be thermodynamically stable, e.g., O/Rh(111) [39]. These studies highlight the complex nature of surface atomic structures that can form for oxygen/TM systems, and how they depend sensitively upon the "environment", i.e., the gas pressure and temperature. Furthermore, the two dimensional nature of these films indicate that they may possess unique properties and functionalities that are distinct to the related bulk phases. The formation and identification of thin surface oxidic structures on TMs has recently been reviewed [40].

In the following we begin with the O/noble-TM systems, which are important catalysts, but bind oxygen and other adparticles only relatively weakly. That they are efficient catalysts is somewhat counter intuative, since it is generally understood that a good catalyst should yield reaction intermediates that have an "intermediate" or "moderate" adsorption energy. In this way, the reactants will be stable under the pressure and temperature conditions of catalysis, but not so strongly that reaction is inhibited. Interestingly, for these systems, on the basis of the *ab initio* atomistic thermodynamics methodology, the calculations predict that at all coverages, in contrast to the "real" TMs (in which the Fermi energy cuts the metal *d*-band), reconstructed surface-oxide like structures are favored over on-surface chemisorbed oxygen, even for very low coverage.

**2.1.1.** O/Ag(111). Silver is a very important heterogeneous catalyst for various oxidation reactions. For example, the partial oxidation of methanol to formaldehyde [41, 42], as well as the selective oxidation of ethylene to epoxide [43]. For this reason, there have been numerous studies into the interaction of oxygen with the surface of silver. In particular, from early experiments a  $(4 \times 4)$  structure was observed which was proposed to be closely related to a (111) layer of the most stable bulk oxide, Ag<sub>2</sub>O [44, 45].

With the aim of shedding light on the atomic structure of this phase, and into the interaction of oxygen with the Ag(111) surface in general, as well as gaining insight into the nature of the active species, a host of recent experimental and theoretical studies have been performed. A recent review can be found in Ref. [29]. From the theoretical side, Li *et al.* [25, 30] performed extensive DFT calculations for many conceivably relevant oxygen configurations at Ag(111). Some of the basic sites are shown in figure 1, namely, on-surface hollow sites and sub-surface sites under the first metal layer. Using *ab initio* thermodynamics, the surface free energies



Figure 1. Highly-coordinated adsorbate sites at an fcc(111) or hcp(0001) surface. Upper: top view of the surface where the two threefold coordinated hollow sites are indicated. Lower: local atomic geometries of three high-symmetry interstitial sites under the first substrate layer. Metal and oxygen atoms are shown as large and small spheres, respectively.

of adsorption as a function of the oxygen chemical potential were obtained, which using equation 2, are correlated with the  $O_2$  gas pressure and temperatures. The results are shown in figure 2. Here, only the lowest energy structures are plotted. In this study a (4 × 4) structure with coverage 0.375 mL was considered which had been predicted on the basis of scanning tunneling microscopy experiments [27, 28], and was found to have the lowest energy for a range of the oxygen chemical potential. A similar finding was reported in Ref. [26]. The atomic configuration of the (4 × 4) structure is like that illustrated in figure 3(a), except there are two additional Ag atoms in the fcc and hcp sites of the surface unit cell. It can be described as consisting of honey-comb-like, silver-oxide "rings" on top of the unreconstructed Ag(111) substrate. In the center of each "ring" there are either no additional atoms, or an Ag atom in a hollow site, which is not coordinated to O.



Figure 2. Left: Surface Gibbs free energies of adsorption for O/Ag(111) for various low energy structures as a function of the O chemical potential, which is defined with respect to half the total energy of the free oxygen molecule: On-surface chemisorbed oxygen with coverages 1/16, 1/9, and 1/4 mL, the (4 × 4) structure (labeled "0.375 mL") (see text), (2 × 2) oxide-like structures with coverages 0.75, 1.25, and 2.25 mL. The corresponding temperatures are given for two selected pressures (cf. equation (2)), one corresponding to UHV conditions and the other to atmospheric pressure. The various "types" of surfaces are indicated by the shaded regions, and labeled at the top of the plot (adapted from Ref. [25]). The dot-dashed line is the lowest energy structure considered with the geometry shown in figure 3(b). Right: Atomic geometry of the 0.50, 0.75, and 1.25 mL (2 × 2) oxide-like structures: (upper) fcc oxygen plus sub-surface oxygen in the tetra-I site, (middle) same but with additional oxygen in the tetra-II site, (lower) as latter but with additional oxygen under the second Ag layer in the tetra-I and tetra-II sites. The average adsorption energy with respect to the clean Ag(111) substrate and free oxygen atoms, as well as the corresponding coverage, are given at the bottom of each figure. The relative variation of the first and second interlayer spacings with respect to the bulk value is also given to the right of the figures. Large pale grey and small dark circles represent silver and oxygen atoms, respectively (from Ref. [15]).



Figure 3. Two surface-oxide-like structures considered in the O/Ag, O/Cu, and O/Au studies. The metal atoms are the larger light grey spheres and the oxygen atoms the smaller dark spheres. The intact underlying metal (111) surface can be seen below as the large pales spheres. (a) This structure is denoted as "p4" in figure 4 for O/Cu(111), and as "struc. a" in figure 5 for O/Au(111). (b) This structure is denoted in figure 4 for O/Cu(111) as "p4-OCu<sub>3</sub>" and as "struc. g" in figure 5 for O/Au(111).

