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Modeling Microenvironmental Effects in Heterogeneous Catalysis

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Modeling Microenvironmental Effects in Heterogeneous Catalysis

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ABSTRACT

Heterogeneous catalysis involves a complex interplay of adsorption, charge transfer, and catalyst restructuring at solid-gas or solid-liquid interfaces. While first-principles methods such as KS-DFT and AIMD accurately describe chemisorbed species, they struggle to capture weakly bound or dynamic molecules subject to thermal fluctuations. Continuum models provide macroscopic insight into electrostatics and transport but often neglect interfacial molecular structure, especially within the Stern layer. The challenge is even greater at gas-solid interfaces, where the gas phase is typically ignored, giving rise to the long-standing pressure gap between theory and experiment. This Perspective advocates a statistical-mechanical description of interfacial species using approaches like classical density functional theory (cDFT), in which physisorption and gas/liquid-phase inhomogeneity near catalytic surfaces are represented by probability density distributions rather than fixed atomic configurations. More importantly, we emphasize the necessity of integrating KS-DFT with such microenvironmental models, and we propose several potential strategies for coupling electronic-structure calculations with continuum and statistical approaches. By merging first-principles, continuum, and statistical approaches within open-system, physics-informed frameworks, it becomes possible to bridge electrochemical and thermocatalytic regimes-

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-from localized chemisorption to diffuse physisorption--and reveal the true complexity of catalytic interfaces.

KEYWORDS: implicit gas phase model, probability density distributions, solution-corrected constant potential model (CPM-sol), electric double layer (EDL), multiscale framework

Introduction

Catalysis plays a vital role in modern society, with heterogeneous catalysis constituting a major branch of the field.¹ The development of high-performance solid catalysts is of great significance in technologies such as hydrogen production and carbon dioxide conversion, which are vital for both reducing our reliance on fossil fuels and curbing environmental pollution. A fundamental understanding of catalytic activity and a clear structure-performance relationship are essential for mechanism-guided catalyst design, enabling the rational and efficient development of advanced catalytic materials.² In particular, the widespread application of first-principles calculations has greatly enhanced our ability to probe catalytic processes at the atomic and electronic levels, offering deep insights into reaction mechanisms.^{3,4} More recently, machine learning (ML) methods have emerged as powerful tools in catalyst design, particularly through the development of machine learning potentials (MLPs), which significantly accelerate simulations over large spatial and temporal scales while maintaining near first-principles accuracy.^{5,6}

Despite significant progress in computational catalyst design, a notable gap persists between existing theoretical models and industrial catalytic reactions. This discrepancy is commonly known as the "materials gap" and the "pressure gap".⁷⁻¹⁰ The former refers the disparity between the highly simplified model catalysts used in fundamental research and the complex, heterogeneous materials used in industrial practice, and the latter arises from the vast difference in pressure between the conditions of surface science experiments and those of industrial processes.

Due to computational limitations, first-principles methods such as Kohn-Sham density functional theory (KS-DFT) calculations are typically restricted to systems containing only tens to a few hundred atoms. As a result, theoretical simulations often focus solely on the immediate vicinity of active sites, neglecting the influence of surrounding molecular species. While *ab initio* molecular dynamics (AIMD) simulations can account for thermal fluctuations, they are usually limited to closed systems and time scales of only a few picoseconds. This means that even with advanced experimental characterization pinpointing active sites, theoretical models may fail to capture the dynamic evolution of the catalyst surfaces and their interactions with nearby adsorbates -- giving rise to the materials gap.

In gas-solid heterogeneous catalysis, the atomic-scale active structures responsible for catalytic enhancement often form only under actual reaction conditions, typically at high temperatures and pressures, rendering them undetectable under ultra-high-vacuum (UHV) and low-temperature techniques.¹¹ At low pressures, a catalyst surface might be mostly clean or covered by only few reactant molecules. However, at high pressures, the surface can be completely covered, or "poisoned," by a high concentration of reactant or product molecules. The high-pressure environment can also induce fundamental changes in the catalyst structure, such as surface reconstruction or even the formation of a new phase (e.g., an oxide layer), which wouldn't occur under UHV conditions. Moreover, as emphasized by Blomberg,⁷ the active phase is not only dependent on the pressure applied but also on gas compositions. The low density of gaseous species often leads to their omission in first-principles simulations, further widening the pressure gap.

In electrocatalysis, the so-called "interfacial gap" arises from the formation of an electrical double layer (EDL) at the electrode-solution interface, which profoundly affects electrocatalytic

performance and has attracted increasing attention.^{12–14} Mainstream approaches to address this include explicit solvent models, wherein AIMD is used to simulate the solvent directly. However, the high computational cost of AIMD restricts its use to small systems and short timescales, typically insufficient to characterize the EDL behavior and pH-dependent surface chemistry. For example, Zhang et al.¹⁵ demonstrated that, while AIMD could estimate the Helmholtz capacitance at oxide-electrolyte interfaces, it failed to capture the equilibrium ion distribution within the EDL due to the limited simulation length and cell size. To overcome these limitations, semi-empirical force fields and multiscale modeling -- especially the recent advances in MLPs -- have enabled large-scale molecular-dynamics simulations with near-DFT accuracy, allowing for the investigation of interfacial phenomena such as water dissociation and proton transfer.¹⁶ While AIMD based on KS-DFT can, in principle, yield accurate atomic-level insights and macroscopic observables of the EDL, MLPs extend the feasible system size and time scale. Nevertheless, these approaches still rely on explicit solvent representations and are often implemented in canonical (NVT) ensembles, which lack rigorous physical foundations for capturing the full complexity of the EDL behavior.

An alternative strategy involves implicit solvent models, grounded in liquid-state theories to account for electrolyte effects with rigorous physical derivations. These models approximate the dominant features of the interfacial environment without explicitly simulating solvent molecules. A classic example is the Poisson-Boltzmann (PB) equation, which describes the distribution of ions under applied electrode potentials.¹⁷ More sophisticated approaches include classical density functional theory (cDFT), which operates under the grand canonical (μ VT) ensemble, allowing for fluctuations in particle number. Unlike continuum approaches, cDFT does not rely on macroscopic variables as the input; instead, it is based on a specific description of intermolecular interactions

similar to that in molecular dynamics (MD). By minimizing the grand potential, cDFT determines the spatial distributions of molecular species, offering a powerful and physically consistent framework for modeling the microscopic behavior of electrochemical interfaces.^{18,19} Crucially, cDFT avoids trajectory sampling and directly outputs equilibrium density profiles for ionic species, making it particularly well-suited for interfacial studies where capturing the spatial organization of the electrolyte solution is essential. However, cDFT lacks an explicit description of electronic structure, and the accuracy of cDFT simulations depends on the quality of the underlying force fields, which may limit chemical specificity. These limitations highlight the need for hybrid strategies to bridge electronic and statistical-mechanical descriptions of the reactive species and local environment, respectively.

First-principles electronic-structure methods such as Hartree–Fock (HF) and KS-DFT treat electronic states quantum mechanically and capture electronic delocalization at the orbital level. However, atoms and molecules in these approaches are typically represented by well-defined, fixed positions corresponding to local or global minima on the potential energy surface. We argue that statistical considerations, in which atoms and molecules in the reaction environment are represented by continuous probability density distributions, deserve greater attention. For strongly chemisorbed molecules, which are immobilized at specific adsorption sites, explicit positional treatment is appropriate. However, in cases of physisorption and liquid/gas-phase molecules, a probabilistic representation of the molecular densities offers a more realistic picture of their spatial behavior. This rationale supports the development of an implicit gas-phase model for thermocatalysis -- analogous to implicit solvent models -- where the gas environment is described as a diffuse medium governed by spatial probability distributions.

For describing chemical reactions in liquid environments, atomistic models based on AIMD or MLPs have the advantage of directly simulating the configurations of solvent molecules. Meanwhile, liquid-state theories representing the solvent by a coarse-grained model are often more physically grounded and suitable for large-scale systems. Both modeling strategies come with distinct strengths and limitations. Their integration offers a promising pathway to harness complementary advantages. One of the most successful examples of such integration is the implicit solvent model.^{20,21} This approach treats the solvent as a continuous dielectric medium with a defined electrostatic response, enabling the computation of a solute's electronic structure via KS-DFT in the presence of the dielectric continuum. However, the simplicity of this treatment can overlook important local solvent structure and solute-solvent interactions. To improve upon this, the Joint DFT framework incorporates the modified PB (MPB) equation to simulate the distribution of solute species near electrodes with fixed potentials.^{22,23} This refinement more accurately captures solute-specific effects and represents a significant advancement in combining quantum-mechanical and statistical-mechanical perspectives within implicit solvation models.

In summary, both explicit and statistical-mechanical approaches offer valuable frameworks for modeling complex chemical microenvironments, each with its unique strengths and inherent limitations. Their integration holds great potential to complement each other, mitigating individual shortcomings while enhancing overall accuracy and efficiency. While improvements within each method continue to evolve, this perspective does not intend to elaborate on those internal advancements. Instead, we focus specifically on the integration of liquid state theory model with first-principles calculations and their application in heterogeneous catalysis. The emphasis is placed on how these two frameworks can be effectively combined, what key aspects require careful attention, what technical or conceptual challenges currently hinder their integration, and how

overcoming these obstacles can significantly enhance our ability to model catalytic interfaces with both electronic and thermodynamic fidelity.

1. Gas-Solid Interface

In describing catalytic reactions at a gas-solid interface, KS-DFT simulations are typically conducted under vacuum conditions due to the inherently low density of gas-phase molecules. For instance, at 503 K and 50 bar, the bulk density of CO₂ is less than 1 molecule/nm³. Under such dilute conditions, introducing a few isolated gas molecules in KS-DFT simulations can lead to substantial statistical noise and sampling errors. Such low densities also make it difficult to accurately represent the gas composition near the catalyst surface, potentially introducing significant deviations in the predicted behavior. While one might attempt to mitigate this by adding a large number of gas molecules into a supercell and averaging over their configurations, this approach falls into the realm of “large system + statistical sampling,” which is not the strength of conventional DFT calculations. Nevertheless, neglecting gas-phase species entirely creates a “pressure gap,” indicating that their influence is non-negligible and must be properly accounted for.

However, as summarized in Figure 1, gas-phase molecules can affect the reaction in three keyways: (i) occupy and compete for active sites, (ii) stabilize or destabilize reaction intermediates, and (iii) promote reaction events through kinetic collisions. To better bridge the gap between theoretical modeling and experimental conditions, we propose the development of an implicit gas-phase model that statistically incorporates the influence of gas-phase species without the computational burden of explicit sampling. The hybrid approach could provide a more accurate and efficient means to capture the effects of the gas environment in heterogeneous catalysis.

