

# Grand-canonical approaches to understand structures and processes at electrochemical interfaces from an atomistic perspective

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Electrochemical interfaces between an electrode and an electrolyte are often covered by ions from the solution. These adsorbed ions can strongly modify the properties of the interfaces. Furthermore, in electrocatalysis the reacting species typically have to get into contact with the surface of the electrocatalyst where then the reaction proceeds. Hence the understanding of the interaction of solvated species with electrode surfaces and the determination of the resulting adsorbate structures as a function of electrochemical control parameters such as electrode potential and electrolyte concentrations are crucial in electrochemistry. Here, grand-canonical theoretical approaches to derive adsorbate structures at electrochemical interfaces from an atomistic perspective will be reviewed. Special emphasis will be put on the distinction between the validity of the approach and the approximations that are typically made when using this approach.

## I. INTRODUCTION

Electrochemical processes typically occur at the interface between an electron conductor, the electrode, and an ion conductor, the electrolyte solution [1, 2] which in electrochemistry is often just called *electrolyte*. Furthermore, the electrolyte solution is usually formed by the dissociation of a salt in a solvent, and often solvated anions adsorb specifically on electrode surfaces whereas cations usually adsorb non-specifically, i.e., with their solvation shell still being intact. From a theoretical atomistic point of view, the reliable description of structures and processes at such interfaces represents a severe challenge [3, 4]: first, due to the liquid nature of the electrolyte, determining local minima of potential energy surfaces is not sufficient to identify stable surface structures. Instead, in principle time-consuming statistical averages over a sufficiently large number of different electrolyte configuration have to be performed [5–9]; second, the electrode potential is a crucial control parameter in electrochemistry which has to be appropriately considered in any theoretical modeling [10–12].

These challenges have hampered the progress in the theoretical description of electrochemical interfaces [2, 13]. However, as structures and processes at electrochemical interfaces are scientifically very interesting and technologically extremely important in the context of energy conversion and storage of renewable energies [14], these technical obstacles have not prevented theoreticians from addressing these topics. Although certainly no complete picture of electrochemical interfaces has been developed yet, still significant progress has been made in recent years [15]. This progress is to a large extent caused by a clever combination of atomistic calculations with grand-canonical approaches, which in the field of surface science and heterogeneous catalysis has been coined *ab initio*

thermodynamics [16] and in electrochemistry the computational hydrogen electrode (CHE) [17, 18]. The progress made in electrochemistry through this approach has recently even been called the “CHE revolution” [13, 19].

In the application of these approaches, typically severe approximations have been made [17, 18, 20–26]. Still, this approach has been rather successful in yielding sometimes even quantitative agreement with electrochemical experiments [25, 27]. Here we will try to contemplate why these severe approximations are applicable and justified. Yet, it is crucial to admit that the approximations typically made in the application of the CHE lead to limits in the validity of the studies applying these approximations. The recognition of these limitations have led to so-called “beyond CHE” approaches [13, 28]. However, in my opinion, using a “beyond CHE” nomenclature mixes the validity of the approximations entering most realizations of the grand-canonical schemes with the validity of the CHE scheme itself. Here I will try to clarify the foundations of the grand-canonical approaches, review some recent applications of this approach and sketch routes for improvements.

## II. GRAND-CANONICAL SCHEMES TO DETERMINE STABLE INTERFACE STRUCTURES

As it is conceptually easier, I will first present the concept of *ab initio* thermodynamics [16], which before being used in heterogeneous catalysis had already been employed to derive thermodynamically stable surface structures of compound materials (see, e.g. [29]). Thus, we will first consider adsorption at solid-gas interfaces in thermodynamic equilibrium, as illustrated in Fig. 1a. Formally, we subdivide the system into three subsystems, the catalyst or solid, the gas phase, and an interface region in between the two other systems. We assume that both the solid and the gas phase act as thermodynamic reservoirs, i.e., adding or removing particles from these phases does not change their thermodynamic properties.

