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Dynamic solvation fields: a paradigm shift in solvent effects on chemical reactivity

Markus Becker

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Traditional solvent descriptors—such as dielectric constant, donor number, or polarity scales—reduce complex, fluctuating environments to static averages. While valuable for capturing bulk trends, these parameters fail to account for the localized, time-resolved interactions that govern many chemical transformations. This perspective argues for a conceptual shift: treating solvents as dynamic solvation fields, characterized by fluctuating local structure, evolving electric fields, and time-dependent response functions. Drawing on a synthesis of experimental, computational, and theoretical work from 2015–2025, we show how solvent dynamics modulate transition state stabilization, steer nonequilibrium reactivity, and reshape interfacial chemical processes. We critically examine the limitations of continuum and linear-response models and highlight emerging tools—from ultrafast spectroscopy to machine-learned potentials—that expose the active role of the solvent in chemistry. Finally, we propose a conceptual framework for a general theory of dynamic solvation fields, with implications for catalysis, nucleation, and thin-film formation. This approach offers a more faithful and predictive understanding of solvent effects in modern physical chemistry.

Fraunhofer Institute for Surface Engineering and Thin Films IST, 38108 Braunschweig, Germany. E-mail: markus.becker@ist.fraunhofer.de; Tel: +49 531 2155-509

Markus Becker

Markus Becker is currently a scientific researcher at the Fraunhofer Society, where he leads a working group on solution-based and electrochemical thin-film deposition, with applications in photovoltaics, catalysis, and surface functionalization. He holds a PhD in chemistry and has extensive experience in solvent engineering, interfacial science, and multiscale modelling of reactive systems. His research bridges theoretical and experimental approaches to understand how solvent structure and dynamics influence material formation and chemical reactivity. His current focus is on developing new conceptual frameworks to describe solvent effects beyond classical parameters, aiming to establish dynamic solvation as a central paradigm in physical chemistry.

Introduction

Solvents play a pivotal role in nearly every chemical transformation, influencing rates, selectivities, equilibria, and mechanisms. They stabilize intermediates, mediate charge redistribution, modulate transition state energies, and facilitate bond making and breaking. Despite their fundamental importance, solvent effects are still most often described using static, averaged parameters—such as dielectric constants, donor and acceptor numbers, Gutmann polarity scales, or the ET(30) parameter. These empirical and continuum-based descriptors have long been useful for rationalizing reactivity trends in homogeneous environments.[1,2] However, they are increasingly inadequate for capturing the full complexity of solvent behavior in modern chemical systems, particularly in heterogeneous or time-dependent scenarios. Recent nanoscale studies of interfacial water on graphite and 2D materials have directly visualized such spatial and temporal heterogeneity, revealing transient hydration layers and dynamic restructuring at solid–liquid interfaces.[3]

It is important to note that this perspective focuses specifically on how dynamic solvation influences chemical reactivity and interfacial processes. Time-dependent solvent relaxation and spectral shifts have long been recognized in the context of spectroscopic solvation dynamics—pioneering work by Maroncelli and co-workers in the 1990s already demonstrated the non-instantaneous solvent response following optical excitation.[4] Building on such insights, the present discussion extends these concepts to reactive systems, where solvent fluctuations and delayed reorganization directly modulate transition-state stabilization, energy barriers, and reaction pathways. Recent work on solvation effects in spectroscopy provides valuable conceptual parallels.[5]

In particular, three limitations of the classical view of solvation are becoming apparent. First, solvation is rarely homogeneous: the molecular environment around reactive species is shaped by directional interactions, interfacial gradients, and nanoscale fluctuations. Second, solvent responses are not instantaneous: they evolve on timescales that can compete with or exceed those of chemical reactions, as already noted in early theoretical work on solvent-controlled electron transfer.[6,7] Third, the solvent is not a passive medium: it actively participates in shaping the energy landscape of reactivity, not only by stabilizing species, but by steering mechanisms and modulating barriers in space and time.

Recent experimental and theoretical advances are driving a re-evaluation of how solvation is understood and modeled. Time-resolved studies have shown that solvent molecules undergo complex, coordinated motions during chemical reactions, indicating that inertia, friction, and structural reorganization play active roles in determining chemical outcomes.[8] Editorial contributions have emphasized the emergence of solvation science as a distinct discipline, focused on time-dependent, non-equilibrium solvent behavior at interfaces and in complex systems.[9] Investigations of ionic liquids have demonstrated that local solvation dynamics can outpace bulk viscosity effects, enabling rapid charge transfer in highly structured and heterogeneous environments.[10] Ultrafast spectroscopic evidence has revealed that even single solvent molecules can influence product identity in photoreactions, highlighting the critical importance of transient solute–solvent interactions.[11]

Computational simulations have provided further evidence that solvent reorganization can dynamically reshape reaction coordinates and energy landscapes. For instance, the presence or absence of short-lived ion pairs can hinge on the timing of solvent shell reorientation, fundamentally altering barrier heights and mechanistic interpretations.[12] Surveys of ultrafast solvent–solute dynamics have shown that solvation fluctuations modulate excited-state lifetimes and branching ratios, defying static solvent polarity assumptions.[13,14] Advances in solvation modeling frameworks have addressed the shortcomings of continuum dielectric models, proposing time-dependent solvent response functions and hybrid discrete–continuum approaches to better capture solvent heterogeneity and dynamics.[15,16]

Experimental observations in electrochemical systems indicate that solvent structure near charged interfaces evolves with applied potential and reaction progress, impacting activation entropy and intermediate stabilization in ways not described by conventional models.[17] Even strongly bound ionic solvation shells, such as those surrounding lithium in batteries, exhibit femtosecond exchange of solvent molecules, challenging the notion of rigid coordination environments.[18] In the realm of biological systems, interfacial water has been shown to respond across a broad range of timescales, suggesting that fluctuating hydration layers contribute to biomolecular function and conformational energy landscapes.[19] Machine-learned reactive potentials have recently emerged as effective tools for simulating these dynamic solvent influences with quantum accuracy across diverse chemical environments.[20]

This perspective aims to articulate and support this shift in conceptual framework. It draws on literature from ultrafast spectroscopy, interfacial science, multiscale modeling, and reaction dynamics to highlight where and how static solvent models break down, and to propose a path forward based on dynamic solvation fields. The article begins by examining time-resolved solvation processes in both bulk and interfacial environments. It then explores the influence of nonequilibrium solvent fluctuations near transition states (TSs), the structuring and reorganization of solvents at solid–liquid interfaces, and the various modeling strategies—from *ab initio* molecular dynamics to field-theoretical formalisms—that seek to capture these effects.

