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-methylimidazolate)$_2$ 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:

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

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:

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

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 or surface roughness.[17,27] On the other hand, soft-shell particles, such as oil droplets, metal nanoparticles coated with a polymer layer, proteins clusters, and even living cells,[28] present complications to DLVO theory as solvent intercalation, ion adsorption,[29] 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,[23,30] impart improved thermodynamic stability and, in some cases, unique optical behavior.[31,32] 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 polymolecular particle dispersed in a medium" with "at least in one direction a dimension roughly between 1 nm and 1 μm".[33] 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.[34] 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.[35,36] 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,[37,38] represent another key example of nanoparticles that find utility only by surface functionalization. Through favorable interactions with solvent, surfactant ligands to prevent Ostwald ripening,[39,40] allowing nanoparticles to remain stable at precise sizes that dictate their tunable
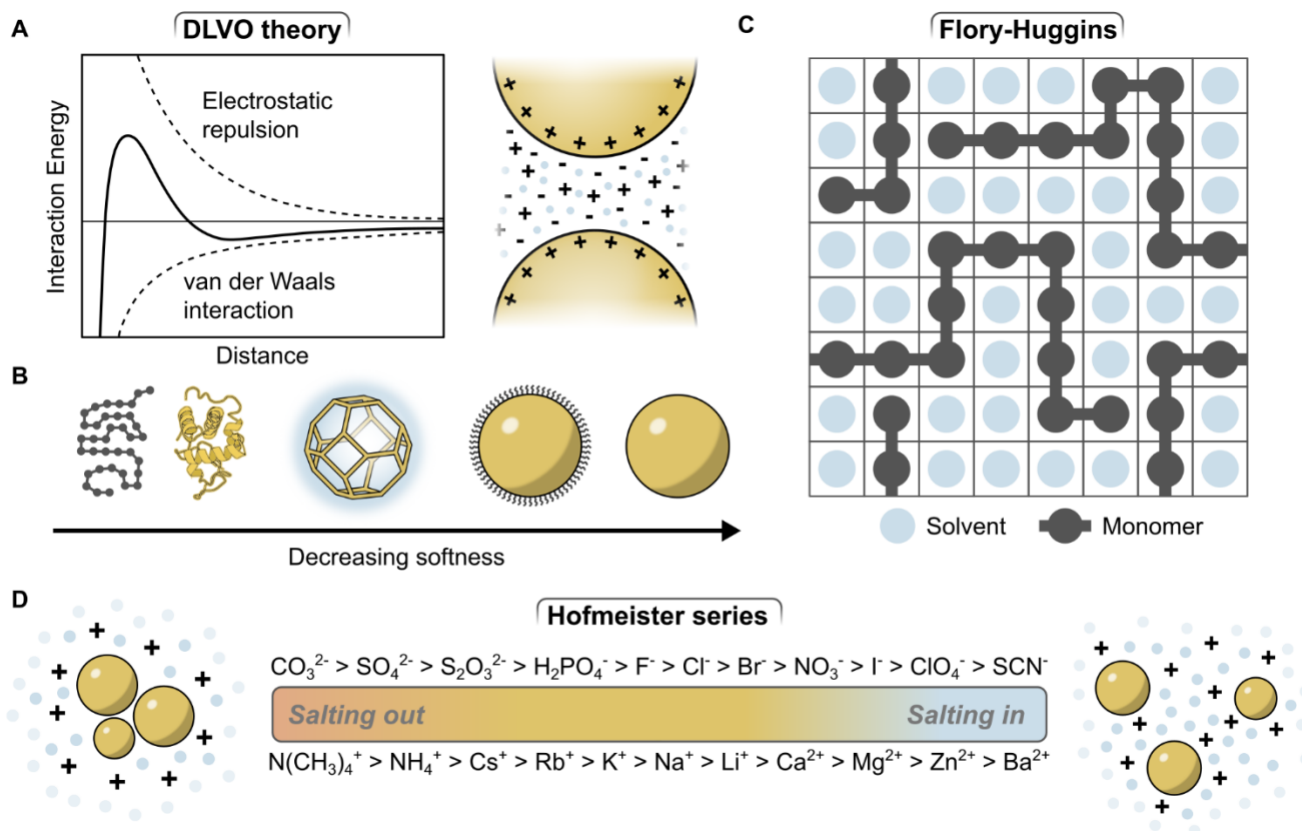
Figure 1. A) Typical DLVO graph, showing the interaction energy as a sum of electrostatic repulsion and attractive van der Waals interactions. **B)** Illustration of the soft-to-hard range of nanoscale materials, ranging from polymers/proteins to hard spheres, such as metal-oxide nanoparticles. **C)** 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.[41–43] Functionalizing quantum dots with either a inorganic shell also diversifies the available solvents for dispersion.[44,45] Most notably, the addition of water-soluble ligands, such as citrates,[46] polymers,[47,48] or other small molecules[49,50] 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.[51,52] 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,[53] this chemical decomposition generates a heterogeneous and rough surface with mixed valence sites.[54,55] An alternate approach that avoids surface oxidation was achieved by synthesizing bare copper

