1. INTRODUCTION

“Principles. You can’t say A is made of B or vice versa. All mass is interaction!” Richard P. Feynman

Global warming, fossil fuel energy shortage, and environmental pollution are increasingly important issues and are driving strong demand for the development of green chemistry. On consideration of the basic principles of green chemistry, a core issue is developing new green solvents and catalysts. Ionic liquids (ILs), which consist of only cations and anions and are liquids near room temperature, have attracted broad attention from the scientific and industrial communities because of their unique features, including an environmentally friendly nature, tailorable structure, and adjustable properties. More importantly, due to their rich interactions and microstructures (which researchers can modulate), ILs function as both solvents and catalysts, rendering them broadly useful in green chemistry and opening new directions in green chemical engineering.

The development of ILs goes back to 1914, when the liquid ethylammonium (containing a small amount of water) was first synthesized. However, ILs were not explored much further until the late 1970s, when Osteryoung and Wilkes prepared liquid chloroaaluminate (\([\text{AlCl}_3\]) melts and used them in electrochemical applications. In the early 1980s, the research groups of Seddon and Hussey regarded ILs containing \([\text{AlCl}_3\]) as nonaqueous, polar, green solvents for studying the electrochemical aspects of transition-metal complexes and spectroscopic chemistry. In the 1990s, for the first time, Chauvin et al. and Wilkes et al. used ILs as solvents for homogeneous transition-metal catalysts. Subsequent to their initial exploration and emergence, ILs are now established media in green chemistry.

Recently, much research on ILs has focused on cutting-edge research fields such as separations, catalysis, electrochemistry, biomolecular analysis, and drug synthesis. For example, Zhang’s group focused on the multiscale nature and function of ILs and applied ILs to industrial processes such as CO\(_2\) capture and utilization, lignin dissolution and transformation, new energy storage, and thermal management of nanoelectron devices. MacFarlane et al. synthesized ILs of trihexyl tetradecyl phosphonium chloride as a proton conductor and constructed an electrochemical nitrogen reduction reaction system with a high ammonia generation rate, high Faraday efficiency, and long-term stable operation. Rogers et al. used IL systems to dissolve...
cellulose, chitin, and other bio-based resources and further prepared high-value chemicals. Huang et al. and others used ILs to prepare new materials such as perovskite batteries that exhibit substantially improved performance in comparison with conventional batteries.

Notably, although substantial progress has been made in the applications of ILs, the reason for ILs having such excellent functions remains unclear. Especially when it is considered that ILs consist entirely of ions, many experimental technologies cannot be directly applied to IL systems. Furthermore, some processes (such as ultrahigh gas solubility, mass transfer mechanisms, and reaction intensification processes) cannot be explained well simply via traditional theoretical models. More importantly, a scientific understanding of the interactions and structures of ILs is the basis for designing task-specific ILs, which remains a major challenge.

A unique class of hydrogen bonds (HBs) dominates the unique properties and functions of ILs. The unique HBs in ILs, namely Z-bonds, always couple with the strong electrostatic interactions between the cations and anions and further facilitate the formation of complex nanostructures (including ionic pairs, aggregates, or even ionic clusters)—thus, the corresponding effects on the performance of ILs in typical applications are substantial. Furthermore, the structure and properties of an IL change substantially when it meets a solid substrate (for instance, an electrode, catalyst, or support matrix). The equilibrium state of interfacial ILs should be a function of the corresponding interactions between the ILs and the solid surface structures. The Z-bonds in ILs couple with the solid surface and thus facilitate the formation of interfacial ILs with relatively ordered structures (much different from those of pure liquids and solids), termed quasi-liquids. The complex structure of quasi-liquids establishes various microenvironments that enable various functionalities, such as CO2 capture and transformation, energy-storage devices, low-friction materials, and field-effect transistor functionalities. Hence, understanding the basic interactions and structures of ILs and their corresponding interfaces is the key to the rational design of IL-based applications in chemical and related fields.