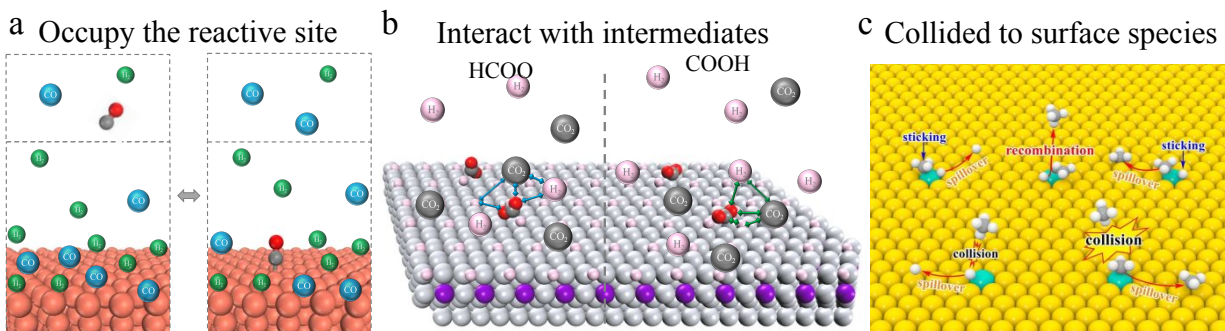


Figure 1 a. Schematic representation of a multiscale approach for modeling CO adsorption on a metal surface in an H₂/CO gas mixture. The ball-and-stick model shows a CO molecule adsorbed on the metal surface (orange sphere), simulated using KS-DFT. Green and blue spheres represent H₂ and CO molecules, respectively, modeled through cDFT. Note that these colored spheres illustrate statistical distributions, rather than fixed atomic positions. Reprinted with permission from ref ²⁴. Copyright 2025 Royal Society of Chemistry. b. Conceptual diagram of surface intermediates and the microenvironment during CO₂ hydrogenation on PdZn alloy catalysts. Grey and purple spheres represent Pd and Zn atoms, respectively, and pink spheres denote dissociated hydrogen atoms. Reprinted with permission from ²⁵. Copyright 2025 Advanced Science published by Wiley - VCH GmbH Open Access Article. c. Illustration of CH_x intermediate spillover induced by methane collision. Yellow, green, grey, and white spheres correspond to Au atoms, active site Au atoms, carbon atoms, and hydrogen atoms, respectively. Reprinted with permission from ref ²⁶. Copyright 2024 John Wiley & Sons.

2.1 Surface Occupation by Gas-Phase Species

Variations in adsorption strength and interfacial energetics among gas-phase species result in compositionally heterogeneous boundary layers at catalyst surfaces. In our previous work,²⁷ we proposed a hybrid framework to address this complexity. The structure of catalyst surface and various intermediates is computed using KS-DFT, while the spatial distribution of gas-phase molecules near the active site is modeled using cDFT. We first compute the structures and energies of the catalyst surface and intermediates in vacuum and then embed them into the microenvironmental system to obtain the overall grand potential from cDFT. Notably, interactions between gas-phase molecules and the surface/intermediates may induce structural changes; a more accurate treatment therefore incorporates these microenvironment-induced forces into KS-DFT and iterates the KS-DFT–cDFT coupling until convergence. Unlike explicit models that fix molecular positions, cDFT describes gas species as continuous density distributions, which better reflect their dynamic, delocalized nature of molecules in the gas phase. Using this hybrid

framework, we investigated how gas-phase components affect the CO₂ hydrogenation pathways on Cu and PdZn surfaces. As shown in Figure 2a and 2b, we found that, due to the strong attraction of CO₂ molecules by metal surfaces, the local CO₂ density can be several hundred times higher than its bulk value. In contrast, the interaction between metal surfaces and H₂ is much weaker, resulting in surface H₂ densities close to their bulk values. This disparity leads to a significantly lower H₂: CO₂ ratio at the solid-gas interface compared to that in the feed gas, which helps explain why experimental systems often require a high H₂: CO₂ feed ratio to achieve desired performance. This phenomenon highlights the pronounced inhomogeneity of the gas-phase environment near catalytic surfaces, where local gas densities depend strongly on molecular identity, surface metal composition, temperature, and pressure, and can differ substantially from bulk values. Moreover, the surface gas density does not increase linearly with bulk pressure, underscoring the necessity of explicitly modeling gas-phase microenvironments at catalytic interfaces.

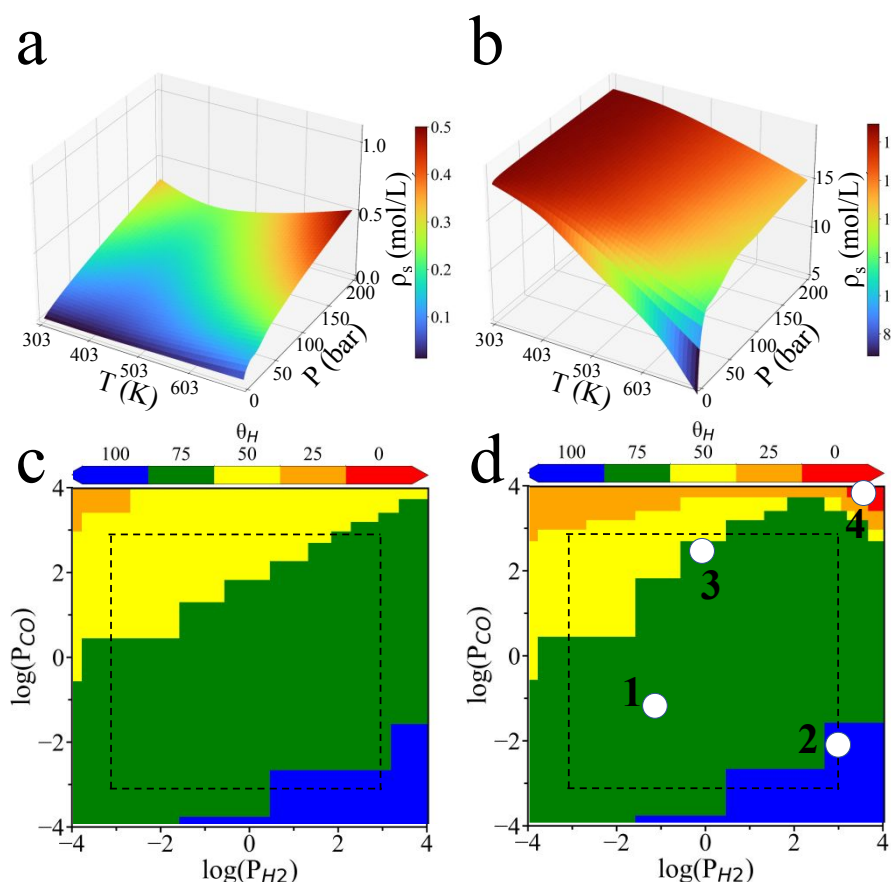


Figure 2 The surface density (ρ_s) versus temperature and pressure for H₂ (a) and CO₂ (b) on Cu (111) surface, respectively. The feed gas ratio was set to H₂:CO₂:CO = 6:1:1. Adapted with permission from ref ²⁷. Copyright 2025 Royal Society of Chemistry. c. Surface phase diagram predicted from the Gibbs energy of formation (G_{form}). d. Surface phase diagram predicted from the grand potential of formation (Ω_{form}). The surface is fully occupied by CO or H, i.e., $\theta_{\text{CO}} = 100 - \theta_{\text{H}}$, with θ_{H} shown in the color bar. Reprinted with permission from ref ²⁴. Copyright 2025 Royal Society of Chemistry.

Furthermore, as illustrated in Figure 1a, the chemisorption of a reactant molecule often requires displacement of gas molecules in the reaction microenvironment that are accumulated near the active site. Traditional KS-DFT calculations typically do not explicitly treat the statistical accumulation of physisorbed gas molecules in the vicinity of active sites, and often approximate the adsorption energy of a reactant to its bond energy with the surface, using the standard expression:

$$E_{ad} = E_{*adsorbate} - E_{*} - E_{adsorbate} \quad (1)$$

where E_* , $E_{\text{adsorbate}}$, and $E_{*\text{adsorbate}}$ denote the ground-state energies of the clean surface, the isolated adsorbate in a vacuum, and the surface bonded with the chemisorbed species, respectively. This formulation neglects the presence of originally physisorbed gas-phase molecules around the active sites, and therefore does not account for their displacement during adsorption. To address this shortcoming, we propose that microenvironmental effects should be incorporated through a modified adsorption energy, which accounts for both the chemical bonding and the inhomogeneous distribution of the surrounding gas molecules:

$$\Omega_{ad} = G_{ad} + \Omega_{cDFT-ad} \quad (2)$$

Here, G_{ad} represents the adsorption free energy obtained via KS-DFT, reflecting the intrinsic interaction between the adsorbate and the active site (i.e., the bond energy), while $\Omega_{cDFT-ad}$ captures the change in the grand potential of the reaction microenvironment upon chemisorption. The latter term is evaluated within cDFT using classical interaction models, such as Lennard–Jones-type force fields, to describe the physical adsorption of gas-phase molecules and their interactions with the active site. We refer to this latter term as a penalty energy, reflecting the free-energy cost of displacing physically adsorbed gas molecules to allow for chemisorption. This penalty arises from the substantial entropy loss associated with transitioning from a loosely bound, dynamic gas-phase distribution to a fixed chemisorbed configuration. Alternative ab initio approaches either with or without dispersion interactions have also been reported.^{28,29} For example, studies of the quantum nuclear motion of helium and molecular nitrogen clusters confined in carbon nanotubes illustrate that accurately describing weak adsorption and the transition from physisorption to chemisorption may require high-level electronic-structure methods, particularly when multireference effects become relevant near the energy barrier.³⁰ By contrast, the framework discussed here emphasizes the statistical-mechanical contribution of the surrounding environment

to adsorption thermodynamics. Notably, unlike bond energy, $\Omega_{cDFT-ad}$ depends not only on the strength of catalyst-gas interactions but also on the accessible volume near the surface sites. While chemisorbed molecules have defined positions and numbers, physically adsorbed gas molecules exhibit diffusive, probabilistic occupancy with no fixed count or atomic structure. Consequently, the local density and interaction strength of gas molecules vary across different adsorption sites, resulting in corrections to the apparent adsorption energetics that may deviate from trends based on bond strength alone. Such corrections may significantly alter the ranking and identity of the most favorable adsorption sites. These shifts in adsorption site preference have profound implications in selecting subsequent reaction pathways and predicting catalytic performance.³¹

As shown in our previous work, the change in grand potential associated with the displacement of pre-adsorbed gas molecules during chemisorption can exceed 10 kcal/mol.^{24,27} This substantial energetic shift significantly impacts the surface coverage of gas-phase species. For example, Figure 2c presents the surface phase diagram showing the coverages of H and CO, constructed based on their formation Gibbs free energies (G_{form}). In contrast, Figure 2d shows the revised phase diagram where surface coverages are determined using the formation grand potential (Ω_{form}), incorporating corrections from cDFT simulations. Although these phase diagrams exhibit similar overall shapes, they predict notably different phase boundaries across specific ranges of temperature and pressure, leading to distinct predictions of the most stable surface phases. A direct comparison of Figures 2c and 2d reveals that the Ω_{form} -based surface phase diagram predicts preferential H adsorption over CO under low-pressure conditions. Furthermore, it more accurately captures the sharp rise in CO coverage observed at ultra-high CO partial pressures, in closer agreement with experimental results.^{32–35} These findings underscore the importance of accounting

for microenvironmental effects via the grand potential framework when modeling gas-solid catalytic interfaces.