Finally, conceptual requirements for a general theory of dynamic solvation are outlined, concluding with an outlook on experimental and theoretical opportunities. The aim is not to propose a single replacement for existing models, but to motivate a rethinking of solvent effects as fundamentally dynamic, evolving, and system-specific phenomena—worthy of direct inclusion in the reaction coordinate and in the conceptual vocabulary of modern chemical theory.

Time-resolved solvation dynamics: watching the solvent in action

Traditional solvation models often presume an instantaneous, homogeneous response of the solvent to solute charge redistributions—implicitly assuming that solvent reorganization is much faster than the chemical process it accompanies. However, advances in ultrafast spectroscopy and molecular simulations have revealed a more intricate picture: solvent molecules reorient, restructure, and fluctuate on femtosecond (fs) to nanosecond (ns) timescales, and these dynamics can strongly couple to the reaction coordinate. Crucially, such findings expose a deep theoretical shortcoming: the solvent is not simply an averaged dielectric medium but an evolving, structured field of forces that may exert directional and time-gated influence on the solute. This realization undermines the core assumptions behind much of classical solvation theory.

Before discussing examples, we distinguish electronic from nuclear solvent response. The ultrafast electronic polarization of the medium—captured by the optical dielectric/refractive index—tracks charge redistribution essentially instantaneously. In contrast, orientational/translational nuclear modes relax on picosecond (ps)–ns scales and dominate nonequilibrium friction and reorganization relevant to reaction coordinates. Refractive-index terms represent the fast electronic component in continuum formalisms (*e.g.*, Lippert–Mataga), whereas rate theories for electron transfer separate optical and static dielectric contributions in the reorganization energy. Our focus below is on these slower collective nuclear dynamics that render the solvation field time dependent for chemical reactivity.[21–24]

Time-resolved fluorescence, 2D infrared (2D-IR), and pump–probe spectroscopy have been instrumental in resolving solvent relaxation into distinct components: a sub-100 fs inertial phase corresponding to ballistic motion of nearby solvent molecules, followed by a slower, ps-scale diffusive reorientation. These experiments provide direct evidence that solvation is not a single-step dielectric relaxation, but a multi-modal process sensitive to solute structure, local interactions, and hydrogen bonding networks. Yet despite the technological sophistication, many studies remain descriptive, lacking a unifying dynamic solvation framework. For instance, Yusof *et al.* showed that proton transfer in aqueous phenol radical cations occurs within ∼0.1 ps, mediated by solvent-compressed O···O distances and involving a fast deactivation of the radical intermediate.[25] Similarly, Brünig *et al.* analyzed proton hopping in HCl solution and identified a broad waiting time distribution (∼200–300 fs) and a fast transfer-path duration (∼14 fs), directly linking IR spectral features to solvation shell dynamics.[26] These insights build on foundational work by Dahms *et al.*, who used ultrafast 2D-IR to show that excess protons in water undergo large-amplitude, ultrafast hopping motions through Zundel-like configurations with strong damping within 20–40 fs,[27] and by Fournier *et al.*, who confirmed persistent asymmetric $H_5O_2^+$ structures in acid solutions using broadband 2D-IR.[28]

In photoinduced reactions, especially charge transfer or bond breaking, the solvent may not reorient fast enough to keep up with changes in solute electronic distribution. This results in a "solvent lag," wherein the polarization environment around a reacting species is mismatched with its instantaneous charge state, destabilizing or delaying critical steps such as TS crossing. The widespread assumption that solvent polarization tracks the reaction coordinate adiabatically is thus demonstrably false for such systems. Biasin *et al.* demonstrated coherent fs hydrogen-bond network motions in water during intramolecular electron transfer in an Fe–Ru complex, with solvent dynamics unfolding in less than 100 fs and actively influencing charge redistribution.[29] Similar dynamics were observed earlier by Haldrup *et al.*, who used ultrafast X-ray spectroscopy and scattering to track the sub-ps reorganization of water molecules around photoexcited Fe complexes.[30] In the photodissociation of triiodide ions (I_3^-), Nimmrich *et al.* observed solvent-specific cage escape and recombination dynamics *via* ultrafast X-ray solution scattering, highlighting how solvent structure affects bond-breaking and geminate recombination timescales.[31] Fig. 1 illustrates the power of time-resolved X-ray solution scattering in capturing dynamic solvation effects during a prototypical photodissociation reaction.