In this Perspective, we summarize key progress on ILs, especially relating to two basic and new concepts: the Z-bond and quasi-liquid (Figure 1). For the Z-bond, we analyze the intrinsic difference between a Z-bond and a conventional HB and discuss Z-bond-induced ionic clustering and corresponding applications in separations and catalysis. Then, we elucidate the dynamic formation process, structural characteristics, and universality of quasi-liquids and discuss their prospects and potential applications. Finally, we also thoroughly analyze the opportunities and challenges of the Z-bond and quasi-liquid in ILs, with a particular focus on quantitative descriptions, new preparation and characterization methods of the Z-bond, and quasi-liquids based on new applications. This Perspective provides an essential and fundamental understanding of the basic interactions and structures of ILs and further supports the development of IL-based applications.

Figure 1. Illustration of typical cations and anions, Z-bond, and quasi-liquid in ILs, where the Z-bond is the intrinsic reason for many of the special properties of ILs, and a quasi-liquid broadly exists in real applications based on ILs.
2. Z-BONDS IN IONIC LIQUIDS

2.1. Definition of Hydrogen Bond

HBs are common in natural and synthetic materials\textsuperscript{63,81,82} (such as those with applications to chemistry, chemical engineering, biology, materials, and energy). Although HBs have been known for almost a century and every scientist is familiar with them, the exact definition of the HB remains vague and elusive. Before we discuss the Z-bond in ILs, it is necessary to clarify the definition of conventional HBs—a difficult task, considering the extensive number and range of characteristics ascribed to HBs.\textsuperscript{63}

The International Union of Pure and Applied Chemistry updated their definition of the HB in 2011;\textsuperscript{83} this definition provides a list of the evidence and characteristics of HBs and a short history of HBs. To clearly understand and clarify the scientific nature of HBs, several typical definitions of an HB\textsuperscript{63} are based on general chemical, geometrical, charge density distribution, infrared (IR), and nuclear magnetic resonance (NMR) data, summarized in Figure 2a. Steiner\textsuperscript{82} proposed the most popular definition: “an \(X-H\cdots A\) interaction is called an HB, if 1. it constitutes a local bond and 2. \(X-H\) acts as proton donor to \(A\).” The second point represents that an HB can be interpreted as an incipient proton-transfer reaction from \(X-H\) to \(A\).\textsuperscript{82} In addition to a chemical description, the HB can also be defined via the geometries of \(X-H\cdots A\), where the HB in water has a clearly defined, short-distance geometry \((d_{H\cdots A})\) and a linear angle \((\angle XHA)\). The chemical interactions and specific geometry of HBs also induce a change in the charge density distribution. If there is an HB, a direct bond path forms and connects the H and A atoms in the map of the charge density distribution, where the point of minimal charge density is termed the bond critical point.\textsuperscript{84} The nonzero electron density at the bond critical point implies that one can use the formation of the HB and the corresponding electron density values to measure the strength of the HB. In addition to the theoretical aspects of HBs, there are also specialized experimental methods (IR and NMR spectroscopy).\textsuperscript{82,83,86} IR spectra mainly corresponds to the vibrational modes of the functional groups in the system, where the HB can affect the vibrational intensities and directions of the corresponding functional groups, especially the stretching vibration \((\nu_{X-H})\) of the donor \(X-H\). One can correlate the shift of \(\nu_{X-H}\) between free \(X-H\) and bonded \(X-H\cdots A\) by using the H\cdots A distance: \(\Delta \nu_{X-H} = \beta (d_{H\cdots A})\). Such a correlation is valid for different types of HBs, including organic and inorganic systems. Furthermore, NMR spectroscopy can use the \(1H\) downfield shift to reflect the HB length that is due to proton transfer within a single HB.\textsuperscript{86} In general, the HB length or \(d_{H\cdots A}\) decreases with an increasing chemical shift in the \(1H\) spectrum. In summary, the red shift of the \(X-H\) vibrational stretching mode or increase in the NMR intensity is an indicator of an HB.

The definitions of an HB discussed in the previous paragraphs are only suitable under specific conditions. For example, the van der Waals (vdW) cutoff definition for the HB in the context of geometry \((d_{H\cdots A} < r_H + r_A)\); the last two terms are the vdW radii) is too strict and should be applied cautiously.\textsuperscript{82} Furthermore, the HB can even be identified visually via atomic force microscopy (AFM); for example, the HB formed between 8-hydroxyquinoline molecules adsorbed on a Cu(111) surface under cryogenic conditions.\textsuperscript{87} Although such a method is direct, it only works for a small number of systems where the molecules are in the same plane. Hence, we advise researchers use (whenever possible) several methods to determine whether there is an HB in a system.

