

Solvation of Nanoscale Materials

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ABSTRACT: The utility of colloidal nanomaterials in energy storage devices, high-definition displays, and industrial coatings depends on their solution processibility and stability. Traditional theories of solvation and colloidal stability, namely Derjaguin-Landau-Verwey-Overbeek (DLVO) and Flory-Huggins theories, describe classical approaches to solvation and colloidal stability of hard-shell colloids and macromolecules, respectively. In contrast, the solution-state behavior of polymers, proteins, and related macromolecules must be understood in terms of solvent interactions, which become especially important due to the accessible cavities of hydrophobic and hydrophilic moieties in these systems. The colloidal stability of permanently porous materials, such as nanoparticles of metal-organic frameworks (nanoMOFs), on the other hand, challenges conventional notions of colloidal stability due to the presence of both internal and external surfaces, and because their external surfaces are mostly empty space. To develop nanoMOFs and other porous colloids into useful materials, we must understand the solvation of porous interfaces. Here, we discuss classical models of solvation and colloidal stability for non-porous and pseudo-porous (proteins and polymers) materials as a basis to propose that the colloidal stability of porous materials likely involves self-assembled solvation shells and strong solvent interactions with the molecular components of the nanomaterial.

INTRODUCTION

The solvation of nanoscale materials challenges basic notions of dissolution and colloidal stability. Take for example, a 5 nm metal-organic framework (MOF) nanoparticle of Zn(2-methylimidazole)₂ dispersed in *N,N*-dimethylformamide (DMF).^{1,2} The particles remain stable in solution without the need for surface ligands to protect against particle aggregation and retain their sizes for weeks or months. In any case, attempts at surface functionalization would face the challenge that MOF particles are mostly empty space. Instead, they readily disperse into a select group of solvents with one commonality: they are the only solvents to dissolve the building blocks of the MOF and small enough to squeeze into the pores. Unlike a 5-nm quantum dot that demands careful surface functionalization for colloidal stability, the solvation behavior of a MOF nanoparticle more closely resembles the dissolution of a 5 nm protein or polymer. This example begs the questions: *Are porous nanocrystals dissolved or colloidal suspensions? What does surface even mean?* MOF nanoparticles are not alone. In solution, the behavior of systems ranging from polyoxometalate clusters and proteins to carbon nanotubes and zeolite nanoparticles becomes inextricably linked to solvation structure and dynamics. In this Perspective, we outline current theories for understanding solvation and colloidal stability, highlight their points of tension, and how a combination of these concepts might help explain the peculiar behavior of solvated nanoscale materials and why it matters.

1. SOLVATION AT NON-POROUS INTERFACES

1.1 Colloidal Stability and Solvation

In the 1940s, two teams of researchers independently studied the forces contributing to particle colloidal stability. Boris Derjaguin and Lev Landau in the Soviet Union presented their theory of colloidal stability that invoked short-range van der Waals attractions between particles overcome by electrostatic surface repulsions.³ While the electrical double layer had previously

been introduced by Hermann von Helmholtz (1853),⁴ Louis Georges Gouy (1910),⁵ David Leonard Chapman (1913),⁶ and Otto Stern (1924),⁷ Derjaguin and Landau pioneered the notion of electrostatic potentials at curved interfaces where the surface electric field decays as a function of the particle radius. Meanwhile, in the Netherlands, Evert Verwey and Theodoor (Jan) Overbeek developed the now-ubiquitous potential energy curves of two interacting spherical particles as a function of interparticle distance and electrolyte concentration.^{8,9} Ultimately, a model of the forces governing nanoparticle stability in solution was named DLVO theory for the four authors involved.¹⁰ DLVO theory has been thoroughly derived to describe the colloidal stability of hard-shell nanoparticles in a variety of electrolyte concentrations,^{11,12} surface charge composition,^{13,14} solvent environments,¹⁵ and many other scenarios.^{15–20} For the purposes of this perspective, DLVO theory can be summarized by Eq. 1:

$$W(D) = W_{vdw} + W_{elec} \quad (1)$$

where $W(D)$ represents the interaction energy between neighboring particles, W_{vdw} is the attractive energy due to van der Waals interactions and W_{elec} is the repulsive electrostatic energy (Figure 1A). The entropy and steric pressures of the system have been incorporated into extended DLVO theory (XDLVO)^{21,22} as described by Eq. 2:

$$W(D) = W_{vdw} + W_{elec} + W_{osmotic} + W_{entropic} \quad (2)$$

where the addition of the $W_{osmotic}$ term accounts for the repulsive energy caused by neighboring nanoparticles with an increased overlap region (typically due to increased surface sterics), while the $W_{entropic}$ term accounts for the attractive energy arising from an increase in solvent entropy upon particle coalescence. This entropy-driven aggregation is often termed the hydrophobic effect.

Although developed as a general model, DLVO theory applies best to “hard” colloidal systems, such as colloidal quantum dots, core-shell metallic nanoparticles, or metal oxides with well-defined boundaries between the nanoscale object and the

suspending solution. Whereas hard-shelled colloids maintain their rigidity in solution, “soft-shelled” particles stretch and adapt to nearby fluid interfaces (Figure 1B).^{23–26} Hard-shell particles are convenient systems to study as short-range van der Waals interactions decay exponentially as a function of distance from the particle without the need to consider interfacial charge-screening. On the other hand, soft-shell particles, such as oil droplets, metal nanoparticles coated with a polymer layer, proteins clusters, and even living cells,²⁷ present complications to DLVO theory as solvent intercalation, ion adsorption,²⁸ spontaneously ordered solvation shells, and surface roughness,¹⁷ together comprising so-called “non-DLVO forces”. Experimental attempts to bridge these two types of systems, such as core-shell colloids with soft exteriors and hard interiors,^{23,29} impart improved thermodynamic stability and, in some cases, unique optical behavior.^{30,31} Theoretical models of such systems account only for the hard-soft interface, while neglecting the possibility of low density and heterogeneous surfaces and their associated energetics.

According to the IUPAC definition, a colloid involves a “molecule or polymeric particle dispersed in a medium” with “at least in one direction a dimension roughly between 1 nm and 1 μm”.³² Examples of colloids include a solid in a gas (smoke), a liquid in a gas (aerosol), or a liquid in a liquid (emulsion), in addition to many other dispersion types that do not require solvent as a medium. Understanding the stability of heterogeneous mixtures in solution is critical to their implementation

in displays, coatings, or membranes, but the clear phase boundary creates significant challenges because of the difficulty in studying the chemistry that emerges at the colloidal interface. The process of dissolution, by contrast, involves the formation of a single, homogeneous phase.³³ Unlike solutions, the heterogeneity of colloidal dispersions creates thermodynamic instability resulting in their eventual phase separation. Suspended particles can be filtered out or mechanically separated, whereas separating dissolved particles requires additional chemical transformations.^{34,35} In the following sections, we provide a brief overview of the chemistry underlying the colloidal stability of non-porous inorganic nanoparticles with and without functionalized surfaces, and how it critically involves solvent.

1-2. Capped Colloidal Nanoparticles

Nearly all non-porous inorganic nanoparticles require surface functionalization for long-term stability. The strong van der Waals attractions between bare metallic surfaces results in nearly instantaneous aggregation and sedimentation. Semiconductor nanocrystals, specifically quantum dots, the topic of the Nobel Prize in Chemistry in 2023,^{36,37} represent another key example of nanoparticles that find utility only by surface functionalization. Through favorable interactions with solvent, surfactant ligands to prevent Ostwald ripening,^{38,39} allowing nanoparticles to remain stable at precise sizes that dictate their tunable

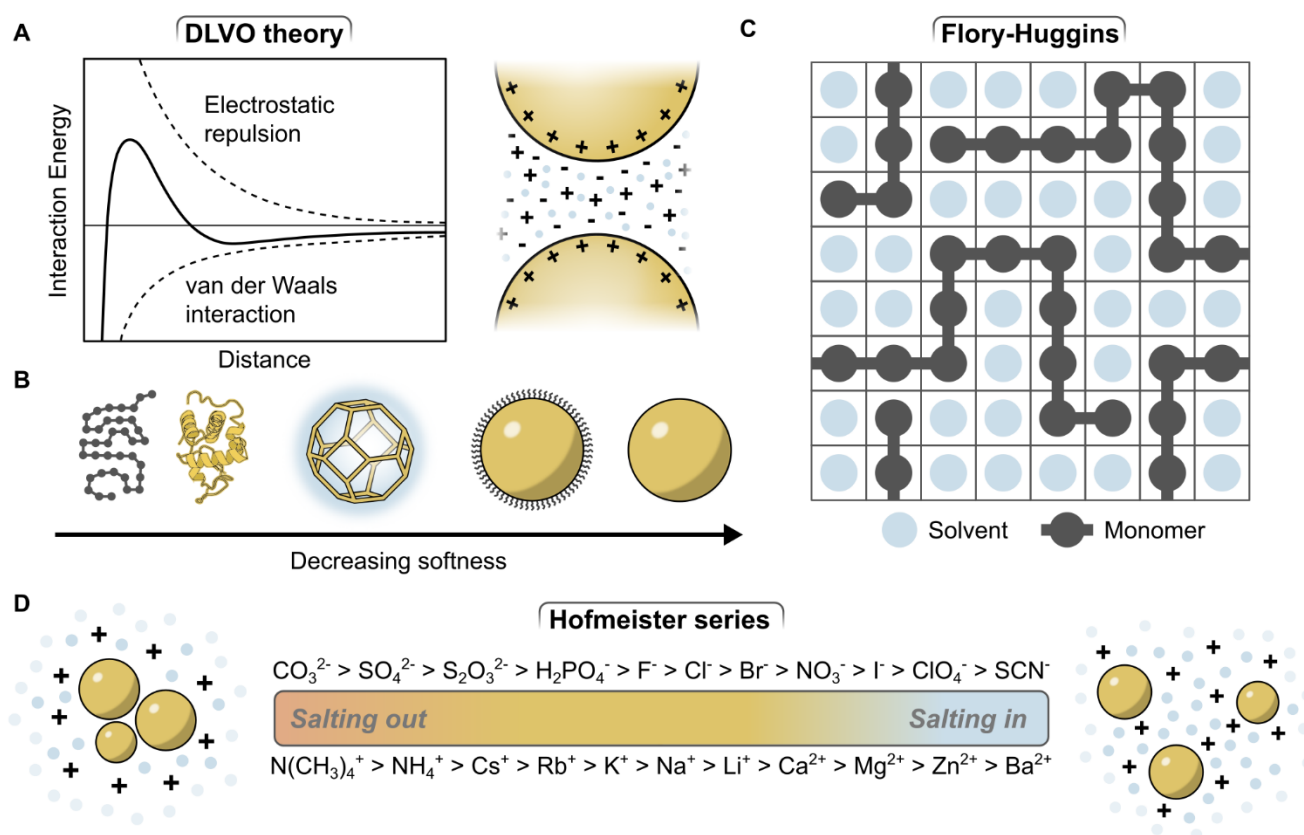


Figure 1. A) Typical DLVO graph, showing the interaction energy as a sum of electrostatic repulsion and attractive van der Waals interactions. B) Illustration of the soft-to-hard range of nanoscale materials, ranging from polymers/proteins to hard spheres, such as metal-oxide nanoparticles. C) The lattice model of polymer solvation as described by Flory-Huggins theory. D) Illustrations and ion examples in relation to the Hofmeister series of solvation.

optical properties.^{40–42} Functionalizing quantum dots with either a inorganic shell also diversifies the available solvents for dispersion.^{43,44} Most notably, the addition of water-soluble ligands, such as citrates,⁴⁵ polymers,^{46,47} or other small molecules^{48,49} allows for the use of metallic nanoparticles within cellular media. A wide variety of ligands have been studied for their interaction with various solvent media.^{50,51} By contrast, nearly all porous colloidal materials, as described below, require no surface functionalization for colloidal stability. Therefore, for context, we must understand the mechanism of colloidal stability for nanoparticles prepared without capping agents.