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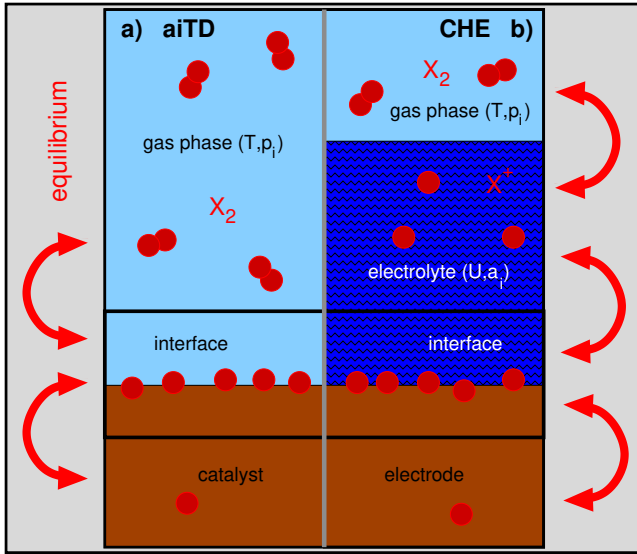


FIG. 1. Illustration of the grand-canonical schemes to determine the equilibrium structure of gas-solid interfaces (panel a) using the concept of *ab initio* thermodynamics (aiTD) [16] and of electrode-electrolyte interfaces (panel b) using the concept of the computational hydrogen electrode (CHE) [17, 18]. The interface region in both cases is given by the area in the box.

All three subsystems shall be in thermodynamic equilibrium which means that the corresponding chemical potentials of the species present in the system are constant throughout the whole system. The appropriate thermodynamic potential to describe such a system is the Gibbs free energy  $G(T, p, N_i)$ , where  $T$  is the temperature,  $p$  the pressure, and the  $N_i$  are the particle numbers of the various species  $i$ .

The surface will become covered by adsorbates in equilibrium when the free energy of the interface region is reduced upon the adsorption of particles from the gas phase, i.e., when the free energy difference

$$\Delta G^{ads}(T, p) = G(T, p, N_{ads}) - G(T, p, 0) - N_{ads} \mu_i(T, p) \quad (1)$$

for the adsorption of  $N_{ads}$  particles of species in the interface region is negative. Here the chemical potential  $\mu_i = \partial G / \partial N_i$  of the adsorbate species  $i$  as a function of temperature and pressure is introduced. For the sake of convenience we first consider only one adsorbate species. Note that in order to derive the thermodynamically stable surface coverage, we have to refer the free energy gain to the surface area as this is the stability determining quantity, i.e., we have to consider the free energy of adsorption of  $N_{ads}$  species on a surface area  $A_s$

$$\begin{aligned} \Delta \gamma(T, p) &= \gamma(T, p, N_{ads}) - \gamma_{clean}(T, p, 0) \\ &= \frac{1}{A_s} \Delta G^{ads}(T, p) \end{aligned} \quad (2)$$

Up to here, everything is exact as long as thermodynamic equilibrium is assumed. However, the numerical

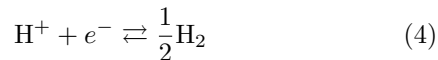
evaluation of free energies is usually rather tedious as it involves statistical averages which have to be derived by, for example, thermodynamic integration schemes. Hence the free energy of adsorption is typically approximated by the total adsorption energy, which can be relatively conveniently obtained using periodic density functional theory (DFT) calculations. Thus the free energy of adsorption is often evaluated by

$$\Delta \gamma(T, p) \approx \frac{N_{ads}}{A_s} (E_{ads} - \Delta \mu_{ads}(T, p)) \quad (3)$$

Here,  $\Delta \mu_{ads}(T, p)$  corresponds to the temperature and pressure dependent part of the chemical potential of the adsorbate in the gas-phase, and  $E_{ads}$  is the total adsorption energy per particle.  $E_{ads}$  is usually evaluated for vacuum conditions at zero temperature. The approximations entering Eq. 3 were carefully discussed by Reuter and Scheffler [16]. They estimate that neglecting pressure and entropy terms under typical conditions leads to uncertainties in the range of  $10 \text{ meV}/\text{\AA}^2$  which is within the reliability of DFT results using standard exchange correlation functionals. Note that omitting the gas phase in these calculations is indeed appropriate considering the fact that the impingement rate of gas-phase particles on surfaces is typically rather small, even at ambient conditions. Note furthermore that in Eq. 3 the dependence of the free energy of adsorption  $\Delta \gamma(T, p)$  on temperature and pressure is entirely determined by the corresponding dependence of the chemical potentials of the species in the gas phase. In spite of these approximation, applications of the *ab initio* thermodynamics using the approximate expression Eq. 3 have often been rather successful in reproducing surface phase diagrams, for example in oxidation catalysis [22, 30].

