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On the Thermodynamic Equivalence of Grand Canonical, Infinite-Size, and Capacitor-Based Models in First-Principle Electrochemistry

Georg Kastlunger,^{*[a]} Sudarshan Vijay,^[a] Xi Chen,^[b] Shubham Sharma,^[b] and Andrew Peterson^{*[b, c]}

This paper is dedicated to Jens Nørskov's outstanding contribution to the theory of electrocatalysis

First principles-based computational and theoretical methods are constantly evolving trying to overcome the many obstacles towards a comprehensive understanding of electrochemical processes on an atomistic level. One of the major challenges has been the determination of reaction energetics under a constant potential. Here, a theoretical framework was proposed applying standard electronic structure methods and extrapolating to the infinite-cell size limit where reactions do not alter the potential. Today, electronically grand canonical modifications to electronic structure methods, holding the potential constant by varying the number of electrons in a finite simulation cell, become increasingly popular. In this perspective, we show that

these two schemes are thermodynamically equivalent. Further, we link these methods to capacitive models of the interface, in the limit that the capacitance of the charging components (whether continuum or atomistic) are equal and invariant along the reaction pathway.

We benchmark the three approaches with an example of alkali cation adsorption on Pt(111) showing that all three approaches converge in the cases of Li, Na and K. For Cs, however, strong deviation from the ideal conditions leads to a spread in the respective results. We discuss the latter by highlighting the cases of broken equivalence and assumptions among the approaches.

Introduction

Simulating electrochemical processes is challenging, owing to the complexity of the electrochemical interface and to the fact that the reaction energetics are not solely functions of temperature and pressure, but that the applied electrode potential and the electrolyte pH drastically influence the reaction energetics.^[1] In corresponding experimental setups, the electrode potential is fixed throughout the course of a reaction by a potentiostat by allowing a flow of electrons between electrodes. Incorporating

such reaction conditions into *ab initio* simulations is far from straightforward, and the practical models are often chosen to balance the computational demand with the degree of approximation.

Scheme 1 illustrates the inherent problem in the simulation of electrochemical adsorption processes, as well as kinetics. In a conventional periodic DFT calculation, performed in finite unit cells with a fixed number n of electrons, the electrode potential ϕ in the simulation changes from the potential of the bare electrode surface ϕ^* upon adsorption of a chemical species A, to ϕ_{A^*} . We symbolize the degree of polarization by the formal charge q on A after adsorption, which is counteracted by a charge $-q$ in the metal electrode. The resulting dipole creates an electric field changing ϕ_{A^*} with respect to ϕ^* . In fact, changes of up to several volts may occur in reasonably sized unit cells for proton-electron transfers^[2-4] or chemical reactions involving polar intermediates.^[5,6] While several approaches exist to counteract the potential drift during a reaction in post-processing,^[4,7-10] two schemes try to approach the constant potential situation directly within the simulation.

Already in 2008, Nørskov and colleagues suggested that a potential drift along an electrochemical reaction path can, in principle, be mitigated by extrapolating the simulation to a single event on an infinitely large electrode.^[11] As outlined in Scheme 1 in this hypothetical limit, there is no change in ϕ upon the adsorption of a polar intermediate. This limit corresponds to the physical scenario where electrochemical reaction events are rare and a single elementary reaction does not influence the electrode potential. In practice, this limit can