1-3. Bare Nanoparticle Solvation

Few reports have documented bare nanoparticles exhibiting long-term colloidal stability. The examples described below are restricted in their industrial applications due to highly defective surfaces, the necessity of a stabilizing supporting material, and the need for post-synthetic cleaning or filtration. For example, while it has been shown that metallic nanoparticles can be stabilized by a partially oxidized surface,⁵² this chemical decomposition generates a heterogeneous and rough surface with mixed valence sites.^{53,54} An alternate approach that avoids surface oxidation was achieved by synthesizing bare copper nanoparticles with an electron-donating gadolinium support.⁵⁵ Implementing nanoparticles in biological sensing applications cannot be achieved, however, with a bulky and potentially toxic supporting material. Another approach involves “sterilization” of bare gold nanoparticles by autoclave.⁵⁶ Studies suggest that < 5-nm particles assemble into larger 10-30 nm particles during this process. This size-focusing serves as a form of filtration to achieve a narrow size dispersity, but size selection does not always ensure colloidal stability.⁵⁷ Because these few examples of bare nanoparticles are short-lived colloids, they are often quickly drop-casted back to their solid state.^{58–61}

In the few studies of bare metallic nanoparticles in solution without a stabilizing support, the ionic structure of the supporting electrolyte and the resulting electrical double layer at the surface has proven to be a key, but poorly understood feature contributing to colloidal stability. Simulations suggest that facet-specific ion adsorption and an ordered primary solvation shell promote gold nanoparticle stability in water.^{54,62} Experimental studies also suggest water stability of bare nanoparticles arises from ion adsorption dependent on electrolyte concentration and following the so-called Hofmeister series for anions.^{56,63–65} The colloidal stability of nanoparticles in solvents without electrolyte, however, have only been studied as computational simulations of bare particles⁶⁶ or through weakly ligated experimental systems where a portion of the surface remains deliberately exposed.⁶⁷ Thus, achieving a metal nanoparticle colloid stabilized by solvation forces alone remains an open challenge and would open an avenue for tuning the opto-electronic and electrochemical electrical properties of metallic nanoparticles in a wide variety of solutions. To understand the colloidal stability of bare nanomaterials, therefore, we instead turn to the supramolecular solvation chemistry of polymers and proteins.

2. SOLVATION AT PSEUDO-POROUS INTERFACES

2-1. Polymer Solubility

At nearly the same time that Derjaguin, Landau, Verwey, and Overbeek developed their model of colloidal stability, Paul

Flory and Maurice Huggins independently considered how polymers could dissolve despite distinct differences in molecular size from the surrounding solvent.^{68,69} While the entropy of mixing a simple molecule in solution can be described by Gibbs energy of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \quad (3)$$

where H is enthalpy, T is temperature, and S is entropy, this relationship only considers the gross interaction between a molecule and its surroundings. It neglects synergistic behavior between individual units within a chain, such as in a polymer (Figure 1C). Flory and Huggins adapted the Gibbs energy of mixing for polymers as:

$$\Delta G_{mix} = RT(n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}) \quad (4)$$

which now considers the number of moles (n_i) and the volume fraction (ϕ_i) of the solvent (component 1) and polymer (component 2). χ_{12} is material-specific and describes the synergistic interaction between the polymer and the solvent, allowing for specific descriptions of polymer solubility.

We introduce the term “pseudo-porosity” to describe the solvation of polymers and related systems. While polymers lack permanent porosity (the ability to maintain a rigid, porous structure when suspended in solution), their solvation mechanism depends on the large solvent accessible surface areas carved out by the wrapping of individual monomer units. In Flory-Huggins theory, a polymer solution is modeled as a lattice of cells containing either polymer monomer units or a solvent molecule. Based on this image, the individual mixing components of a monomer unit with the polymer is well described by equation 4. However, realistic intermolecular forces from hydrophobicity,⁷⁰ ionic screening,⁷¹ and other polymer or solvent-specific interactions^{72,73} integral to solvation and polymer conformation are absent from eq. 4.

In addition to the pseudo-porosity of conventional polymers, intrinsically porous polymers and porous polymer membranes also exist. Typical examples of porous polymer membranes include polycarbonate, polyester, or cellulose with pore diameters ranging from nanometers to 10s of μm s. The narrow, one-dimensional confinement of these pores within a membrane have led to a versatile platform for studying solvent-controlled ion-transport under spatial confinement akin to the ion-transport across cellular membranes and carbon nanotubes.^{74,75} Chemical functionalization of these materials leads to specific ion effects, such as appended carbonate groups showing preferential binding of metal cations.⁷⁶ Polymers of intrinsic microporosity (PIMs), on the other hand, contain voids of 2 nm or less.⁷⁷ Controlling the solubility of PIMs is critical for creating robust films with consistent pore sizes.⁷⁸ The commonly used PIM-1, however, dissolves only in tetrahydrofuran (THF) and chloroform (CHCl_3), leading to reduced solution processability and restricting the incorporation of fillers or other composites. Recent work has introduced post-synthetic modifications of PIMs to improve their solubility,⁷⁹ with the key result that specific solvent interactions with appended moieties improves solubility. In understanding the solvation of porous materials discussed in Section 3, these reports of porous polymers offer the insight that solution stability of nanoscale materials benefits from monomer units accessible to solvent.

2-2. Hydration of Proteins

Proteins comprise another class of macromolecules whose solvation depends on solvent interacting with accessible building

blocks, yet with the added compositional diversity of amino acid mixtures and H-bonding networks. For proteins, solvation can be described as monomer-by-monomer solubility or by secondary structure solvation via protein folding to bury hydrophobic moieties. As a result, proteins arrange into secondary structures, like helices or sheets, and fold into native states to satisfy solvent interactions with their respective amino acid chains. Numerous studies have quantified surface interactions between proteins and water in solution,^{80,81} with one notable computational investigation into the hydrogen bonding of a protein in water as a function of solvent accessible surface area and protein conformation.⁸² These authors report that the solvation free energy of a protein decreases linearly as a function of the solvent accessible surface area of the protein. This finding suggests that an increase in the surfaces available for solvation promote stability in solution. As the basis of Flory-Huggins theory, leveraging enthalpically favorable solvent-material interactions is critical for solubility and stability. In a permanently porous material, as explained below, the unparalleled solvent accessible surface areas provide increased sites for solvation interactions via internal and external surfaces.

The unique folding ability of a protein allows it to adapt to an otherwise thermodynamically unstable environment. In contrast, porous framework materials, such as metal-organic frameworks (MOFs), cannot protect select components by geometrical reconfiguration. Protein folding or unfolding can be induced by addition of ions that “salt-in” or “salt-out” the macromolecule of interest (protein, polymer, nanoparticle, etc.) *vis-à-vis* the Hofmeister series (Figure 1D). Ion specific effects in protein precipitation was introduced by Franz Hofmeister in the late 1880s to describe how different salts impact the solubility of proteins despite possessing the same net charges.^{83,84} Kosmotropes, or “structure-makers” are ions that interact more strongly with water than with the protein themselves, causing the protein to remain in its native folded state and salt-out of solution. Common examples of kosmotropes include citrate, sulfate, and phosphate anions or magnesium, calcium, or lithium cations. On the other hand, chaotropes, or “structure-makers” interact closely with individual protein units, promoting an unfolded, solubilized state of the protein. Chaotropes include iodide, nitrate, and tetrafluoroborate anions or calcium, magnesium, and aluminum cations. Polyoxometalates (POMs), for example, are super-chaotropes due to their large, delocalized charge and low surface densities.⁸⁵ While Hofmeister’s initial experiments provide a basis for harnessing specific-ion effects, recent work has produced a more detailed understanding of salts and their impact on colloidal stability and solubility, especially cooperative contributions from ion pairs.^{86–89} Vibrational spectroscopy and molecular dynamic simulations reveal that cations follow the Hofmeister series through strong backbone-salt interactions and weaker interactions with negatively charged side chains.⁹⁰ Anions, however, despite following the Hofmeister series at the backbone, exhibit a reversed trend on positively charged amino acid residues. For this reason, the Hofmeister series for anions holds only when the backbone-salt interactions outweigh the salt interactions with side chains. Tuning the colloidal stability of metal-based nanoparticles requires understanding the specific-ion effect in solvents beyond water.^{91,92} A comprehensive study of the ion effects in non-aqueous solvents found that water is not unique in its role in the Hofmeister series.⁹³ In fact, aprotic solvents also show an ion specificity due to the inherent molar volume and electrostriction of the ion, or the ability of the ion to slightly deform. These results confirm

that a Hofmeister trend persists regardless of solvent identity, thereby providing a basis for tailoring the colloidal stability of non-aqueous materials.

Specific ion effects are critical to the colloidal stability of bare nanoparticles. In one study, gold nanoparticles without any organic ligands at the surface were stabilized by as little as 10 μM of a chaotropic anion.⁶³ The electrolyte solutions were added during nanoparticle synthesis, thereby acting as a non-organic capping ligand. Additional electrolyte may destabilize colloids, however. Reports indicate that increasing salt concentration to the mM regime often leads to nanoparticle aggregation, as exhibited by metallic nanosheets titrated with potassium salts of varying valency anions⁹⁴ and other metal nanoparticles.^{95,96} A likely cause is that with increased salt concentrations electrolyte ions screen the effective charge density that normally prevents aggregation. Nevertheless, tuning salt concentrations could serve as a promising strategy for controlling the solvation of porous nanoparticles with bare surfaces.

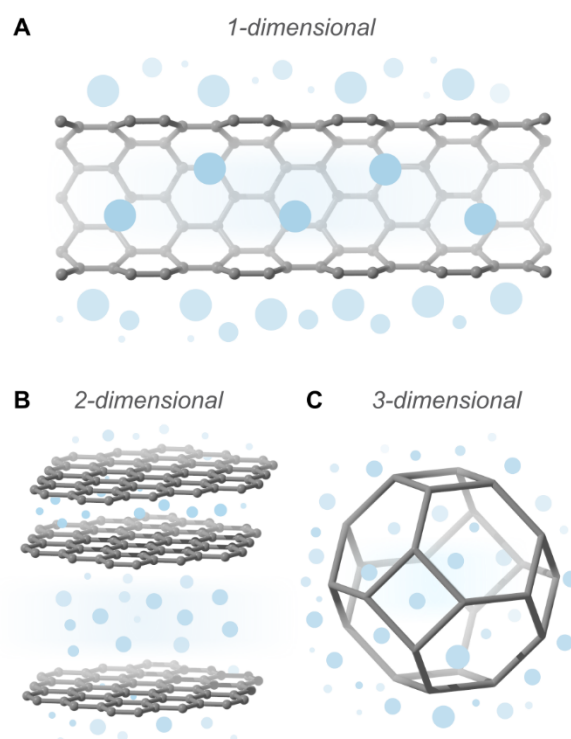


Figure 2. Illustration of (A) 1-dimensional (polymers, nanotubes), (B) 2-dimensional (layered or sheet-like materials) and (C) 3-dimensional structures (porous materials) and their possible solvent interactions.

3. SOLVATION AT POROUS INTERFACES

To understand the solubility and stability of porous colloids, we suggest using the aforementioned models of solvation, namely electrostatic or steric repulsion, the hydrophobic effect, monomer-by-monomer solubility, and specific ions interactions. By possessing both internal and external surfaces, porous colloids exhibit surface area-to-volume ratios and accessible void spaces far exceeding any class of non-porous or pseudo-porous material.⁹⁷ For example, the surface density of the commonly studied zeolitic imidazolate framework ZIF-8 ($\text{Zn}(\text{2-methylimidazolate})_2$), has a surface density of 7 atoms/ nm^2 while non-porous ZnO has a surface density of 78 atoms/ nm^2 . Additionally, as

illustrated by the example above, the internal and external surfaces of porous materials resemble the heterogeneous surfaces of proteins. We expect the surface of porous materials to be susceptible to specific solvent-surface interactions as opposed to generalized hard-shell interactions between a homogeneous nanoparticle surface or surfactant ligands and the supporting solvent. In the following sections, we describe common permanently porous materials (*i.e.*, materials that retain porosity in solution) and propose mechanisms for their colloidal stability and solubility. This research field is nascent, without consensus around theory that explains the colloidal stability of porous materials. We propose, given the examples below, that specific solvent-surface interactions, such as through ordered solvation shells and chemical interactions between the material building blocks and the solvent provide the colloidal stability of porous materials.

3-1. Simple Porous Structures

As a starting point, solved nanotubes serve as a basis for understanding the solvation of a one-dimensional porous material (Figure 2A). The pores, or tunnels, of a nanotubes can range from 0.5-2 nm in diameter and are typically grown from a metal catalyst via chemical vapor deposition. One might assume that water should exclude from the nanotube interior due to its hydrophobicity and because water absorption is entropically disfavored.⁹⁸ Surprisingly, water adsorbs inside the pores of carbon nanotubes, leading to the phenomenon of “water wires”.⁹⁹ One explanation proposes that water-wires and carbon nanotube solubility results from the entropy of water flowing through the pores and from free rotation of water molecules. Studies also suggest dissolution in water does not involve favorable enthalpic interactions between water and the nanotube, suggesting water solubility of other hydrophobic materials through entropy-favored interactions. Changing the nanotube polarity, via simulations or experimental crystal engineering, allows for tuning of the water wire mobility, specifically in terms of water migration from one opening of the tube to the other, functioning as a nanosized garden hose. Carbon nanotubes also dissolve in ionic liquids,^{100,101} where both solvation shells and internal hydrogen bonding are postulated to stabilize the particles. Similar solvation behavior has been observed for carbon nanotubes in benzene,¹⁰² alcohols,¹⁰³ and polymer solutions,¹⁰⁴ however nearly all studies are computational. Although challenging, experimental studies of nanomaterials solvation will lay the foundation for designing their application in solution state applications, such as drug delivery or membranes.