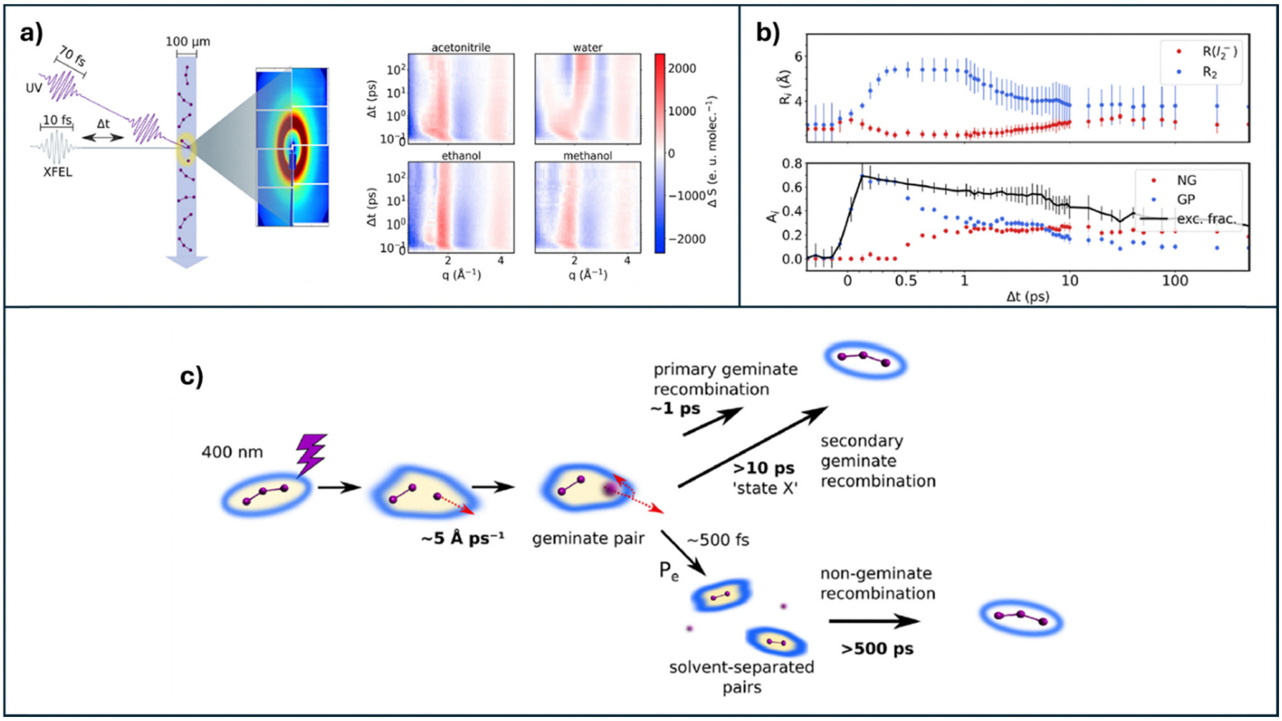

Fig. 1 (a) Schematic representation of the experimental setup. The XFEL pulse and laser pump pulse (400 nm, 70 fs fwhm) are overlapped at the sample position. Scattering patterns are recorded with the octal MPCCD detector. The time-dependent difference scattering signals for the four solvents studied (top left to bottom right: acetonitrile, water, ethanol, and methanol) are presented. The data covers time delays from −0.1 to 500 ps and a *q*-range of 0.5 to 4.5 Å^{-1}. (b) Optimized parameters from the structural refinement for I_3^- in acetonitrile. The two panels present the optimized structural parameters (top) and population dynamics (bottom). A linear scale is used for the first 1 ps to highlight the fastest dynamics; later time points are presented on a logarithmic scale. (c) Scheme of the reaction mechanism of the photodissocation and recombination of I_3^-. Reprinted with permission from the American Chemical Society, 2023.[31]

Fig. 1(a) shows the experimental setup and time-resolved scattering signals across four solvents, highlighting the sensitivity of the structural response to solvent environment. Fig. 1(b) presents the solvent-dependent evolution of key structural parameters—bond lengths and population fractions of geminate and nongeminate species—revealing how the solvent modulates both cage escape and recombination dynamics on ultrafast timescales. Fig. 1(c) summarizes the mechanistic pathway derived from these observations, emphasizing how ballistic bond rupture, solvent-cage interactions, and delayed recombination collectively define a dynamic solvation landscape. Panman *et al.* confirmed such effects for CH_2I_2 photodissociation in cyclohexane, quantifying how 85% of nascent radical pairs remain caged within the original solvent shell. In addition, time-resolved scattering reveals how the molecule breaks into $I^•$ radicals, how those nascent radicals collide with solvent molecules, and how a transient isomer (iso-CH_2I–I) forms.[32] Taken together, these findings argue for a rethinking of solvent ''response'' as a temporally discrete and sometimes mechanistically determining agent.

Beyond timescales, ultrafast spectroscopy has also revealed the heterogeneity of solvent environments during reactions. Rather than sampling a continuum of solvation states, solutes often experience discrete solvent configurations—''solvent cages''—that transiently stabilize or trap reactive intermediates. This undermines the Gaussian fluctuation assumptions behind linear-response theories. Katayama *et al.* observed a two-step ligand flattening in a copper(I) complex photosensitizer, where the first flattening step induced coherent motion in acetonitrile solvent molecules, which in turn damped further structural change in the solute.[33] In another example, Markmann *et al.* tracked the ultrafast solvation response following halide photoionization and confirmed that water shell reorganization occurs on the ∼0.5–1 ps timescale, influencing charge recombination dynamics.[34] Related results by van Driel *et al.* showed how ultrafast coordination of acetonitrile solvent molecules to a reactive iridium complex modulates excited-state reactivity in real time.[35]

Molecular dynamics (MD) simulations—both classical and *ab initio*—have corroborated these experimental findings. They show that solvent shells undergo stochastic restructuring, including solvent exchange events and orientational flips, which generate a rich distribution of local solvation environments. However, these simulations also highlight a methodological gap: although trajectory-resolved solvent behavior is visible, its impact on observables (*e.g.*, rate constants, branching ratios) is not systematically captured. Zederkof *et al.* demonstrated with QM/MM (quantum mechanics/molecular mechanics) nonadiabatic dynamics that explicit hydrogen bonding between water and ligands in an Fe(II) complex is essential to reproduce MLCT (metal-to-ligand charge transfer) dynamics, with solvent reorganization occurring within 50 fs.[36] Similarly, Albrechtsen *et al.* directly observed, *via* fs pump–probe, stepwise solvation of Na^+ in helium nanodroplets and quantified Poisson-distributed solvation dynamics on the 1–2 ps timescale.[37] Earlier work by Yuan *et al.* and Markland *et al.* established that proton hopping and chemical exchange in aqueous HCl occurs *via* concerted hydrogen-bond rearrangements on ∼1 ps timescales,[38] while Lu *et al.* proposed that solvent fluctuations ahead of the reaction coordinate can lower the effective reorganization energy and accelerate electron transfer, which, in turn, show behaviors that deviate from the predictions of the classic Marcus theory.[39]

Together, these findings motivate a shift from a view of the solvent as a background dielectric to a time-dependent, heterogeneous field with active influence over reaction dynamics. The very notion of a scalar solvation energy should be replaced by a vectorial, time-encoded field that evolves jointly with the reaction coordinate. In time-resolved solvation dynamics, the timing, trajectory, and identity of solvent fluctuations matter—often as much as solute structure—suggesting that reactivity should be interpreted through a spatiotemporal solvent field framework. What we lack is a quantitative language for these fields—a solvodynamic theory that elevates local fluctuations to the level of chemical determinants. This section therefore sets the stage for a broader reimagining of how we conceptualize, measure, and model solvent action in chemistry.

Solvent fields and transition states: breaking the linear response paradigm

In classical transition state theory (TST), solvent effects are incorporated *via* equilibrium solvation energies—assuming that the solvent polarization equilibrates instantaneously with the charge distribution along the reaction coordinate. This approximation underpins both continuum solvation models and linear-response theories, where reorganization energies are treated as quadratic corrections. Yet mounting evidence challenges this paradigm: the solvent not only responds to but actively modulates the position and shape of the TS, especially under ultrafast or nonequilibrium conditions. For example, Carpenter and co-workers highlight several cases in which hot, non-equilibrated intermediates and non-instantaneous solvent response distort the assumptions of classical TST.[40]

Several experimental and computational studies have shown that the solvent's internal electric field can shift the energy and geometry of the TS. These shifts are not symmetric around the reactant and product wells, violating the assumptions of harmonic free energy surfaces implicit in Marcus-type models. For example, solute–solvent coupling in charge-transfer reactions can introduce anharmonic fluctuations that bias the system toward early or late TSs depending on local field configurations. This has been observed in ultrafast photochemical pathways where solvents selectively stabilize different electronic states at the TS, steering the relaxation trajectory.[13] The consequence is a non-parabolic free energy landscape with asymmetric activation barriers.