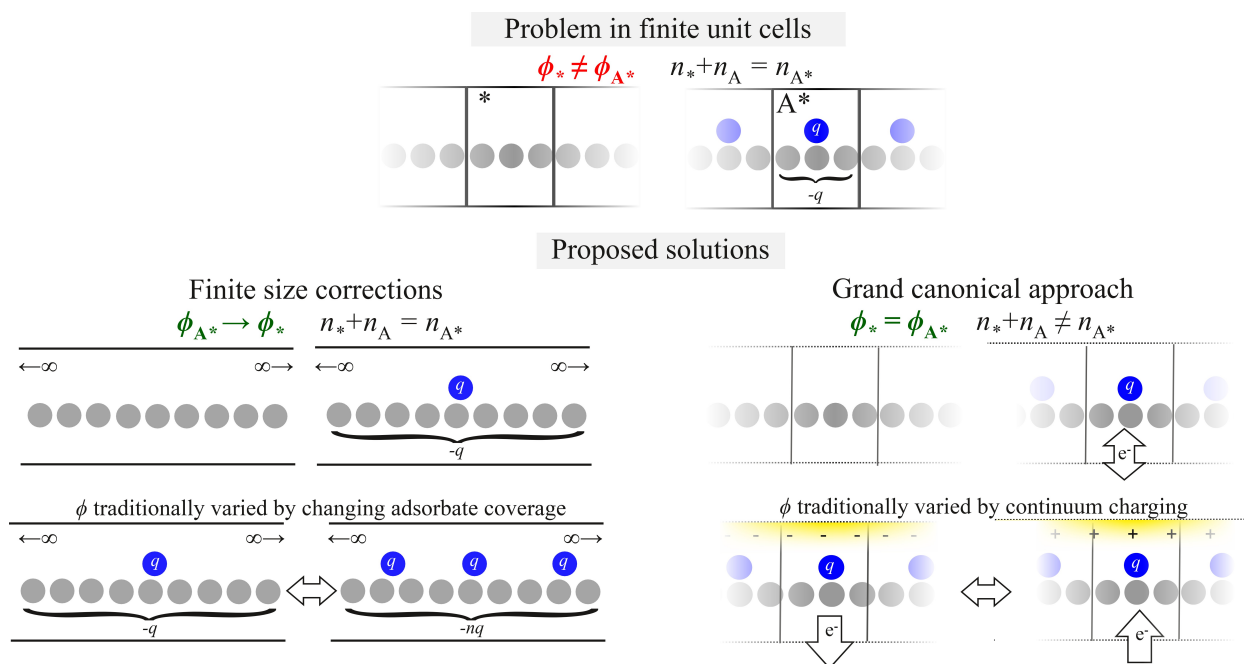
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Scheme 1. Illustration of the challenge in simulating electrochemical processes including polarized adsorbates or kinetics, namely the fact that the potential varies from the initial to the final state of the reaction and the two proposed solutions prominently discussed in this perspective.

be determined in computations through an extrapolation from simulations in a series of finite-sized cells^[2,11,12] of the interface, or with a single cell via a capacitor model of the interface.^[4,8,9] Traditionally, a range of potentials can be screened in this approach by varying the coverage of polarized adsorbates or protons included in a water bilayer.

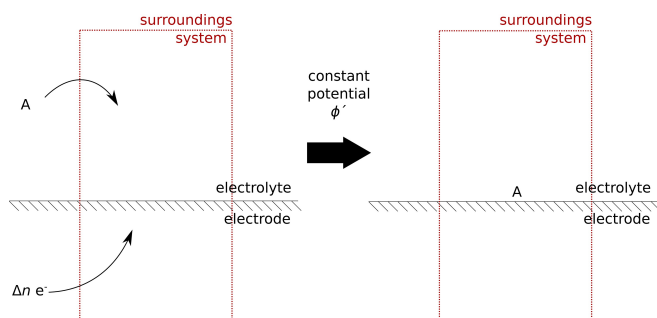
Another proposed solution is the grand canonical approach, where the number of electrons in the simulation is varied continuously to hold the potential constant, through the application of various continuum charging approaches (some of which also continuously vary counter-ion concentrations).^[27] In most electronically grand canonical implementations, the interface is connected to an external electron reservoir – as it is in a physical potentiostat – which supplies electrons to keep the potential constant throughout the reaction process. The number of explicit (quantum mechanically treated) ions, on the other hand, is kept constant and only a corresponding electrostatic contribution is varied within the applied continuum charging schemes to hold the charge balanced.^[4–7,10,14,15,17,20–26] The diverse streams of method development in recent years has led to many differing approaches, each with its own underlying assumptions and capabilities, in the simulations of electrochemical thermodynamics and kinetics.

In this perspective, we 1) show that the energetics from a canonical treatment at infinite cell size are equivalent to those of grand canonical simulations and 2) review how the infinite cell size result can be obtained by finite cell size simulations using a capacitor model of the interface. (In contrast to the derivations in Ref. [8], our derivation for the equivalence in point (1) is based on a general thermodynamic formulation, independent of a capacitor model of the interface.) We end

with examples of cation adsorption using a grand canonical, capacitor and cell extrapolation approach to illustrate their equivalence and the latter's breakdown. We hope that this short note resolves outstanding controversies relating to the different approaches, by showing they are able to yield the same results, with differences due solely to the implementation details, and not the inherent model framework.

Equivalence of a Grand Canonical Approach and Infinite-Size Extrapolation

We start by describing what happens at the level of atoms and electrons when an elementary reaction takes place at a potential-controlled electrode. Here, we intend to describe the actual physical process, and not the particulars of any specific method of simulating such a process. As an example, we examine the adsorption of a species A on an electrode surface, shown in Scheme 2. At this stage, we consider A to be generic – it may be ionic or non-ionic, and the adsorbed state may be a locally stable state, a transition state, or at an arbitrary geometry. When A enters the system and adsorbs, the circuit needs to provide $n\Delta$ electrons (which may be positive, negative, or zero) to hold the electrode's potential constant at ϕ' . The flow of electrons may be needed for a variety of reasons, such as to compensate for a transfer of electrons between A and the electrode surface, or to offset changes to the surface-normal dipole that would otherwise have the effect of changing the potential. We compactly write this constant-potential process as:



Scheme 2. The thermodynamic system corresponding to an elementary electrochemical step, associated with the reaction of species A (coming from a reservoir) and Δn electrons (also coming from a thermodynamic reservoir).