At electrochemical electrode/electrolyte interfaces, the situation is more complex than at gas/surface interfaces, as illustrated in Fig. 1. Instead of a dilute gas, now typically a liquid electrolyte is present above the electrode that contains dissolved anions and cations to make it electrically conductive. Furthermore, the reference for the calculation of adsorption energies is no longer an atom or a molecule in the gas phase, but rather a dissolved species. Hence the determination of the energy gain upon adsorption requires to evaluate solvation energies which can be numerically rather demanding [31]. In order to avoid the evaluation of the proton solvation energy in water, Nørskov *et al.* suggested the following approach [17]: “By setting the reference potential to be that of the standard hydrogen electrode, we can relate the chemical potential (the free energy per H) for the reaction ( $\text{H}^+ + \text{e}^-$ ) to that of  $1/2 \text{H}_2$ ”. This is the basis of the concept that was later (in 2010) coined the “Computational Hydrogen Electrode” [18]. However, the details of this concept were only revealed in the supporting information (SI) of that later article [18]. We will recapitulate the derivation given in the SI of this article. Interestingly, instead of employing the standard hydrogen electrode (SHE) as in Ref. [17], here the authors refer to

the zero voltage definition with respect to the reversible hydrogen electrode (RHE), given by the equilibrium of the reaction



at all pH values and temperatures with  $\text{H}_2$  at 1 bar pressure. This also means that at this conditions the chemical potential of the educts and products are the same, i.e.,  $\tilde{\mu}_{\text{H}^+(\text{aq})} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2(\text{g})}$  so that the electrochemical potential of the proton can be derived from the chemical potential of gas-phase hydrogen. For varying electrode potential, the electrode potential of the proton-electron pair is then simply given by

$$\tilde{\mu}_{\text{H}^+(\text{aq})} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2(\text{g})} - eU_{\text{RHE}}. \quad (5)$$

The question arises whether the computational hydrogen electrode is a concept based on the reversible or the standard hydrogen electrode. This discussion is in principle obsolete, as the CHE is concerned with electrochemical potentials in equilibrium where the chosen electrode potential does not matter [32]. Hence, the electrode potential of the proton-electron pair can equally well been expressed with respect to the standard hydrogen electrode

$$\tilde{\mu}_{\text{H}^+(\text{aq})} + \tilde{\mu}_{e^-} = \frac{1}{2}\mu_{\text{H}_2(\text{g})} - eU_{\text{SHE}} - k_{\text{B}}T \ln(10)\text{pH}, \quad (6)$$

where now the pH value explicitly enters. Still, the electrochemical potential will be the same, no matter whether the SHE or the RHE reference for the electrode potentials is used, as the same total thermodynamic driving forces enter.

In principle, this concludes the presentation of the CHE, Eqs. 4-6 capture everything that enters this concept. As mentioned above, this concept is very powerful in order to derive reference energies of the adsorbing species in the reservoir given by the electrolyte. In equilibrium, the CHE gives the correct reference energies. Hence there is in principle no room to go “beyond CHE”, unless one questions equilibrium thermodynamics or one wants to treat non-equilibrium situations.

The CHE concept has been mainly used to address stable adsorbate structures at electrochemical electrode/electrolyte interfaces [13, 20, 24, 25] and the potential dependent adsorption energies of reaction intermediates in electrocatalysis [17, 18, 26, 33]. It is important to note that the concept of the CHE is not restricted to the treatment of protons. Any solvated ionic species for which a corresponding standard potential exists can be considered within this concept. Take as an example a redox couple such as  $\frac{1}{2}\text{A}_2 + e^- \rightleftharpoons \text{A}^-$  [20, 24] appropriate for a halide  $\text{A}^-$  yielding an electrochemical potential of

$$\tilde{\mu}(\text{A}^-(\text{aq})) - \mu(e^-) = \frac{1}{2}\mu(\text{A}_2(\text{g})) + e(U_{\text{SHE}} - U^0) + k_{\text{B}}T \ln a_{\text{A}^-}. \quad (7)$$