2.2. Scientific Connotation of the Z-Bond in ILs

It is noteworthy that the HBs in ILs substantially differ from those in water or organic solvents, particularly considering the ionic nature of ILs. In other words, both the donor and acceptor in HBs for ILs are charged species, rather than near-neutral groups or molecules. Considering the charge state, one can identify a series of HBs (Figure 2b). The original or prototypical HB is the weak interaction within the water system,\textsuperscript{88} where two water molecules form a \(O^\cdots H^\cdots O\) interaction. The HB interaction mainly arises from the electrical force or weak ionic dispersion between \(H^\text{+}\) and \(O^\text{−}\) atoms. Over time, researchers expanded the requirement for an O atom in an HB to other electronegative atoms (\(X-H\cdots A\) where \(X\) and \(A\) can be \(O, C, N, F, P, S, Cl, Br, I\); the H atom always localizes to the more electronegative atom). Furthermore, if \(X\) or \(A\) is a charged species or the HB is between an ion and a neutral molecule, the HB can be represented as \([X-H]\cdots [A]^{-}\) or \([X-H]\cdots A^{-}\). Such an HB can be termed an ionic HB, which is common in biology and acid–base chemistry. For example, researchers have comprehensively...
studied and evaluated the HB between a water molecule and either a cation (R₃NH⁺) or an anion (Cl⁻). Physically, an ionic HB has a shorter H···A distance and stronger interactions in comparison with conventional HBs in water but is still dominated by the HB interactions.

If we focus on the HBs in ILs, we find that both the acceptor and the donor in HBs are charged species: i.e., [X⁻H]⁺···[A]⁻ or [X⁻H]⁺···[A]⁺. There are four main types of cations in ILs (i.e., quaternary ammonium, quaternary phosphonium, imidazole, and pyrrole ions), whereas anions are commonly e.g. halide, tetrafluoroborate (BF₄⁻), or hexafluorophosphate (PF₆⁻) ions (Figure 1). Figure 3 shows the possible HBs between various cations and anions. On consideration of the location of the H atom in the cation or anion, HBs with different geometries, energies, and vibrations can form in ILs. Furthermore, HBs can be present between a cation and an anion, and also in interaction, cation–cation, and even anion–anion pairs, suggestive of the tailorable nature of HBs in ILs. Using 1-ethyl-3-methylimidazolium chloride (EmimCl) as an example, there are several types of HBs: [Im–C₃–H]⁺···[Cl]⁻, [Im–C₅–H]⁺···[Cl]⁻, [Im–C₅–H]⁺···[Cl]⁻, and [Im–C_chain–H]⁺···[Cl]⁻. On the basis of theoretical simulations, the transferred

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Typical HBs in the ILs, where the dashed lines represents the HBs: (a) HBs between Emim⁺ and Cl⁻/SCN⁻/NO₃⁻; (b) HBs between N1111⁺ and Cl⁻/SCN⁻/NO₃⁻; (c) HBs between Epy⁺ and Cl⁻/SCN⁻/NO₃⁻; (d) HBs for cation–cation; (e) HBs for anion–anion; (f) intra-HB of a cation with a long chain; (g) π⁺–π⁺; (h) π⁺–anion.

![Figure 4](https://example.com/fig4.png)

**Figure 4.** (a–e) The zigzag configurations in different crystal ILs, where the red dashed lines represent the HBs and the gray, blue, pink, light blue, yellow, red, orange, and white sticks represent C, N, P, F, S, O, B, and H atoms, respectively (a) 1-ethyl-3-methylimidazolium hexafluorophosphate (EmimPF₆); (b) 1,2,4-triazolium perfluorobutanesulfonate (TAZpfBu); (c) 1,3-dimethylimidazolium chloride (MmimCl); (d) 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF₄); (e) 1-butyl-3-methylimidazolium chloride (BmimCl). The solid line indicates the zigzag arrangement of ions. (f) The HB in the ice one cubic (Ic), where the dashed light lines represents the HBs.
electron from Cl\(^{-}\) to \(\text{Emim}^{+}\) is up to 0.3 e and the angle of the HB is ca. 150\(^{\circ}\), which is quite different from that of the weak and linear HBs in water. The unique structure of HBs in ILs may be attributable to the coupling interactions between the HBs and electrostatic interactions. In other words, the HBs in ILs differ from the HBs in water or organic systems and also differ from ionic HBs with a single ion as the proton donor or acceptor.