Whereas nearly all nanotubes are homogenous and comprised of carbon, the solvation of 2D materials introduces the probability of surface heterogeneity (Figure 2B). In addition to the atomically homogeneous example of graphene, 2D materials include the heterogeneous boron nitride, metal chalcogenides, or metal oxides. In these materials, solvent accessible surface areas exist between sheets (interlayer), introducing another unique solvation environment in addition to interior and exterior pores. Despite their enhanced surface areas, most nanosheets require a surfactant or post-synthetic modification for long-term colloidal stability, similar to 3D, non-porous inorganic analogs.¹⁰⁵⁻¹⁰⁷ As illustrated by the examples below, electrical double layers are thought to spontaneously assemble at the surface of nanosheets, providing a large electrostatic surface repulsion (as measured by zeta potential) and site-specific

water interactions at the surface. These results suggest that in high-surface area materials without deliberately added surface capping agents, specific solvent interactions are important for colloidal stability. Surprisingly, hydrophobic 2D materials, including graphene and MoS₂, disperse in aqueous solutions via exfoliation-induced oxidation.^{108,109} Studies suggest that ultrasonication causes etching of edge-groups that improves the solubility in water. In a notable study, graphene ultrasonicated at high-temperatures exhibited long-term colloidal stability in water while the sample sonicated at low-temperatures maintained a pristine morphology and was unstable in water.¹¹⁰ The introduction of edge-site functionalization to graphene oxide in the form of hydroxyl and carboxyl groups also contributes to the increased water stability. However, for heterogeneous nanosheets of hexagonal boron nitride, MoS₂, WS₂, and MoSe₂, colloidal stability in water was achieved after sonication at both high- and low-temperatures and no surface functionalization was observed.

3D porous materials with relatively simple compositions include microporous nanoparticles such as silica and zeolites (Figure 2C). Mesoporous silica (SiO₂) has pore diameters of 2-50 nm, while microporous silica has much smaller pores below 2 nm. Zeolites are aluminosilicates with even smaller pore diameters ranging from 0.3-0.8 nm. As with colloidal nanoparticles, polymers, and proteins detailed above, the colloidal stability of 3D porous nanomaterials depends on proper electrolyte concentration,¹¹¹ surfactant surface coverage,^{112,113} and polymer coatings.¹¹⁴ Studies remain largely empirical and an underlying mechanism of colloidal stability remains unclear. Representative studies include the finding that mesoporous silica is typically synthesized with a surfactant like hexadecyltrimethylammonium bromide (CTAB) acting as both a structure-directing molecule (to synthesize a specific shape) and a stabilizing capping ligand.¹¹⁵⁻¹¹⁷ These surfactant-capped materials can be stable for upwards of a year in water.¹¹⁸ Mesoporous silica nanoparticles can also be surface functionalized as hydrophobic, which renders them useful drug delivery agents.^{119,120} Little is known about the solvation and colloidal stability of mesoporous silica, although recent work suggests that performing dialysis solvent exchange or coating the nanoparticles with proteins improves dispersability.^{121,122}

A potential method for probing mechanisms of colloidal stability in porous materials would rely on surface functionalization. Although porous, silica and zeolites lack chemical tunability beyond their typical inorganic compositions, however (Figure 3). Instead, organic-inorganic framework materials assemble from a wide variety of metallic and organic-compounds, resulting in a diverse range of pore diameters, aperture shapes, solvent-accessible surface area, morphology, and well-developed methods for post-synthetic modulation of surface compositions.

3-2. Porous Frameworks

Understanding the colloidal stability of porous frameworks attracts intense recent attention, in part because 3D porosity challenges conventional mechanisms of solvation, such as the notion of electrostatic forces between smooth, uniform, hard spheres. Porous framework materials such as covalent-organic frameworks (COFs) and

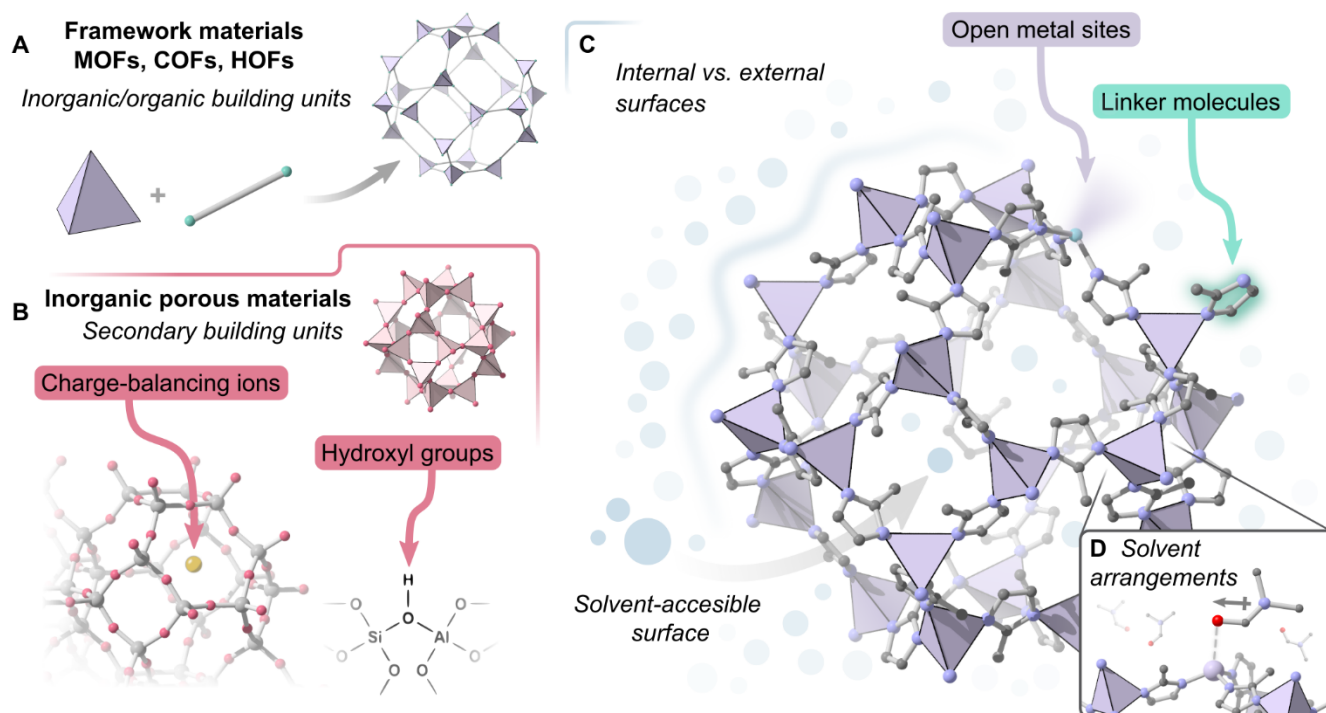


Figure 3. Representation of (A) framework materials, comprised of inorganic/organic building units that are assembled into porous frameworks, and (B) inorganic porous materials, which are made up of secondary building units. (C) Both material classes show distinct internal vs. external surfaces due to their high surface areas and, consequentially, large solvent-accessible surface areas. (D) Distinct functional groups or open metal sites within the materials may induce different solvent arrangements, further affecting their solvation.

metal-organic frameworks (MOFs) are pursued for a wide range of applications due to their unparalleled performance at selective gas separation, water filtration, carbon sequestration, and other areas leveraging tunable guest-host interactions (Figure 3A). Practical implementation as solution processible and reusable materials, such as thin film membranes, demands their ability to suspend as uniform, stable colloids in a range of solvents. Stability in water would facilitate their utility in biological applications, for example, while compatibility with low-boiling solvents would render them amenable to spraying coating and other forms of industrial production at-scale. In addition to a lack of knowledge of solvation structure, few studies exist for any form of surface functionalization. Reported surface ligands deviate from those well studied with conventional quantum dots.¹²³ Solvent interactions likely dictate the interaction of porous materials with polymers in the so-called mixed matrix membranes envisioned for chemical separation technologies. Little is known about microscopic aspects of the polymer-porous colloid interface, except that great care must be taken to prevent polymers from intercalating and clogging pores,^{124,125} which can be detrimental to gas sorption and chemical separation applications. In this section, we will describe the current theories of colloidal stability for porous frameworks and the challenges in studying them.

COFs constitute organic polymers with crystalline, porous topologies. Due to their dispersibility in organic solvents, studying the solution chemistry of COFs could inform on the solvation chemistry of porous colloids in general, but frequently these materials form gels rather than colloidal suspensions. In one notable study, the polar solvents dimethylacetamide

(DMAc) and water were used to stabilize COF nanoparticles in solution and prevent aggregation.¹²⁶ Yet, with the removal of water or with the substitution of dimethyl sulfoxide (DMSO) for DMAc, COF gels formed instead of the crystalline nanoparticles. These results suggest that not only does polarity of the solvent influence colloidal stability, but the reactivity of the surface species with the solvent can impart unfavorable products. In another study, water-soluble amino monomer units were used to form a colloidal COF in water, indicating that the importance of favorable solvent interactions with individual building blocks, similar to the solvation of polymers.¹²⁷ However, higher concentrations of the monomer unit induced gel formation, as is commonly noticed for COF syntheses.^{128,129} While these gels can be useful for casting films, they are typically mechanically weak¹³⁰ and difficult for studying solvent-based stabilizing interactions. To prevent the development of gels, careful selection of the solvent identity and concentration is necessary to achieve the highest likelihood of stabilizing solvent-surface interactions.

Unlike typical, nonporous nanoparticles, MOFs exhibit colloidal stability without the need for conventional capping ligands.¹ In fact, while traditional surfactants such as dodecanoic acid or cetyltrimethylammonium bromide can be included in a MOF synthesis to impart size or shape control,^{131,132} these ligands do not remain with the MOF nanoparticles after washing, as we have observed by nuclear magnetic resonance spectroscopy, thermogravimetric analysis, and other analytical techniques.^{1,2} Instead, while post-synthetic addition of ligand dyes¹²³ or DNA/protein coronas¹³³ leads to functionalized surfaces, few if any studies detail how they impact colloidal

stability. Instead, we recently demonstrated that the solvent identity plays a greater role in stabilizing the surface as only solvents that can dissolve the organic linker can suspend the MOF nanoparticle.¹ This result strongly suggests that the interaction of MOF nanoparticles resembles the dissolution of cage molecules, polymers, and other macromolecules systems where solubility depends solvent-monomer energetics and accessible void spaces (Figure 3C,D).

In addition to specific solvent-surface interactions, classical electrostatic arguments of DLVO theory could explain the stability of uncharged MOF nanoparticles, where surface charges would arise from deprotonated linker molecules or open metal sites. Electrostatics alone is unlikely to account for the full mechanism of colloidal stability, however.¹³⁴ Recent reports of zeta potentials—indicators of net surface charge—typically at the border (± 30 mV) of values required for colloidal stability by DLVO theory.^{1,135} These reduced zeta potentials can be attributed to the low surface density of porous nanoparticles and the weak, short-range electrostatic fields produced by surface defects that quickly decayed through porous channels.¹³⁶ Binding of solvent or polymers to open metal sites at the surface of MOF nanoparticles improve colloidal stability, while also reduce the apparent surface charge.^{2,125} In other words, zeta potentials may not relate directly to MOF colloidal stability.

Instead of traditional electrostatics, we suggest the intrinsic porosity of nanoMOFs improves colloidal stability through entropic effects. For nonporous colloids, entropy favors aggregation because it removes solvation shells and disorders excluded solvent. This process is termed the “hydrophobic effect”. It is introduced as a mechanism to describe porous nanoparticles,¹³⁷ where the total amount of ordered solvent must be lower than nonporous colloids due to the low density surfaces. As a result, the potential energy favoring aggregation decreases as well. To examine the interaction of solvent with porous interfaces, we recently pioneered the use of vibrational sum frequency scattering spectroscopy (VSFSS)—an interface-specific technique—with colloidal nanoparticles.² Spectra revealed spontaneously assembly of ordered solvation shells of *N,N*-dimethylformamide (DMF) or water at the exterior of ZIF-8 colloids. Although predicted to exist, solvation shells of colloids were previously documented only by atomic force microscopy and x-ray studies.^{138–142} In addition to providing a protective shell of steric repulsion, we propose that solvent interactions with open metal sites and linker monomer units improves solvation energetics akin to Flory-Huggins theory. We also observed that the bridging 2-methylimidazolate linkers spontaneously align at the solvent interface in a manner that expands the internal pore volumes. This lattice flexibility, like a protein, may further enhance favorable solvent interactions and colloidal stability. Taken together, these recent reports provide a roadmap for preparing and stabilizing porous materials in solution.