Here, * is used to represent the electrode system before A is present, and A* represents the electrode system after A enters and adsorbs.

Properly, the A* state has a net charge of $-\Delta n$ relative to the earlier state (*), but we will avoid writing $A^{*-\Delta n}$ for brevity. We make no assumptions about where within the system the extra n electrons localize.

The change in free energy of this reaction at the potential ϕ' is

$$\begin{aligned} \Delta G_{\text{rxn}}[\phi'] &= G_{A^*}[n_* + n_A + \Delta n, \phi'] - G_*[n_*, \phi'] \\ &\quad - \mu_A[n_A] - \Delta n \mu_e[\phi'] \end{aligned} \quad (2)$$

where G_i refers to the free energy stored in the system (as defined in Scheme 2) in state i , and n_i refers to the number of electrons associated with each state. μ_A and μ_e refer to the chemical potentials of the adsorbing species and electrons, respectively. Both the adsorbing species and the added electrons are initially located in thermodynamic reservoirs and enter the system over the course of the reaction; thus these species' chemical potentials μ_i are those of their respective reservoirs. The reservoir of A is located above the electrode surface and can be, for example, a gas-phase species (such as CO₂ at 1 atm) or a species solvated in bulk solution (such as a proton whose chemical potential is defined by the solution pH). Since this reservoir is electronically disconnected from the electrode, its chemical potential does not depend on ϕ , but only on the nature of A. μ_e , on the other hand, is set by the electrode potential, with $\mu_e[\phi] = \mu_e[\phi_{\text{ref}}] - e(\phi - \phi_{\text{ref}})$, where e is the (positive) electronic charge in atomic units, or the Faraday constant in molar units; ϕ_{ref} is an arbitrary reference state, which will cancel out in the overall reaction process.

Grand canonical treatment. Using an electronically grand canonical electronic structure method, the electrode potential of the system can be directly set to a specified value ϕ by varying the number of electrons in the simulation.^[6,14–19,21] We note that from a thermodynamic perspective, the electrons entering the system are no different than other reactants or products that enter or leave the system in conventional

catalysis; that is, while electronic structure calculations trying to explicitly incorporate the described electrochemical scenario may be referred to as “grand canonical” in electrons, the net reaction thermodynamics are analyzed identically to any catalytic reaction, for example, with a gas-phase species entering the simulation cell; see Lindgren *et al.*^[54] for a more detailed description. However, in practice, electronically grand canonical calculations allow any fractional change in the number of electrons, while the number of explicitly included adsorbates is bound to integer numbers. Thus, μ_A is generally considered in energetic differences (such as ΔG_{rxn}), while the reference state for the electrons (μ_e) is conventionally built into the free energy of each individual state transforming it into the grand canonical free energy $\Omega \equiv G - n\mu_e$. This transformation results in single-state energies that are consistent with the atomic forces, and allows routines such as saddle-point searches to operate smoothly.^[27]

Substitution of Ω into equation (2) results in an exact cancellation of the electronic term:

$$\Delta G_{\text{rxn}}[\phi'] = \Omega_{A^*}[\phi'] - \Omega_*[\phi'] - \mu_A \quad (3)$$

That is, free energy changes can be evaluated directly from the output of grand canonical simulations,^[28] as long as Ω is used, since the chemical potential of the entering/exiting electrons are automatically incorporated through the use of grand canonical energies.

Canonical treatment. Next, we'll examine a similar system that is closed to the flow of electrons, to understand if and when it is thermodynamically equivalent to the open system described above. This comparison will allow us to link the cell-extrapolation method to grand canonical calculations. Let's examine the same reaction occurring with a fixed number of electrons $n' \equiv n_* + n_A$ (and with a non-constant potential), as would be simulated in a traditional calculation:



The free-energy change of such a reaction is

$$\Delta G_{\text{rxn}}[n'] = G_{A^*}[n', \phi' + \Delta\phi] - G_*[n_*, \phi'] - \mu_A[n_A] \quad (5)$$

Note that at this stage, $\Delta G_{\text{rxn}}[n']$ does not have a well-defined potential. To facilitate comparison with the grand canonical treatment, we take as a basis that the initial state (A + *) in both the open and closed systems are identical; that is, they both have $n_* + n_A$ electrons and the electrode has the potential ϕ' . That is, G_* is identical in equations (5) and (2). However, the A* states in equations (2) and (5) are at two subtly different conditions, differing by n electrons and $\Delta\phi$ potential from one another. For the moment we'll assume that the states in both ensembles have identical geometries – and when Δn and $\Delta\phi$ are very small they should, since stationary points found in one ensemble are always stationary points in the other^[27,29,30] – so we can relate the final-state free energies by

$$G_{A*}[n' + \Delta n, \phi'] = G_{A*}[n', \phi' + \Delta\phi] + \int_{n'}^{n'+\Delta n} \mu_e[\phi(n)] dn \quad (6)$$

which is a thermodynamic identity at fixed temperature, pressure, and atomic positions, since $\mu_e \equiv \left(\frac{\partial G}{\partial n}\right)_{T,P,\{\bar{r}_i\}}$.