Here,  $U^0$  is the reduction potential of the halide vs.  $U_{\text{SHE}}$  and  $a_{\text{A}^-}$  its activity coefficient. Note furthermore that this concept can also be extended to several species in the reservoir [22, 25]. The equilibrium adsorbate structure then correspond to the one with the lowest free energy of adsorption [25],

$$\Delta\gamma = \frac{1}{A_{\text{S}}}\left(G_{\text{ads}} - \sum_i n_i \Delta\tilde{\mu}_i(T, a_i, U)\right), \quad (8)$$

as a function of temperature  $T$ , activity coefficients  $a_i$  of the considered solvated species, and electrode potential  $U$  where  $G_{\text{ads}}$  is taken with respect to the surface area  $A_{\text{S}}$ . Again I like to stress that Eq.(8) is in principle exact in thermal equilibrium as long as the free energy  $G_{\text{ads}}$  is correctly determined (which is of course practically still not possible given the current status of first-principles technologies). All uncertainties are related to the approximations that enter the evaluation of  $G_{\text{ads}}$ .

### III. APPLICATION OF GRAND-CANONICAL SCHEMES TO ADDRESS STRUCTURES AND PROCESSES AT ELECTROCHEMICAL ELECTRODE/ELECTROLYTE INTERFACES

One first famous application of the concept of the CHE was the elucidation of the origin of the overpotential in the oxygen reduction reaction (ORR) by Nørskov *et al.* [17]. The main ideas are illustrated in Fig. 2 for the four electron process. All energies of the reaction intermediates are shift by  $-n_i eU$ , where  $n_i$  is the number of electrons involved. For example, in the formation of  $\text{O}_2(\text{g})$  from two water molecules four protons and electrons are involved, so that the state  $\text{O}_2(\text{g})$  is associated with  $n_i = 4$ . Figure 2a illustrates the case of an ideal catalyst, for which the free energy difference between successive reaction intermediates should be 1.23 eV. Then at the equilibrium potential of 1.23 V a flat free energy diagram results.

Nørskov *et al.* [17] explicitly calculated the reaction energies using periodic DFT calculations in combination with the grand-canonical scheme just discussed. In fact, they specifically addressed the approximations that entered the concrete calculations. First of all, the presence of water was modeled by just one bilayer of water. Still, for the small adsorbates considered, the adsorption energies are hardly modified by the presence of water [34, 35]. Furthermore, the presence of electric fields and thus also varying electrode potentials hardly influences the adsorption energies [17, 36–38] which is probably due to the good screening properties of metallic electrodes [39].

The corresponding calculations of the adsorption energies of the ORR reaction intermediates [17] revealed that they do not follow the ideal behavior illustrated in Fig. 2a. Instead, they rather exhibit a behavior that is schematically illustrated in Fig. 2b. As the differences between the adsorption energies of consecutive reaction intermediates do not correspond to the ideal value of

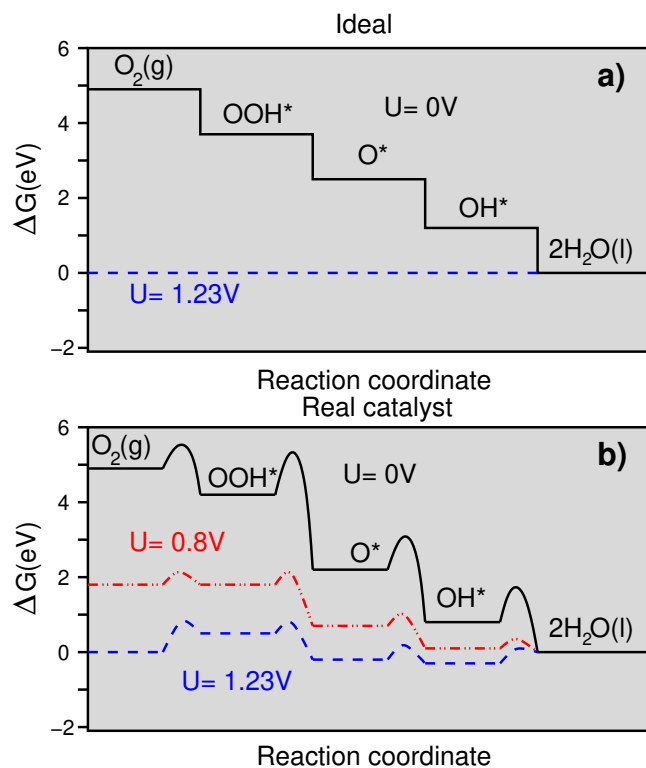


FIG. 2. Schematic free energy diagrams of the four steps in the oxygen reduction reaction for various electrode potentials. a) Ideal catalyst, b) Realistic catalyst also including reaction barriers.