In a groundbreaking ultrafast study, Biasin *et al.* used fs X-ray spectroscopy to reveal that solvent shell reorganization around a photoexcited Fe–Ru complex occurs within ∼100 fs and exhibits coherent coupling to electron transfer.[29] These coherent solvent fluctuations actively influence the timing and energetics of barrier crossing. Similar coupling was found in photoredox reactions, where the escape of radical pairs from the solvent cage, governed by solvent viscosity and structure, directly modulates reaction efficiency and yield.[41] Such effects are most pronounced when the timescale of solvent response overlaps with the timescale of electronic transition, resulting in nonequilibrium solvation trajectories that bypass canonical minima.

Ab initio MD (AIMD) simulations further support these findings. Leitold *et al.* developed a solvent coordinate for an S_N2 reaction that quantifies the nonequilibrium polarization state of water around the TS, capturing key solvent contributions missed by conventional reaction coordinates.[42] Bernasconi and co-workers demonstrated that glycosylation reactions can transition between S_N1 and S_N2-like mechanisms depending on the solvent's ability to stabilize or delay intermediate formation.[43] Roytman and Singleton showed that in carbocation reactions, the majority of TSs proceed before full solvation is achieved, challenging the very definition of an equilibrium TS.[12]

Even subtle solvent interactions can disproportionately influence the TS. Vik *et al.* found that weak hydrogen bonds, formed transiently at the TS, can provide several kcal mol^{-1} of stabilization, far exceeding their static interaction energy.[44] Zhang *et al.* showed *via* machine learning-enhanced simulations that different solvents stabilize the TS of a Diels–Alder reaction to varying degrees, with water leading to a lower activation barrier than methanol.[20] These findings argue that solvent-induced field effects cannot be understood merely by bulk polarity or viscosity.

Time-dependent friction and memory effects are also important. Dalton *et al.* demonstrated that molecular isomerization rates in viscous solvents are not solely governed by bulk viscosity but depend on how solvent friction is distributed in time (non-Markovian behavior).[45] García-Meseguer and Carpenter emphasized that the dividing surface of the TS in solution may not align with the saddle point geometry, due to persistent solvent relaxation delays.[46]

Such behavior is irreconcilable with static solvation models. It suggests that the TS should be treated not as a fixed geometry but as a field-sensitive, solvent-embedded configuration subject to time-dependent forces. Wang *et al.* quantified how different solvent cages modulate recombination *versus* separation in photoredox reactions, providing a kinetic link between solvent structure and product yield.[41] Fig. 2 illustrates how solvent cage dynamics act as directional, time-dependent fields that modulate TS access and reaction outcomes beyond classical linear-response frameworks. Fig. 2(a) outlines the formation and fate of radical ion pairs within solvent cages, emphasizing how solvent structure governs escape *versus* recombination. Fig. 2(b) shows how the cage escape yield (Φ_{CE}) varies nonlinearly across donor–acceptor combinations, defying predictions based on bulk polarity alone. Fig. 2(c) presents a Marcus-type free energy landscape, where solvent-induced asymmetries reshape barrier positions and activation energies. Finally, Fig. 2(d) correlates escape yields with overall reaction efficiency, highlighting the central role of nonequilibrium solvent fields in determining photoredox performance.

This shift in perspective implies that reactivity cannot be fully captured without accounting for solvent–TS feedback: how solvent structure affects the TS, and how the evolving TS in turn modifies the solvent field. Capturing this interplay requires dynamic solvation field models that explicitly couple the nuclear coordinates of the solute with the spatiotemporal evolution of the solvent environment.

The next section will explore the implications of this paradigm shift for interfacial systems, where solvent dynamics and surface interactions intersect in complex, spatially heterogeneous environments.

Interfaces, solvent reorganization, and dynamic heterogeneity

At solid–liquid interfaces, solvent behavior diverges fundamentally from its bulk characteristics. Rather than acting as a homogeneous, inert medium, interfacial solvent layers exhibit spatial structuring, restricted mobility, and directionally dependent interactions. These features lead to a distinct form of dynamic heterogeneity that significantly influences chemical reactivity, particularly in surface-bound processes such as electrocatalysis, redox reactions, adsorption, and surface coordination chemistry.

One of the most striking features of interfacial solvents is their structural layering. Solvent molecules often form quasi-ordered layers in response to surface potentials and the chemical nature of the substrate. Atomic-resolution 3D-AFM (atomic force microscopy) and X-ray reflectivity experiments confirm this behavior at graphite and graphene surfaces, showing 1–3 short-lived hydration layers (≈ 0.3 nm spacing) that can be replaced by hydrocarbon layers upon surface aging—an archetype of dynamically evolving interfacial solvation fields.[3] Uhlig *et al.* visualized this layering using 3D-AFM and MD simulations, showing tightly bound water at hydrophilic surfaces and depleted, loosely organized layers at hydrophobic interfaces.[47] Fig. 3 illustrates how solvent structure and reorganization at solid–liquid interfaces give rise to spatially and temporally heterogeneous solvation environments. Fig. 3(a) compares 3D-AFM and force–distance profiles at a hydrophobic surface, revealing pronounced layering on mica. Fig. 3(b) combines MD simulations and experimental data to demonstrate how substrate-dependent solvent organization translates into distinct local field responses. Fig. 3(c) highlights the temporal evolution of interlayer distances, emphasizing that interfacial solvent structuring is dynamically unstable and highly sensitive to surface history. Together, these observations underscore the limitations of continuum models and highlight the role of fluctuating, anisotropic solvent fields in interfacial reactivity. Nauman and Willard reviewed how these structures lead to steep dielectric gradients and anisotropic polarization effects not captured by classical continuum models.[48] The resulting stratification generates local microenvironments with different dielectric properties, hydrogen bonding capabilities, and reorganization rates. This heterogeneity is