2.2 Interactions Between Gas-Phase Species and Reaction Intermediates

During thermocatalytic reactions, structural transformations or conformational changes of surface intermediates can alter their interactions with surrounding gas-phase species, thereby influencing their stability and reactivity. As illustrated in Figure 1b, we combined cDFT simulations of the gas-phase microenvironment with KS-DFT calculations to investigate simulated two elementary hydrogenation pathways for CO₂ on PdZn alloy surfaces -- proceeding via *HCOO and *COOH intermediates.²⁵ Our analysis revealed that the initial configurations and the respective transition states of these two pathways exhibit distinct interaction energies with gas-phase species, which in turn modulate the catalyst activity and selectivity. Although the changes in grand potential due to conformational variations are typically on the order of a few kcal/mol -- comparable to standard Gibbs free energy corrections -- they can have non-negligible effects on the relative reaction energetics and thus the selection of different reaction pathways.²⁵ Besides, gas-intermediate interaction energies generally increase with surface gas density, but their differences across conformations are complex and non-monotonic. This is due to the combined influence of long- and short-range interactions between the catalyst and the surrounding molecules, which vary with the surface conformation.

2.3 Collisions Between Gas-Phase Molecules and Reaction Intermediates

The kinetic energy carried by gas-phase molecules can promote surface reactions by facilitating energy transfer to adsorbed species. As illustrated in Figure 1c, Lin and co-workers systematically investigated the spillover dynamics of *H and *CH_x species following methane dissociative adsorption on a Rh/Cu (111) single-atom alloy surface.²⁶ Using a machine learning

potential trained on KS-DFT data to construct a high-dimensional potential energy surface, they demonstrated that collisions with gas-phase molecules under realistic catalytic conditions can transfer energy to surface intermediates, thereby mitigating catalyst poisoning at active sites. These findings highlight a critical yet underexplored aspect of heterogeneous catalysis: the role of gas-phase collisions in altering reaction dynamics. Incorporating gas-phase kinetic energy and collision probabilities into theoretical frameworks presents a valuable opportunity for further development.

3. Liquid-Solid Interface

The influence of the electrolyte solution on electrocatalytic activity has garnered increasing attention in recent years.^{12,14,36,37} For instance, Su et al.³⁸ investigated the microscopic interactions between solvated ions and electrode surfaces via AIMD, while Ringe et al.³⁹ employed continuum transport models to describe the mesoscale behavior of electrolytes. However, significant opportunities remain to bridge mesoscale liquid-state theories more rationally with first-principles electronic-structure calculations. For example, Lorenzutti et al.⁴⁰ computed reaction energy barriers using first-principles calculations, and subsequently employed a continuum transport model based on the Poisson-Nernst-Planck (PNP) formalism to describe solute concentration profiles in the diffusion layer. The resulting interfacial concentrations -- specifically those at the outer Helmholtz plane (OHP) -- were then incorporated into a microkinetic model (MKM) to simulate the reaction kinetics. This multiscale framework elegantly integrates the strengths of diverse theoretical approaches. Nevertheless, in such a scheme, the liquid-state model merely provides local solute concentrations as input for kinetic simulations, offering only an indirect coupling to the underlying first-principles energetics.

The central focus of this Perspective is, therefore, to elucidate how solvent effects can be more rigorously incorporated into first-principles simulations and how these interfacial phenomena influence the electronic structure of the electrode surface. In Section 3.1, we revisit the formation mechanism of the electric double layer (EDL) and establish a conceptual framework that links first-principles and liquid-state theories by connecting key physical quantities -- including the potential drop between the electrode and the OHP, surface charge density, electric field, interfacial capacitance, and dielectric response. A physically accurate description of these quantities requires a reliable model of the Stern layer, which we discuss in detail in Section 3.2. There, we outline the essential parameters and structural considerations for constructing a physically meaningful Stern-layer model. Finally, in Section 3.3, we compare various liquid-state theoretical approaches for modeling the diffuse layer, highlighting their applicability and limitations.

3.1 Formation of the EDL and Causal Relationships Among Physical Quantities

At the interface between an electrode and the surrounding solution, the electric potential difference leads to the reorganization and spatial distribution of solute species near the surface, resulting in the formation of an EDL. Accurately constructing a physically grounded model of the EDL is essential for understanding the interfacial mechanisms governing electrocatalytic reactions. As illustrated in Figure 3, when an electrode is immersed in an electrolyte, a spontaneous potential difference arises at the interface due to the mismatch between the intrinsic energy levels of the electrode material and the electrochemical potentials of solvent molecules and ions in the solution. This potential difference generates an electric field that drives the redistribution and orientation of ions and solvent molecules near the surface, leading to the formation of the EDL -- a spatially structured charge layer arising from electrostatic interactions between surface charges and

counterions in the electrolyte. Even in the absence of an externally electrode potential, the interface can carry a net charge due to factors such as contact potential differences, interfacial electron redistribution, surface chemical reactions (e.g., protonation or deprotonation), or specific ion adsorption. When the electrode potential (ψ_{Ele}) is tuned such that the net surface charge becomes zero, the system reaches the so-called potential of zero charge (PZC). At PZC, ion rearrangement within the EDL is minimized, and the interface adopts its most symmetric and stable configuration. In this case, the surface charge density on the electrode (σ_e) is zero, and correspondingly, there is no compensating charge density within the EDL (σ_{EDL}).

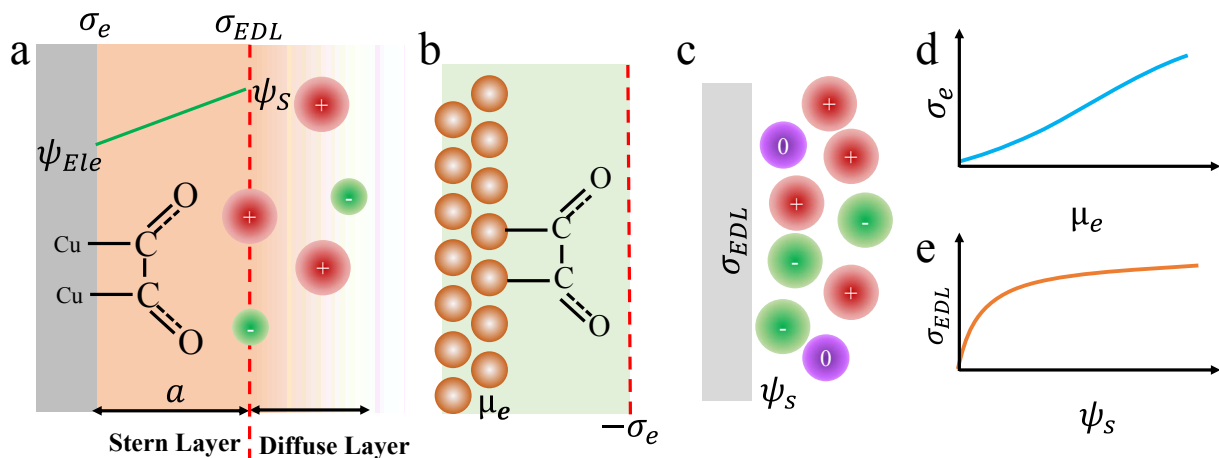


Figure 3 a. Schematic of the Stern layer and diffuse layer separated by the outer Helmholtz plane (OHP, dashed line); b. the system setup for KS-DFT calculations to establish the surface charge density (σ_e) and Fermi energy (μ_e) relationship in a dielectric medium, as shown schematically in panel (d). c. the electric double layer (EDL) described by cDFT, which predicts the EDL charge density (σ_{EDL}) as a function of the surface potential (ψ_s), as shown schematically in panel (e). At a fixed electrode potential, the charge neutrality is satisfied in both KS-DFT and cDFT calculations. However, we may have $\sigma_e \neq \sigma_{EDL}$ due to approximations in both quantum and classical models, leading to inconsistency in the theoretical modeling. The red, green, and purple spheres represent cations, anions, and neutral reactants (e.g., CO_2), respectively. Panel a reproduced with permission from ref⁴¹. Copyright 2025 American Chemical Society. Panel b-e reproduced with permission from ref⁴² Copyright 2025 Chinese Chemical Society.

When the electrode potential ψ_{Ele} deviates from PZC, the EDL structure begins to change significantly. On one hand, the traditional constant-potential model (CPM) assumes a linear relationship (with a slope of unity) between the electrode's Fermi level (μ_e) and the externally electrode potential (ψ_{Ele}), which leads to the estimation of μ_e at a given ψ_{Ele} :

$$\mu_e = \psi_{Ele} - \psi_{ref} - \psi_{sol} \quad (3)$$

Here, ψ_{ref} is the reference electrode potential, and ψ_{sol} accounts for solvation-related potential contributions. With this defined μ_e , the surface charge density (σ_e) for each adsorbed intermediate during the reaction is computed in the KS-DFT CPM framework. On the other hand, conventional EDL theories posit that ψ_{Ele} induces a redistribution of ions in the EDL, generating an opposing charge density (σ_{EDL}) that counterbalances the altered electrode potential. It is crucial to recognize that σ_e and σ_{EDL} are generally not equal. While σ_e depends on the electrode surface structure and the nature of adsorbed intermediates, σ_{EDL} varies with the type and concentration of ions in the electrolyte. The mismatch between these two charge densities results in a net interfacial charge imbalance, which creates an additional electric field across the interface. This, in turn, drives the redistribution of electrons and ions to restore charge neutrality. Despite its importance, this interfacial re-equilibration process is rarely considered in theoretical modeling, largely because KS-DFT CPM framework and EDL simulations are typically conducted independently. As a result, the impact of post-equilibration charge rearrangement on interfacial properties is often overlooked. Furthermore, the renormalization of σ_e and σ_{EDL} can itself influence both the Fermi level and the EDL local potential. This implies that the relationship between μ_e and ψ_{Ele} is not strictly linear or universal -- it is system-specific and dependent on both the electrode material and the electrolyte composition.