In the cell-extrapolation technique, one repeats constant-charge simulations in larger and larger unit cells, while allowing only a single reaction event to take place regardless of cell size, as we outline in section 1 of the SI. The argument of the integral varies monotonically from $\mu_e[\phi']$ to $\mu_e[\phi' + \Delta\phi]$, which differ by $e\Delta\phi$. As the system size grows to infinity and only a single reaction takes place, $\Delta\phi \rightarrow 0$, and therefore $\mu_e[\phi']$ can be pulled from the integral. However, note that Δn does not approach zero as the system size grows; it is independent of the system size as it is tied to the number of reaction events. Thus, the integral becomes exactly $-\Delta n\mu_e[\phi']$ in the limit of infinite size, and

$$\lim_{\text{area} \rightarrow \infty} G_{A*}[n', \phi' + \Delta\phi] = \lim_{\text{area} \rightarrow \infty} G_{A*}[n' + \Delta n, \phi'] - \Delta n\mu_e[\phi'] \quad (7)$$

which shows that equations (2) and (5) are identical in the limit of infinite area, noting that the free energy of electrons entering the system is exactly equivalent to the chemical potential within the system (μ_e) at constant potential. Therefore,

$$\Delta G_{\text{rxn}}[\phi'] = \lim_{\text{area} \rightarrow \infty} \Delta G_{\text{rxn}}[n'] \quad (8)$$

Thus, when the system work functions are the same, this relationship shows the equivalence of ΔG when evaluated in either the grand canonical framework (equation (2)), or the canonical framework (equation (5)), with the system size being extrapolated to infinity.

Of course, in the practical implementation of grand canonical and infinite-size calculations, researchers may make different modeling simplifications, which can still lead to differing results. Further, artifacts of periodicity may be present in one system but absent in another. However, in the hypothetical case where all modeling choices are equivalent, the two methods of calculation are equivalent for a single reaction.

Capacitor Model in Canonical Simulations

We next make the connection to capacitor-based models, which under certain assumptions can link finite-sized canonical calculations to constant-potential results without the need for infinite-size extrapolation.

In traditional (charge-neutral) canonical calculations, the potential of the simulation (which is manifested as the topside work function) cannot be set explicitly; rather, it is an output of the calculation. In practice, one changes the atomic geometry of the simulation in order to adjust the simulated potential^[2,11] (cf. lower left panel of Scheme 1). For example, adding an extra H atom into a water layer will result in a ground-state electronic configuration that exhibits charge separation, with a positively charged proton in the water layer and a negatively charged

surface. In this case, this will lower the work function of the electrode, making the simulated potential more negative. Removing a hydrogen, or adding an atom that forms an anion (such as Cl^-) will have the opposite effect, making the simulated potential more positive. To a lesser degree, adding adsorbates to the surface affects the work function, allowing one to use coverage as another tool to fine-tune the simulated potential.

For similar reasons, the simulated potential will change over the course of a reaction in a finite canonical simulation. *E.g.*, in the proton-deposition (Volmer) reaction, the initial state contains a positively-charged proton in the water layer and an equal amount of negative charge on the electrode surface, resulting in a relatively negative potential. In the final state, the hydrogen is adsorbed on the surface in a relatively charge-neutral manner, resulting in a more positive potential than the initial state. The transition state is likely to have a potential in between these extreme values.^[27]

Several approaches^[4,7,8,24,25,31–33] have modeled changes to the simulated potential as a capacitor. The metal–electrolyte interface within a canonical simulation is envisioned to be a parallel-plate capacitor, where the metal slab and the electrolyte make up the two plates, analogous to Helmholtz' model of the electrochemical double layer.^[34] As before, we consider the reaction in equation (4). In a finite unit cell, the introduction of A onto the surface will cause a shift $\Delta\phi$ in the simulated potential with respect to the adsorbate-free surface. Thus, if a reaction at constant potential is to be simulated, this finite-size effect needs to be countered. By applying the assumption that the free energy of the interface changes as a parallel-plate capacitor with a constant capacitance C , we can correct the free energies of the two states in order to correspond to energies at an infinite cell size and, hence, equal potential. We note that in our treatment here we have assumed an ideal case where the capacitances of all charging components are equal and invariant along the reaction path. Capacitance mismatch amongst the components can occur with variations in the parameterization of the implicit model,^[15] the addition of an explicit water layer (which pushes implicit electrolyte farther from the electrode),^[24,25] or when considering the adsorption of species of very different sizes, high coverages and dipole moments.^[5,6] In general, the capacitance in a real system does not shift in the course of a single elementary reaction, but it can occur within a simulation in a finite cell size.