Interestingly, subsequent studies identified still lower energy structures [29] such as those depicted in figures 3(a) and 3(b), where the latter has the (slightly) lower energy. The dot-dashed line in figure 2 represents the surface free energy for this configuration. From figure 2 it can be seen that the calculations predict that the structure shown in figure 3(b) is thermodynamically most stable for values of the oxygen chemical potential from -0.72 eV up to where the bulk oxide, Ag<sub>2</sub>O, becomes stable ( $\mu_{\rm O} = -0.325 \text{ eV}$ ). More recently, new experiments have led to the proposal of a different structure [31, 32] involving a closer packing of Ag atoms in the (4 × 4) surface unit cell, i.e., consisting of 12 Ag (and 6 O) atoms. Surprisingly, however, DFT calculations do not find this structure to be lower in energy than the one shown in figure 3(b) [31, 32].

**2.1.2.** O/Cu(111). Copper-based catalysts are important for various heterogeneous reactions, including methanol synthesis [47] and the partial oxidation of methanol. as well as the water-gas shift reaction [48]. With the aim of obtaining a deeper understanding of the behavior of Cu as an oxidation catalyst, many experimental investigations have been carried out. Complicated surface structures have been observed on exposing Cu(111) to an oxygen environment, which have been reported to resemble the basic structure of a layer of  $Cu_2O(111)$ . Recently, Soon *et al.* [17] carried out analogous studies for the O/Cu(111) system to those of O/Ag(111)described above. The results are shown in figure 4. It can be seen that for values of the oxygen chemical potential of less than  $-1.65 \,\text{eV}$ , the clean Cu(111) surface is thermodynamically most stable. For higher values, from -1.65 to -1.24 eV, so-called p4-OCu<sub>3</sub> [figure 3(b)], p4 [figure 3(a)], and p4+O<sub>F</sub> (as for figure 3(a)) but with an additional O atom in the fcc site) structures are most favorable. The bulk Cu<sub>2</sub>O oxide phase is thermodynamically most stable for values of the oxygen chemical potential greater than  $-1.24 \,\text{eV}$ . Like for O/Ag(111), on-surface chemisorbed oxygen is not found to be stable for any values of the oxygen chemical potential. In contrast to O/Ag(111), however, the surface oxidic structures are not thermodynamically stable under typical catalytic conditions of, e.g., >300 K and atmospheric pressure, due to the relatively large heat of formation of  $Cu_2O$ .



Figure 4. (A) Calculated Gibbs free energy of adsorption for low energy structures of the O/Cu(111) system. Unfavorable surface phases are indicated by light gray lines. Structures with the (2 × 2) periodicity ("p2-structures") are also indicated, where the geometries are like those depicted in figure 2, right side. The atomic geometry of the phases p4-OCu<sub>3</sub> and p4 are shown in figures 3(b) and 3(a), respectively. The p4 + O<sub>F</sub>, p4 + O<sub>H</sub>, and p4 + O<sub>FH</sub> structures are as for that shown in figure 3(a), but there is an additional O atom in the fcc (F), hcp (H), and fcc+hcp (FH) sites, respectively, of the surface unit cell. (B) same as (A) but on a larger scale. (C) The stability range of the most stable configurations plotted in (*p*, *T*)-space (from Ref. [17]).

This result indicates that in oxidation reactions, the active material will actually be surfaces of bulk copper oxide (assuming thermodynamic equilibrium can be obtained).

2.1.3. O/Au(111). It is interesting to extend the comparison of O/Ag(111) and O/Cu(111) to the O/Au(111) system. Although Au(111) is largely inert to dissociative adsorption of  $O_2$ , it can be oxidized by other oxygen carrying species, such as ozone [49]. Supported Au nanoparticles exhibit a high reactivity for a number of catalytic reactions, including low temperature oxidation of carbon monoxide [50]. Various explanations have been put forward to explain this high reactivity, which is in stark contrast to that of the low index pure metal surfaces, including the role of oxidized gold atoms. Calculations employing *ab initio* atomistic thermodynamics, analogous to the systems described above have been performed [46], where the results are presented in figure 5. Similarly to the previous two systems, it can be seen that on-surface adsorption of oxygen is only metastable, and the thin surface oxide-like structure shown in figure 3(b) is predicted to be stable for values of  $\mu_0$ from -0.4 to  $-0.17 \,\text{eV}$ , up to where bulk Au<sub>2</sub>O<sub>3</sub> becomes stable. Interestingly, the stability region of this thin surface-oxide-like structure corresponds to a temperature region of 200–420 K at a pressure of 1 atm, thus suggesting that such structures could exist under the conditions of low temperature oxidation reactions and play a role in the activity.