1.23 eV, at the equilibrium potential of 1.23 V two steps result that are uphill in energy. These energy differences then act as an effective barrier suppressing the activity of the ORR. Only for a value of about 0.8 V, no uphill steps occur. This would correspond to an overpotential of about 0.4 V which is very close to experimental observations [40]. Later it has been found that there are scaling relations between the adsorption energies of the OH and OOH intermediates which lead to universality in oxygen reduction electrocatalysis on metal surfaces [41].

Thus in general, a situation where the free energy differences between all reaction intermediates fulfil the condition  $\Delta G \sim 0$ , as represented in Fig. 2a for the equilibrium potential, is considered to be preferable for a high catalytic activity. However, recently this issue has drawn some attention [19, 42, 43]. Lindgren *et al.* [19] addressed the hydrogen evolution reaction (HER) on Pt(111) by a combination of density functional theory calculations and microkinetic modeling in a very elaborate study. In particular, from the electronic structure calculations they derived fully potential-dependent reaction barriers. Traditionally one considers the hydrogen atoms adsorbed in the three-fold hollow sites, also called underpotential deposited (UPD) hydrogen, to be the reaction intermediates in the HER [3]. However, based on their microkinetic analysis, Lindgren *et al.* could demonstrate that rather hydrogen atoms weakly bound to the top positions of

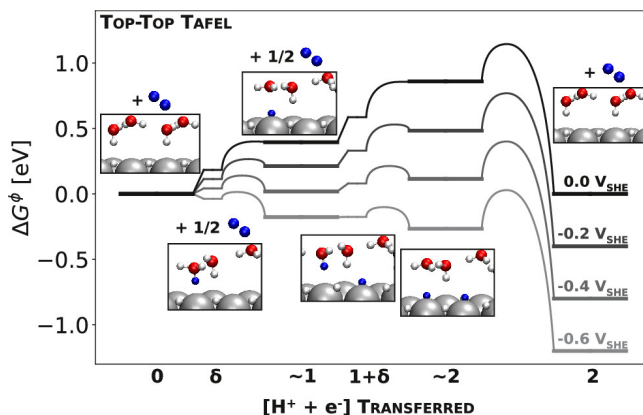


FIG. 3. Calculated free energy diagram of the hydrogen evolution reaction. Reprinted with permission from Ref. [19], P. Lindgren, G. Kastlunger, A.A. Peterson, A challenge to the G 0 interpretation of hydrogen evolution, ACS Catal. 2020, 10:121 .

Pt(111), after the three-fold hollow positions have been filled, are the active species, as illustrated in Fig. 3. The important role of these overpotential deposited (OPD) hydrogen atoms in the HER on Pt(111) has in fact already been pointed out before [44].

This basically confirms the obvious fact that in order to fully understand trends in catalysis, it is not sufficient to only consider thermodynamics, kinetic effects might also play a crucial role. I have indicated this by additionally including activation barriers in Fig. 2b. This is in the spirit of distinguishing between rate-determining and potential-determining steps, as presented by Koper [45]. Still, as Koper demonstrates, the simpler concept of potential-determining step is often sufficient to capture the essence of reaction mechanisms, but there are important exceptions as just presented above.

I will now address two examples where the application of the concept of the computational hydrogen electrode yields results that are almost in quantitative agreement with experiment. The first example concerns the co-adsorption of hydrogen and halogen atoms on Pt(111) [25]. In this computational study, the adsorption energies of more than 100 different halogen and hydrogen adsorption structures in various geometries were considered. Using these energies, the Pourbaix diagram, i.e., a phase diagram as a function of pH and the electrode potential, was constructed. In fact, in the determination of the adsorption energies, the presence of the aqueous electrolyte was entirely neglected. Still, the calculations were able to semi-quantitatively confirm the experimentally observed competitive adsorption behavior of halides and hydrogen [46]. This is due to the fact that the adsorption energies of atoms at metal electrodes are hardly influenced by the presence of water [5, 17, 34, 35]