As a first approach within this framework, Chan and Nørkov suggested a means to correct the reaction energy between two states from the finite to the infinite cell size.^[4,7] This so-called *charge extrapolation* method elegantly transforms the reaction energy in a finite cell (with differing potentials in the two states) to the infinite cell size (with identical potentials) by applying a correction term of the form $\frac{1}{2}\Delta q\Delta\phi$ mitigating finite size effects to *extrapolate* the reactant to the product's potential (cf. section 1 of the SI for further details), or vice versa:

$$\lim_{\text{area} \rightarrow \infty} \Delta G[n', \phi'] = G_{A*}[n', \phi' + \Delta\phi] - G_*[n_*, \phi'] - \mu_A[n_A] - \frac{\Delta q\Delta\phi}{2} \quad (9)$$

$$\lim_{\text{area} \rightarrow \infty} \Delta G[n', \phi' + \Delta\phi] = G_{A^*}[n', \phi' + \Delta\phi] - G_*[n_*, \phi'] - \mu_A[n_A] + \frac{\Delta q \Delta\phi}{2}$$

where Δq is the change of charge stored in a hypothetical capacitor upon transitioning between the two states of the reaction. Note that in this work Δq refers to a (hypothetical) charge rearrangement *within the simulated system*, while Δn refers to electrons entering or exiting the system from or to an *external reservoir*.

Although efficient, as it only necessitates one canonical DFT calculation of each state involved to get the constant-potential energy at both the initial and final state potentials, the *charge extrapolation* method relies on a scheme to determine Δq , which is not an observable in DFT. As Δq can be envisioned as the charge transferred onto an adsorbate, originally, Bader charge partitioning^[35,36] was applied.^[4,7] However, more recently an atomic force based method has been developed, leading to an alternative method to estimate Δq .^[37]

A scheme to avoid the need to know the (unobservable) value of Δq has been proposed recently.^[8,9] In this so-called *mean-potential method*, the reaction energy is assumed to change linearly with potential at the infinite cell size. In principle, we can use equations (9) and (10) to extrapolate to the potential of the initial and final states of a reaction, respectively. In a second step we can then transfer the results to the mean potential of the two states via

$$\lim_{\text{area} \rightarrow \infty} \Delta G[n', \bar{\phi}] = \lim_{\text{area} \rightarrow \infty} \frac{\Delta G[n', \phi'] + \Delta G[n', \phi' + \Delta\phi]}{2} \quad (11)$$

assuming a linear dependence of the reaction energy at the infinite cell size on the potential. Substituting equation (9) and (10) into (11) cancels the size dependent term ($\mp \frac{\Delta q \Delta\phi}{2}$) and leads to the equality:

$$\Delta G[\phi] = \lim_{\text{Area} \rightarrow \infty} \Delta G[n', \phi] = G_{A^*}[n', \phi + \Delta\phi] - G_*[n_*, \phi] - \mu_A[n_A] \quad (12)$$

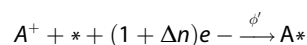
which shows that a constant-potential reaction energy can be estimated from constant- n calculations in a finite unit cell by linking to the mean potential of the two end states and incorporates all three discussed frameworks. An additional graphical derivation of this final equation is provided in the Supporting information.

To summarise, within certain assumptions and limitations, the energetics of electrochemical reaction processes at a fixed electrode potential can be validly calculated in the three discussed ways, *i.e.*, by application of a grand canonical framework or a canonical framework either by extrapolation to an infinite unit cell or a finite unit cell evaluated at the mean potential. However, we emphasize that for the latter equivalence to hold we must assume that the change in potential upon charge rearrangement inside the cell, Δq , is an equivalent process to the introduction of electrons into the cell, Δn , and is always linear and equal in slope (that is, following a single constant capacitance).

We note that recently, the use of continuum charging (10) techniques for varying the potential within the constant-charge framework is gaining considerable popularity.^[8,24,25,30–33,38,39] Here, adding arbitrary, but identical, amounts of charge to the two states of a reaction of interest changes their respective potential gradually, while the potential difference between the states remains virtually constant, save for polarization effects of the adsorbates. This allows the decoupling of coverage and potential within canonical simulations. The addition of such a continuum charge does not alter the upcoming argumentation, as only the change in potential in the course of the reaction defines the potential response.