Figure 5. Surface free energies of adsorption for O at Au(111) for various low energy structures as a function of the O chemical potential, where the energy zero of  $\Delta \mu_0$  is taken as the total energy of the free oxygen molecule: On-surface chemisorbed oxygen with coverages 0.06, 0.11, 0.25 mL, (4 × 4) surface oxide-like structures, where those labeled "struc. a" and "struc. g" correspond to the configurations shown in figure 3(a) and 3(b), respectively. The structure labeled "(2 × 2)-O +vac" corresponds to 0.25 mL on the surface plus a surface Au vacancy. The corresponding temperatures are given for two selected pressures, one corresponding to UHV conditions and the other to atmospheric pressure (from Ref. [46]).

2.1.4. O/Rh(111). We now turn to discuss two O/TM systems which bind oxygen notably stronger, namely O/Rh(111) and O/Ru(0001), for which a different behavior to those discussed above is predicted on the basis of *ab initio* atomistic thermodynamics. For oxygen adsorption on Rh(111), a number of ordered phases have been identified, including  $(2 \times 2)$  and  $(2 \times 1)$  structures for coverages 0.25 and 0.50 mL, respectively [51], as well as  $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$  and  $(2 \times 2)$ -30 phases [52]. In these structures, the oxygen atoms occupy the on-surface hep or fcc sites (cf. figure 1). For higher oxygen exposures, a structure with a periodicity close to  $(9 \times 9)$  is observed. This phase gives rise to a morié pattern, which may be understood as corresponding to a hexagonal over-layer on the (111) substrate which has a larger in-plane distance. Recent studies employing scanning tunneling microscopy (STM) and high-resolution core-level spectroscopy, together with *ab initio* atomistic thermodynamics, have characterized the O/Rh(111) system. In particular, for the " $(9 \times 9)$ " phase, it is proposed to correspond to a trilayer-type of surfaceoxide [39] (see figure 6(b)). The phase diagram is presented in figure 6. What is quite striking is that the calculations reveal that the structure is only metastable with respect to the bulk oxide formation. Thus, this phase is "kinetically stabilized", that is, notable energy activation barriers prevent the system from reaching thermal equilibrium under the experimental conditions. This was also the case for the  $(2\sqrt{3} \times 2\sqrt{3})R30^{\circ}$  and  $(2 \times 2)$ -30 structures [52] which are less stable than this surface-oxide phase. The trilayer-like structure can be described as an  $(8 \times 8)$ hexagonal surface oxide on a  $(9 \times 9)$  Rh(111) surface unit cell. The DFT calculations



Figure 6. (a) Calculated surface Gibbs free energy of adsorption for O/Rh(111) and (b) lowest energy structures for oxides with 2 (O-Rh-O), 3, and 4 layers (L) of oxygen on a Rh(111) ( $2 \times 2$ ) supercell. Oxygen atoms are shown as bonds only, except for the bottom oxygen layer. The chemical potential is related to the temperature and the oxygen partial pressure *p* through the ideal gas equation (from Ref. [39]).

showed that the stability of the structure is very similar to that obtained when calculated using a smaller  $(2 \times 2)$  cell, which could be described as a  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  oxide layer on a  $(2 \times 2)$  Rh(111) surface unit cell [39].

**2.1.5. O/Ru(0001).** The motivation for investigating oxygen adsorption and oxide formation at the Ru(0001) surface, originates from the observation that supported Ru catalysts [53], as well as Ru(0001) single crystals [54], have a high reactivity for CO oxidation under high-pressure and temperature conditions, however, under UHV conditions [55], the turnover frequency is extremely low. This behavior is a clear example of system that exhibits a so-called "pressure gap" [2]. Therefore it was highly desirable to understand the underlying reasons for this phenomenon on the microscopic level.

This system has been studied using *ab initio* thermodynamics, through consideration of many possible atomic configurations [5]. The results are displayed in figure 7. It can be seen that the overall qualitative behavior is similar to O/Rh(111), with the difference that bulk oxide formation is predicted at a lower value of the oxygen chemical potential due to the greater heat of formation of RuO<sub>2</sub>. Specifically, for  $\mu_{\rm O}$  < -2.7 eV the clean surface is most stable, while five different O adsorbate phases (with oxygen occupying the hcp site, cf. figure 1) with increasing coverages become progressively more stable for more O-rich environments; namely,  $(2 \times 2)$ ,  $(2 \times 1)$ ,  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O, (for a very small range of  $\mu_{\rm O}$ ), (2 × 2)-3O, and (1 × 1). All of these structures have been experimentally verified, with the exception of the  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O configuration. For  $\mu_{\rm O} > -1.4\,{\rm eV}$ , bulk RuO<sub>2</sub> represents the most stable phase, thus the  $(1 \times 1)$  structure is only metastable. The stability range of the bulk oxide is large, and it encompasses all realistically attainable pressures for temperatures below about 600 K, pointing to oxidized Ru metal being the active phase under typical (oxidizing) catalytic conditions, consistent with experiment [56]. If thermodynamic equilibrium is not reached, i.e., if the system