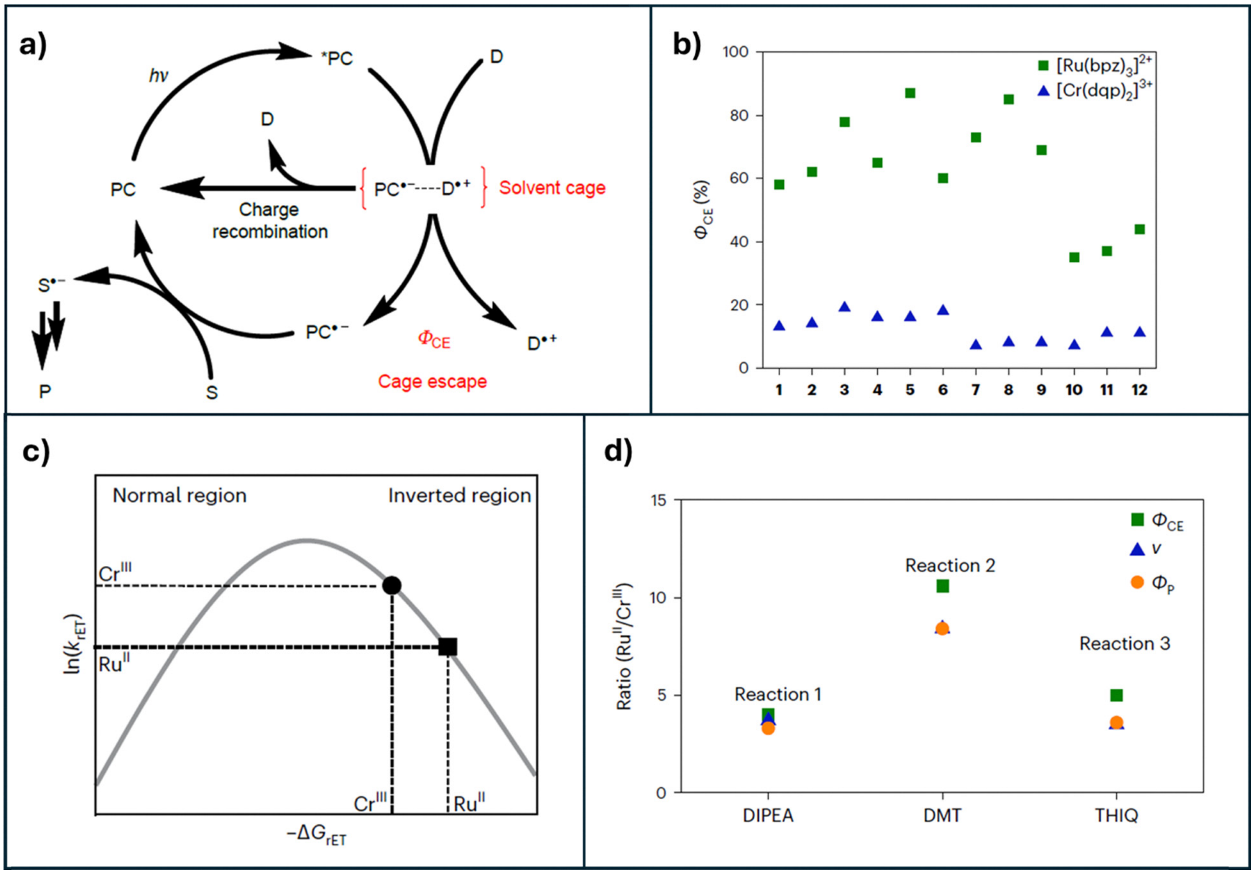

Fig. 2 (a) Catalytic cycle of a photocatalyst (PC) reacting with an electron donor (D) *via* a so-called reductive quenching mechanism (oxidative quenching mechanisms are also common but are not considered here). Following excitation of the photocatalyst, photoinduced electron transfer leads to the reduced photocatalyst and the oxidized donor embedded in a solvent cage. Escape from this solvent cage competes with unproductive thermal reverse electron transfer (charge recombination). Only successful cage escape can lead to productive photoredox chemistry, here electron transfer to the substrate (S), which reacts onwards to the desired product (P) in subsequent (light-independent) elementary reaction steps. (b) Cage escape quantum yields (Φ_{CE}) obtained with $[Ru(bpz)_3]^{2+}$ and $[Cr(dqp)_2]^{3+}$ for the electron donors 1–12 (bpz, 2,2′-bipyrazine; dqp, 2,6-di(quinolin-8-yl)pyridine). (c) Generic Marcus parabola illustrating the dependence of the rate constant for in-cage reverse electron transfer (k_{rET}) on its driving force (ΔG_{rET}). For a given electron donor, in-cage reverse electron transfer with the reduced RuII complex (black square) occurs more deeply in the inverted regime and thus is slower than in-cage reverse electron transfer with the reduced CrIII complex (black circle). (d) Experimentally determined ratios of the cage escape quantum yield (Φ_{CE}), the initial product formation rate (ν) and the initial product formation quantum yield (Φ_P) for $[Ru(bpz)_3]^{2+}$ and $[Cr(dqp)_2]^{3+}$ in the three photochemical reactions using DIPEA (*N*,*N*-diisopropylethylamine), DMT (*N*,*N*-dimethyl-*p*-toluidine) and THIQ (2-phenyl-1,2,3,4-tetrahydroisoquinoline), respectively, as electron donors. Reprinted with permission from Springer Nature, 2024.[41]

not merely static—it actively shapes the energetic landscape for molecular adsorption, ion pairing, and chemical transformation.

Solvent molecules in the interfacial region also experience altered dynamics. Time-resolved VSFG (vibrational sum frequency generation) studies by Nihonyanagi *et al.* have demonstrated that hydrogen-bond reorientation near surfaces proceeds more slowly and heterogeneously than in the bulk.[49] Yuan and Fayer further characterized a boundary layer of interfacial water with reorientation times up to 13 ps, distinct from both directly adsorbed and bulk-like layers.[50] These findings show that interfacial water exists as a layered dynamic ensemble with depth-dependent relaxation timescales. Ryan *et al.* showed that applied electrode potentials can dramatically alter hydrogen-bond lifetimes in water bound to self-assembled monolayers, demonstrating direct control over solvent relaxation by interfacial electric fields.[51]

Such constraints on solvent mobility and reorganization have kinetic implications. Zhang, Stirnemann, and Laage employed an extended jump model to show how electrode polarization suppresses hydrogen-bond exchange at graphene–water interfaces, slowing reorientation dynamics.[52] In complementary simulations, Zhang *et al.* demonstrated that strong electric fields at graphene electrodes can induce spatially extended dipolar ordering of interfacial water layers, altering vibrational response and reorientation timescales.[53] These studies underscore how interfacial electric fields can tailor both the spatial and temporal characteristics of solvent behavior.