Testing the Equivalence

Next, we construct computational systems to test the equivalence of the three methods in practice. We will study the adsorption of alkali cations from solution on a platinum fcc(111) surface, which we can represent as



Such reactions present a formidable test case as the ion's (partial) discharge upon adsorption leads to significant potential/charge changes; meanwhile, the fact that they are single ions reduces the noise of geometric rearrangement.

To describe the reaction above, we will modify equation (2) to reference each cation to its standard redox potential ϕ_{A^+/A^+}^0 ^[40] and its deviation at the potential of interest ϕ , via $\mu_{A^+/A^+}^{+e} - [n_A] = \mu_{A^+}^0 [n_A] - e(\phi - \phi_{A^+/A^+}^0)$. This leads to the adsorption energy

$$\Delta G[\phi] = G_{A^*}[\phi] - G_*[\phi] - \mu_{A^+}^0 + e\phi_{A^+/A^+} + e(1 + \Delta n)\phi \quad (13)$$

in the grand canonical framework, where $1 + \Delta n$ is defined by the difference in the total number of electrons in $*$ and A^* at the potential ϕ . As mentioned before, we emphasize that, if the grand canonical energies are calculated directly (*e.g.*, with SJM) the last term in equation (13) is already implicitly contained in the subtraction of the grand free energies of the two states. Also note that in the case of this reaction Δn is negative, as a consequence of the need to extract electrons from A^* with respect to $*$.

In the case where we extrapolate the electrochemical adsorption to an infinite unit cell the definition changes into

$$\lim_{\text{area} \rightarrow \infty} \Delta G[n'] = \lim_{\text{area} \rightarrow \infty} (G_{A^*}[n'] - G_*[n_*]) - \mu_{A^+}^0 + e(\phi_\infty - \phi_{A^+/A^+}), \quad (14)$$

where ϕ_∞ represents the potential corresponding to a given adsorbate coverage at an infinite unit cell, as further described in section 1 of the supporting information. Note that, while in the grand canonical case the potential will be an input of the calculation, in the cases of the capacitor approach and the extrapolation to an infinite cell size the potential will be determined as an output of the DFT calculation.

Finally, the analogue definition applying the mean potential approach for this reaction is

$$\lim_{\text{area} \rightarrow \infty} \Delta G[n', \bar{\phi}] = G_{A^*}[n'] - G_*[n_*] - \mu_{A^*}^0 + e(\bar{\phi} - \phi_{A/A^*}), \quad (15)$$

where $\bar{\phi}$ represents the arithmetic mean of the output workfunction of * and A*, which is the potential the reaction energy is defined at.

Figure 1 shows the results of the potential-dependent adsorption energy of hydrogen and a range of alkali cations. In the canonical cases, the electrode potential was tuned by changing the adsorbate coverage (see schematic in Scheme 1 section 1 of the SI for further details). In the grand canonical case, the potential can be tuned directly based on grand canonical continuum charging,^[17] and thus the potential and coverage were varied independently. The respective adsorption energies were calculated applying equations (13)–(15). Note that for *H, *Li and *Na we increased the adsorbate coverage up to a quarter of a monolayer. For *K and *Cs, we observed depolarization of the adsorbates at coverages exceeding 0.14 and 0.11 monolayers, respectively, as we show in Figure S7. Depolarization would lead to a non-linear behaviour in the relationship of ΔG vs potential.^[41,42] Addressing the physicality of such a behaviour is beyond the scope of this letter, thus we chose to exclude the depolarized coverages for *K and *Cs in Figure 1.

The determined effective slope gives insights into the nature of the adsorption process. For *H, we find a slope of about 1 eV/V. This is expected given that upon adsorption H⁺ is fully absorbed into the metal bandstructure, hence fully

discharged. In this case the workfunction is virtually unchanged upon the change of hydrogen coverage. Hence, both the capacitor and infinite cell size approaches (represented by circles and triangles, respectively) collapse in a single point at $\phi \approx 5.1$ V. On the other hand, the grand canonical approach allows the manual variation of the potential, in order to move along the x-axis of Figure 1, exhibiting the slope of 1 eV/V. This result is consistent with the result of a traditional computational hydrogen electrode^[43] (CHE)-based model, where by default a complete discharge and a slope of 1 eV/V is assumed.

In contrast to *H, we find varying slopes of ΔG with ϕ for alkali cation adsorption on Pt(111). These deviations suggest only partial discharge of the cations upon adsorption and the creation of a significant surface dipole. Thus, cation adsorption potentials might be overestimated significantly by using CHE alone and the use of the methods described herein is crucial. The potential response of the free energy of adsorption shown in Figure 1 ranges from 0.6 to 0.3 for the studied cations, with a reducing value descending the periodic table. Interestingly, we find a correlation of the potential dependence of ΔG with the Pauling electronegativity of the cations, as shown in Figure 2. Further investigation of this correlation might allow an *a priori* estimation of the potential response of adsorbing ionic species. Such a study, however, is beyond the scope of this perspective.