Conventional HBs and electrostatic attractions couple with each other in ILs, which constitutes new interactions that dominate the structural directionality, arrangement order, and even ionic aggregates of ILs. Physically, the solid state of matter can represent the intrinsic feature of a weak interaction, especially HBs.\(^{82}\) In ice, linear HBs always form between different water molecules. However, in IL crystals, the HB substantially deviates from a linear geometry and induces the imidazolium cation to form a zigzag packing chain motif, where the anion localizes between these zigzag chains.\(^{82}\) These unique HBs link the cation and anion (Figure 4), forming distinct zigzag configurations in crystal ILs, including \(\text{EmimPF}_6\), \(\text{EmimBF}_4\), 1,3-dimethylimidazolium chloride, 1-butyl-3-methylimidazolium chloride (BmimCl), and 1,2,4-triazolium perfluorobutanesulfonate (TAZPfBu). Physically, the formation of zigzag chains is mainly attributable to the following reasons: (1) the coupling interactions between the HB and electrostatic interactions, where the strong electrostatic attractive forces correspond to a bent HB bond, and (2) stabilization of the entire system or minimization the total potential energy, for which HBs should form between the cation and anion to the maximum extent. Hence, such a structural packing is attributable to the unique coupling interactions between the cations and anions in ILs: namely, the Z-bond.\(^{85}\) In addition to conventional ILs, polynionic liquids (PILs) are important members of the IL family. From the level of the HB bond, the cations and anions in PILs can also form Z-bonds that are similar to those in conventional ordinary ILs. However, PILs do not readily form zigzag configurations (Figure 4) because of the strong chemical constraint within the polymeric ionic monomer.

In the content of the Z-bond, HBs can provide both an attractive force (at a long distance) and a repulsive force (at a short distance) and exhibit a direction because of the spatial orientations of the H and A atoms. However, the electrostatic interaction mainly serves as the attractive force, especially considering the charge transfer between the H and A atoms. The HB and electrostatic interaction are both present in ILs, resulting in the formation of Z-bonds. Physically, the Z-bond can also be described as an electrostatic dipole–dipole interaction.\(^{93}\) However, the Z-bond bears more resemblance to covalent bonds than to traditional HBs. Furthermore, the Z-bond is directional and strong, and one atom may form several Z-bonds, leading to a complex Z-bond network in ILs. From theoretical and experimental results, one can compare information on Z-bonds and HBs in water (Figure 5). The Z-bond energy spans 2 orders of magnitude, ranging from 0.2 to 40 kcal/mol,\(^{83}\) whereas the HB energy for the water system is ca. 4.72 kcal/mol.\(^{94}\) Using EmimCl as an example, the p orbital exhibits a distinct orbital overlap and a bond angle of \(\sim 150^{\circ}\), whereas there is no orbital overlap in the linear HB of water.\(^{93,94}\) Furthermore, the lifetimes of the Z-bond and HB are on the scale of nanoseconds and picoseconds, respectively, which agrees well with the high stability of IL systems.

Hence, we propose that the Z-bond exhibits the following features.\(^{83,85}\) (a) The general structure of the Z-bond is \([\text{X–H}\cdots \text{A}]\), where X and A are electronegative atoms (including O, N, F, C, P, Cl, Br, I, and S). (b) Z-bonds correspond to the coupling interactions in IL systems, especially the induced and electrostatic interactions. Furthermore, electron transfer between the proton acceptor and donor is more evident than that in water or organic systems, resulting in the intrinsic nature of the covalent bond. (c) The energy of a Z-bond is much greater than that of a HB due to the coupling effect, almost 10 times that of an HB in water. (d) The angle of the Z-bond always ranges from 120 to 150\(^{\circ}\), which is bent in comparison with an HB and can form a zigzag motif. The \(d_{\text{H}...\text{A}}\) bond is longer than that of a conventional HB because of the nonlocal charge distribution in the cation or anion. (e) With regard to the Z-bond, there is always orbital overlapping, leading to the characteristics of a \(\sigma\) orbital. The overlap also results in a shift in the frequency of the HB vibration.