However, this is not necessarily true when the adsorption of molecules at electrode/electrolyte interfaces is considered. In a recent study, the adsorption of sul-

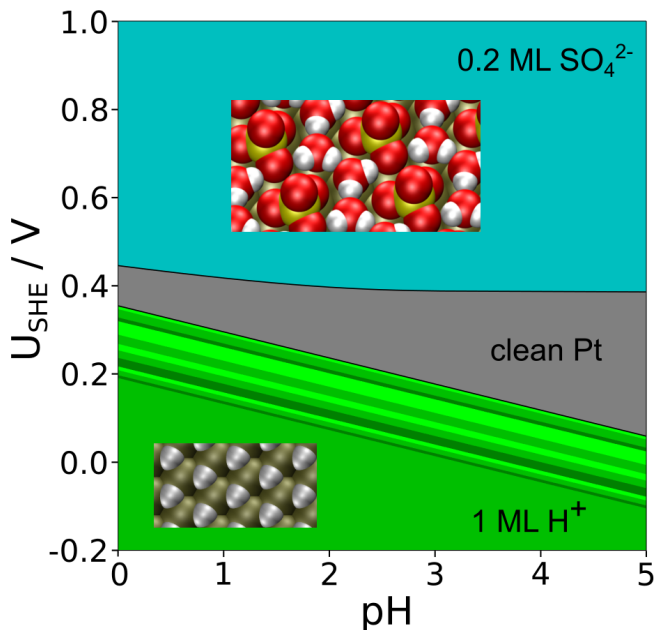


FIG. 4. Calculated Pourbaix diagram showing the stable phases of co-adsorbed sulfate and hydrogen on Pt(111) as a function of pH and electrode potential. The sulfate concentration corresponds to an activity of 0.1 (adapted from Ref. [27], F. Gossenberger, F. Juarez, A. Groß, Sulfate, bisulfate, and hydrogen co-adsorption on Pt(111) and Au(111) in an electrochemical environment, *Front. Chem.* 2020, **8**:634, under the Creative Commons Attribution License (CC BY)).

fate and hydrogen on Pt(111) and Au(111) were considered [27]. Sulfate is known to adsorb on Pt(111) at potentials of about 0.5 V in a row-like  $\sqrt{3} \times \sqrt{7}$  structure [47]. A corresponding structure is also observed on Au(111), but at potentials of about 1 V [48]. Yet, calculated surface phase diagrams as a function of the electrochemical potentials of sulfate and protons obtained using the CHE concept could not reproduce any stable row-like sulfate structures on Pt(111) and Au(111) at the experimentally observed conditions [27], as long as the presence of water was neglected in the calculations. Even when the water was included within an implicit solvent model [49], no agreement with experiment could be obtained.

However, using a combination of the implicit solvent model with explicitly considered water molecules, a very satisfactory agreement with the experiment has been obtained. This is demonstrated in Fig. 4 where a Pourbaix diagram for the co-adsorption of sulfate and hydrogen on

Pt(111) is shown. At low electrode potentials, Pt(111) is hydrogen-covered, and at about 0.4 V the so-called double layer region starts, followed by the onset of sulfate adsorption. The stable sulfate structure is illustrated in the inset of Fig. 4. The sulfate row-like structures become strongly stabilized by the presence of two explicit water molecules per sulfate anion linking the sulfate rows. Note that the calculations also reproduce the experimentally observed displacement of sulfate adsorption to higher potentials for decreasing pH, in particular for  $\text{pH} \leq 2$  [50].

#### IV. CONCLUSIONS

By the combination of atomistic first-principles electronic structure calculations with grand-canonical concepts such as *ab initio* thermodynamics and the computational hydrogen electrode, interface structures and processes under operating conditions in heterogeneous and electro-catalysis can be rather successfully reproduced. This is often rather surprising as in the applications of these concepts for practical reasons often considerable approximations enter. Due to the severe nature of these approximations, in particular as far as electro-catalysis is concerned, the whole approach of using these grand-canonical concepts has been questioned. However, it is important to realize that these concepts are exact within a grand-canonical equilibrium description of the systems. Hence instead of questioning the concepts, the atomistic modelling of the interfaces shall be improved, which can be successfully done, also for electrochemical electrode/electrolyte interfaces, as demonstrated in this contribution.

#### V. DECLARATION OF INTERESTS

none

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