Beyond aqueous systems, non-aqueous and mixed-solvent interfaces also exhibit pronounced dynamic heterogeneity. Li *et al.* used AFM to reveal nanostructured, quasi-2D ion aggregates in protic and aprotic ionic liquids at mica surfaces, with extremely slow diffusion compared to the bulk.[54] Schmelz and

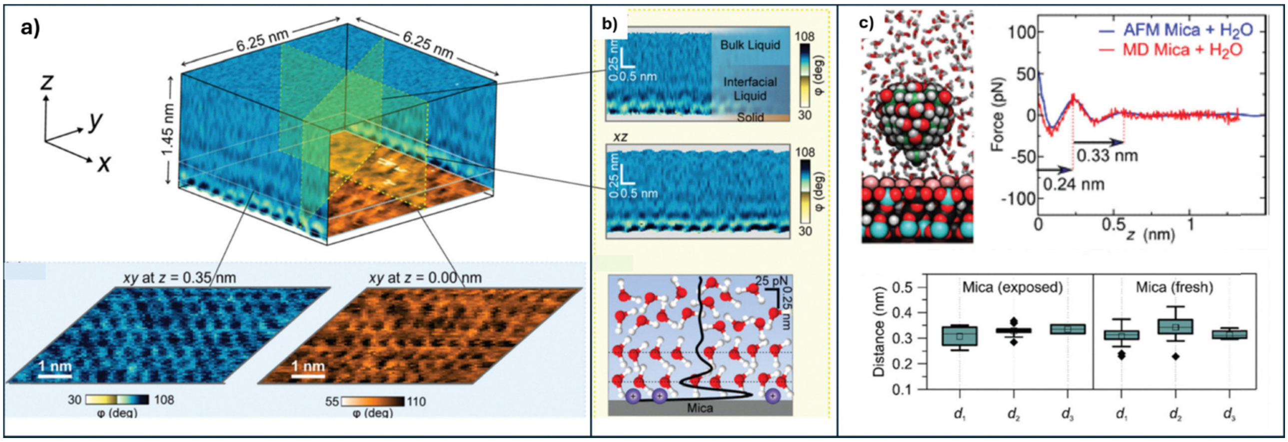

Fig. 3 (a) 3D-AFM image of a solid–water interface. (top) Mica–water interface. The 3D image can be split up into different 2D maps and images. An image of the mica lattice is shown at the bottom. (bottom) 2D images parallel to the mica surface taken at different z distances. Lateral ordering of the water is seen, *e.g.* in the image taken at z = 0.35 nm. ((b), top) 2D maps of the mica–water interface taken at different orientations with respect to the mica basal plane. The maps represent the tip's phase shift as a function of the tip's position ($x_i y_j$, z). ((b) bottom) Force distance curve obtained by processing the xz-panel of ((b), top). (c) Molecular dynamics simulations compared to experiments. MD snapshots of a model AFM tip asperity near a mica–water interface ((c) top left). For clarity, only a cross section of the solvent molecules is shown. Atoms are shown as spheres (H, white; graphite C, gray; other C, green; oxygen, red; K^+, pink; Al, black; Si, cyan). ((c) top right) Comparison between experimental FDCs (function of the distance, blue and grey curves) and MD (red) obtained on a mica surface in water. ((c), bottom) Time-evolution of the interfacial water structures on mica. Interlayer distances of purified water on mica (box plots). The interlayer distances do not depend on the time the mica surface was exposed to ambient air. All the values are centered around 0.32 nm. Reprinted with permission from The Royal Society of Chemistry, 2021.[47]

colleagues showed *via* SFG (sum frequency generation) spectroscopy that in ''water-in-salt'' electrolytes, the interfacial solvent composition shifts rapidly with applied potential, favoring weakly bonded over hydrogen-bonded water in a potential-dependent manner.[55] These studies illustrate how even subtle changes in interfacial composition or bias can restructure solvent coordination and reorganizational dynamics.

Together, these observations confirm that interfacial solvent layers are not passive but dynamic agents. Their structural and dynamic heterogeneity affects not only local solvation environments but also the kinetics of bond making and breaking at surfaces. Magnussen and Groß have emphasized the need to integrate transient, collective solvent rearrangements into mechanistic models of interfacial catalysis and electrochemistry.[56] Understanding and controlling solvent behavior at interfaces thus holds the key to designing responsive, efficient, and tunable interfacial reaction systems.

Modeling dynamic solvation: from AIMD to field theory

Capturing dynamic solvation requires theoretical models that go beyond static parameters like polarity, dielectric constant, or donor number. Conventional continuum solvation models, while useful for estimating equilibrium free energies, are fundamentally limited in describing time-dependent solvent–solute interactions, solvent fluctuations, and spatially resolved solvation environments. To address these challenges, recent years have seen the development of multi-scale modeling frameworks that range from atomistic to coarse-grained, and even field-theoretic descriptions, each offering distinct insights into the evolving nature of solvation.

At the atomistic level, AIMD remains a cornerstone for studying solvation phenomena with quantum mechanical accuracy. Herron *et al.* used AIMD to model methanol oxidation on solvated Pt(111), showing how explicit water stabilizes charged TSs and lowers bond cleavage barriers under applied potentials.[57] Similarly, Zederkof *et al.* applied nonadiabatic dynamics to an iron complex in water, revealing solvent reorganizations on ∼50 fs timescales that strongly influence excited-state relaxation.[36] These studies highlight how AIMD can resolve solute–solvent coupling on ultrafast timescales and under reactive conditions.

To extend simulation timescales, hybrid schemes like QM/MM provide a balance between quantum accuracy and system size. Boereboom and co-workers benchmarked several QM/MM protocols on a nucleophilic addition, showing that adaptive dual-sphere QM/MM models correctly capture solvent rearrangement along the reaction coordinate.[58] Duster *et al.* further reviewed adaptive QM/MM techniques, which allow for dynamic redefinition of the QM region, especially important in aqueous systems where solvation shells evolve during bond formation or proton transfer.[59] Using large-scale nonadiabatic VC/MM (vibronic coupling/molecular mechanics) dynamics simulations of $[Fe(CN)_4(bipy)]^{2-}$ in explicit water, Polonius *et al.* resolved ultrafast, anisotropic solvent reorganization on sub-100 fs timescales, revealing a directed hydrogen-bond migration mechanism driven by evolving electronic states. The work exemplifies how modern trajectory-based approaches can capture coupled solute–solvent dynamics in full spatial and temporal resolution, surpassing the capabilities of traditional