nanoparticles with an electron-donating gadolinium support.[56] 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.[57] 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.[58] Because these few examples of bare nanoparticles are short-lived colloids, they are often quickly drop-casted back to their solid state.[59–62]

In the few studies of bare metallic nanoparticles in solution without a stabilizing support (detailed below), 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.[55,63] 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.[57,64–66] The colloidal stability of nanoparticles in solvents without electrolyte, however, have only been studied as computational simulations of

bare particles[67] or through weakly ligated experimental systems where a portion of the surface remains deliberately exposed.[68] 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, 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.[69,70] While the entropy of mixing a simple molecule in solution can be described by Gibbs energy of mixing:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{3}$$

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:

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

which now considers the number of moles (n) and the volume fraction (ϕ) 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. With the exception of intrinsically porous polymers (such as PIM-1),[71] polymers lack permanent porosity (the ability to maintain a rigid, porous structure when suspended in solution).[72] However, the mechanism of polymer solvation depends on the large solvent accessible surface areas carved out by the unwrapping of individual monomer units.[73] 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,[74] ionic screening,[75] and other polymer or solvent-specific interactions[76,77] 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 μms. 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.[78,79] Chemical functionalization of these materials leads to specific ion effects, such as appended carbonate groups showing preferential binding of metal cations.[80] Polymers of intrinsic microporosity (PIMs), on the other hand, contain voids of 2 nm or less.[81] Controlling the solubility of PIMs is critical for creating robust films with consistent pore sizes.[82] The commonly used PIM-1, however, dissolves only in tetrahydrofuran (THF) and chloroform (CHCl₃), 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,[83] 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.[84–86] 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,[87,88] 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.[89] 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.[90,91] 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.[92] 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.[93–96] 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.[97] 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.[98,99] A comprehensive study of the ion effects in non-aqueous solvents found that water is not unique in its role in the Hofmeister series.[100] 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.[64] 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 anions[101] and other metal nanoparticles.[102,103] A likely causes 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.

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.[104] For example, the surface density of the commonly studied zeolitic imidazolate framework ZIF-8 (Zn(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
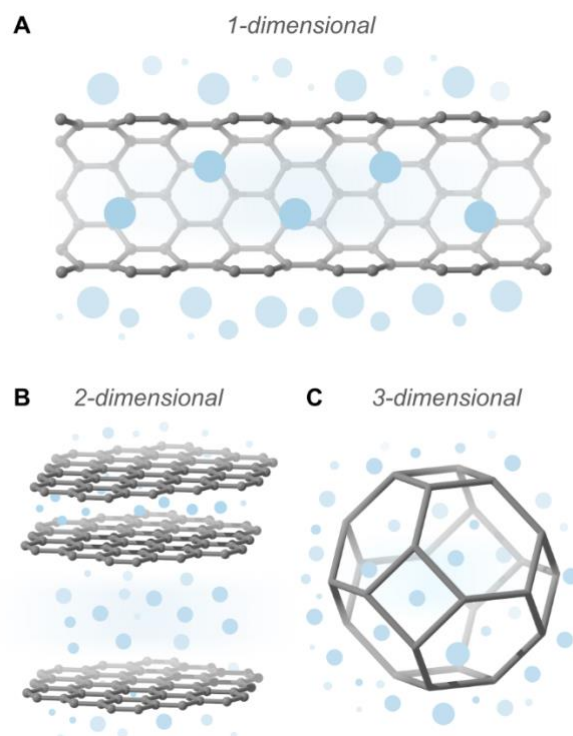
Figure 2. Illustration of (**A**) 1-dimensional (polymers, nanotubes), (**B**) 2-dimensional (layered or sheet-like materials) and (**C**) 3-dimensional structures (porous materials) and their possible solvent interactions.