The linear fit of ΔG with ϕ in Figure 1 is nearly perfect for *H, *Li, *Na and *K. The adsorption of Cs on the other hand led to considerable noise. Several reasons can be thought of being responsible for the creation of noise in this case, which we outline in more detail in the next section.

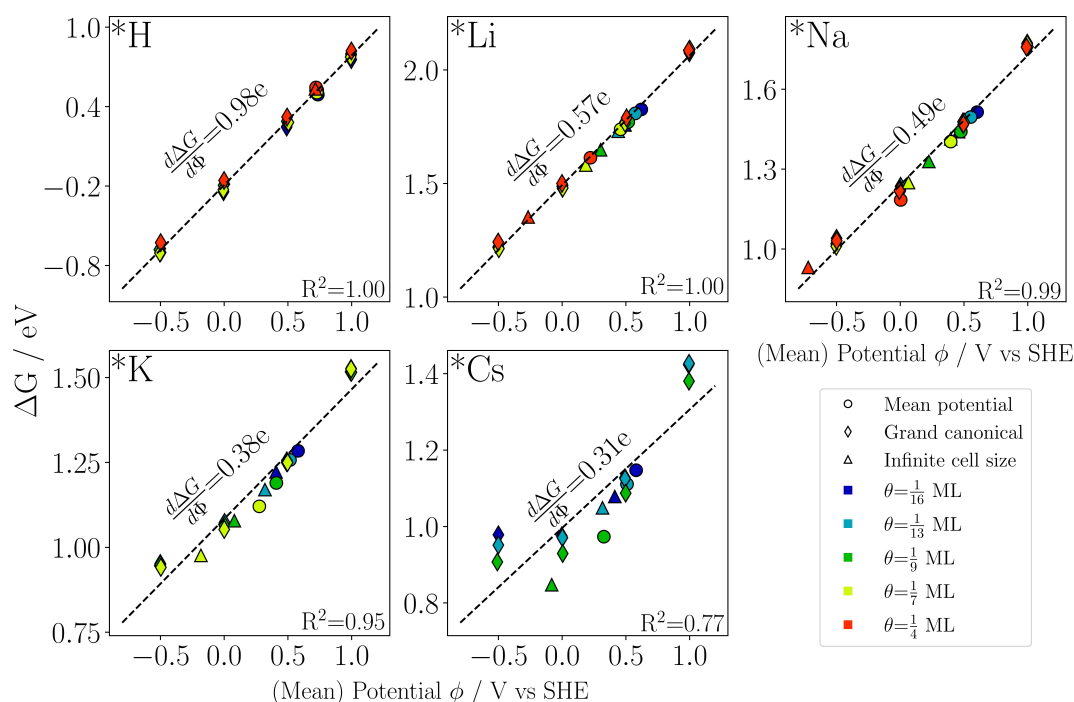


Figure 1. Binding energy of a proton (H⁺) and alkali cations on a Pt(111) surface at varying potential, where all three discussed frameworks have been applied. For H⁺ the slope is 1 eV/V as expected from CHE. The cations do not fully discharge upon adsorption. Hence, the slope deviates from ideal CHE behaviour. All three methods account for this deviation with equal outcome.

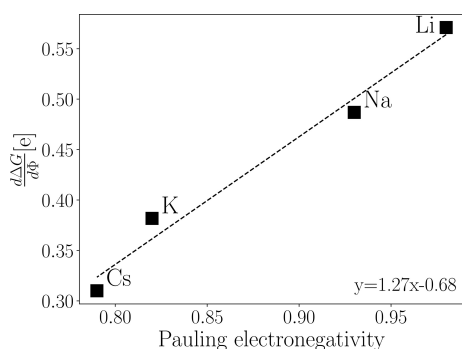


Figure 2. Relationship of potential dependence of adsorption and the electronegativity of the respective cations.

Our results in Figure 1 further show that the alkali cation coverage at potentials relevant for electrocatalysis ($2 \text{ eV} < e\phi < 6 \text{ eV}$, with $e\phi_{\text{SHE}} \approx 4.4 \text{ eV}$) is generally negligible. The plating potential $E_{1/2} = \phi_{1/2} - \phi_{\text{SHE}}$; that is, the potential of $\Delta G = 0$ where the coverage reaches 0.5, can be estimated from Figure 1. The resulting $E_{1/2}$ are 0.20 V, -2.62 V , -2.55 V , -2.84 V , -3.21 V , vs SHE, in descending order from H to Cs, in reasonable vicinity to $E^0[\text{A}/\text{A}^+]$ of the cations. A deviation from $E^0[\text{A}/\text{A}^+]$ is generally a consequence of chemical interaction upon bond formation. However, given the simplified model in our calculations we do not expect to reach quantitative accuracy.