3-3. Designing a Stable, Porous Colloid

Recent evidence suggests that specific solvent-surface interactions dictate the stability of colloidal, porous nanoparticles. The design of surface atomic structure and composition, and solvent identity provide tools for designing solvation energetics. Our recent VSFSS study indicates that the ordering of solvation shells correlates with colloidal stability, with strong similarities to protein hydration shells and the Hofmeister series.² Binding of solvent through covalent or van der Waals forces with monomer units also improves the stability of bare inorganic,

organic, or porous colloids. As with the dissolution of proteins, favorable enthalpic interactions between solvent and the components of a porous colloid improve stability, such that solvent that dissolves the constituent components also disperses the particle. Therefore, accessible void spaces in polymers, proteins, and porous colloids help to maximize these interactions. Binding of solvent or polymer to open metal sites at the surface¹²⁵ has been shown to improve colloidal stability despite decreasing net surface charges on the colloid. Simulations of solvent adsorption at functionalized porous surfaces similarly suggest that the external surface dictates particle-solvent interactions^{143,144} and that surface composition, such as rough pore apertures¹⁴⁵ or framework flexibility,¹⁴⁶ gate-keep the ability of solvent to interact with colloid internal voids. At porous surfaces and in confined void spaces, traditional notions of hydrophobicity and uniform electrostatic interactions break down, giving rise to unexpected solvation phenomena of water wires in nanotubes, the hydrophobic effect, and dense clusters water clusters at the metal sites of otherwise hydrophobic MOF interiors.

Deploying porous materials into real-world applications requires their solution processability and, therefore, a microscopic understanding of their solvation structure and energetics. Given the examples above, we propose that colloidal stability benefits from specific solvent interactions with the external surface of the porous material through ordered solvation shells, ionic binding, or steric coatings. The role of internal surface solvation, on the other hand, remains an open question. Our recent evidence suggests that porous colloidal solubility increases when solvent can penetrate the interiors.¹ Additional studies are needed to understand how the presence of interior surfaces contributes to the conventional factors governing colloidal stability such as electrostatic forces, steric repulsion, and favorable enthalpic interactions. Taken together, the solvation of porous colloids challenges the electrostatic basis of DLVO theory, while resembling elements of Flory-Huggins theory: porous colloids depend on interactions with monomer units, accessible-surface areas, and the need for structural flexibility that produces the secondary structure of proteins. At the frontier of this research remains fundamental questions surrounding how solvation of porous materials deviates from proteins and other familiar examples and demands entirely new modes of thinking.

3-4. Implications for Electrochemical Systems

Solvation plays a key role in most electrochemical processes. In Marcus theory, solvent reorganization energetics strongly influences electron transfer rates.^{147–151} The properties of wide-ranging technologies from electrocatalysts and capacitors to metal plating electrodes and potential-swing chemical separators, therefore, depend on solvent interactions with dissolved species and heterogeneous interfaces.^{152–154} Here, we highlight two recent developments from our group where electrochemical performance depends on solvation structure and dynamics.

Thermoelectrochemical cells offer a strategy for converting thermal energy to electrical power.¹⁵⁵ As solution-state thermoelectric devices, they comprise of two electrodes submerged in a solution containing redox-active electrolyte and a thermal gradient between the two electrodes. Because temperature controls the equilibrium constant of the redox couple, a difference in free energies forms between the two electrodes. Once connected, the circuit performs work. Most redox couples show little if any temperature dependence because the entropy change

associated with their redox (ΔS_r) is small. Because the Seebeck coefficient S_e , a measure of $\Delta V/\Delta T$, relates directly to ΔS_r ,¹⁵⁶ electrolyte with large ΔS_r lead to large free energy differences

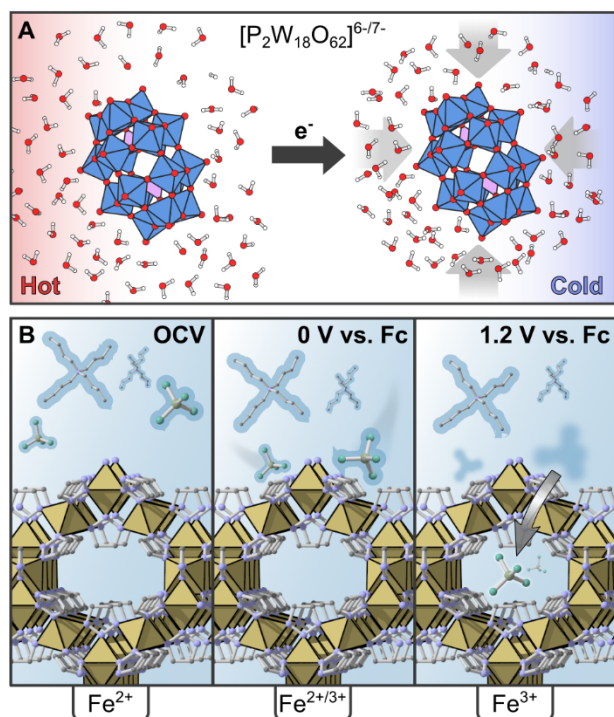


Figure 4. Illustrative examples of how solvation affects electrochemical processes in nanoscale materials. **A)** Illustration of how the superchaotropic properties of a Wells-Dawson polyoxotungstate anion, $[P_2W_{18}O_{62}]^{6-/7-}$, can be used in thermogalvanic applications: the difference in solvation of the two charge states is associated with a large change in entropy, allowing the conversion from thermal to electric energy as the reduction is more favorable at lower temperatures. **B)** Intercalation of BF_4^- upon oxidation of Fe^{2+} centers in $Fe(1,2,3\text{-triazolate})_2$, for which it was observed that the redox potential of surface vs. interior iron sites is shifted by ~ 1.2 V (Fc: ferrocene/ferrocenium), due to the requirement of desolvating the anions as they enter the pores.

across the thermoelectrochemical cell. Although research in this area remains a frontier, recent examples have demonstrated that synthetic manipulation of the solvation environment serves as a pathway for enhancing ΔS_r and the energy density of the cell. For example, solvent mixtures,¹⁵⁷ the use of dissolved polymers that undergo phase changes upon redox,¹⁵⁸ metallocages that intercalate charge balancing ions through a desolvation process,¹⁵⁹ and polyoxometalate anions¹⁶⁰ all involve large supra-molecular changes to solvation structure (Figure 4A). We predict that the ability of solvent to intercalate into pores and the frustration solvent to assemble into ordered shells at porous surfaces will strongly influence the thermoelectrochemical behavior of porous colloids.

Nearly all electrochemistry occurs at interfaces. While most electrochemistry assumes smooth and uniform interfaces, thin film electrodes of porous nanoparticles contain internal, external, and inter-particle interfaces. We recently reported the electrochemical behavior of conductive nanoparticle thin films of the MOF $Fe(1,2,3\text{-triazolate})_2$ ($Fe(TA)_2$). Although the MOF contains two crystallographically distinct Fe sites, their chemical environments are so similar that Mössbauer spectroscopy

shows just one Fe species.¹⁶¹ Nevertheless, cyclic voltammogram traces of $Fe(TA)_2$ nanoparticle colloids and thin films for any particle size show at least two reversible redox waves separated by nearly 1.5 V in tetrabutylammonium tetrafluoroborate supporting electrolyte (Figure 4B).¹⁶² Repeating this experiment with the larger anion hexafluorophosphate caused the more positive of the two redox waves to disappear, however. Through a suite of complementary techniques, we showed that the less positive feature corresponds oxidation of Fe at the particle external surfaces while the more positive feature arises from oxidation of internal Fe sites. Whereas most MOF pore apertures exceed 1 nm, those of $Fe(TA)_2$ are only 0.4 nm, thereby frustrating the anion intercalation needed to charge balance Fe^{3+} . The 1.5 V additional potential arises solely from desolvation, solvent reorganization, and cooperative anion intercalation energetics. These remarkable results provide a roadmap for modulating the voltage of other redox intercalation electrodes, such as those ubiquitous in batteries, and are made possible by the unique combination of both external and internal surfaces of porous colloids.

CONCLUSION

The solvation mechanisms proposed for porous nanomaterials are inspired by traditional solvation methods used for hard-shell colloids, such as DLVO theory, and approaches for dissolving soft macromolecules like polymers and proteins. Porous nanomaterials, due to their increased solvent-accessible surface area, utilize specific solvent-surface interactions to solvate the material's component unit-by-unit. This approach differs from the reliance on a separate layer of surfactant or capping ligand typically used for the colloidal stability of hard-shell nanoparticles. By adapting traditional techniques, including vibrational spectroscopy and redox chemistry, to examine these unique surfaces, we can gain a deeper understanding of how the internal and external interfaces of bare, porous nanomaterials contribute to their unexpected colloidal stability.

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REFERENCES

- (1) LeRoy, M. A.; Perera, A. S.; Lamichhane, S.; Mapile, A. N.; Khaliq, F.; Kadota, K.; Zhang, X.; Ha, S.; Fisher, R.; Wu, D.; Risko, C.; Brozek, C. K. Colloidal Stability and Solubility of Metal–Organic Framework Particles. *Chem. Mater.* **2024**, *36* (8), 3673–3682. <https://doi.org/10.1021/acs.chemmater.3c03191>.
- (2) Mapile, A. N.; LeRoy, M. A.; Fabrizio, K.; Scatena, L. F.; Brozek, C. K. The Surface of Colloidal Metal–Organic Framework Nanoparticles Revealed by Vibrational Sum Frequency Scattering Spectroscopy. *ACS Nano* **2024**. <https://doi.org/10.1021/acsnano.4c03758>.
- (3) Derjaguin, B.; Landau, L. Theory of the Stability of Strongly Charged Lyophobic Sols and of the Adhesion of Strongly Charged Particles in Solutions of Electrolytes. *Progress in Surface Science* **1993**, *43* (1), 30–59. [https://doi.org/10.1016/0079-6816\(93\)90013-L](https://doi.org/10.1016/0079-6816(93)90013-L).
- (4) Helmholtz, H. Ueber Einige Gesetze Der Vertheilung Elektrischer Ströme in Körperlichen Leitern Mit Anwendung Auf Die Thierisch-Elektrischen Versuche. *Annalen der Physik* **1853**, *165* (6), 211–233. <https://doi.org/10.1002/andp.18531650603>.
- (5) Gouy, M. Sur la constitution de la charge électrique à la surface d'un électrolyte. *J. Phys. Theor. Appl.* **1910**, *9* (1), 457–468. <https://doi.org/10.1051/jphystap:019100090045700>.
- (6) Chapman, D. L. LI. A Contribution to the Theory of Electrowetting. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science* **1913**, *25* (148), 475–481. <https://doi.org/10.1080/14786440408634187>.
- (7) Stern, O. Zur Theorie Der Elektrolytischen Doppelschicht. *Zeitschrift für Elektrochemie und angewandte physikalische Chemie* **1924**, *30* (21–22), 508–516. <https://doi.org/10.1002/bbpc.192400182>.
- (8) Verwey, E. J. W. Theory of the Stability of Lyophobic Colloids. *J. Phys. Chem.* **1947**, *51* (3), 631–636. <https://doi.org/10.1021/j150453a001>.
- (9) Verwey, E. J. W.; Overbeek, J. Th. G. *Theory of the Stability of Lyophobic Colloids*; Elsevier: Amsterdam, 1948.
- (10) Derjaguin, B. V.; Churaev, N. V.; Muller, V. M. The Derjaguin–Landau–Verwey–Overbeek (DLVO) Theory of Stability of Lyophobic Colloids. In *Surface Forces*; Derjaguin, B. V., Churaev, N. V., Muller, V. M., Eds.; Springer US: Boston, MA, 1987; pp 293–310. https://doi.org/10.1007/978-1-4757-6639-4_8.
- (11) Trefalt, G.; Szilagy, I.; Borkovec, M. Poisson–Boltzmann Description of Interaction Forces and Aggregation Rates Involving Charged Colloidal Particles in Asymmetric Electrolytes. *Journal of Colloid and Interface Science* **2013**, *406*, 111–120. <https://doi.org/10.1016/j.jcis.2013.05.071>.
- (12) Trefalt, G.; Ruiz-Cabello, F. J. M.; Borkovec, M. Interaction Forces, Heteroaggregation, and Deposition Involving Charged Colloidal Particles. *J. Phys. Chem. B* **2014**, *118* (23), 6346–6355. <https://doi.org/10.1021/jp503564p>.
- (13) Trefalt, G.; Cao, T.; Sugimoto, T.; Borkovec, M. Heteroaggregation between Charged and Neutral Particles. *Langmuir* **2020**, *36* (19), 5303–5311. <https://doi.org/10.1021/acs.langmuir.0c00667>.
- (14) Obstbaum, T.; Sivan, U. Thermodynamics of Charge Regulation near Surface Neutrality. *Langmuir* **2022**, *38* (27), 8477–8483. <https://doi.org/10.1021/acs.langmuir.2c01352>.
- (15) Russel, W. B.; Saville, D. A.; Schowalter, W. R. *Colloidal Dispersions*; Cambridge Monographs on Mechanics; Cambridge University Press: Cambridge, 1989. <https://doi.org/10.1017/CBO9780511608810>.
- (16) Leckband, D.; Sivasankar, S. Forces Controlling Protein Interactions: Theory and Experiment. *Colloids and Surfaces B: Biointerfaces* **1999**, *14* (1), 83–97. [https://doi.org/10.1016/S0927-7765\(99\)00027-2](https://doi.org/10.1016/S0927-7765(99)00027-2).
- (17) Eom, N.; Parsons, D. F.; Craig, V. S. J. Roughness in Surface Force Measurements: Extension of DLVO Theory To Describe the Forces between Hafnia Surfaces. *J. Phys. Chem. B* **2017**, *121* (26), 6442–6453. <https://doi.org/10.1021/acs.jpcc.7b03131>.
- (18) Tran, E.; Richmond, G. L. Interfacial Steric and Molecular Bonding Effects Contributing to the Stability of Neutrally Charged Nanoemulsions. *Langmuir* **2021**, *37* (43), 12643–12653. <https://doi.org/10.1021/acs.langmuir.1c02020>.
- (19) Yang, L.; Wen, J. Can DLVO Theory Be Applied to MOF in Different Dielectric Solvents? *Microporous and*