following sections, we describe common permanently porous materials (*i.e.*, materials that retain porosity in solution), propose mechanisms for their colloidal stability and solubility and outline key factors that impact porous nanomaterial solubility. Additionally, we consider the thermodynamic factors of solvation in terms of the packing and charge density of solvent revealed from simulations. 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.[105] Surprisingly, water adsorbs inside the pores of carbon nanotubes, leading to the phenomenon of "water wires".[106] 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,[107,108] 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,[109] alcohols,[110] and polymer solutions,[111] 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.[112–114] 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 MoS_2, disperse in aqueous solutions via exfoliation-induced oxidation.[115,116] 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.[117] 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, MoS_2, WS_2, and $MoSe_2$, 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 (SiO_2) 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,[118] surfactant surface coverage,[119,120] and polymer coatings.[121] 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.[122–124] These surfactant-capped materials can be stable for upwards of a year in water.[125] Mesoporous silica nanoparticles can also be surface functionalized as hydrophobic, which renders them useful drug delivery agents.[126,127] 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.[128,129]

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,
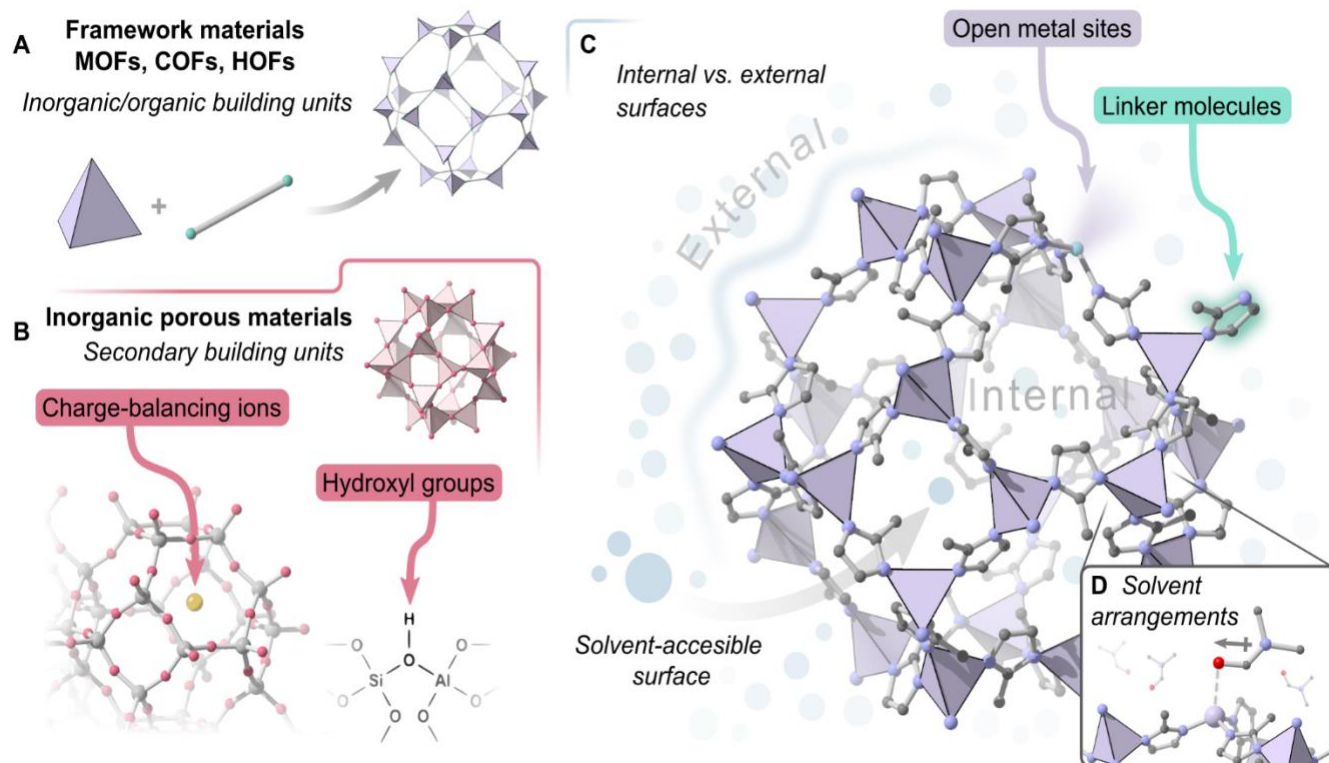
Figure 3. Representation of (**A**) framework materials, comprised of inorganic/organic building units that are assembled into porous frameworks, and (**B**) inorganic porous materials, which are made up of secondary building units. (**C**) Both material classes show distinct internal vs. external surfaces 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.