Figure 7. Calculated surface free energy of adsorption for low energy O/Ru(0001) structures. The chemical potential is given with respect to half the total energy of the free oxygen molecule. The various stable phases are listed along the bottom of the plot, where the label "2/3 mL" indicates the  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O structure which is only stable for a very narrow region of the oxygen chemical potential. The favorable surface phases are:  $(2 \times 2)$ -O,  $(2 \times 1)$ -O,  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O,  $(2 \times 2)$ -3O,  $(1 \times 1)$ -O, and the "trilayer+O" configuration (see right, lower figure). The three paler thin lines for the structure not labeled are less stable structures and correspond to chemisorbed O at 0.33 mL, and the trilayer-like  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  configuration on a  $(2 \times 2)$  surface unit cell configuration [see description above for O/Rh(111)], with and without an O atom adsorbed on top. The vertical continuous line marks the theoretical heat of formation of RuO<sub>2</sub> per O atom (adapted from Ref. [5]).

is kinetically hindered, surface oxide-like structures could be stabilized at the surface, such as the the "trilayer" or "trilayer+O" configurations depicted to the right of figure 7.

To summarize the behavior of the O/TM systems, *ab initio* atomistic thermodynamic studies show that for the noble metal (111) substrates, of Cu, Ag, Au, surface-oxide-like formation is energetically preferred right away, with on-surface adsorption being only metastable. Further, it is apparent that copper binds O more strongly than silver, and silver more strongly than gold. The hexagonal close-packed Ru and Rh substrates bind oxygen more strongly and on-surface chemisorbed oxygen phases are predicted to be stable, where for higher values of the oxygen chemical potential, the bulk oxide is thermodynamically stable. Thus, for these cases, thin surface-oxide-like structures are only metastable, but could possibly be stabilized due to kinetic hindering, as found for O/Rh(111). To date, no thin surface oxide-like structures have been observed on Ru(0001), with STM experiments showing a coexistence of the on-surface (1 × 1) phase and patches of bulk oxide [56].

The theoretical approach of *ab initio* atomistic thermodynamics, is of course applicable to all solid surfaces; for example, it has been used to obtain a first-principles surface phase-diagram for hydrogen on gallium nitride surfaces [57], and numerous other applications.

# 2.2. Restricted or "constrained" thermodynamics

**2.2.1.** CO + O<sub>2</sub>/RuO<sub>2</sub>(110). It is clearly of interest to also describe surfaces which are in contact with two (or more) gas phase species, which is often the case in heterogeneous catalysis or crystal growth. This can be achieved with the *ab initio* thermodynamics formalism outlined above, with the assumption that the gas phase species do not react with each other and that they have separate reservoirs. In *full* thermodynamic equilibrium, however, exothermic reactions between gas phase species (e.g., O<sub>2</sub> and H<sub>2</sub>:  $1/2O_2 + H_2 \rightarrow H_2O$ ) would of course occur. The assumption relies on the reaction barrier in the gas phase being sufficiently high that the reaction plays no role on the time scales of interest.

As an example of this approach, we discuss the RuO<sub>2</sub>(110) surface in contact with a gas phase of CO and O<sub>2</sub> [58]. The expression for the Gibbs surface free energy is just as in equation (1), but with the addition of the carbon atom chemical potential term ( $-N_{CO}\mu_{CO}$ ) on the right-hand-side, and the reference slab system is the metal oxide with which the surface is in equilibrium, as well as with the gas phase. Through consideration of various possible surface geometries involving CO and O adsorption, the surface phase diagram shown in figure 8 was obtained. It can be seen that there are four different surface structures, namely, O<sup>br</sup>/CO<sup>cus</sup>, CO<sup>br</sup>/CO<sup>cus</sup>, O<sup>br</sup>/-, and O<sup>br</sup>/O<sup>cus</sup>, which correspond to occupation of the two main adsorption sites (bridge site (br) and the coordinatively unsaturated (cus) site) by CO or O, or remaining empty (-). These structures are depicted in the right side of figure 8. In particular, for very low CO chemical potential and low oxygen chemical potential (corresponding to low gas pressure of CO and O<sub>2</sub>), the termination with O at only the bridge site is stable. On raising the O chemical potential, additional oxygen is adsorbed at the cus sites. For increasing CO chemical potential, CO becomes preferentially bound



Figure 8. Left: Surface phase diagram for  $RuO_2(110)$  in "constrained equilibrium" with an O<sub>2</sub> and CO environment. For T = 300 K and T = 600 K, the corresponding pressure scales are given. Regions in which phase coexistence may occur are marked by white hatching. Above the dashed white line,  $RuO_2$  is unstable against CO-induced decomposition, so the surface structures are only metastable there in this region. Right: Atomic geometry of the various low energy structures, and illustration of the adsorption sites on the surface (from Ref. [58]).

at the cus site instead of oxygen  $(O^{br}/CO^{cus})$ . Finally, at high CO and low O chemical potential, CO can also be stabilized at the bridge site  $(CO^{br}/CO^{cus})$ . Interestingly, with regard to the CO oxidation reaction over this surface, a very high reactivity has been found for different environmental conditions, which all lie near the boundary between the  $O^{br}/CO^{cus}$  and  $O^{br}/O^{cus}$  phases. This points to the importance of such regions (phase boundaries) for catalysis. In these regions of high activity, however, the validity of "constrained equilibrium" may breakdown. As to providing a first, or general, understanding of a surface in contact with a complex gaseous environment, "constrained thermodynamics" provides a valuable picture.