- Mesoporous Materials* **2022**, *343*, 112166. <https://doi.org/10.1016/j.micromeso.2022.112166>.
- (20) Peng, B.; Liao, P.; Jiang, Y. A Meta-Analysis to Revisit the Property–Aggregation Relationships of Carbon Nanomaterials: Experimental Observations versus Predictions of the DLVO Theory. *Langmuir* **2024**, *40* (13), 7127–7138. <https://doi.org/10.1021/acs.langmuir.4c00274>.
- (21) van Oss, C. J. Chapter Three - The Extended DLVO Theory. In *Interface Science and Technology*; van Oss, C. J., Ed.; The Properties of Water and their Role in Colloidal and Biological Systems; Elsevier, 2008; Vol. 16, pp 31–48. [https://doi.org/10.1016/S1573-4285\(08\)00203-2](https://doi.org/10.1016/S1573-4285(08)00203-2).
- (22) Boström, M.; Deniz, V.; Franks, G. V.; Ninham, B. W. Extended DLVO Theory: Electrostatic and Non-Electrostatic Forces in Oxide Suspensions. *Advances in Colloid and Interface Science* **2006**, *123–126*, 5–15. <https://doi.org/10.1016/j.cis.2006.05.001>.
- (23) Buchcic, C.; Tromp, R. H.; Meinders, M. B. J.; Stuart, M. A. C. Harnessing the Advantages of Hard and Soft Colloids by the Use of Core–Shell Particles as Interfacial Stabilizers. *Soft Matter* **2017**, *13* (7), 1326–1334. <https://doi.org/10.1039/C6SM02159J>.
- (24) Style, R. W.; Isa, L.; Dufresne, E. R. Adsorption of Soft Particles at Fluid Interfaces. *Soft Matter* **2015**, *11* (37), 7412–7419. <https://doi.org/10.1039/C5SM01743B>.
- (25) Abate, A. R.; Han, L.; Jin, L.; Suo, Z.; Weitz, D. A. Measuring the Elastic Modulus of Microgels Using Microdrops. *Soft Matter* **2012**, *8* (39), 10032–10035. <https://doi.org/10.1039/C2SM26108A>.
- (26) Tan, S.; Sherman, R. L.; Ford, W. T. Nanoscale Compression of Polymer Microspheres by Atomic Force Microscopy. *Langmuir* **2004**, *20* (17), 7015–7020. <https://doi.org/10.1021/la049597c>.
- (27) Wennerström, H.; Vallina Estrada, E.; Danielsson, J.; Oliveberg, M. Colloidal Stability of the Living Cell. *Proceedings of the National Academy of Sciences* **2020**, *117* (19), 10113–10121. <https://doi.org/10.1073/pnas.1914599117>.
- (28) Molina-Bolívar, J. A.; Galisteo-González, F.; Hidalgo-Alvarez, R. The Role Played by Hydration Forces in the Stability of Protein-Coated Particles: Non-Classical DLVO Behaviour. *Colloids and Surfaces B: Biointerfaces* **1999**, *14* (1), 3–17. [https://doi.org/10.1016/S0927-7765\(99\)00020-X](https://doi.org/10.1016/S0927-7765(99)00020-X).
- (29) Singh, R. S.; Hernandez, R. Modeling Soft Core-Shell Colloids Using Stochastic Hard Collision Dynamics. *Chemical Physics Letters* **2018**, *708*, 233–240. <https://doi.org/10.1016/j.cplett.2018.08.032>.
- (30) Cao, W.; Xiang, C.; Yang, Y.; Chen, Q.; Chen, L.; Yan, X.; Qian, L. Highly Stable QLEDs with Improved Hole Injection via Quantum Dot Structure Tailoring. *Nat Commun* **2018**, *9* (1), 2608. <https://doi.org/10.1038/s41467-018-04986-z>.
- (31) Park, Y.-S.; Lim, J.; Klimov, V. I. Asymmetrically Strained Quantum Dots with Non-Fluctuating Single-Dot Emission Spectra and Subthermal Room-Temperature Linewidths. *Nature Mater* **2019**, *18* (3), 249–255. <https://doi.org/10.1038/s41563-018-0254-7>.
- (32) Everett, D. H. Manual of Symbols and Terminology for Physicochemical Quantities and Units, Appendix II: Definitions, Terminology and Symbols in Colloid and Surface Chemistry. *Pure and Applied Chemistry* **1972**, *31* (4), 577–638. <https://doi.org/10.1351/pac197231040577>.
- (33) Clarke, J. B.; Hastie, J. W.; Kihlberg, L. H. E.; Metselaar, R.; Thackeray, M. M. Definitions of Terms Relating to Phase Transitions of the Solid State (IUPAC Recommendations 1994). *Pure and Applied Chemistry* **1994**, *66* (3), 577–594. <https://doi.org/10.1351/pac199466030577>.
- (34) *Standard Methods for the Examination of Water and Wastewater*, 23rd edition.; Bridgewater, L. L., Baird, R. B., Eaton, A. D., Rice, E. W., American Public Health Association, American Water Works Association, Water Environment Federation, Eds.; American Public Health Association: Washington, DC, 2017.
- (35) Butler, B. A.; Ford, R. G. Evaluating Relationships between Total Dissolved Solids (TDS) and Total Suspended Solids (TSS) in a Mining-Influenced Watershed. *Mine Water Environ* **2018**, *37* (1), 18–30. <https://doi.org/10.1007/s10230-017-0484-y>.
- (36) Beard, M. C.; Peng, X.; Hens, Z.; Weiss, E. A. Introduction to Special Issue: Colloidal Quantum Dots. *The Journal of Chemical Physics* **2020**, *153* (24), 240401. <https://doi.org/10.1063/5.0039506>.
- (37) Bawendi, M. G.; Brus, L. E.; Yekimov, A. The Nobel Prize in Chemistry 2023.
- (38) Rossetti, R.; Nakahara, S.; Brus, L. E. Quantum Size Effects in the Redox Potentials, Resonance Raman Spectra, and Electronic Spectra of CdS Crystallites in Aqueous Solution. *The Journal of Chemical Physics* **1983**, *79* (2), 1086–1088. <https://doi.org/10.1063/1.445834>.
- (39) Cardellini, A.; Alberghini, M.; Rajan, A. G.; Misra, R. P.; Blankschtein, D.; Asinari, P. Multi-Scale Approach for Modeling Stability, Aggregation, and Network Formation of Nanoparticles Suspended in Aqueous Solutions. *Nanoscale* **2019**, *11* (9), 3979–3992. <https://doi.org/10.1039/C8NR08782B>.
- (40) Zarghami, M. H.; Liu, Y.; Gibbs, M.; Gebremichael, E.; Webster, C.; Law, M. P-Type PbSe and PbS Quantum Dot Solids Prepared with Short-Chain Acids and Diacids. *ACS Nano* **2010**, *4* (4), 2475–2485. <https://doi.org/10.1021/nn100339b>.
- (41) Bae, W. K.; Joo, J.; Padilha, L. A.; Won, J.; Lee, D. C.; Lin, Q.; Koh, W.; Luo, H.; Klimov, V. I.; Pietryga, J. M. Highly Effective Surface Passivation of PbSe Quantum Dots through Reaction with Molecular Chlorine. *J. Am. Chem. Soc.* **2012**, *134* (49), 20160–20168. <https://doi.org/10.1021/ja309783v>.

- (42) Zhang, J.; Gao, J.; Miller, E. M.; Luther, J. M.; Beard, M. C. Diffusion-Controlled Synthesis of PbS and PbSe Quantum Dots with in Situ Halide Passivation for Quantum Dot Solar Cells. *ACS Nano* **2014**, *8* (1), 614–622. <https://doi.org/10.1021/nn405236k>.
- (43) Kovalenko, M. V.; Scheele, M.; Talapin, D. V. Colloidal Nanocrystals with Molecular Metal Chalcogenide Surface Ligands. *Science* **2009**, *324* (5933), 1417–1420. <https://doi.org/10.1126/science.1170524>.
- (44) Bederak, D.; Sukharevska, N.; Kahmann, S.; Abdu-Aguye, M.; Duim, H.; Dirin, D. N.; Kovalenko, M. V.; Portale, G.; Loi, M. A. On the Colloidal Stability of PbS Quantum Dots Capped with Methylammonium Lead Iodide Ligands. *ACS Appl. Mater. Interfaces* **2020**, *12* (47), 52959–52966. <https://doi.org/10.1021/acsmi.0c16646>.
- (45) Alam, A.-M.; Shon, Y.-S. Water-Soluble Noble Metal Nanoparticle Catalysts Capped with Small Organic Molecules for Organic Transformations in Water. *ACS Appl. Nano Mater.* **2021**, *4* (4), 3294–3318. <https://doi.org/10.1021/acsnm.1c00335>.
- (46) Oh, E.; Delehanty, J. B.; Klug, C. A.; Susumu, K.; Algar, W. R.; Goswami, R.; Medintz, I. L. Utility of PEGylated Dithiolane Ligands for Direct Synthesis of Water-Soluble Au, Ag, Pt, Pd, Cu and AuPt Nanoparticles. *Chem. Commun.* **2018**, *54* (16), 1956–1959. <https://doi.org/10.1039/C7CC08650D>.
- (47) Moore, T. L.; Urban, D. A.; Rodriguez-Lorenzo, L.; Milosevic, A.; Crippa, F.; Spuch-Calvar, M.; Balog, S.; Rothen-Rutishauser, B.; Lattuada, M.; Petri-Fink, A. Nanoparticle Administration Method in Cell Culture Alters Particle-Cell Interaction. *Sci Rep* **2019**, *9* (1), 900. <https://doi.org/10.1038/s41598-018-36954-4>.
- (48) Moore, T. L.; Rodriguez-Lorenzo, L.; Hirsch, V.; Balog, S.; Urban, D.; Jud, C.; Rothen-Rutishauser, B.; Lattuada, M.; Petri-Fink, A. Nanoparticle Colloidal Stability in Cell Culture Media and Impact on Cellular Interactions. *Chem. Soc. Rev.* **2015**, *44* (17), 6287–6305. <https://doi.org/10.1039/C4CS00487F>.
- (49) Arcudi, F.; Westmoreland, D. E.; Weiss, E. A. Colloidally Stable CdS Quantum Dots in Water with Electrostatically Stabilized Weak-Binding, Sulfur-Free Ligands. *Chemistry – A European Journal* **2019**, *25* (63), 14469–14474. <https://doi.org/10.1002/chem.201903908>.
- (50) Owen, J. The Coordination Chemistry of Nanocrystal Surfaces. *Science* **2015**, *347* (6222), 615–616. <https://doi.org/10.1126/science.1259924>.
- (51) Prather, K. V.; Stoffel, J. T.; Tsui, E. Y. Redox Reactions at Colloidal Semiconductor Nanocrystal Surfaces. *Chem. Mater.* **2023**, *35* (9), 3386–3403. <https://doi.org/10.1021/acs.chemmater.3c00481>.
- (52) Sylvestre, J.-P.; Poulin, S.; Kabashin, A. V.; Sacher, E.; Meunier, M.; Luong, J. H. T. Surface Chemistry of Gold Nanoparticles Produced by Laser Ablation in Aqueous Media. *J. Phys. Chem. B* **2004**, *108* (43), 16864–16869. <https://doi.org/10.1021/jp047134+>.
- (53) De Anda Villa, M.; Gaudin, J.; Amans, D.; Boudjada, F.; Bozek, J.; Evaristo Grisenti, R.; Lamour, E.; Laurens, G.; Macé, S.; Nicolas, C.; Papagiannouli, I.; Patanen, M.; Prigent, C.; Robert, E.; Steydli, S.; Trassinelli, M.; Vernhet, D.; Lévy, A. Assessing the Surface Oxidation State of Free-Standing Gold Nanoparticles Produced by Laser Ablation. *Langmuir* **2019**, *35* (36), 11859–11871. <https://doi.org/10.1021/acs.langmuir.9b02159>.
- (54) Li, Z.; Ruiz, V. G.; Kanduč, M.; Dzubiella, J. Highly Heterogeneous Polarization and Solvation of Gold Nanoparticles in Aqueous Electrolytes. *ACS Nano* **2021**, *15* (8), 13155–13165. <https://doi.org/10.1021/acsnano.1c02668>.
- (55) Chung, K.; Bang, J.; Thacharon, A.; Song, H. Y.; Kang, S. H.; Jang, W.-S.; Dhull, N.; Thapa, D.; Ajmal, C. M.; Song, B.; Lee, S.-G.; Wang, Z.; Jetybayeva, A.; Hong, S.; Lee, K. H.; Cho, E. J.; Baik, S.; Oh, S. H.; Kim, Y.-M.; Lee, Y. H.; Kim, S.-G.; Kim, S. W. Non-Oxidized Bare Copper Nanoparticles with Surface Excess Electrons in Air. *Nat. Nanotechnol.* **2022**, *17* (3), 285–291. <https://doi.org/10.1038/s41565-021-01070-4>.
- (56) Johny, J.; van Halteren, C. E. R.; Zwihehoff, S.; Behrends, C.; Bäumer, C.; Timmermann, B.; Rehbock, C.; Barcikowski, S. Impact of Sterilization on the Colloidal Stability of Ligand-Free Gold Nanoparticles for Biomedical Applications. *Langmuir* **2022**, *38* (43), 13030–13047. <https://doi.org/10.1021/acs.langmuir.2c01557>.
- (57) França, Á.; Pelaz, B.; Moros, M.; Sánchez-Espinel, C.; Hernández, A.; Fernández-López, C.; Grazú, V.; de la Fuente, J. M.; Pastoriza-Santos, I.; Liz-Marzán, L. M.; González-Fernández, Á. Sterilization Matters: Consequences of Different Sterilization Techniques on Gold Nanoparticles. *Small* **2010**, *6* (1), 89–95. <https://doi.org/10.1002/sml.200901006>.
- (58) Scroccarello, A.; Álvarez-Diduk, R.; Della Pelle, F.; de Carvalho Castro e Silva, C.; Idili, A.; Parolo, C.; Compagnone, D.; Merkoçi, A. One-Step Laser Nanostructuring of Reduced Graphene Oxide Films Embedding Metal Nanoparticles for Sensing Applications. *ACS Sens.* **2023**, *8* (2), 598–609. <https://doi.org/10.1021/acssensors.2c01782>.
- (59) Mastronardi, V.; Magliocca, E.; Gullon, J. S.; Brescia, R.; Pompa, P. P.; Miller, T. S.; Moglianetti, M. Ultrasmall, Coating-Free, Pyramidal Platinum Nanoparticles for High Stability Fuel Cell Oxygen Reduction. *ACS Appl. Mater. Interfaces* **2022**, *14* (32), 36570–36581. <https://doi.org/10.1021/acsmi.2c07738>.
- (60) Mazzotta, E.; Di Giulio, T.; Mastronardi, V.; Pompa, P. P.; Moglianetti, M.; Malitesta, C. Bare Platinum Nanoparticles Deposited on Glassy Carbon Electrodes for Electroanalytic Detection of Hydrogen Peroxide. *ACS Appl. Nano Mater.* **2021**, *4* (8), 7650–7662. <https://doi.org/10.1021/acsnm.1c00754>.
- (61) Sobhan, M. A.; Withford, M. J.; Goldys, E. M. Enhanced Stability of Gold Colloids Produced by Femtosecond Laser Synthesis in Aqueous Solution of CTAB. *Langmuir* **2010**, *26* (5), 3156–3159. <https://doi.org/10.1021/la903088e>.