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 hydrogen-bonded organic frameworks (HOFs), covalent-organic frameworks (COFs) and 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.[130] 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,[131,132] 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.

Hydrogen bonding facilitates the self-assembly of 2-dimensional and 3-dimensional frameworks. Due to the dynamic nature of hydrogen bonding, HOFs reversibly convert between monomers in solution to extended solids in the crystalline state. Most HOFs contain carboxylic acid motifs, with the first reported HOF consisting of trimesic acid.[133] Despite this structural reversibility, experimental insight into the solvation state of HOFs remains elusive. Preliminary evidence suggests HOFs remain partially intact in solution as fragments ranging between 10-200 nm in diameter.[134] Because HOFs cannot be prepared as spherical nanoparticles, but rather as rods,[135] cages,[136] or larger crystals, their solvation state is difficult to study with typical light scattering techniques. While recent work has utilized fragmented HOF nanoparticles for membrane formations,[134] fundamental studies will be needed to understand how HOF nanoparticles vary in composition as compared to their single crystal counterparts and how they remain colloidally stable in the absence of surface functionalization.

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.[137] 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.[138] However, higher concentrations of the monomer unit induced gel formation, as is commonly noticed for COF syntheses.[139,140] While these gels can be useful for casting films, they are typically mechanically weak[141] 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,[142,143] 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 dyes[130] or DNA/protein coronas[144] 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] Solubility measurements indicated that the dispersibility of MOF nanoparticles correlates with the solubility of the linker, in terms of both solvent identity and overall concentration, regardless of the MOF/linker pair. Additional calorimetry measurements revealed that the enthalpy of solvation of the MOF nanoparticle was akin to that of the linker alone. This experimental evidence suggests individual thermodynamic contributions of solvent-monomer units driving overall nanoparticle solubility, in a similar fashion to Flory-Huggins solubility for polymers. While the rigidity of nanoparticle frameworks differs from the macromolecular flexibility of polymers and proteins, their porosity greatly enhances solvent accessible surface areas. These results and analysis strongly suggests that the interaction of MOF nanoparticles resembles the dissolution of cage molecules, polymers, and other macromolecules systems where solubility depends on solvent-monomer energetics and accessible void spaces (Figure 3C,D). In addition to solubility and calorimetry

measurements with single-solvent systems, we suggest the use of binary solvents (such as one that dissolves the linker and another that does not),[145] and bulky solvents incapable of entering the pores as strategies for understanding the solvation mechanism of porous nanoparticles. Finally, determining the Hansen solubility parameters for MOF nanoparticles will prove useful in comparing bare nanoMOFs to uncapped, hard-shell colloidal nanoparticles.[146]

Instead of capping agents imparting colloidal stability to nanoMOFs, we recently found evidence of specific solvent-surface interactions that mimic binding at the surface but with solvent instead of organic ligands. 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] A unique, blue-shifted C=O feature exhibited in the VSFS spectra was assigned to ordered *N,N*-dimethylformamide (DMF) molecules bound to open Zn^{2+} sites on the surface of ZIF-8. In this case, solvent binds to open metal sites in a similar fashion to ordered capping agents and reduces the energetics at the surface. In addition to linker solubility, we postulate that MOF nanoparticles are only soluble in high-dipole solvents due to the necessity of the solvent molecule to specifically adsorb to the high energy nanoparticle surface.