The nonlinearity between the electrode potential and Fermi level is especially pronounced for non-metal electrodes.⁴³ As reported by Ma and colleagues,⁴⁴ the low density of electronic states near μ_e in graphene causes a notable shift in the Fermi level in response to charge injection or withdrawal. This shift introduces a quantum capacitance in series with the traditional double-layer capacitance, leading to a decomposition of the total electrode potential into two components: the

electrostatic potential across the EDL and the shift in electronic chemical potential. Similarly, Luan and co-workers identified a comparable deviation between μ_e and ψ_{Ele} .⁴⁵ To address this discrepancy, they proposed a novel simulation method termed electric-field-controlled constant potential (EFC-CP), in which the electric field strength in the Helmholtz layer ($|E|$) is used as the primary control variable. This method establishes a one-to-one correspondence between $|E|$ and ψ_{Ele} via the classical Stern model. Nevertheless, the strength of the electric field in the Stern layer is influenced by various factors, including electrolyte composition and electrode surface characteristics. These complexities are not yet fully captured in current implementations of the EFC-CP approach, highlighting the need for further refinement of interfacial modeling strategies in electrochemical systems.

To establish a more accurate and quantitative relationship between μ_e and ψ_{Ele} that fully accounts for the effects of the solution environment, electrode potential, and surface properties, we present a simplified derivation based on reasonable physical assumptions. The results from CPM and cDFT calculations can be utilized to establish a net interfacial charge and an electric field that perturbs both the surface charge density σ_e and the Fermi level. Importantly, the magnitude of this net charge varies as a function of the electrode surface structure, the adsorbed intermediate, the electrolyte composition, and the electrode potential. To simplify this complexity, we propose an effective correction scheme: rather than altering the fundamental linearity between the μ_e and ψ_{Ele} , we reinterpret the microenvironmental correction as a modification to the reference potential. This leads to an adjusted expression:

$$\mu_e = \psi_{Ele} - \psi_{ref} - \psi_{EDL}(\psi_{Ele}, Sur, sol) \quad (4)$$

Here, we emphasize a key distinction: in Eq. (3), ψ_{sol} represents the bulk potential of the solvent, which is a constant for a given electrolyte. In contrast, ψ_{EDL} in Eq. (4) is not a bulk quantity. It

depends sensitively on the interfacial environment, including the surface structure and the identity of the adsorbed reaction intermediate. Even under the same electrode potential, different intermediates lead to different σ_e and thus create different charge imbalances with the surrounding solution ($\sigma_e - \sigma_{EDL}$). This results in varying degrees of electronic and ionic redistribution at the interface, and correspondingly, different values of ψ_{EDL} . As a result, during constant-potential simulations of catalytic reactions, μ_e inherently shifts in response to changes in the surface species. This reconciles two long-standing inconsistencies observed in prior EDL models: (i) the "potential drift" in the traditional constant charge model (CCM), where the electrode potential changes unintentionally across different intermediates, and (ii) the "charge inconsistency" in the CPM, where the surface charge appears discontinuous under a fixed electrode potential. Our framework provides a unified explanation for both, rooted in the varying interfacial field due to environment-specific charge imbalances. Furthermore, since charge difference ($\sigma_e - \sigma_{EDL}$) is also a function of ψ_{Ele} , ψ_{EDL} is not a constant -- it evolves with ψ_{Ele} , introducing a nonlinear correction to what is otherwise assumed to be a linear relationship.

Conventionally, EDL can be further divided into the Stern layer and the diffuse layer, separated by the outer Helmholtz plane (OHP). If one can obtain the functional relationship between the outer Helmholtz potential (ψ_S) and the ψ_{Ele} , the corrected μ_e and surface charge distribution can be determined self-consistently. To begin, assuming $\psi_{EDL} = 0$, which allows for the direct estimation of the initial μ_e and ψ_S under given ψ_{Ele} . Then, using CPM through KS-DFT and cDFT simulations to compute σ_e and σ_{EDL} , respectively. Based on the initial charge imbalance ($\sigma_e - \sigma_{EDL}$), we can apply an additional external electric field ($|E|$) to both the CPM and cDFT simulations. This external field serves to correct the deviation from charge neutrality. Updated values of μ_e and ψ_S are then obtained under the applied field E . Next, we remove the external field

and recalculate σ_e and σ_{EDL} , yielding a new estimate of the charge imbalance. This process is repeated iteratively -- each cycle updating the $|E|$ and recalculating the charge distributions -- until convergence is reached, that is, when $\sigma_e = \sigma_{EDL}$.

A key challenge of the above framework lies in accurately describing of the potential drop ($\Delta\psi = \psi_{Ele} - \psi_S$) between the electrode surface and the OHL. While cDFT effectively models the diffuse layer beyond the OHP -- providing the relationship between electric potential and charge density at the OHP ($\psi_S \sim \sigma_{EDL}$), the region between the electrode surface and the OHP, i.e., the Stern layer, remains a key challenge in interfacial modeling. Within the Stern layer, numerous charged species exist under the influence of complex electrostatic interactions and dynamic polarization effects. As discussed below, the properties of the Stern layer -- such as its effective thickness and dielectric constant -- depend sensitively on the solute type, concentration, applied electrode potential, and the atomic structure of the catalyst surface.

3.2 Modeling the Stern Layer

As a first approximation, the Stern layer can be idealized as a parallel-plate capacitor, allowing the potential drop and related quantities to be described through electrostatic relationships:

$$\Delta\psi = E \times d \quad (5)$$

$$E = \sigma / \epsilon_S \quad (6)$$

$$C_S = \sigma / \Delta\psi \quad (7)$$

where E is the electric field within the Stern layer, d is the effective thickness, ϵ_S is the Stern-layer dielectric constant, and C_S is the corresponding capacitance. In this framework, if the ϵ_S and d can be determined with reasonable accuracy, one can combine cDFT simulations to reconstruct the full potential profile and other interfacial properties. For example, in our previous work,⁴¹ we modeled the Stern layer thickness as the contact radius between the counterion and the electrode

surface, and described the dielectric response of the Stern layer using the Booth model. The field-dependent dielectric constant $\varepsilon_s(|\mathbf{E}|)$ is given by:

$$\varepsilon_s(|\mathbf{E}|) = n^2 + (\varepsilon_b - n^2) \frac{3}{\gamma|\mathbf{E}|} (\coth(\gamma|\mathbf{E}|) - \frac{1}{\gamma|\mathbf{E}|}) \quad (8)$$

where n is the optical refractive index of liquid water, ε_b is dielectric constant without the electric field, and γ is the critical field parameter. This model allows for a semi-quantitative description of how $\Delta\psi$ across the Stern layer varies with the strength of electric field and solution properties. By integrating this with cDFT-derived relationship between electric potential and charge density at the OHP ($\psi_S \sim \sigma_{EDL}$), we constructed a unified electrostatic model of the electrode-solution interface that accounts for both the diffuse and compact layers, thereby enabling a more complete and physically consistent treatment of interfacial potentials in electrochemical simulations.

A more accurate description of the Stern layer requires consideration of several complex interfacial factors, including the orientation and structuring of interfacial water molecules, the size and concentration of solvated ions, specific adsorption phenomena, and electron transfer processes. These factors collectively determine the key properties of the Stern layer such as its effective dielectric constant, thickness, charge distribution, capacitance, and local electric field. This section reviews state-of-the-art approaches for modeling the Stern layer and highlights various factors that influence its behavior.

3.2.1 Dielectric Constant of the Stern Layer

The dielectric constant within the Stern layer deviates significantly from that of bulk water due to the restricted mobility and reorientation of water molecules under strong interfacial electric fields.⁴⁶ This suppression of dipole freedom leads to a reduced effective permittivity in the immediate vicinity of the electrode. Additionally, the presence of specifically adsorbed ions,

charge-transfer processes, and surface heterogeneity can further modulate the local dielectric environment.

A comprehensive understanding of the Stern layer's dielectric behavior requires considering multiple coupled effects. At the electrode surface, subtle interactions between water-metal and water-water hydrogen bonding drive the formation of complex interfacial water structures.^{47,48} The orientation of water molecules is highly surface-dependent and can typically be categorized into three distinct configurations based on the strength of water-surface interactions: O-down, H-down, and weak/flat. These orientation patterns result in anisotropic dielectric behavior that cannot be captured by continuous solvent models. Extensive experimental and theoretical studies have demonstrated that interfacial water adopts specific arrangements depending on surface polarity, roughness, and chemical functionality. Besides, solvated ions significantly affect interfacial water structure. For example, Chen et al. reported that the accumulation of large cations within the EDL disrupts the local hydrogen-bonding network and water distribution, thereby impeding proton transfer from the bulk to the interface.⁴⁹ Lee emphasized that understanding water behavior in electrolyte solutions remains a key challenge in computational chemistry, as solutes introduce heterogeneity that alters both molecular orientation and dielectric response.⁵⁰

The dielectric constant within the Stern layer is also strongly potential-dependent. Experimentally, the double-layer capacitance often exhibits two characteristic peaks as a function of electrode potential -- features attributed to structural changes in the interfacial dielectric environment. Shin et al. demonstrated through first-principles molecular simulations that such capacitance peaks can be reproduced and traced to EDL structural phase transitions.⁵¹ As shown in Figure 4a-c, two bistable interfacial states with different surface charge densities (σ_h and σ_l) coexist at a given cathodic potential (E) resulting in an S-shaped potential-charge curve. Upon

scanning the potential, the EDL transitions from a low-charge to a high-charge phase, with phase coexistence giving rise to the observed capacitance peak -- an insight fully captured at the molecular level. Similarly, Speelman and co-workers investigated the orientational ordering of Stern layer water molecules under applied potential using nonlinear optical spectroscopy.⁵² Their measurements on Ni electrodes at pH 13 revealed a transition from disordered to ordered water structures prior to the onset of Faradaic currents. At +0.8 V, a monolayer of water aligns with oxygen atoms facing the electrode, with an estimated flipping energetic barrier of ~80 kJ/mol. As shown in Figure 4d-e, this transition can be described using a 2D Ising framework, with the Helmholtz free energy per molecule given by:

$$F = (N_{\downarrow})^2 J z / 2 - \beta^{-1} \ln \{ \cosh [\beta \cdot (J z |N_{\downarrow}| + e \cdot \Phi_{tot})] \} \quad (9)$$

where $N_{\downarrow}$ is the molecular dipole alignment term, J is the coupling energy, z is the lattice constant, Φ_{tot} is the total potential, and $\beta = (k_B T)^{-1}$. These results, validated by both AIMD and molecular modeling, showcase the complementary nature of first-principles and statistical-mechanical calculations in capturing the Stern layer dielectric transitions.