- (62) Li, Z.; Ruiz, V. G.; Kanduč, M.; Dzubiella, J. Ion-Specific Adsorption on Bare Gold (Au) Nanoparticles in Aqueous Solutions: Double-Layer Structure and Surface Potentials. *Langmuir* **2020**, *36* (45), 13457–13468. <https://doi.org/10.1021/acs.langmuir.0c02097>.
- (63) Merk, V.; Rehbock, C.; Becker, F.; Hagemann, U.; Nienhaus, H.; Barcikowski, S. In Situ Non-DLVO Stabilization of Surfactant-Free, Plasmonic Gold Nanoparticles: Effect of Hofmeister's Anions. *Langmuir* **2014**, *30* (15), 4213–4222. <https://doi.org/10.1021/la404556a>.
- (64) Oncsik, T.; Trefalt, G.; Borkovec, M.; Szilagyi, I. Specific Ion Effects on Particle Aggregation Induced by Monovalent Salts within the Hofmeister Series. *Langmuir* **2015**, *31* (13), 3799–3807. <https://doi.org/10.1021/acs.langmuir.5b00225>.
- (65) Ziefuß, A. R.; Barcikowski, S.; Rehbock, C. Synergism between Specific Halide Anions and pH Effects during Nanosecond Laser Fragmentation of Ligand-Free Gold Nanoparticles. *Langmuir* **2019**, *35* (20), 6630–6639. <https://doi.org/10.1021/acs.langmuir.9b00418>.
- (66) Lal, M.; Plummer, M.; Smith, W. Solvent Density Effects on the Solvation Behavior and Configurational Structure of Bare and Passivated 38-Atom Gold Nanoparticle in Supercritical Ethane. *J. Phys. Chem. B* **2006**, *110* (42), 20879–20888. <https://doi.org/10.1021/jp0633650>.
- (67) Novelli, F.; Bernal Lopez, M.; Schwaab, G.; Roldan Cuenya, B.; Havenith, M. Water Solvation of Charged and Neutral Gold Nanoparticles. *J. Phys. Chem. B* **2019**, *123* (30), 6521–6528. <https://doi.org/10.1021/acs.jpcc.9b02358>.
- (68) Huggins, M. L. Solutions of Long Chain Compounds. *The Journal of Chemical Physics* **1941**, *9* (5), 440. <https://doi.org/10.1063/1.1750930>.
- (69) Flory, P. J. Thermodynamics of High Polymer Solutions. *The Journal of Chemical Physics* **1942**, *10* (1), 51–61. <https://doi.org/10.1063/1.1723621>.
- (70) Dhabal, D.; Jiang, Z.; Pallath, A.; Patel, A. J. Characterizing the Interplay between Polymer Solvation and Conformation. *J. Phys. Chem. B* **2021**, *125* (20), 5434–5442. <https://doi.org/10.1021/acs.jpcc.1c02191>.
- (71) Athawale, M. V.; Sarupria, S.; Garde, S. Enthalpy–Entropy Contributions to Salt and Osmolyte Effects on Molecular-Scale Hydrophobic Hydration and Interactions. *J. Phys. Chem. B* **2008**, *112* (18), 5661–5670. <https://doi.org/10.1021/jp073485n>.
- (72) Dudowicz, J.; Freed, K. F.; Douglas, J. F. Theory of Competitive Solvation of Polymers by Two Solvents and Entropy-Enthalpy Compensation in the Solvation Free Energy upon Dilution with the Second Solvent. *The Journal of Chemical Physics* **2015**, *142* (21), 214906. <https://doi.org/10.1063/1.4921373>.
- (73) Huang, Y.; Cheng, S. Chain Conformations and Phase Separation in Polymer Solutions with Varying Solvent Quality. *Journal of Polymer Science* **2021**, *59* (22), 2819–2831. <https://doi.org/10.1002/pol.20210526>.
- (74) Siwy, Z.; Kosińska, I. D.; Fuliński, A.; Martin, C. R. Asymmetric Diffusion through Synthetic Nanopores. *Phys. Rev. Lett.* **2005**, *94* (4), 048102. <https://doi.org/10.1103/PhysRevLett.94.048102>.
- (75) Martin, C. R.; Siwy, Z. S. Learning Nature's Way: Biosensing with Synthetic Nanopores. *Science* **2007**, *317* (5836), 331–332. <https://doi.org/10.1126/science.1146126>.
- (76) Bush, S. N.; Ken, J. S.; Martin, C. R. The Ionic Composition and Chemistry of Nanopore-Confined Solutions. *ACS Nano* **2022**, *16* (5), 8338–8346. <https://doi.org/10.1021/acsnano.2c02597>.
- (77) Budd, P. M.; Ghanem, B. S.; Makhseed, S.; McKeown, N. B.; Msayib, K. J.; Tattershall, C. E. Polymers of Intrinsic Microporosity (PIMs): Robust, Solution-Processable, Organic Nanoporous Materials. *Chem. Commun.* **2004**, No. 2, 230–231. <https://doi.org/10.1039/B311764B>.
- (78) Wang, S.; Shi, K.; Tripathi, A.; Chakraborty, U.; Parsons, G. N.; Khan, S. A. Designing Intrinsically Microporous Polymer (PIM-1) Microfibers with Tunable Morphology and Porosity via Controlling Solvent/Nonsolvent/Polymer Interactions. *ACS Appl. Polym. Mater.* **2020**, *2* (6), 2434–2443. <https://doi.org/10.1021/acscpm.0c00386>.
- (79) Wongwilawan, S.; Nguyen, T. S.; Nguyen, T. P. N.; Alhaji, A.; Lim, W.; Hong, Y.; Park, J. S.; Atilhan, M.; Kim, B. J.; Eddaoudi, M.; Yavuz, C. T. Non-Solvent Post-Modifications with Volatile Reagents for Remarkably Porous Ketone Functionalized Polymers of Intrinsic Microporosity. *Nat Commun* **2023**, *14* (1), 2096. <https://doi.org/10.1038/s41467-023-37743-y>.
- (80) Wang, J.; Hou, T. Develop and Test a Solvent Accessible Surface Area-Based Model in Conformational Entropy Calculations. *J. Chem. Inf. Model.* **2012**, *52* (5), 1199–1212. <https://doi.org/10.1021/ci300064d>.
- (81) Janjić, G. V.; Malkov, S. N.; Živković, M. V.; Zarić, S. D. What Are Preferred Water–Aromatic Interactions in Proteins and Crystal Structures of Small Molecules? *Phys. Chem. Chem. Phys.* **2014**, *16* (43), 23549–23553. <https://doi.org/10.1039/C4CP00929K>.
- (82) Pal, P.; Chakraborty, S.; Jana, B. Number of Hydrogen Bonds per Unit Solvent Accessible Surface Area: A Descriptor of Functional States of Proteins. *J. Phys. Chem. B* **2022**, *126* (51), 10822–10833. <https://doi.org/10.1021/acs.jpcc.2c05367>.
- (83) Hofmeister, F. Zur Lehre von der Wirkung der Salze. *Archiv f. experiment. Pathol. u. Pharmakol* **1888**, *24* (4), 247–260. <https://doi.org/10.1007/BF01918191>.
- (84) Kunz, W.; Henle, J.; Ninham, B. W. 'Zur Lehre von Der Wirkung Der Salze' (about the Science of the Effect of Salts): Franz Hofmeister's Historical Papers. *Current*