Other recent examples of the application of so-called restricted or "constrained" thermodynamics is the study of the calcite surface in contact with a gaseous phase containing water and carbon dioxide [59], and of zinc oxide in thermodynamic equilibrium with oxygen and hydrogen [60].

#### 3. Combined Monte Carlo + ab initio lattice-gas or cluster-expansion approaches

The *ab initio* Lattice-gas Hamiltonian or Cluster-expansion plus Monte Carlo (LGH + MC or CE + MC) approaches offer greater flexibility in predictive ability compared to that of *ab initio* atomistic thermodynamics, in the sense that they afford identification of unanticipated geometries and stoichiometries, can describe the coexistence of phases and disordered phases, as well as associated order-order and order-disorder phase transitions.

In the following we will describe the LGH + MC approach, but the CE + MC methodology is very similar and we refer to Refs. [1, 4, 61–65], and references therein, for details. The CE has traditionally been used to describe bulk binary alloys, but has also more recently been applied to surfaces. For a system to be described in the LGH or CE approach, it must consist of well-defined lattice sites, and this is actually one main limitation. The total energy for a given configuration of atoms is written as an expansion of a sum of interactions between these lattice sites. For example, for a system consisting of one adsorbate species and one type of site, the Hamiltonian can be written as [66, 67],

$$H = F \sum_{i} n_i + \sum_{m=1}^{\text{pair}} V_m^{\text{pair}} \sum_{(ij)_m} n_i n_j + \sum_{m=1}^{\text{trio}} V_m^{\text{trio}} \sum_{(ijk)_m} n_i n_j n_k + \cdots,$$
(3)

where  $n_l = 0$  or 1 depending upon on whether site *l* is empty or occupied, and *F* is the free energy of an isolated species, including static and vibrational contributions.  $V_m^{\text{pair}}$  are the two-body (or pair) interaction energies between species at *m*th nearest neighbor sites and  $V_m^{\text{trio}}$  is the energy due to three-body (or trio) interactions. In principle, higher order interaction terms (four-body, five-body..) would follow in this infinite expansion, but in practice, the series is truncated after a finite number of terms. Generalizations to multiple species and sites is straightforward; however, for systems with several sites and species, the construction of the LGH becomes very complicated. Figure 9 (left) illustrates some of these interactions. In other fields, this kind of methodology may be called an "Ising-type model" [63].

Since evaluation of the Hamiltonian involves only performing an algebraic sum over a finite number of terms, it is computationally very fast. The most difficult task is deciding upon the number and kind (e.g., pair, trio, multi-body) of interaction



Figure 9. Left: lateral interactions considered for the O/Ru(0001) system, where the adsorbates can occupy the two threefold hollow sites (hcp and fcc).  $V_n^{\text{pair}}$  (n = 1, 2, 3) are two-body (or pair) interactions at first, second and third nearest neighbor distances of like hollow sites.  $V_n^{\text{trio}}$  (n = 1, 2, 3) are three three-body (or trio) interactions between three atoms in like nearest neighbor hollow sites, and  $V_n^{\text{pair}(h,f)}$  (n = 1, 2, 3) represent pair interactions between atoms that occupy unlike hollow sites (i.e., one in fcc and the other in hcp) (from Ref. [3]). Right: The heat of adsorption of O<sub>2</sub> on Ru(0001) as a function of coverage for various temperatures. The peaks and dips correspond to ordered phases (from Ref. [71]).

terms to include, and extracting these from DFT calculations. We note that there is no *a priori* way to know how many, and what type of, interactions to include in the expansion. While there are some attempts to automatize this procedure [68] the actual implementation is a rather sensitive task. Some criteria to test the convergence of the Hamiltonian include its ability to predict the energies of a number of DFT-computed configurations that were not employed in the fit, or that it reproduces the correct lowest-energy configurations at T=0 K [65]. This is described in a little more detail in section 3.3.

With regard to Monte Carlo simulations, importantly, modern techniques perform the sampling very efficiently by focusing on the parts of the configuration space that contribute most to the partition function of the system. The Metropolis algorithm [6] is a well-known "importance sampling scheme" which proceeds by generating random configurations and, if a new configuration is lower in energy than the previous one, it is "accepted", building-up a sequence of configurations. If the configuration has a higher energy, it still has a Boltzmann-weighted probability of being accepted. The scheme also fulfills "detailed balance", where the forward probability of accepting a new configuration *j* from state *i* is related to the backward probability of accepting configuration *i* from state *j*, by the free energy difference of both configurations. Then, from the average of the system observables of the configurations, the correct thermodynamic averages can be obtained. For more details we refer, e.g., to Refs. [69, 70].