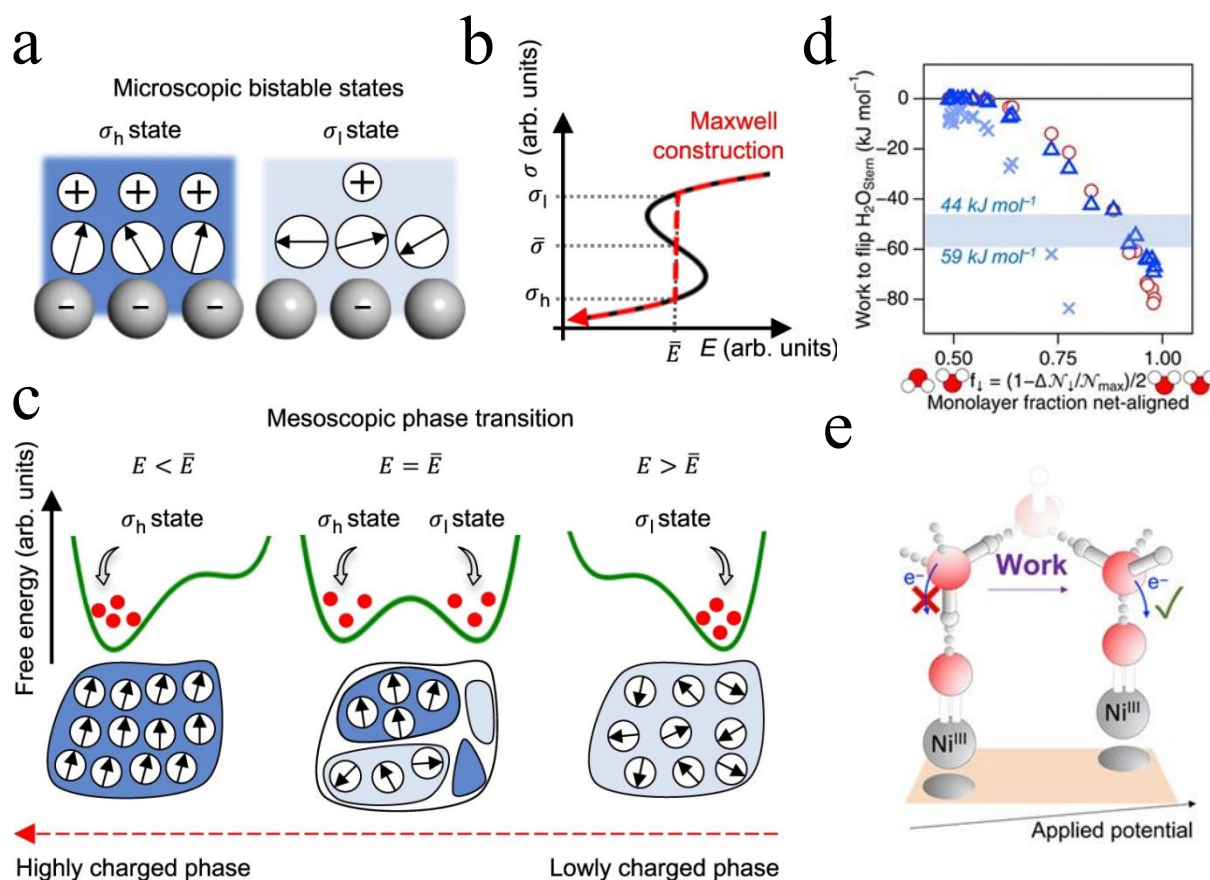


Figure 4 a. Higher charged state with more-aligned water dipoles (that is, large $|\sigma|$ and large ϵ_{eff} ; σ_h state) and lower charged state with less-aligned water dipoles (that is, small $|\sigma|$ and small ϵ_{eff} ; σ_l state) are bistable at the same cathodic potential, E . b Phase transition between bistable states, which is modeled using a Landau-type theory, yields the S-shaped region, at which the Maxwell tie-line is constructed. σ is defined as $(\sigma_h + \sigma_l)/2$, and phase transition occurs at $E = \bar{E}$. c. At mesoscopic interfaces, σ_l state is more populated when $E > \bar{E}$, forming a lowly charged phase (right panels), and σ_h state is more populated when $E < \bar{E}$, forming a highly charged phase (left panels). Negative-potential sweep induces a phase transition from the lowly charged phase to the highly charged phase via a phase coexistence at $E = \bar{E}$. Reprinted with permission from ref⁵¹. Copyright 2022 Springer Nature. d. Work associated with Stern layer water flipping as a function of the fraction of water molecules having a net-orientation with their oxygen atoms pointed toward the electrode. Upper and lower bounds of shaded area indicate range of cohesive energies of liquid water and ice, respectively. Dark blue triangles and light blue x's indicate 2D-Ising model result with $J = -1 \times 10^{-20}$ J and $J = -1 \times 10^{-19}$ J, respectively. e. Cartoon of water flipping concept. Reprinted with permission from ref⁵². Copyright 2025 The American Association for the Advancement of Science.

It is worth noting that the dielectric properties of the Stern layer are not solely governed by molecular orientation. Using classical molecular dynamics simulations, Olivieri et al. found that confinement-induced dielectric reduction in graphene nanochannels is not primarily due to water orientation, but rather the result of long-range dipole-dipole correlations and the excluded volume effects imposed by low-dielectric substrates.⁵³ Furthermore, McGregor and co-workers showed

that variations in electrolyte concentration alter the screening efficiency of the EDL, thereby modifying the effective interfacial electric field experienced by adsorbates.³⁶ Overall, the dielectric behavior of the Stern layer is a complex function of interfacial structure, electrostatics, ion-water-surface interactions, and microenvironmental conditions. Capturing these effects requires synergistic use of molecular simulations and EDL theory modeling. Their combination is essential for quantitatively linking interfacial dielectric properties with observed electrocatalytic behavior.

3.2.2 Stern Layer Thickness

The thickness of the Stern layer is a dynamic quantity that depends on multiple interrelated factors, including electrode surface characteristics, electrolyte composition, proton availability, and the magnitude and polarity of the applied potential. In combination of KD-DFT and EDL models, the Stern layer thickness plays a critical role in determining the electric field strength across the EDL, and therefore directly influences interfacial charge distribution, capacitance, and electrocatalytic activity.

Through extensive AIMD simulations, McGregor and co-workers demonstrated that variations in interfacial electric field strength can be attributed to differences in the distance between cations and the electrode surface.³⁶ This separation distance is strongly influenced by the size and structure of the solvated ions, especially bulky organic cations, and determines the effective thickness of the electrochemical double layer. A closer cation-surface approach leads to a thinner Stern layer and stronger local electric field, while more spatially extended solvation shells result in thicker, more diffuse layers. Brown et al. found that the Stern layer compresses (i.e., becomes thinner) as the electrolyte concentration increases.⁵⁴ This behavior offers a straightforward explanation for the simultaneous increase in surface charge density and decrease in surface and zeta potentials with rising ionic strength. Higher concentrations lead to enhanced

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3 screening, drawing the counterions closer to the electrode and thus compacting the Stern layer.
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5 Furthermore, Favaro and collaborators reported how Stern layer thickness varies not only with
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7 electrolyte concentration but also with applied potential.⁵⁵ Their experimental studies confirmed
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9 that applied bias can modulate the spatial distribution of ions at the interface, leading to a
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11 compression or expansion of the compact layer depending on the electrode polarity and interfacial
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13 interactions. In addition, the formation of ion-intermediate complexes within the Stern layer can
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15 also significantly alter its structure.^{51,56}
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19 Taken together, these findings highlight that the thickness of the Stern layer is not a fixed or
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21 purely geometric parameter -- it is an emergent property of molecular interactions at the interface,
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23 responsive to electrolyte composition, electrode surface properties, and potential. As such,
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25 accurately determining Stern layer thickness requires either direct experimental measurements
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27 (e.g., via X-ray reflectivity or electrochemical impedance spectroscopy) or detailed AIMD
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29 simulations. Once obtained, these thickness values can be used as critical input parameters in
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31 liquid-state theoretical models (e.g., cDFT) to ensure realistic and physically consistent
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33 descriptions of interfacial electrostatics.
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37 38 *3.2.3 Adsorption and Electron Transfer* 39

40 The electrode-electrolyte interface is not an insulating boundary; rather, it permits partial
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42 electronic communication between the electrode and solution.⁵⁷ Electron transfer across the
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44 interface plays a central role in determining the structure and reactivity of the Stern layer, and has
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46 significant implications for interfacial charge distribution, solvent response, and catalytic
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48 performance. Li and co-workers revealed that 30-40% of the excess electronic charge density is
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50 not confined to the metal surface but instead penetrates into the adjacent interfacial water region
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52 at the Pt (111)-water interface.⁵⁸ This charge delocalization is absent in vacuum environments and
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often neglected in molecular simulations using classical force fields, underscoring the necessity of explicitly accounting for quantum-mechanical charge transfer in realistic electrochemical interfaces. The electron transfer implies that interfacial solution species can acquire partial or full charges, significantly altering their structural and dielectric properties compared to those in bulk solutions. To model such effects accurately, it is essential to establish a quantitative relationship between applied potential and charge transfer across the interface.

As illustrated in Figure 5, interfacial electron transfer can be broadly categorized into two mechanisms. Outer-sphere electron transfer (OSET) occurs without direct chemical bonding between the electrode and the reactant. In this case, the reactive species remain solvated and separated from the surface by a solvent layer. By contrast, inner-sphere electron transfer (ISET) is mediated by the direct adsorption of the reactive species onto the electrode surface, involving partial or full chemisorption.⁵⁹ The distinction between these two mechanisms lies in the presence or absence of chemical bonding with the surface. Importantly, they each give rise to different interfacial electric fields, dielectric responses, and Stern layer configurations. Moreover, adsorption and the accompanying electron transfer processes are tightly coupled with the Stern layer properties. On one hand, the local electric field and structure of the EDL modulate the adsorption strength and stability of intermediates. On the other hand, adsorbed species alter the local charge distribution, which feeds back into the Stern layer's electric field, thickness, and dielectric response. Thus, a thorough understanding of interfacial electron transfer requires a holistic approach that simultaneously considers adsorption thermodynamics, quantum charge redistribution, and solvent structure.