- (85) Buchecker, T.; Schmid, P.; Renaudineau, S.; Diat, O.; Proust, A.; Pfitzner, A.; Bauduin, P. Polyoxometalates in the Hofmeister Series. *Chem. Commun.* **2018**, *54* (15), 1833–1836. <https://doi.org/10.1039/C7CC09113C>.
- (86) Rana, B.; Fairhurst, D. J.; Jena, K. C. Ion-Specific Water–Macromolecule Interactions at the Air/Aqueous Interface: An Insight into Hofmeister Effect. *J. Am. Chem. Soc.* **2023**, *145* (17), 9646–9654. <https://doi.org/10.1021/jacs.3c00701>.
- (87) Judd, K. D.; Gonzalez, N. M.; Yang, T.; Cremer, P. S. Contact Ion Pair Formation Is Not Necessarily Stronger than Solvent Shared Ion Pairing. *J. Phys. Chem. Lett.* **2022**, *13* (3), 923–930. <https://doi.org/10.1021/acs.jpcllett.1c03576>.
- (88) Drexler, C. I.; Cracchiolo, O. M.; Myers, R. L.; Okur, H. I.; Serrano, A. L.; Corcelli, S. A.; Cremer, P. S. Local Electric Fields in Aqueous Electrolytes. *J. Phys. Chem. B* **2021**, *125* (30), 8484–8493. <https://doi.org/10.1021/acs.jpccb.1c03257>.
- (89) Schwaab, G.; Sebastiani, F.; Havenith, M. Ion Hydration and Ion Pairing as Probed by THz Spectroscopy. *Angewandte Chemie International Edition* **2019**, *58* (10), 3000–3013. <https://doi.org/10.1002/anie.201805261>.
- (90) Okur, H. I.; Hladílková, J.; Rembert, K. B.; Cho, Y.; Heyda, J.; Dzubiella, J.; Cremer, P. S.; Jungwirth, P. Beyond the Hofmeister Series: Ion-Specific Effects on Proteins and Their Biological Functions. *J. Phys. Chem. B* **2017**, *121* (9), 1997–2014. <https://doi.org/10.1021/acs.jpccb.6b10797>.
- (91) Krishnamoorthy, A. N.; Holm, C.; Smiatek, J. Specific Ion Effects for Polyelectrolytes in Aqueous and Non-Aqueous Media: The Importance of the Ion Solvation Behavior. *Soft Matter* **2018**, *14* (30), 6243–6255. <https://doi.org/10.1039/C8SM00600H>.
- (92) Miranda-Quintana, R. A.; Smiatek, J. Specific Ion Effects in Different Media: Current Status and Future Challenges. *J. Phys. Chem. B* **2021**, *125* (51), 13840–13849. <https://doi.org/10.1021/acs.jpccb.1c07957>.
- (93) Mazzini, V.; Craig, V. S. J. What Is the Fundamental Ion-Specific Series for Anions and Cations? Ion Specificity in Standard Partial Molar Volumes of Electrolytes and Electrostriction in Water and Non-Aqueous Solvents. *Chem. Sci.* **2017**, *8* (10), 7052–7065. <https://doi.org/10.1039/C7SC02691A>.
- (94) Yu, W.; Du, N.; Gu, Y.; Yan, J.; Hou, W. Specific Ion Effects on the Colloidal Stability of Layered Double Hydroxide Single-Layer Nanosheets. *Langmuir* **2020**, *36* (23), 6557–6568. <https://doi.org/10.1021/acs.langmuir.0c01089>.
- (95) Han, X.; Goebel, J.; Lu, Z.; Yin, Y. Role of Salt in the Spontaneous Assembly of Charged Gold Nanoparticles in Ethanol. *Langmuir* **2011**, *27* (9), 5282–5289. <https://doi.org/10.1021/la200459t>.
- (96) Abbas, S.; Yadav, I.; Kumar, S.; Aswal, V. K.; Kohlbrecher, J. Structure and Interaction in Pathway of Charged Nanoparticles Aggregation in Saline Water as Probed by Scattering Techniques. *Chemical Physics Letters* **2017**, *675*, 124–130. <https://doi.org/10.1016/j.cplett.2017.03.024>.
- (97) Rouquerol, J.; Avnir, D.; Fairbridge, C. W.; Everett, D. H.; Haynes, J. M.; Pernicone, N.; Ramsay, J. D. F.; Sing, K. S. W.; Unger, K. K. Recommendations for the Characterization of Porous Solids (Technical Report). *Pure and Applied Chemistry* **1994**, *66* (8), 1739–1758. <https://doi.org/10.1351/pac199466081739>.
- (98) Natarajan, R.; Charmant, J. P. H.; Orpen, A. G.; Davis, A. P. Water Chains in Hydrophobic Crystal Channels: Nanoporous Materials as Supramolecular Analogues of Carbon Nanotubes. *Angewandte Chemie International Edition* **2010**, *49* (30), 5125–5129. <https://doi.org/10.1002/anie.201002418>.
- (99) Hummer, G.; Rasaiah, J. C.; Noworyta, J. P. Water Conduction through the Hydrophobic Channel of a Carbon Nanotube. *Nature* **2001**, *414* (6860), 188–190. <https://doi.org/10.1038/35102535>.
- (100) Shim, Y.; Kim, H. J. Solvation of Carbon Nanotubes in a Room-Temperature Ionic Liquid. *ACS Nano* **2009**, *3* (7), 1693–1702. <https://doi.org/10.1021/nn900195b>.
- (101) Wang, X.; Fu, F.; Peng, K.; Huang, Q.; Li, W.; Chen, X.; Yang, Z. Understanding of Competitive Hydrogen Bond Behavior of Imidazolium-Based Ionic Liquid Mixture around Single-Walled Carbon Nanotubes. *J. Phys. Chem. C* **2020**, *124* (12), 6634–6645. <https://doi.org/10.1021/acs.jpcc.9b11576>.
- (102) Shim, Y.; Jung, Y.; Kim, H. J. Carbon Nanotubes in Benzene: Internal and External Solvation. *Phys. Chem. Chem. Phys.* **2011**, *13* (9), 3969–3978. <https://doi.org/10.1039/C0CP01845G>.
- (103) Hinkle, K. R.; Phelan, F. R. Jr. Solvation of Carbon Nanoparticles in Water/Alcohol Mixtures: Using Molecular Simulation To Probe Energetics, Structure, and Dynamics. *J. Phys. Chem. C* **2017**, *121* (41), 22926–22938. <https://doi.org/10.1021/acs.jpcc.7b07769>.
- (104) Pramanik, C.; Gissinger, J. R.; Kumar, S.; Heinz, H. Carbon Nanotube Dispersion in Solvents and Polymer Solutions: Mechanisms, Assembly, and Preferences. *ACS Nano* **2017**, *11* (12), 12805–12816. <https://doi.org/10.1021/acs.nano.7b07684>.
- (105) Heinz, H.; Pramanik, C.; Heinz, O.; Ding, Y.; Mishra, R. K.; Marchon, D.; Flatt, R. J.; Estrela-Lopis, I.; Llop, J.; Moya, S.; Ziolo, R. F. Nanoparticle Decoration with Surfactants: Molecular Interactions, Assembly, and Applications. *Surface Science Reports* **2017**, *72* (1), 1–58. <https://doi.org/10.1016/j.surfrep.2017.02.001>.

- (106) Jiang, H.; Cai, Q.; Mateti, S.; Yu, Y.; Zhi, C.; Chen, Y. Boron Nitride Nanosheet Dispersion at High Concentrations. *ACS Appl. Mater. Interfaces* **2021**, *13* (37), 44751–44759. <https://doi.org/10.1021/acscami.1c11795>.
- (107) Smith McWilliams, A. D.; Martínez-Jiménez, C.; Matatyaho Ya'akobi, A.; Ginestra, C. J.; Talmon, Y.; Pasquali, M.; Martí, A. A. Understanding the Exfoliation and Dispersion of Hexagonal Boron Nitride Nanosheets by Surfactants: Implications for Antibacterial and Thermally Resistant Coatings. *ACS Appl. Nano Mater.* **2021**, *4* (1), 142–151. <https://doi.org/10.1021/acsnm.0c02437>.
- (108) Li, D.; Müller, M. B.; Gilje, S.; Kaner, R. B.; Wallace, G. G. Processable Aqueous Dispersions of Graphene Nanosheets. *Nature Nanotech* **2008**, *3* (2), 101–105. <https://doi.org/10.1038/nnano.2007.451>.
- (109) Ma, H.; Shen, Z.; Ben, S. Understanding the Exfoliation and Dispersion of MoS₂ Nanosheets in Pure Water. *Journal of Colloid and Interface Science* **2018**, *517*, 204–212. <https://doi.org/10.1016/j.jcis.2017.11.013>.
- (110) Kim, J.; Kwon, S.; Cho, D.-H.; Kang, B.; Kwon, H.; Kim, Y.; Park, S. O.; Jung, G. Y.; Shin, E.; Kim, W.-G.; Lee, H.; Ryu, G. H.; Choi, M.; Kim, T. H.; Oh, J.; Park, S.; Kwak, S. K.; Yoon, S. W.; Byun, D.; Lee, Z.; Lee, C. Direct Exfoliation and Dispersion of Two-Dimensional Materials in Pure Water via Temperature Control. *Nat Commun* **2015**, *6* (1), 8294. <https://doi.org/10.1038/ncomms9294>.
- (111) Schoeman, B. J.; Sterte, J.; Otterstedt, J.-E. Colloidal Zeolite Suspensions. *Zeolites* **1994**, *14* (2), 110–116. [https://doi.org/10.1016/0144-2449\(94\)90004-3](https://doi.org/10.1016/0144-2449(94)90004-3).
- (112) Lam, C. H.; Chi, H.-Y.; Hsu, S.-M.; Li, Y.-S.; Lee, W.-Y.; Cheng, I.-C.; Kang, D.-Y. Surfactant-Mediated Self-Assembly of Nanocrystals to Form Hierarchically Structured Zeolite Thin Films with Controlled Crystal Orientation. *RSC Adv.* **2017**, *7* (77), 49048–49055. <https://doi.org/10.1039/C7RA10679C>.
- (113) Hsu, W.-J.; Huang, P.-S.; Huang, Y.-C.; Hu, S.-W.; Tsao, H.-K.; Kang, D.-Y. Zeolite-Based Antifogging Coating via Direct Wet Deposition. *Langmuir* **2019**, *35* (7), 2538–2546. <https://doi.org/10.1021/acs.langmuir.8b03738>.
- (114) Gözcü, O.; Kayacı, H. U.; Dou, Y.; Zhang, W.; Hedin, N.; Jasso-Salcedo, A. B.; Kaiser, A.; Çınar Aygün, S. Colloidal Stabilization of Submicron-Sized Zeolite NaA in Ethanol–Water Mixtures for Nanostructuring into Thin Films and Nanofibers. *Langmuir* **2023**, *39* (1), 192–203. <https://doi.org/10.1021/acs.langmuir.2c02241>.
- (115) Cai, Q.; Luo, Z.-S.; Pang, W.-Q.; Fan, Y.-W.; Chen, X.-H.; Cui, F.-Z. Dilute Solution Routes to Various Controllable Morphologies of MCM-41 Silica with a Basic Medium. *Chem. Mater.* **2001**, *13* (2), 258–263. <https://doi.org/10.1021/cm990661z>.
- (116) Nooney, R. I.; Thirunavukkarasu, D.; Chen, Y.; Josephs, R.; Ostafin, A. E. Synthesis of Nanoscale Mesoporous Silica Spheres with Controlled Particle Size. *Chem. Mater.* **2002**, *14* (11), 4721–4728. <https://doi.org/10.1021/cm0204371>.
- (117) Kobler, J.; Möller, K.; Bein, T. Colloidal Suspensions of Functionalized Mesoporous Silica Nanoparticles. *ACS Nano* **2008**, *2* (4), 791–799. <https://doi.org/10.1021/nn700008s>.
- (118) Möller, K.; Kobler, J.; Bein, T. Colloidal Suspensions of Nanometer-Sized Mesoporous Silica. *Advanced Functional Materials* **2007**, *17* (4), 605–612. <https://doi.org/10.1002/adfm.200600578>.
- (119) Pyo, C. E.; Chang, J. H. Hydrophobic Mesoporous Silica Particles Modified With Nonfluorinated Alkyl Silanes. *ACS Omega* **2021**, *6* (24), 16100–16109. <https://doi.org/10.1021/acsomega.1c01981>.
- (120) Sabuncu, S.; Montoya Mira, J.; Quentel, A.; Gomes, M. M.; Civitci, F.; Fischer, J. M.; Yildirim, A. Protein-Coated Biodegradable Gas-Stabilizing Nanoparticles for Cancer Therapy and Diagnosis Using Focused Ultrasound. *Advanced Materials Interfaces* **2023**, *10* (2), 2201543. <https://doi.org/10.1002/admi.202201543>.
- (121) Yamamoto, E.; Shimojima, A.; Wada, H.; Kuroda, K. Mesoporous Silica Nanoparticles with Dispersibility in Organic Solvents and Their Versatile Surface Modification. *Langmuir* **2020**, *36* (20), 5571–5578. <https://doi.org/10.1021/acs.langmuir.0c00729>.
- (122) Schneid, A. D. C.; Silveira, C. P.; Galdino, F. E.; Ferreira, L. F.; Bouchmella, K.; Cardoso, M. B. Colloidal Stability and Redispersibility of Mesoporous Silica Nanoparticles in Biological Media. *Langmuir* **2020**, *36* (39), 11442–11449. <https://doi.org/10.1021/acs.langmuir.0c01571>.
- (123) Wang, A.; Barcus, K.; Cohen, S. M. Quantifying Ligand Binding to the Surface of Metal–Organic Frameworks. *J. Am. Chem. Soc.* **2023**, *145* (30), 16821–16827. <https://doi.org/10.1021/jacs.3c04892>.
- (124) Erdosy, D. P.; Wenny, M. B.; Cho, J.; DelRe, C.; Walter, M. V.; Jiménez-Ángeles, F.; Qiao, B.; Sanchez, R.; Peng, Y.; Polizzotti, B. D.; de la Cruz, M. O.; Mason, J. A. Microporous Water with High Gas Solubilities. *Nature* **2022**, *608* (7924), 712–718. <https://doi.org/10.1038/s41586-022-05029-w>.
- (125) DelRe, C.; Hong, H.; Wenny, M. B.; Erdosy, D. P.; Cho, J.; Lee, B.; Mason, J. A. Design Principles for Using Amphiphilic Polymers To Create Microporous Water. *J. Am. Chem. Soc.* **2023**, *145* (36), 19982–19988. <https://doi.org/10.1021/jacs.3c06627>.
- (126) Khalil, S.; Meyer, M. D.; Alazmi, A.; Samani, M. H. K.; Huang, P.-C.; Barnes, M.; Marciel, A. B.; Verduzco, R. Enabling Solution Processable COFs through Suppression of Precipitation during Solvothermal Synthesis. *ACS Nano* **2022**, *16* (12), 20964–20974. <https://doi.org/10.1021/acsnano.2c08580>.
- (127) Hu, F.; Hu, Z.; Liu, Y.; Tam, K. C.; Liang, R.; Xie, Q.; Fan, Z.; Pan, C.; Tang, J.; Yu, G.; Zhang, W. Aqueous Sol–Gel Synthesis and Shaping of Covalent Organic