# 3.1. Oxygen phases on Ru(0001)

The "*ab initio* LGH" approach has been applied to the O/Ru(0001) system, where the surface is in equilibrium with a surrounding gas-phase. Here it is of interest to know how much oxygen is adsorbed at the surface at a certain temperature and pressure in the gas phase and if the oxygen adsorbates form

ordered or disordered phases. Using the LGH approach, Stampfl *et al.* [71] constructed a LGH for this system which contained two kinds of sites (hcp and fcc), pair interactions up to third neighbor, and three trio interactions (see figure 9, left). It was initially used in combination with rate equations [66], to predict temperature programmed desorption spectra, and the heat of adsorption of  $O_2$ . The results of the latter are shown in figure 9, right. It can firstly be seen that the heat of adsorption (energy gained by  $O_2$  dissociatively adsorbing on the surface) is greater at lower coverages.

The noticeable peaks and dips indicate the formation of ordered phases, which are predicted at coverages of 0.25, 0.50, and 0.75 mL. The T=0 K curve shows that the heat of adsorption is greatest (peaks) when at these coverages, which correspond to the surface being fully covered by the particular ordered phase. The curve stops at 1 mL, but the form is consistent with an ordered phase also existing at 1 mL. A weak shoulder can also be noticed at  $\approx 0.65$  mL, hinting at the existence of another ordered phase.

Subsequently, using the same LGH, in combination with MC simulations, McEwen *et al.* [72] determined the phase-diagrams shown in figure 10. It can be seen that in the coverage range considered, i.e., from very low coverage up to 0.75 mL, four ordered structures are predicted. Namely, the  $(2 \times 2)$ -O,  $(2 \times 1)$ -O,  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O, and  $(2 \times 2)$ -3O. As mentioned earlier, these phases have all been verified experimentally, with the exception of  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ -2O, which is awaiting confirmation. This latter phase appears only in a very narrow temperature and coverage window so its identification may prove challenging. Also a disordered lattice-gas was identified, as well as four coexistence regions involving the phases (i)  $(2 \times 2)$ -O and  $(2 \times 1)$ -O, (ii)  $(2 \times 1)$ -O and  $(2 \times 2)$ -3O. The triangles in figure 9 indicate that the transition is of first-order, while the circles represent second-order transitions. Figure 10 (right) shows the corresponding temperature versus O-chemical potential phase diagram, illustrating which phases exist under which (T, p)-conditions (or equivalently  $(T, \mu)$ -conditions) in the gas phase.

Clearly the *ab initio* atomistic thermodynamics and the LGH approaches yield the same results concerning the predicted (single) ordered phases; however, in the former approach, this relied upon the thought to actually consider the 2/3, 3/4, and 1 mL structures (which had not hitherto been experimentally identified in the literature), whereas with the LGH, all phases come out "automatically", without the necessity of such fore-thought or prior knowledge.

Other more recent studies using the LGH+MC or CE+MC approach have been performed; namely, to determine the phase diagram and adsorption-desorption kinetics of CO on Ru(0001) [72] and the surface phase diagram of O/Pt(111) has been obtained [73]. Two other recent interesting applications of the CE approach (not combined with MC) have been carried out: (i) to determine the ground state of hydrogen adsorbed on two-sided graphene sheets [62], and (ii) by Singer *et al.* [74] to predict Li and Co atom structures on Mo(112).

#### 3.2. Oxygen induced segregation and ordering of PtRu

As indicated above, the cluster-expansion in combination with MC simulations methodology, was originally developed for the description of bulk binary alloy systems. A recent extension of the CE+MC approach was the application to study



Figure 10. Temperature-coverage (a) and oxygen chemical potential-temperature (b) phase diagrams for O/Ru(0001), as obtained using the *ab initio* LGH approach in combination with MC calculations. The triangles and circles indicate first and second order transitions, respectively. The identified ordered structures are labeled as:  $(2 \times 2)$ -O (A),  $(2 \times 1)$ -O (B),  $(\sqrt{3} \times \sqrt{3})R30^{\circ}$  (C),  $(2 \times 2)$ -3O (D), and disordered lattice-gas (l.g.) (from Ref. [72]).

the effect of adsorbates on the surface of alloys [75]. This work found that for the  $O/Pt_{1-x}Ru_x$  system, surface segregation can be substantially modified by the presence of oxygen on the surface. In particular, while Pt has the lowest surface energy in vacuum and is expected to fully saturate the surface layer, the segregation is significantly affected by the adsorption of oxygen, where the strong binding between O and Ru on the surface, more than over compensates the higher surface energy.

Han *et al.* [75] described the system using a bulk substrate of PtRu which acts as a reservoir, with constant Pt and Ru chemical potentials, and a surface alloy layer



Figure 11. Monte Carlo simulations and surface structure evolutions as a function of oxygen chemical potential,  $\mu_0$ .  $C_{Ru}^{surface}$  and  $\theta_0$  are the concentration of Ru atoms in the alloy surface layer and the oxygen coverage, respectively. The conditions of (a) are T = 600 K,  $\mu_{Ru} = -1750$  meV and (b) T = 1050 K,  $\mu_{Ru} = -665$  meV (from Han *et al.* [75]).

where each site can be occupied by Pt or Ru, as well as an adsorbate layer on top of this, where the O atoms can occupy fcc sites. The consideration of a single alloy surface layer and adsorbate layer of which the atomic configuration can be varied, can of course be extended to multilayers, but more interactions in the CE would be required. Since the CE describes oxygen adsorption and segregation energetics, as well as the interaction between them, it is possible to equilibrate both segregation in PtRu and oxygen adsorption simultaneously and find the equilibrium states of the system as a function of chemical potential.