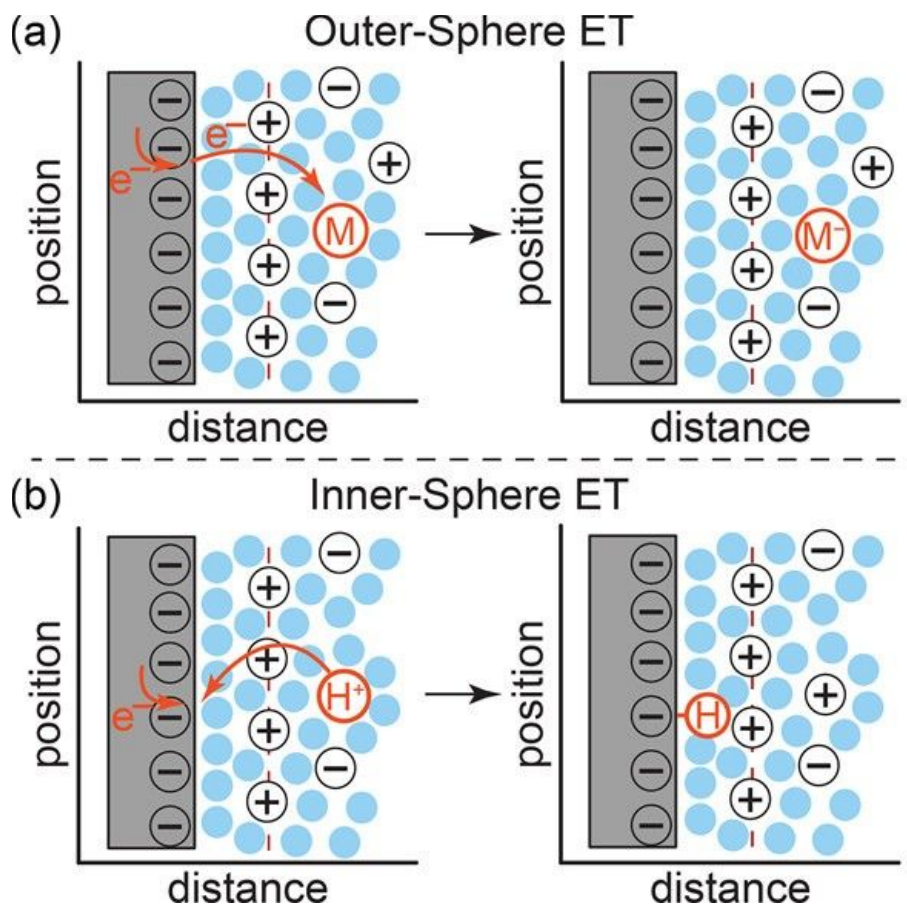


Figure 5 Schematic representations of (a) interfacial OSET between an electrode and a dissolved molecule, M , and (b) interfacial ISET resulting in bond formation between an electrode surface site and a solution-phase proton. Reprinted with permission from ref ⁶⁰. Copyright 2019 American Chemical Society.

In ISET, reactive species form chemical bonds with the electrode surface, analogous to bond formation in molecular reactions. The interfacial environment -- including solvent water molecules, protons (H^+), hydroxide ions (OH^-), solvated electrolyte ions, and reactant molecules -- exhibits diverse adsorption behaviors depending on the electrode material and surface structure. These behaviors are typically studied using first-principles methods such as KS-DFT and AIMD. Electrosorption is not merely a passive surface phenomenon; it is often accompanied by electron transfer between the adsorbate and the electrode. This charge exchange can modulate the electronic structure of the electrode. For instance, Chen et al. demonstrated that modifying Pt surfaces with transition metals of varying oxophilicity tunes the PZC, thereby altering the EDL field strength,

rigidity, and interfacial hydrogen-bond network, ultimately affecting proton transport kinetics under alkaline hydrogen evolution conditions.¹³ In addition to water, protons, and hydroxide ions, solvated ions also play a critical role in interfacial behavior. Using DFT-based molecular dynamics combined with constant electric field methods, Andersson et al. directly calculated the Helmholtz capacitance at the Au (100)/Au (111)-electrolyte interface by accounting for both electronic and ionic degrees of freedom.⁶¹ Their results showed that the electronic response of the gold surface is key to the high Helmholtz capacitance, and that transient adsorption of Cl⁻ ions can induce charge inversion at positively polarized Au (100) surfaces. Similarly, Wang et al. combined experimental results with classical and joint DFT methods to study the charging behavior of Ag (111) electrodes in NaF aqueous solutions.⁶² Their work revealed that F⁻ ions specifically adsorb on positively charged Ag surfaces and play a significant role in modulating interfacial properties. Su and coworkers reported that during C-C coupling on Cu, K⁺ ions exhibit specific adsorption rather than merely remaining at quasi-specific adsorption sites, directly inducing interfacial charge redistribution and enhancing coupling kinetics.³⁸ Moreover, as discussed above, the dynamic evolution of adsorbed intermediates during reaction pathways also influences the electrode's electronic structure.

A major challenge in theoretical modeling of electrocatalysis remains the accurate determination of surface coverage by different solution species under operating conditions. Li et al. emphasized that current theoretical simulations often neglect realistic surface coverage effects, leading to discrepancies between theoretical predictions and experimental observations.⁶³ Under actual reaction conditions, catalyst surfaces are rarely pristine; they may be covered by various species or undergo surface reconstruction, forming new active motifs. Ignoring these effects risks misrepresenting structure–activity relationships and may misguide catalyst design strategies. For

example, Ding et al. employed fully solvated AIMD combined with the slow-growth method to construct partially polarized Ni (111) surfaces with varying *O coverages (1/32 to 1/8 ML).⁶⁴ In this model, non-polar regions were *CO-covered, while polarized regions modified the Ni d-band center, reducing CO and CO₂ poisoning and stabilizing *COOH intermediates. Similarly, Yang et al. identified the formation of hydride Pt-Ce-H sites as key intermediates in selective oxidation catalysis.⁶⁵ Building on this principle, Li et al. used surface Pourbaix diagrams to show that under electrochemical CO₂-to-formate conditions, SnO₂ (110) and (100) surfaces generate 1 ML of oxygen vacancies (*O_V), triggering surface rearrangement and formation of metallic Sn species.⁶³ These changes alter both atomic and electronic structures, thus affecting catalytic activity and selectivity. More sophisticated approaches are emerging to address these challenges. Liu and co-workers used large-scale machine learning-based global optimization to explore millions of Rh bulk, surface, and nanoparticle configurations under hydrogen exposure.⁶⁶ They identified [RhH₆] species -- where surface Rh atoms are coordinated by six hydrogen atoms -- as key intermediates in Rh-catalyzed hydrogen evolution reactions (HER).

The incorporation of liquid-state theories into electronic structure calculations enables the consideration of solution effects at larger length scales. As shown in Figure 6, Huang and co-workers^{46,67} proposed a multiscale framework based on hierarchical modeling strategies. At the atomistic scale, the reaction mechanisms are determined by KS-DFT calculations. At the macroscopic scale, a continuum transport model that accounts for the microscopically non-electroneutral EDL captures the local reaction environment, including the reactant concentrations and the electric field in the reaction zone. Bridging these two scales, a microkinetic model links the KS-DFT results with the continuum transport model, providing more accurate information on surface coverage.

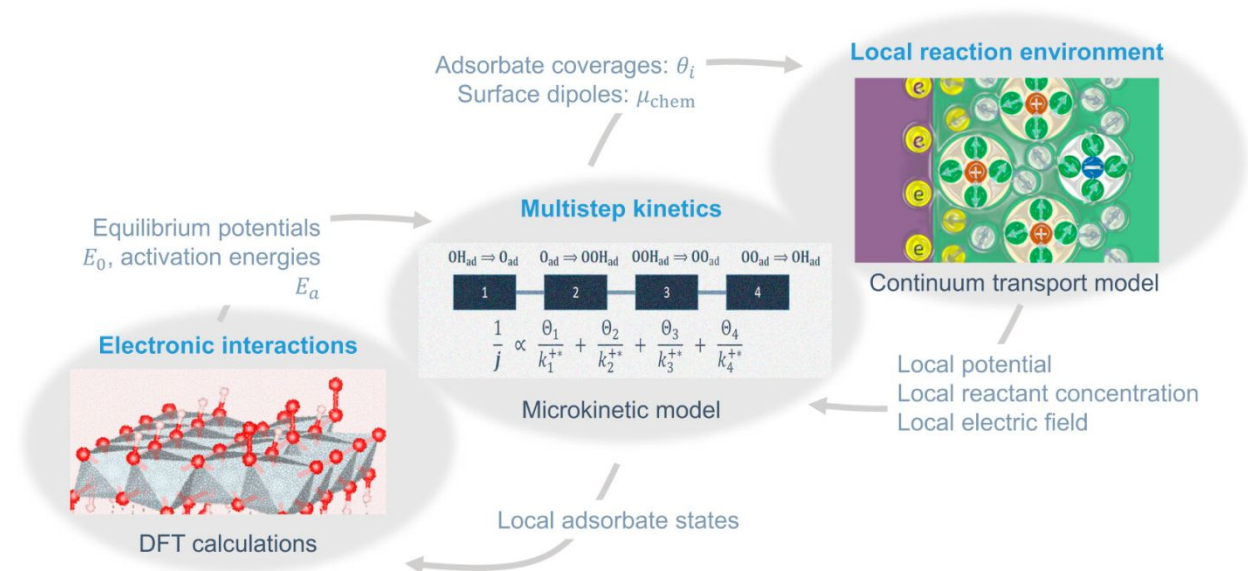


Figure 6 Hierarchical approach to model the EDL effects on electrocatalytic reactions. The approach integrates KS-DFT calculations to determine the reaction mechanism on the atomistic scale, a continuum transport model to describe the local reaction conditions on the macroscopic scale, and a microkinetic model between them to treat the coupled multistep electron transfer kinetics. Reprinted with permission from ref⁴⁶. Copyright 2023 American Chemical Society.

As mentioned above, OSET typically occurs between the electrode and solvated ions or weakly adsorbed neutral reactant molecules. It involves the transfer of an electron from the electrode to a species in the electrolyte solution via quantum tunneling, without the formation of a direct chemical bond between the reactant and the electrode. In this mechanism, the detailed surface chemistry of the electrode plays a less critical role compared to ISET. Instead, the rate of electron transfer is governed by solvent dynamics and can be quantitatively described by the Marcus-Hush theory, which emphasizes that reaction rates are controlled by solvent reorganization -- specifically, the slow polarization modes related to dipole reorientation.⁶⁸ Ojha et al. conducted detailed capacitance measurements at the Pt (111)-electrolyte interface near the PZC, in the presence of electrolytes composed of non-specifically adsorbing cations and anions.⁶⁹ By combining the Gouy-Chapman-Stern (GCS) model with a mean-field model that accounts for water reorientation on platinum near the PZC and attractive ion-surface interactions beyond the GCS scope, they successfully reproduced experimental observations on the capacitance

dependence on the electrode potential. It is important to note that this model explicitly treats the ions as hydrated species, reinforcing the physical picture of OSET as occurring through an extended, solvated interfacial region. Neutral, non-hydrogen-bonding molecules like CO₂ typically exhibit weak adsorption on the electrode, making them likely candidates for OSET. For instance, Xu and co-workers conducted extensive studies on CO adsorption on metal electrodes, proposing experimental thermodynamic strategies to measure the enthalpy and entropy of CO adsorption.⁷⁰ On Cu surfaces, the enthalpy of CO adsorption was found to be positive, suggesting that the stability of adsorbed CO arises mainly from entropy gains. This implies that CO₂ may first undergo electron transfer to form *COO⁻, which then binds to the surface -- highlighting a likely OSET pathway. However, such stepwise electron-adsorption sequences are difficult to resolve using conventional KS-DFT, which cannot disentangle the chronology of charge transfer and surface binding. Besides, the OSET process is strongly modulated by the ionic structure of the Stern layer. For example, Wang et al. used molecular dynamics simulations to show that K⁺ ions play a critical role in electrostatically stabilizing adsorbed NO₃⁻ species on negatively polarized cathodes.⁷¹ However, excessive ion concentrations can lead to undesired blocking effects. Yan et al. reported that local CO availability -- and hence CO reduction performance -- varies significantly depending on the type of cation present.⁷² Highly hydrated ions like Li⁺ can hinder surface accessibility by forming compact hydration shells, reducing local CO coverage and lowering catalytic efficiency compared to more weakly hydrated cations like K⁺.