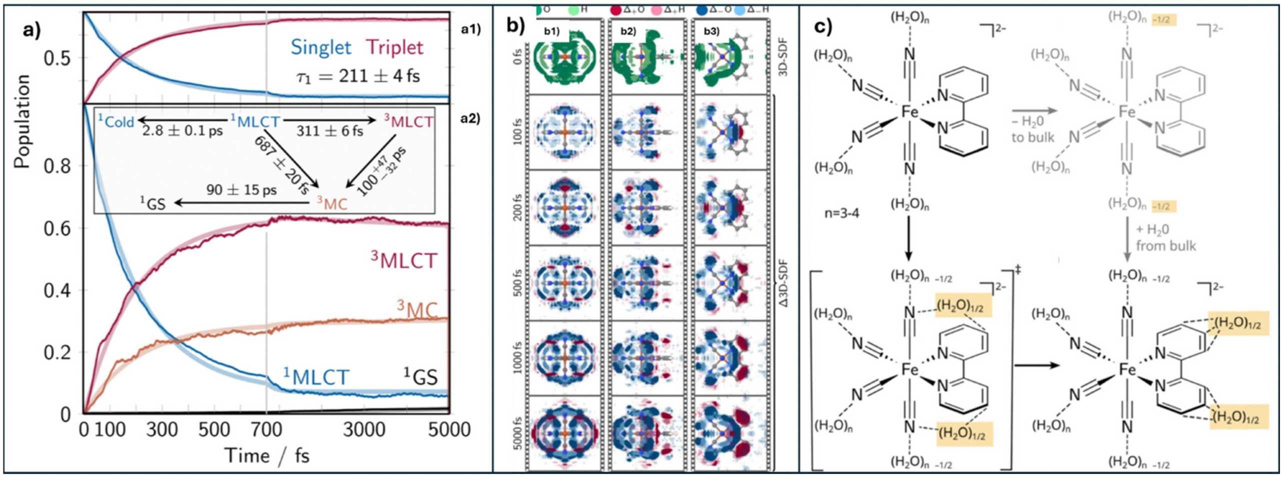

Fig. 4 (a) Time-resolved electronic population dynamics. (a1) Total singlet and triplet populations (thin lines) and corresponding mono-exponential fits (thick semitransparent lines). (a2) Time-dependent diabatic populations (thin lines) for the ground state (GS, black), the 1MLCT states that was excited into (blue), the 3MC states (orange), and the 3MLCT states comprising all other triplet states (majorly MLCT character, red). The thick lines indicate the global fitting results from the shown kinetic model. (b) Symmetry-adapted three-dimensional spatial distribution functions (3D-SDFs) of water oxygen and hydrogen atoms at $t = 0$ fs and time-dependent difference 3D-SDFs thereafter. In all panels at $t = 0$ fs, spatial regions with an occurrence higher than 2.5 times the average are colored green for oxygen atoms and light green for hydrogen atoms. For the D3D-SDFs at $t > 0$ fs, the iso value is set to 0.5 and 0.3 times the average with solid and shaded colors respectively; positive deviations are colored with red colors and negative deviations with blue colors with oxygens in the darker and hydrogens in the lighter shade. Panels (b1)–(b3) show different orientations of the system. (c) Schematic representation of the initial hydrogen bonding state of $[Fe(CN)_4(bipy)]^{2-}$ in the ground state (upper left)—with three to four hydrogen bonds per cyanide—and the rearrangement (top right and bottom left) and final hydrogen bonding state (bottom right) in the 3MLCT states. The upper right pathway shows a hypothetical bulk exchange mechanism, whereas the lower left pathway illustrates the direct migration pathway found for $[Fe(CN)_4(bipy)]^{2-}$. Reprinted with permission from The Royal Society of Chemistry, 2025.[60]

continuum or RDF-based (radial distribution functions) models.[60] Fig. 4 illustrates how advanced nonadiabatic dynamics simulations reveal the field-like nature of solvent reorganization around electronically excited species. Fig. 4(a) shows the evolution of electronic state populations in a photoexcited iron complex, where ultrafast intersystem crossing is accompanied by a rapid solvent response. Fig. 4(b) presents time-resolved solvent density maps, capturing the directional migration of water molecules in response to the changing solute charge distribution. Fig. 4(c) schematically highlights the mechanism of solvent field reorganization, driven by concerted hydrogen-bond switching rather than stochastic diffusion. Together, these insights demonstrate that solvent reorganization is an active, state-specific process—breaking the assumptions of linear response and equilibrium solvation models.

Beyond individual trajectories, statistical sampling techniques such as umbrella sampling and metadynamics are frequently used to reconstruct free energy profiles of solvent-coupled reactions. However, they depend critically on the quality of the underlying force field or electronic structure method.

To describe collective solvent behavior over longer timescales, classical MD with polarizable or reactive force fields has become essential. Zhang and van Duin introduced a second-generation ReaxFF (reactive force-field) model for water that accurately captures OH^- diffusion, proton transfer, and dielectric relaxation, enabling simulations across a broad pH range.[61] Schröder and Heid reviewed such techniques in detail, emphasizing validation strategies and best practices for computing solvation time correlation functions and linking them to spectroscopic observables.[62]

At the mesoscale, coarse-grained and field-theoretic models provide a complementary view. Peter and Pivkin developed a polarizable water model for dissipative particle dynamics that reproduces dielectric screening and ionic response under electric fields.[63] In parallel, Pipolo *et al.* reformulated the polarizable continuum model to include real-time solvent polarization dynamics, enabling time-resolved simulations of solvent relaxation following photoexcitation.[64] A more recent field-based method by Li *et al.* combines dynamic density functional theory (DFT) with orientational polarization fields, capturing the heterogeneous response of polar solvents around a suddenly charged solute.[65]

Machine learning is emerging as a powerful tool across all these scales. Schran *et al.* trained DeepMD neural network potentials on aqueous interfaces and ion solvation systems, achieving DFT-level accuracy for complex solvent dynamics at greatly reduced cost.[66] Their models were validated on metal–oxide interfaces, capturing both structural layering and time-resolved hydrogen-bond dynamics.

Overall, modeling dynamic solvation requires a layered approach that bridges molecular detail with collective behavior. While AIMD and QM/MM elucidate short-time, local interactions, classical MD and field theories reveal longer-time and spatially extended features of solvent structure and response. Together, these tools are enabling a shift from static solvation models toward dynamic, multiscale representations that better reflect the fluctuating, field-like nature of the solvent environment in real chemical systems.

Toward a general theory of dynamic solvation fields

Recent advances across experimental and computational studies have revealed that solvent effects are neither instantaneous nor homogeneous, but rather spatially and temporally structured. Time-resolved spectroscopy, interfacial characterization, and multiscale simulations all converge on a common insight: solvent–solute interactions evolve dynamically, exhibit local heterogeneity, and respond nonlinearly to chemical perturbations. These observations increasingly challenge the traditional frameworks used to describe solvation in chemistry.