In constructing the CE, Han et al. [75] used the DFT results of 127 atomic configurations and included 40 terms, comprising pair, trio, and quarto interactions. The types and values thereof, were determined by a cross-validation approach [4], which is effectively an average measure of how well each atomic configuration is predicted when left out of the fit to the DFT energies. Figures 11(a) and (b) show equilibrated oxygen isotherms at two different temperatures (T = 600 and 1050 K) and Ru chemical potentials (-1750 and -665 meV), respectively, that is, the oxygen coverage and the Ru concentration in the surface layer as a function of oxygen chemical potential. For low Ru chemical potential (figure 11(a)), the oxygen coverage initially gradually increases for increasing O-chemical potential, whereafter it remains constant up until around  $-500 \,\mathrm{meV}$ , at which point it abruptly increases. Here also the concentration of Ru in the surface layer abruptly increases. Finally, a full oxygen-covered Ru surface is obtained. Snapshots from the Monte Carlo simulation are shown as insets for two values of the oxygen chemical potential. The first (left-most in figure 11(a)) shows oxygen adsorbed on the Pt(111) surface, while in the other, it can be seen that segregation of Ru has occurred and the Ru atoms cluster together, on which O atoms are preferentially adsorbed. This results in a surface microstructure consisting of islands of Pt surrounded by regions of O/Ru.

Both figures 11(a) and 11(b) show that under a high enough oxygen partial pressure, Ru will segregate to the surface. But there are some notable differences: In figure 11(a) the oxygen coverage is always larger than the Ru concentration in the surface layer, but at higher Ru chemical potential (figure 11(b)), corresponding to

a larger Ru bulk concentration, the Ru concentration at the surface exceeds the oxygen concentration. Furthermore, it is apparent that for figure 11(b), the oxygen adsorption and Ru segregation are strongly coupled, occurring suddenly at a critical oxygen chemical potential. The results of this study show the striking effect that adsorbates can induce on alloy surfaces and provides valuable insight into the *initial* stages of oxidation.

Other recent applications of the CE approach to alloy surfaces (without MC) include the determination of a phase diagram for the binary alloy CoAl(100) surface [76] and for the ordering of  $Ni_{90}Al_{10}$  surfaces [77]. Early studies investigating phase diagrams of binary alloy surfaces by the CE in combination with MC simulations should be noted, e.g., alloy surfaces of Cu-Pd [78], which have lead the way for the current future investigations where the number and type of interactions included in the expansion have increased significantly, and consequently the methodology has become more advanced and the results more accurate.

#### 3.3. Order-disorder phase transitions of Na/Al(001)

The adsorption of sodium on Al(001) results in a rich series of phase transformations as a function of coverage and temperature. The stable adsorption site for Na is the surface substitutional site, where the Na atoms kick-out Al atoms and take their place. At low temperature, an ordered  $(\sqrt{5} \times \sqrt{5})R27^{\circ}$  structure forms (see inset of figure 13(b)). At temperatures in the range of 220–300 K on the other hand, the Na atoms undergo a phase transition to a disordered arrangement. Also, as a function of Na coverage, reversible order-disorder phase transitions occur; namely, for  $\theta_{\text{Na}} < 0.17 \text{ mL}$  the Na atoms are disordered, while for coverages in the range  $0.17 \text{ mL} < \theta_{\text{Na}} < 0.23 \text{ mL}$  the  $(\sqrt{5} \times \sqrt{5})R27^{\circ}$  phase forms. For  $\theta_{\text{Na}} > 0.23 \text{ mL}$ a disordered phase occurs again, which, for higher coverages transforms into a  $c(2 \times 2)$  structure with a coverage of 0.5 mL.

Borg *et al.* [79] have studied this system using the *ab initio* LGH + MC approach outlined above. Here, pair interactions up to sixth nearest neighbor, and two trio, and one quarto interaction, were included in the expansion for the Hamiltonian. These resulting values of the parameters are depicted in figure 12, left. They were obtained from N=25 DFT calculations for various configurations, where the "Leave-Many-Out Cross-Validation" (LMO-CV) scheme [80, 81] was used to determine the interaction parameters. In LMO-CV, N - d DFT-calculated structures are used in a least-squares fit to obtain the interaction parameters, and the remaining d structures are used to calculate the root-mean-square of the deviations between the LGH-obtained energies, and the DFT energies (so-called "prediction errors"). By doing this for many random divisions of the total set, an average prediction error is obtained. This procedure is performed for a number of different possible sets of interaction parameters (in Ref. [79] 24 sets were considered). The interactions yielding the lowest average prediction error are then chosen. With the thus constructed LGH, the experimental results outlined above could be reproduced with standard Metropolis MC. Because, however, the Metropolis scheme is rather inefficient for finding phase transition temperatures, extracting the specific heat, and directly determining the free energy and entropy, the scheme introduced by Wang and Landau [7] was used. This formalism performs a random walk in "energy space" and obtains an accurate estimate of the so-called (configurational) density of states (CDOS), g(E), which is the number of system configurations with