In summary, ISET involves chemisorption and is well-described by KS-DFT and AIMD, particularly for modeling adsorbate-surface interactions and reaction intermediates. However, capturing coverage-dependent effects and dynamic surface environments may require larger-scale methods such as MLPs or grand-canonical simulations. In contrast, OSET does not involve direct

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3 bonding and is largely determined by solvent reorganization and interfacial dielectric properties,
4 making it more amenable to modeling via liquid-state theories and continuum frameworks (e.g.,
5 the Marcus-Hush theory).⁷³ Understanding whether a reaction proceeds via ISET (adsorption
6 followed by electron transfer, rate-limited by adsorption energy) or OSET (electron transfer
7 followed by adsorption, rate-determined by solvent reorganization) is crucial for accurate
8 mechanistic interpretation. Addressing this distinction requires the integration of first-principles
9 electronic structure methods and liquid-state theories, enabling a holistic, multiscale view of
10 electrochemical electron transfer processes.
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21 *3.2.4 Other Effects on Stern Layer*

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23 In addition to dielectric properties, thickness, and electron transfer, the structure and behavior
24 of the Stern layer can also be strongly influenced by other interfacial processes, such as surface
25 reactions and geometric confinement. These factors introduce additional layers of complexity in
26 modeling electrochemical interfaces and further highlight the need for multi-scale, multi-physics
27 simulation approaches.
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35 *3.2.4.1 Surface Reactions*

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37 In some cases, the electrode surface can actively participate in chemical transformations of
38 interfacial species -- for example, by promoting water dissociation. Advincula et al. reported
39 proton accumulation at the water-graphene interface, with hydrated protons primarily localized
40 within the first contact layer of water, while hydroxide ions exhibited a bimodal distribution --
41 partially clustering near the surface and partially dispersed into the bulk.⁷⁴ Using path-integral MD
42 (PIMD) simulations on the nanosecond timescale, Cao et al. showed that nuclear quantum effects
43 (NQE) lead to significant proton delocalization, enabling rapid and frequent proton transfer events
44 between water molecules, facilitate spontaneous water dissociation on surfaces like Ru (0001).⁷⁵
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The dissociation of water, or any catalytic reaction that consumes protons or hydroxide ions, alters the local pH within the Stern layer, leading to substantial deviations from the bulk electrolyte conditions.

3.2.4.2 Geometric Confinement

Geometric confinement introduces additional modifications to water structure and dynamics.⁴⁸ Tang and co-workers performed extensive MD simulations to study confined water between α -Al₂O₃ layers.⁷⁶ They found that several unique features of confined water -- such as ordered molecular structures, anisotropic and highly connected hydrogen-bond networks, extremely low (even locally negative) dielectric constants, and suppressed self-diffusion -- were especially pronounced in interfacial water layers and largely independent of the confinement scale. In contrast, other anomalies, such as enhanced in-plane diffusion and overall dielectric suppression, emerged across the entire confined region due to geometric constraints and exhibited strong scale dependence. Notably, the transition threshold between confined and bulk-like water behavior was determined to be within the 10-20 nm range. The study also explored how ion concentration, pH, surface functional groups, and net dipole orientation affect the dielectric and dynamic properties of confined water. These findings are particularly relevant for modeling porous catalysts, nanogap electrochemical systems, and 2D material interfaces, where confinement effects reshape the Stern layer and must be explicitly included in theoretical treatments to capture interfacial transport, reactivity, and electrodynamic behavior accurately.

Together, these additional effects demonstrate that the Stern layer is not merely a static dielectric slab, but a dynamic, chemically responsive region coupled with electrode activities. Modeling this complexity requires integrating quantum simulations (to capture electronic and reactive events), classical or machine-learning-based molecular dynamics (to model ion/water

structuring and dynamics), and liquid-state theories (to describe statistical distributions of underlying chemical species and their local potentials).

3.3 Distribution and Diffusion of Reactants

The dissolution of gaseous reactants into solution and their subsequent transport to the electrode surface is a prerequisite for electrochemical reactions. Once dissolved, molecular species must traverse the electrolyte through a combination of diffusion, migration, and convection, processes that collectively define the mass transport limitations of the electrochemical system. Computational methods -- ranging from continuum transport models to fully atomistic simulations -- provide the critical link between these macroscopic transport phenomena and microscopic interfacial processes.^{77,78} Based on AIMD simulations, Awoonor-Williams et al. reported that CO behaves like a hydrophobic solute in water, forming few hydrogen bonds and exhibiting limited interaction with the solvent.⁷⁹ Other than reactant molecules, the interfacial pH can deviate significantly from the bulk value, especially in proton-consuming reactions such as HER and OER. When interfacial reactions are sluggish, the rapid consumption of H_3O^+ at the surface outpaces replenishment from the bulk, resulting in a non-equilibrium local pH.⁸⁰ This interplay between pH, mass transport, and reaction kinetics critically shapes catalytic behavior.

Accurately describing the spatial distribution and mass transport of reactant molecules in solution -- particularly near electrochemical interfaces -- remains a major challenge. KS-DFT is ill-suited for modeling these processes due to its closed-system nature and limited timescales. AIMD suffers from finite-size effects and statistical arbitrariness when attempting to simulate long-range transport or rare events. To overcome these limitations, several alternative approaches have been proposed. For example, Andrade and co-workers combined MLPs, enhanced sampling, and grand-canonical Monte Carlo simulations to model CO_2 chemisorption in liquid ammonia.⁸¹

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3 Their results revealed that CO₂ capture proceeds through sequential steps, forming a metastable
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5 zwitterionic intermediate. The simulations also showed that solvent-mediated proton transfer and
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7 solvent dynamics significantly influence both the reaction pathway and the chemisorption
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9 efficiency. Recently, we employed cDFT to simulate the static distribution of CO₂ in ionic
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11 liquids.⁴² We quantified the interaction energies between CO₂ and both cations and anions,
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13 showing that although strong anion-CO₂ interactions enhance solubility, they also hinder access
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15 of CO₂ to the catalyst surface. This highlights that solubility and reactivity may not follow the
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17 same trend. While the static distribution models can capture such trade-offs, they are limited to
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19 equilibrium states. To address the dynamic aspects of reactant transport, especially under non-
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21 equilibrium conditions, physical models such as the Poisson-Nernst-Planck (PNP) equation are
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23 commonly used. Butt et al. emphasized that local reaction conditions near the electrode --
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25 especially those shaped by EDL formation and steric constraints -- can significantly affect CO₂
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27 availability.⁸² They developed a size-modified PNP (SMPNP) model that incorporates steric
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29 effects into transport equations and adopts the Frumkin correction to Tafel kinetics. Similarly,
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31 Bohra et al. employed a generalized modified PNP (GMPNP) approach to self-consistently
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33 calculate concentration and potential distributions in CO₂ electroreduction systems.⁸³ Those results
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35 in more realistic concentration and potential profiles near the interface. However, as Johnson et al.
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37 pointed out, while PNP models are effective at long length scales and low electrolyte
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39 concentrations, they fail within ~1 nm of the electrode, where ion-specific interactions, high local
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41 concentrations, and polarization effects dominate -- phenomena better captured by MD
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43 simulations.⁸⁴ Moreover, PNP models often reverse-engineer transport processes based on the
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45 consumption rate of CO₂, rather than predicting them from first principles. To better capture solute
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47 dynamics under external fields and interactions, dynamic cDFT (DDFT) offers a time-resolved
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extension of cDFT may have potential.⁸⁵ Besides, Chen et al. developed an Electrochemical Knowledge-Integrated Neural Network (ECINN) model that embeds core electrochemical principles (e.g., Butler-Volmer, Nernst, and diffusion equations) into a neural network framework.⁸⁶ Applied to experimental voltammetry data, ECINN successfully extracted kinetic and transport parameters for redox couples.

A wide variety of computational methods have been used to describe how mass transport constraints and diffusion layer formation couple to the EDL's electronic, ionic, and molecular structure. However, each method has its own strengths and limitations: KS-DFT and AIMD provide detailed atomic-level insights but are limited by scale and timespan; MLPs with enhanced sampling offers scalability for complex dynamics; cDFT captures equilibrium distributions but cannot resolve transport; PNP models describe macroscopic concentration profiles but fail near interfaces; and ML-integrated frameworks help bridge data and theory but often lack atomic specificity. To move forward, there is a clear need for open-system simulation approaches that combine first-principles accuracy, multi-scale physics, and machine learning -- capable of capturing both reactant transport and interfacial restructuring under realistic conditions.

4. Other Developments

4.1 Hybrid Approaches

Advanced ab initio-based strategies have demonstrated that surrounding fluid can be explicitly captured even in highly quantum mechanical settings.^{29,87,88} In representative studies, an ab initio description of He-surface interactions was coupled with zero-temperature time-dependent density functional theory for superfluid ⁴He droplets to follow the short-time collision dynamics of Au@⁴He₃₀₀ clusters impinging on TiO₂(110) surfaces.⁸⁷ This composite framework revealed that the helium droplet acts as a quantum-mechanical buffer, enabling droplet-assisted “soft

landing” of metal species at very low kinetic energies, and provided a theoretical explanation for experimentally observed helium-droplet-mediated deposition of metal nanoparticles on solid substrates. More broadly, these studies exemplify a general methodological paradigm in which quantum chemistry calculations for reactive species and surfaces are consistently integrated with a continuous density-functional description of the surrounding fluid. In such approaches, the embedding medium is represented as a quantum or quasi-quantum density field, while the adsorbates and substrates are treated explicitly at the electronic-structure level, enabling a physically rigorous treatment of weak interfacial interactions, solvation, and energy dissipation processes. These developments provide valuable conceptual insights into how electronic-structure methods can be combined with density-based descriptions of complex microenvironments.

While advancing first-principles and cDFT-based simulations is not the central theme of this perspective, integrating ML offers promising pathways to enhance both approaches. A major challenge lies in the fundamentally different dielectric behaviors of metallic electrodes (electronic conductors, ionic insulators) and electrolytes (ionic conductors, electronic insulators). At electrochemical interfaces, strong local electric fields require ML potentials that can faithfully capture the field-dependent dielectric response. In such systems, electrolytes primarily respond through ionic migration, dipole reorientation, and bond deformation while metals respond mainly via electronic polarization. For instance, the dielectric constant of bulk water (~ 78) stems mostly from orientational polarization, with electronic contributions being minimal (~ 1.8). This dielectric asymmetry underscores the need for differentiated ML treatments for electrode and electrolyte regions. Zhu and co-workers⁵ highlighted that, due to the fundamentally different dielectric responses, a hybrid scheme of MLPs is needed to treat electrochemical interfaces (ec-MLP). The hybrid approach integrates distinct modeling strategies: Wannier center-based methods for

electrolytes and the Siepmann-Sprik polarizable electrode approach for metals. The ec-MLP model successfully reproduced the bell-shaped differential capacitance curve of Pt (111)-electrolyte interfaces as a function of potential. Similarly, combining first-principles atomic simulations with physically grounded liquid-state models, and enhancing both via ML, offers a promising direction forward.