- Frameworks. *J. Am. Chem. Soc.* **2023**, *145* (50), 27718–27727. <https://doi.org/10.1021/jacs.3c10053>.
- (128) Martín-Illán, J. Á.; Rodríguez-San-Miguel, D.; Castillo, O.; Beobide, G.; Perez-Carvajal, J.; Imaz, I.; Maspoch, D.; Zamora, F. Macroscopic Ultralight Aerogel Monoliths of Imine-Based Covalent Organic Frameworks. *Angewandte Chemie International Edition* **2021**, *60* (25), 13969–13977. <https://doi.org/10.1002/anie.202100881>.
- (129) Tao, X.; Wang, Z.; Zhang, Q.-P.; Liu, N.; Sun, Y.-L.; Niu, R.-X.; Sun, R.; Wang, X.; Tan, B.; Zhang, C. Covalent Organic Framework Nanohydrogels. *J. Am. Chem. Soc.* **2023**, *145* (46), 25471–25477. <https://doi.org/10.1021/jacs.3c10296>.
- (130) Carrington, M. E.; Rampal, N.; Madden, D. G.; O’Nolan, D.; Casati, N. P. M.; Divitini, G.; Martín-Illán, J. Á.; Tricarico, M.; Cepitis, R.; Çamur, C.; Curtin, T.; Silvestre-Albero, J.; Tan, J.-C.; Zamora, F.; Taraskin, S.; Chapman, K. W.; Fairen-Jimenez, D. Sol-Gel Processing of a Covalent Organic Framework for the Generation of Hierarchically Porous Monolithic Adsorbents. *Chem* **2022**, *8* (11), 2961–2977. <https://doi.org/10.1016/j.chempr.2022.07.013>.
- (131) Romero-Angel, M.; Castells-Gil, J.; Rubio-Giménez, V.; Ameloot, R.; Tatay, S.; Martí-Gastaldo, C. Surfactant-Assisted Synthesis of Titanium nanoMOFs for Thin Film Fabrication. *Chem. Commun.* **2021**, *57* (72), 9040–9043. <https://doi.org/10.1039/D1CC02828F>.
- (132) Zheng, G.; Chen, Z.; Sentosun, K.; Pérez-Juste, I.; Bals, S.; Liz-Marzán, L. M.; Pastoriza-Santos, I.; Pérez-Juste, J.; Hong, M. Shape Control in ZIF-8 Nanocrystals and Metal nanoparticles@ZIF-8 Heterostructures. *Nanoscale* **2017**, *9* (43), 16645–16651. <https://doi.org/10.1039/C7NR03739B>.
- (133) Wang, S.; Park, S. S.; Buru, C. T.; Lin, H.; Chen, P.-C.; Roth, E. W.; Farha, O. K.; Mirkin, C. A. Colloidal Crystal Engineering with Metal–Organic Framework Nanoparticles and DNA. *Nat Commun* **2020**, *11* (1), 2495. <https://doi.org/10.1038/s41467-020-16339-w>.
- (134) Ding, S.; Zhang, Y.; Lou, F.; Aslam, M. K.; Sun, Y.; Li, M.; Duan, J.; Li, Y.; Chen, S. “Uncapped” Metal–Organic Framework (MOF) Dispersions Driven by O₂ Plasma towards Superior Oxygen Evolution Electrocatalysis. *J. Mater. Chem. A* **2022**, *10* (39), 20813–20818. <https://doi.org/10.1039/D2TA05387J>.
- (135) Jongert, T. K.; Slowinski, I. A.; Dao, B.; Cortez, V. H.; Gredig, T.; Plascencia, N. D.; Tian, F. Zeta Potential and Size Analysis of Zeolitic Imidazolate Framework-8 Nanocrystals Prepared by Surfactant-Assisted Synthesis. *Langmuir* **2024**, *40* (12), 6138–6148. <https://doi.org/10.1021/acs.langmuir.3c03193>.
- (136) Yakin, F. E.; Barisik, M.; Sen, T. Pore Size and Porosity Dependent Zeta Potentials of Mesoporous Silica Nanoparticles. *J. Phys. Chem. C* **2020**, *124* (36), 19579–19587. <https://doi.org/10.1021/acs.jpcc.0c04602>.
- (137) Chen, C.-Y.; Hsieh, M.-J.; Raj, A.; Peng, W.-C.; Hamaguchi, H.; Chuang, W.-T.; Wang, X.; Wang, C.-L. Missing Piece in Colloidal Stability—Morphological Factor of Hydrophobic Nanoparticles. *Langmuir* **2023**, *39* (8), 2922–2931. <https://doi.org/10.1021/acs.langmuir.2c02582>.
- (138) Zobel, M.; Neder, R. B.; Kimber, S. A. J. Universal Solvent Restructuring Induced by Colloidal Nanoparticles. *Science* **2015**, *347* (6219), 292–294. <https://doi.org/10.1126/science.1261412>.
- (139) Zobel, M. Observing Structural Reorientations at Solvent–Nanoparticle Interfaces by X-Ray Diffraction – Putting Water in the Spotlight. *Acta Crystallogr A Found Adv* **2016**, *72* (6), 621–631. <https://doi.org/10.1107/S2053273316013516>.
- (140) Thomä, S. L. J.; Krauss, S. W.; Eckardt, M.; Chater, P.; Zobel, M. Atomic Insight into Hydration Shells around Faceted Nanoparticles. *Nat Commun* **2019**, *10* (1), 995. <https://doi.org/10.1038/s41467-019-09007-1>.
- (141) Israelachvili, J. N.; McGuiggan, P. M. Forces Between Surfaces in Liquids. *Science* **1988**, *241* (4867), 795–800. <https://doi.org/10.1126/science.241.4867.795>.
- (142) Israelachvili, J. N.; Wennerstroem, H. Entropic Forces between Amphiphilic Surfaces in Liquids. *J. Phys. Chem.* **1992**, *96* (2), 520–531. <https://doi.org/10.1021/j100181a007>.
- (143) von Wedelstedt, A.; Chen, H.; Kalies, G.; Snurr, R. Q. Do Internal and External Surfaces of Metal–Organic Frameworks Have the Same Hydrophobicity? Insights from Molecular Simulations. *Langmuir* **2020**, *36* (43), 13070–13078. <https://doi.org/10.1021/acs.langmuir.0c02527>.
- (144) von Wedelstedt, A.; Bockel, L.; Flehmig, N.; Klauk, M.; Kalies, G. How Important Is the Internal Hydrophobicity of Metal–Organic Frameworks for the Separation of Water/Alcohol Mixtures? *Langmuir* **2022**, *38* (50), 15672–15682. <https://doi.org/10.1021/acs.langmuir.2c02475>.
- (145) Li, L.; Lin, J.; Fu, F.; Dai, Z.; Zhou, G.; Yang, Z. Molecular-Level Understanding of Surface Roughness Boosting Segregation Behavior at the ZIF-8/Ionic Liquid Interfaces. *Langmuir* **2022**, *38* (14), 4175–4187. <https://doi.org/10.1021/acs.langmuir.1c02922>.
- (146) Grenev, I. V.; Shubin, A. A.; Solovyeva, M. V.; Gordeeva, L. G. The Impact of Framework Flexibility and Defects on the Water Adsorption in CAU-10-H. *Phys. Chem. Chem. Phys.* **2021**, *23* (37), 21329–21337. <https://doi.org/10.1039/D1CP03242A>.
- (147) Marcus, R. A. Electrostatic Free Energy and Other Properties of States Having Nonequilibrium Polarization. I. *The Journal of Chemical Physics* **1956**, *24* (5), 979–989. <https://doi.org/10.1063/1.1742724>.
- (148) Marcus, R. A. Exchange Reactions and Electron Transfer Reactions Including Isotopic Exchange. Theory of Oxidation-Reduction Reactions Involving Electron Transfer. Part 4.—A Statistical-Mechanical Basis for Treating Contributions from Solvent, Ligands, and Inert Salt. *Discuss.*

- Faraday Soc.* **1960**, 29 (0), 21–31.
<https://doi.org/10.1039/DF9602900021>.
- (149) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. I. *The Journal of Chemical Physics* **1956**, 24 (5), 966–978.
<https://doi.org/10.1063/1.1742723>.
- (150) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. II. Applications to Data on the Rates of Isotopic Exchange Reactions. *The Journal of Chemical Physics* **1957**, 26 (4), 867–871.
<https://doi.org/10.1063/1.1743423>.
- (151) Marcus, R. A. On the Theory of Oxidation-Reduction Reactions Involving Electron Transfer. III. Applications to Data on the Rates of Organic Redox Reactions. *The Journal of Chemical Physics* **1957**, 26 (4), 872–877.
<https://doi.org/10.1063/1.1743424>.
- (152) Noble, B. B.; Konovalova, A.; Moutarlier, L. J.; Brogden, V.; Kempler, P. A. Electrochemical Chlor-Iron Process for Iron Production from Iron Oxide and Salt Water. *Joule* **2024**, 8 (3), 714–727.
<https://doi.org/10.1016/j.joule.2024.01.001>.
- (153) Kuo, F.-Y.; Jerng, S. E.; Gallant, B. M. Dual Salt Cation-Swing Process for Electrochemical CO₂ Separation. *ACS Cent. Sci.* **2023**, 9 (9), 1750–1757.
<https://doi.org/10.1021/acscentsci.3c00692>.
- (154) Oener, S. Z.; Foster, M. J.; Boettcher, S. W. Accelerating Water Dissociation in Bipolar Membranes and for Electrocatalysis. *Science* **2020**, 369 (6507), 1099–1103.
<https://doi.org/10.1126/science.aaz1487>.
- (155) Poletayev, A. D.; McKay, I. S.; Chueh, W. C.; Majumdar, A. Continuous Electrochemical Heat Engines. *Energy and Environmental Science* **2018**, 11 (10), 2964–2971.
<https://doi.org/10.1039/c8ee01137k>.
- (156) Hupp, J. T.; Weaver, M. J. Solvent, Ligand, and Ionic Charge Effects on Reaction Entropies for Simple Transition-Metal Redox Couples. *Inorganic Chemistry* **1984**, 23 (22), 3639–3644. <https://doi.org/10.1021/ic00190a042>.
- (157) Inoue, H.; Zhou, H.; Ando, H.; Nakagawa, S.; Yamada, T. Exploring the Local Solvation Structure of Redox Molecules in a Mixed Solvent for Increasing the Seebeck Coefficient of Thermocells. *Chem. Sci.* **2023**.
<https://doi.org/10.1039/D3SC04955H>.
- (158) Zhou, H.; Matoba, F.; Matsuno, R.; Wakayama, Y.; Yamada, T. Direct Conversion of Phase-Transition Entropy into Electrochemical Thermopower and the Peltier Effect. *Advanced Materials* **2023**, 35 (36), 2303341.
<https://doi.org/10.1002/adma.202303341>.
- (159) Xia, K. T.; Rajan, A.; Surendranath, Y.; Bergman, R. G.; Raymond, K. N.; Toste, F. D. Tunable Electrochemical Entropy through Solvent Ordering by a Supramolecular Host. *J. Am. Chem. Soc.* **2023**.
<https://doi.org/10.1021/jacs.3c10145>.
- (160) Svensson Grape, E.; Huang, J.; Roychowdhury, D.; Debela, T. T.; Chang, H.; Jenkins, A.; Schimpf, A. M.; Hendon, C. H.; Brozek, C. K. Converting Heat to Electrical Energy Using Highly Charged Polyoxometalate Electrolytes. *ACS Appl. Energy Mater.* **2024**.
<https://doi.org/10.1021/acsaem.4c00036>.
- (161) Park, J. G.; Aubrey, M. L.; Oktawiec, J.; Chakarawet, K.; Darago, L. E.; Grandjean, F.; Long, G. J.; Long, J. R. Charge Delocalization and Bulk Electronic Conductivity in the Mixed-Valence Metal-Organic Framework Fe(1,2,3-Triazolato)2(BF₄)_x. *Journal of the American Chemical Society* **2018**, 140 (27), 8526–8534.
<https://doi.org/10.1021/jacs.8b03696>.
- (162) Huang, J.; Marshall, C. R.; Ojha, K.; Shen, M.; Golledge, S.; Kadota, K.; McKenzie, J.; Fabrizio, K.; Mitchell, J. B.; Khaliq, F.; Davenport, A. M.; LeRoy, M. A.; Mapile, A. N.; Debela, T. T.; Twight, L. P.; Hendon, C. H.; Brozek, C. K. Giant Redox Entropy in the Intercalation vs Surface Chemistry of Nanocrystal Frameworks with Confined Pores. *J. Am. Chem. Soc.* **2023**, 145 (11), 6257–6269. <https://doi.org/10.1021/jacs.2c12846>.

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