Figure 12. Left: Sodium interaction energies: pair interactions to the left and the two considered trio interactions and quarto interaction to the right. The units are eV and a positive value indicates a repulsive interaction. The adsorption energy of an isolated Na atom is given on the dark grey atom (left). For the case of pair interactions, the values of the interactions written on the various "atoms", the interaction is between this atom and the darker shaded atom. For example, the second nearest-neighbor pair interaction is 0.107 eV. Right: Specific heat,  $C_V(T)$ , as obtained from Wang-Landau MC simulations, at different coverages. Inset: Critical temperature  $T_c$  (as determined from the peak positions) as a function of Na coverage. The highest critical temperature occurs for the  $(\sqrt{5} \times \sqrt{5})R27^{\circ}$ -Na/Al(100) phase at 0.2 mL (from Ref. [79]).



Figure 13. (a) Density of configurational states (CDOS) as a function of energy for 0.2 mL of Na. Inset: The logarithm of the canonical distribution  $P(E, T) = g(E)e^{-E/k_BT}$  at the critical temperature. (b) Free energy F(T) and internal energy U(T) as a function of temperature, derived from the CDOS. The cusp in F(T) and discontinuity in U(T) at 301 K indicate the occurrence of the first-order disorder-order phase transition, experimentally observed in the temperature range 220–300 K. Inset: The structure of the  $(\sqrt{5} \times \sqrt{5})R27^{\circ}$ -Na/Al(100) phase at 0.2 mL (from Ref. [79]).

a certain energy, E. This quantity is independent of temperature. From g(E) all major thermodynamic functions can be directly determined, e.g., the canonical distribution, the free energy, the partition function, the internal energy, the entropy and the specific heat.

Figure 13(a) shows the calculated density of configurational states, g(E), and 13(b) shows the internal and free energies. In the latter two quantities, distinct changes can be seen corresponding to the first-order phase transition at 301 K. The free energy decreases with increasing temperature; the reason for

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this is the entropic contribution (difference in the free and internal energies), the magnitude of which significantly increases at the transition temperature and continues to increase thereafter. The configurational entropy is clearly the crucial aspect in the simulation and understanding of this order-disorder phase transition.

#### 4. Conclusion

Recent theoretical approaches for predicting surface structures and phase transformations at surfaces have been discussed. In particular, the value of the *ab initio* atomistic thermodynamics approach was demonstrated for a series of oxygen/ transition-metal systems. This method allows a comparison of the relative stability of surface structures as a function of relevant atom chemical potentials, and under varying gas-pressure and temperature conditions. The main limitation of this method is that its predictive ability is limited to the explicitly considered surface structures and there is always the risk that a lower energy structure exists, which has not been not included. An additional drawback is that the structures have to be periodic due to the supercell approach typically employed in state-of-the-art first-principles electronic structure codes.

Using the concept of a Lattice-gas Hamiltonian (LGH) or Cluster-expansion (CE) in combination with Monte Carlo (MC) simulations, represents a so-called "multi-scale" approach, in which meso- or macro-scopic properties can be determined on the basis of *ab initio* electronic structure calculations. These methodologies are more powerful than *ab initio* atomistic thermodynamics, in that unanticipated structures can be found; also, coexistence and order-disorder phase transitions can be described, and configurational entropy is included. The LGH + MC approach was determined, and the CE + MC for describing oxygen-induced segregation and ordering of PtRu alloys surfaces. For the Na/Al(100) system, the application and advantages of the Wang-Landau MC algorithm was demonstrated for describing a temperature-induced order-disorder phase transition. This scheme offers a more efficient determination of phase transition temperatures, specific heat, and the free energy and entropy.

Such coarse-grained lattice models as the LGH or CE, in which the real Hamiltonian is described as expansions in terms of certain interactions, are valid and necessary for many surface phase transformation problems, since to calculate all necessary configurations (e.g., those generated in MC simulations) from first-principles, given that the configurational space of most materials surface science problems is extremely large, to obtain meaningful statistics would require a prohibitively large (e.g., 10<sup>6</sup>) number of calculations. Since in practice the expansions can only comprise a finite number of terms, there is always the risk of overlooking a relevant interaction, and at present there are no fully automated schemes to reliably and efficiently determine which terms to include in the expansion. For more complex systems, the procedure will become increasingly cumbersome, and even the mapping onto lattices themselves will be problematic. Future developments in overcoming these limitations may be the development of adaptive, self-refining approaches, which will be of high importance to ensure the general applicability of the associated statistical techniques.

#### Acknowledgements

Fruitful collaboration with Matthias Scheffler, Aloysius Soon, Hongqing Shi, Mira Todorova, Wei-Xue Li, Micke Borg, Juergen Kreuzer, Stephen Payne, Jean-Sabin McEwen, Karsten Reuter, Veronica Ganduglia-Pirovano, is gratefully acknowledged. We thank E. Lundgren, G. Kresse, K. Reuter, G. Ceder, B. C. Han for kindly assisting with, and providing, figures.

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