Conventional models typically treat solvent influence in terms of static parameters—such as dielectric constant, polarity indices, or reorganization energy—embedded within linear response formalisms. These simplifications, while powerful for interpreting bulk-phase reactions, often fail when applied to heterogeneous environments, nonequilibrium processes, or strongly coupled solvent–solute systems. In such scenarios, the solvent cannot be meaningfully described by averaged properties alone; instead, its dynamical organization becomes the critical factor modulating reactivity. Havenith emphasized this paradigm shift by proposing a bottom-up, molecular-level description of solvation, where the solvent acts as an active participant rather than a passive background.[9]

A more general theoretical framework is thus required—one that conceptualizes solvent effects not as scalar descriptors, but as spatiotemporal fields that evolve in tandem with molecular transformations. Orr-Ewing provided a detailed review showing how fluctuating solvent environments alter reaction dynamics in solution, including coupling to the reaction coordinate, solvation cage effects, and restructuring of solvent shells during chemical transformations.[14] Within such a framework, solvation is characterized by fluctuating polarization, density, and hydrogen-bond configurations, each possessing intrinsic length scales, relaxation times, and directional biases. These fields must be treated as dynamically coupled to the reaction coordinate, especially in cases where barrier crossing depends on local solvent rearrangement or when the timescales of solvent relaxation and chemical change are comparable.

Emerging theoretical frameworks offer promising approaches. Kirchberg *et al.* extended Onsager's model by introducing a time-dependent solvent cavity, allowing dynamic variations in dielectric response to influence dipole relaxation and friction.[67] Dubey, Stuyver, and Shaik have similarly proposed that local electric fields—arising from solvent molecules, proteins, or catalysts—function as dynamic forces that actively modulate TS energetics.[68] Meanwhile, Lu and Zhong demonstrated experimentally that nonequilibrium solvent fluctuations can synchronize with ultrafast electron transfer events, enhancing reaction rates and challenging classical Marcus theory.[39]

To describe solvation beyond static models, Huang *et al.* introduced the interaction-reorganization solvation (IRS) framework, decomposing solvation into direct solute–solvent interactions and solvent structural reorganization, both accessible through explicit MD simulations.[69] This approach captures time-dependent solvent restructuring as an intrinsic component of reactivity.

Despite these advances, substantial theoretical challenges remain. A predictive model of dynamic solvation would require coupling solvent fields to reaction pathways in a self-consistent manner—accounting for nonlinearity, memory effects, and the breaking of local equilibrium. It must also integrate multiple length and timescales, from fs fluctuations to long-range structuring. Perhaps most importantly, it must remain general enough to apply across solvents, interfaces, and reaction types.

The conceptual transition from static parameters to dynamic solvation fields represents more than a theoretical refinement—it redefines how solvent effects are understood and modeled in chemistry. It opens a path toward a new class of solvent descriptors: field-based, multiscale, and inherently dynamic. The implications for reaction design, catalysis, and materials processing are significant. Yet realizing this vision will require not only conceptual innovation but also methodological integration between simulation, theory, and experiment.

Outlook: opportunities and open questions

The recognition of solvation as a dynamic, field-like phenomenon marks a conceptual turning point in the theory and application of solvent effects. This perspective has outlined how experimental evidence, interfacial studies, and multiscale modeling collectively support a departure from classical static descriptors in favor of time-dependent, spatially resolved frameworks. Yet the transition to a fully predictive and mechanistically grounded theory of dynamic solvation is only just beginning. Several key opportunities and open questions merit particular attention.

(1) Toward universal solvent field descriptors: despite recent progress, there remains no standardized set of dynamic solvent descriptors capable of replacing traditional parameters like dielectric constant or polarity. Future work must identify measurable quantities—such as time-resolved polarization fluctuations, local electric field vectors, or dynamic coordination numbers—that can serve as transferable, context-sensitive solvent descriptors across chemical systems. Yu *et al.* highlighted how real-time visualization of solvation processes could provide access to such dynamic properties.[70] (2) Linking solvent dynamics to chemical kinetics: it remains challenging to directly correlate fluctuating solvation environments with observable reaction rates or product distributions. Bridging this gap will require novel kinetic theories that incorporate delayed solvation response, solvent memory effects, and the statistical nature of rare solvent configurations. Ilgen *et al.* suggested the use of probabilistic field representations of interfacial properties to account for these

dynamic fluctuations in reactivity models.[71] (3) Interface-specific solvation theories: interfaces introduce extreme gradients in electric fields, coordination environments, and molecular mobility—making them a critical testbed for dynamic solvation theories. However, current models often treat the solvent response at interfaces using bulk-like or continuum approximations. Zhang *et al.* emphasized the importance of incorporating explicit solvation and potential-dependent effects when modeling interfacial dynamics on single-atom electrocatalysts.[72] (4) Experimental probes of solvent fields: advances in time-resolved spectroscopy, nonlinear optics, and interfacial X-ray methods now allow for increasingly precise measurements of solvent orientation, mobility, and polarization under reactive conditions. Hunt reviewed progress in ultrafast IR and multidimensional spectroscopy, predicting that real-time visualization of solvent reorganization across fs to ms timescales will soon become routine.[73] (5) Integration with data-driven methods: machine learning presents an opportunity to reverse-engineer solvent field characteristics from molecular trajectories, spectroscopic data, or reaction outcomes. Zhang *et al.* and others have proposed combining field-theoretical models with data-driven force fields to better simulate interfacial phenomena and guide solvent or catalyst design.[72,74] (6) Solvent design beyond bulk properties: a dynamic field view of solvation opens the door to solvent design strategies that target not only bulk properties but also time-dependent behaviors. Tailoring relaxation timescales, directional field effects, or coordination fluctuation spectra may allow for more precise control of reaction pathways, surface processes, and self-assembly dynamics.

In summary, the conceptual shift from static solvent parameters to dynamic solvation fields has far-reaching implications across chemical theory, catalysis, materials design, and spectroscopy. Realizing its full potential will require close coordination between theoretical innovation, experimental validation, and computational refinement. The groundwork has been laid—but the construction of a general, predictive theory of dynamic solvation is an open and exciting challenge for the coming decade.

Author contributions

The author confirms sole responsibility for conceptualization, literature analysis, writing, and revision of the manuscript. Text editing and structural suggestions were supported by ChatGPT (OpenAI, ChatGPT Plus, version 4o), with all material reviewed and approved by the author.

Conflicts of interest

There are no conflicts to declare.

Data availability

No new data were created or analysed in this study. Data sharing is not applicable to this article.

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