In addition to specific solvent-surface interactions, classical electrostatic arguments of DLVO theory could explain the stability of uncapped 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.[147] 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.[1,148] 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 decay through porous channels.[149] Binding of solvent or polymers to open metal sites at the surface of MOF nanoparticles improves colloidal stability, while also reducing the apparent surface charge.[2,132] While one may expect that smaller nanoparticles to possess a greater volumetric density of surface defects, experimental evidence of size-dependent zeta potentials is lacking. Instead, studies have focused on the influence of synthetic conditions (such as modulator), on nanoparticle surface chemistry,[148] with most systems having hydrodynamic diameters of 100-300 nm. In other words, zeta potentials may not relate directly to MOF colloidal stability, especially where steric hindrance from solvent or polymer might reduce the overall surface charge and impart a repulsive osmotic pressure to the system.

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, termed the "hydrophobic effect", is introduced as a mechanism to describe porous nanoparticles,[150] 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. Our recent VSFSS spectra revealed spontaneously assembly of ordered solvation shells of 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 and lacked chemical specificity.[151–155] 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.

While experimental evidence of porous nanomaterial solvation is slowing emerging, theoretical results also provide insight into these buried interfaces. Molecular dynamics (MD) simulations of ZIF-8 indicate that nanoparticle solubility increases in solvents with higher molar densities, suggesting solvation benefits from a higher density of enthalpically favorable interactions.[1] Other simulations have probed the role of solvent removal in framework collapse.[156] as well as the impact of solvent impurities on forming framework defects.[157] Although deleterious to MOF applications, these results provide insight into specific solvent-linker or solvent-metal interactions which can impart colloidal stability in the presence of ordered solvent.

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 surface[132] 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[158,159] and that surface composition, such as rough pore aperatures[160] or framework flexibility,[161] 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.[162–166] 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.[167–169] 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.[170] 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,[171] electrolyte with large ΔS_r lead to large free energy differences 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,[172] the use of dissolved polymers that undergo phase changes upon redox,[173] metallocages that intercalate charge balancing ions through a desolvation process,[174] and polyoxometalate anions[175] all involve large supramolecular 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 colloid.

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-triazolate)$_2$ (Fe(TA)$_2$).
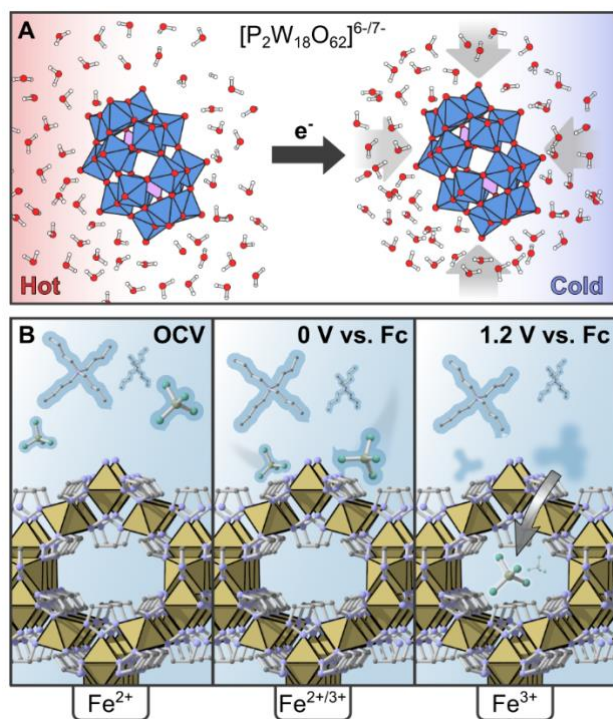
Figure 4. Illustrative examples of how solvation affects electrochemical processes in nanoscale materials. **A)** Illustration of how the superchaotropic properties of a Wells-Dawson polyoxotungstate anion, $[P_2W_{18}O_{62}]^{6-}$, can be used in thermogalvanic applications: the difference in solvation 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-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.

Although the MOF contains two crystallographically distinct Fe sites, their chemical environments are so similar that Mössbauer spectroscopy shows just one Fe species.[176] 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).[177] 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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Table of Contents Artwork:

Solvation of Nanoscale Materials

Colloidal stability — Interfacial chemistry — Internal vs. external surfaces