4.2 Three-Phase Interfaces

Three-phase interfaces -- where gas, solid, and liquid meet -- present additional complexity. In gas diffusion electrodes (GDEs), the local electric field, interfacial water network, and ion-assisted gas adsorption and transport follow intricate mechanisms.⁸⁹ Effective CO₂ reduction (CO₂RR) depends on optimizing mass transfer and stabilizing gas-solid-liquid catalytic interfaces. For example, McKee et al. demonstrated that hydrophobic assembly of molecular catalysts at such interfaces drives highly selective CO₂ electromethanation.⁹⁰ Similarly, Deng and co-workers reported pressurized electrolyzers for high-rate NH₃ synthesis from NO_x, while Tan et al. designed CuS microtube catalysts with hierarchical porosity to create stable and efficient triple-phase boundaries, enhancing CO₂ solubility and transport.^{91,92}

These cases underscore the importance of understanding gas-liquid interfaces. The air-water interface, approximately 6-8 Å thick and anisotropic, significantly influences reactivity and the kinetics of gas solubilization.⁹³ Using AIMD, Chen and co-workers revealed that water molecules at nanodroplet interfaces prefer donor-acceptor dimer configurations due to structural heterogeneity, while planar interfaces exhibit uniform H-bond networks.⁹⁴ This local structural difference -- quantified by solvation entropy -- lowers reaction barriers by 1-2 kcal/mol at flat interfaces, enhancing reactivity. This highlights that even the size of gas-liquid interfaces can affect interfacial chemistry.

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3 Solid-liquid interfaces also merit further attention. For instance, Mi et al. explored CO₂RR at
4 interfaces between electrodes and polyelectrolytes, where solvent is absorbed into polymer
5 networks -- akin to nanoconfined microenvironments.⁹⁵ These complex interfaces are well-suited
6 for modeling via polymer density functional theory, i.e., applications of cDFT to polymer
7 systems.⁹⁶
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10 11 12 13 14 15 **4.3 Surface Reconstruction**

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17 Heterogeneous microenvironments can impact not just surface coverage but also trigger
18 surface reconstruction. For example, Sun et al. reported oscillatory redox behavior in CuO under
19 H₂ via a Mars-van Krevelen (MvK) mechanism involving cyclic reconstruction.⁹⁷ Gao and co-
20 workers combined DFT with millisecond-resolved environmental kinetic Monte Carlo (EKMC)
21 simulations to uncover a unique particle hopping and condensation (PHC) sintering mechanism in
22 CO-rich microenvironments.⁹⁸ Qin et al. found that co-adsorption of H and CO on Cu surfaces can
23 drive the formation of Cu-(CO)_x clusters via intermediate dissolution and aggregation.⁹⁹ Increasing
24 Cu²⁺ concentration or applying potential can suppress this sintering. Zhang used GCMC, EKMC,
25 and DFT to systematically study CO and H co-adsorption-induced reconstruction on Cu (100),
26 showing atomic vacancy formation and square-cluster assembly. Chen et al. elucidated, via the
27 coupled crystal-field theory, the dynamic restructuring mechanisms of Cu-N-C single-atom
28 catalysts (SACs) at electrochemical interfaces.¹⁰⁰ Li et al. revealed that tuning the
29 microenvironment around metal clusters -- e.g., surface gas layers or support defects -- can
30 overcome the classic activity -- stability trade-off.¹⁰¹ An oxygen-rich CO oxidation atmosphere
31 induced in situ redispersion of Ag nanoparticles into clusters, stabilized via adsorbed oxygen
32 species and interfacial hydroxyls. These examples highlight the vital role of interfacial
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microenvironments and suggest that coupling KS-DFT with multiscale modeling of the catalyst structure and reaction environment could offer deeper insights into the dynamic catalytic behavior.

5. Conclusion and Outlook

Modeling the heterogeneous structure of catalytic interfaces -- spanning gas-solid thermal catalysis to electrochemical gas-liquid-solid systems -- requires a unified multiscale strategy that goes beyond the traditional boundaries of atomistic and continuum theories. For gas-solid interfaces, especially under catalytic conditions, capturing the probabilistic distribution of gas-phase species in an open ensemble is essential for describing physisorption, surface coverage, and adsorption-desorption dynamics. Embedding KS-DFT-based surface models into an implicit gas-phase microenvironment, as treated in the grand-potential frameworks, offers a promising direction for capturing these effects. For solid-liquid interfaces, understanding the EDL structure is crucial for establishing the connection between surface charge, applied potential, electrolyte composition, and surface intermediates. First-principles calculations combined with liquid states theory provides a powerful toolkit for resolving both the electronic structure and ion distributions in the diffuse layer. However, the detailed nature of the Stern layer -- encompassing orientation and dissociation of water, physical and chemical adsorption, and potential-dependent electron transfer -- demands a deeper integration of first-principles accuracy with liquid-state theoretical rigor. Moreover, liquid-state approaches provide essential capabilities for describing solute distributions and transport processes, effectively complementing the limitations of MD methods.

Ultimately, first-principles simulations and liquid-state theories each offer distinct strengths. Their integration can yield a more complete and physically grounded picture of interfacial behavior, thereby enabling predictive modeling of electrochemical performance under realistic operating conditions. Looking ahead, the next generation of modeling tools must transcend the existing

dichotomy. We envision a new class of open-system, distribution-respecting simulation frameworks that blend first-principles calculations, statistical mechanics, continuum electrostatics, and physics-informed machine learning. These approaches should be capable of resolving interfacial charge transfer, dielectric response, solvation structure, and dynamic solute distributions and transport processes in chemically realistic and computationally scalable ways.

ASSOCIATED CONTENT

Supporting information

None.

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Notes

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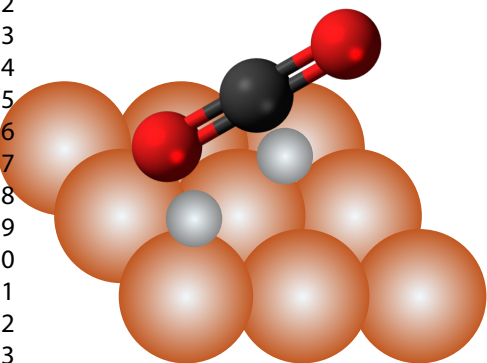
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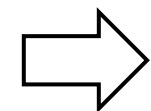
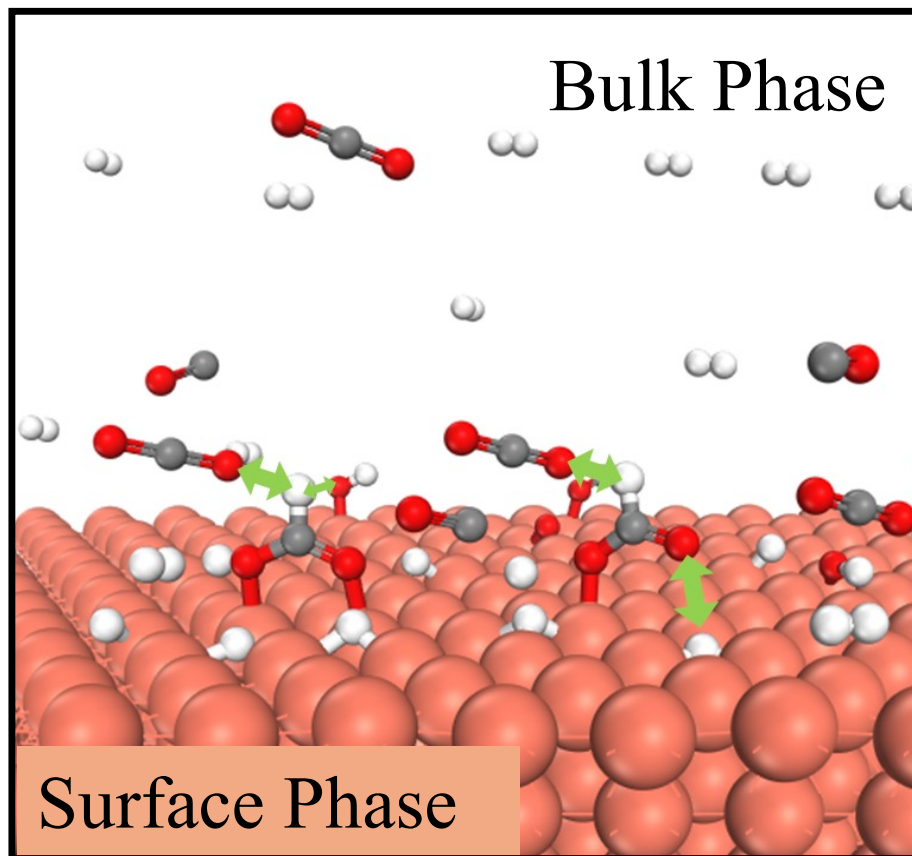
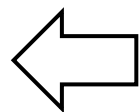
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Surface Structure

$$\mathbf{R} \equiv (\mathbf{r}_1, \mathbf{r}_2, \dots)$$

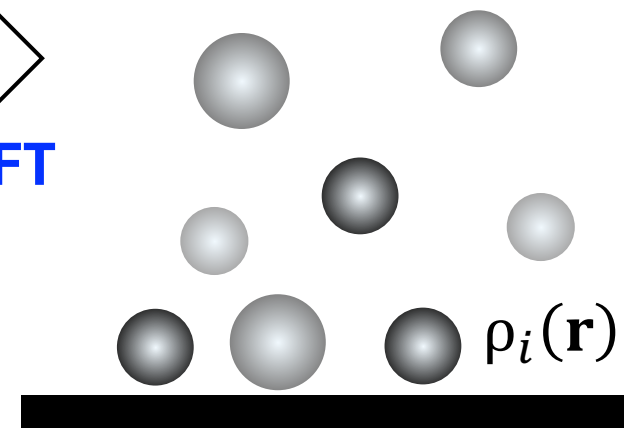


KS-DFT



cDFT

Reaction
Environment
 $[T, V, \mu_i]$



$$\Omega[\mathbf{R}, T, V, \mu_i] = E_{KS-DFT}(\mathbf{R}) + G_{corr}(\mathbf{R}) + \Omega_{cDFT}[\rho_i(\mathbf{r}), T, V, \mu_i]$$