Outlook, Limitations, and Comparative (Dis)Advantages

We have shown that canonical calculations at the infinite-cell size limit are thermodynamically equivalent to a grand canonical description, and that under a capacitor-model approximation one can extrapolate to the infinite-cell limit with a single calculation at finite size. We emphasize that these equivalences are applicable only when certain assumptions are satisfied.

Independent of the choice within the three presented frameworks, if specific (local) interactions of the electrolyte and reaction intermediates are significant, then the separate consideration of the chemical potentials of ions and electrons will lead to errors in the analysis.^[44]

Further, we have assumed that the capacitance of all charging components - the charges coming in from the electron reservoir, polar adsorbates and explicit ions - are equivalent. In practice, differences in capacitances associated with different charging components lead to variations in the local potential drop and therefore the reaction energetics. In particular, note that when explicit water is added to a simulation, the continuum electrolyte is shifted away from the electrode, which effectively reduces the corresponding capacitance to about $5\text{--}10 \text{ mF}/\text{cm}^2$.^[25] It has been proposed that this challenge could be mitigated when an effective surface charge density is considered as the driving force for the reactions instead of the work function. Since surface charge is proportional to the field at the surface, it approximates the local potential drop which drives the reaction process.^[24]

A depolarization of reactants due to adsorbate-adsorbate interactions and a change in capacitance upon adsorption have not been addressed so far. Upon increasing coverage of polar adsorbates the partial charge upon them can reduce as a consequence of their repulsive interaction. We observe such a behaviour for *K and *Cs as we show in Figure S7. This behaviour results in a non-constant potential dependence of ΔG .^[45] Hence, we note that simulations should always be performed at polar adsorbate coverages expected close to the actual potential of interest.

Similarly, a change in the capacitance with the change in adsorbate coverage can lead to a deviation from the linear behavior, as visible in the grand canonical results for *K and *Cs in Figure 1. Here the curvature is proportional to the difference in capacitance, as we derive in detail in section 3 of the SI. We note that care is needed in the physical interpretation of a capacitance mismatch, as a change of capacitance due to a single reaction event is unlikely and might just be an artifact of the applied implicit solvent model. Since implicit solvent schemes are effective models relying on a range of parameters a change in the atomic geometry alone can lead to a change in capacitance. For example in the implicit solvent model applied in this work the solvent accessible surface is defined on the basis of the van der Waals radii of the explicit atoms.^[46] Since Cs has a van der Waals radius, which is twice as large as Na, this difference alone leads to the scatter present in the lower left panel of Figure 1.

Both a depolarization and a change in capacitance can, in principle, be captured by both a grand canonical description and the capacitor approach, where for the latter the introduction of an additional term in equation (9) is needed.^[5,6] However, the straightforward application of the mean-potential method as described above is only valid at equal capacitance, as we further discuss in section 2 of the SI.

A high coverage of strongly polarized adsorbates can lead to an unphysical situation where electrons start to spill out into the vacuum region above the slab, giving rise to work functions approaching zero.^[3,17,47] Such high coverages can not be described by a pure capacitor approach; however, the problem can be mitigated by additionally adding a positive continuum charge on the electrode surface in an analogous fashion to the grand canonical approach of equal magnitude in both states of the reaction. In such a way the workfunction could be altered into a reasonable region avoiding artificially weak bound electrons in the simulation. The grand canonical description does not suffer from such a limitation, since the potential can be shifted manually into regions where electrons do not spill out into the vacuum.

Finally, we note that simulations of electrochemical reactions might suffer from artificial co-adsorption of an unwanted species. Prominent examples of this issue include the spontaneous adsorption of OH^- in the simulation of alkaline protonation reactions in constant-charge simulations,^[48] and the change in the average water adsorption strength in the two states of a reaction in constant-charge molecular dynamics simulations.^[49] Both artifacts are, in principle, avoided in a grand canonical framework.^[1,50] We note, though, that the application

of constant-potential molecular dynamics frameworks is still in its infancy.^[51,54]

All the mentioned practical challenges should be kept in mind when applying these methods in the study of electrochemical reaction energetics. In practical simulations, both constant-charge and constant-potential approaches can have advantages. For example, constant-charge simulations are attractive since they can work in any DFT code without the need for a specialized grand-canonical implementation, which lets them avoid the potential-equilibration cost (and stability) associated with grand canonical schemes. Controlled-potential calculations are attractive for a number of reasons, including that they allow direct specification of the potential, they ensure that the relaxed geometry is valid at the potential of interest, and avoid some of the collision pitfalls described above.

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in consistency_of_inifinite_cell_and_GC at https://github.com/CatTheoryDTU/consistency_of_inifinite_cell_and_GC.

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