### 2.3. Z-Bond-Induced Networks and Ionic Clusters

As discussed in the previous paragraphs, an individual cation or anion may have multiple Z-bond sites, which enables ILs to form a continuous and complex HB network. On consideration of the strong bond energy, long lifetimes, and unique zigzag motif, the Z-bond-induced network will be more stable and distinct than that in water or organic systems. From theoretical simulations, we found that various ionic clusters form in a 1-dodecyl-3-methylimidazolium bromide (C\(_{12}\) mimBr) solution,\(^{103-105}\) for example, spherical vesicles or rodlike micelles. In accordance with the progress of the simulations, the randomly distributed ions first formed several small micelles, and then these small vesicles moved closer to form one large vesicle (Figure 6a).\(^{100}\) Rodlike micelles also formed in accordance with the concentration of C\(_{12}\) mimBr (Figure 6b). Furthermore, transmission electron microscopy (TEM) clearly indicated that the spherical vesicles transformed to rodlike micelles and then back to the vesicle morphology as the C\(_{12}\) mimBr concentration increased from 0.06 to 0.96 mol L\(^{-1}\) (Figure 6c). With regard to ILs in solution, several basic forces and interactions between the cations and anions (for example, Z-bonds, vdW forces, long-range electrostatic interactions, and hydrophobic interactions between the alkyl chain in the cations) mainly dominate the dynamic formation of ionic clusters. Ionic clusters can also be present in pure ILs, as revealed by theoretical simulations and
spectral experiments. For example, the hydroxyl-functionalized cation 1-(2-hydroxyalkyl)pyridinium can form a heterogeneous aggregation region in ILs because of the polarization and hydrophobic interactions of the long side chain. Under the concomitant influence of these basic interactions, a single ion, an ion pair, a Z-bonding network of multiple ions, large ionic clusters, and even complex nanostructures can form and evolve in the dynamic and fast-changing microenvironments in ILs.

The long-tail chains in the cations mainly interact with each other via hydrophobic interactions, whereas the anion is bound to the cluster via the Z-bond (Figure 6a). The local rearrangement and charge separation substantially affect the properties of ILs, such as viscosity and dissolution. In industrial applications, the viscosity of ILs is usually high and imparts constraints on the mass transport and reaction processes, where researchers prepare and use water—IL mixtures rather than pure ILs to decrease the viscosity. However, our previous work has indicated that a small amount of water can unexpectedly increase the viscosity of Bmim acetate (Figure 6d). The abnormal increase in the viscosity is attributable to a chainlike anion—water—anion cluster structure, where the chain length of the cluster increases with the IL concentration when the water content is less than 2%. The chainlike cluster does not disrupt the Z-bond within the ILs and can enhance the diffusive resistance, leading to a substantial increase in the viscosity. However, the viscosity of the water—BmimBF4 mixture decreases gradually with increasing water content. This is because a spherical cluster is more stable than a chainlike cluster in the BmimBF4 system, where the spherical cluster disrupts the Z-bond between the cation and anion and further decreases the viscosity.

The Z-bond-induced cluster can play a key role in many applications. For instance, a dimethyl sulfoxide—IL mixture can dissolve cellulose because the formation of the IL cluster can directly expose the anion to the cellulose. Furthermore, the ionic cluster can catalyze conversion of CO2 and ethylene oxide to dimethyl carbonate, which exhibits a relatively lower energy barrier in comparison to that in the single IL pair. In general, ionic clusters are present in mixed systems of ILs and other

Figure 6. (a) Evolution of a cluster in a C12mimBr—water mixture, transforming from a random cluster to a micelle. Reproduced with permission from ref 100. Copyright 2015 American Chemical Society. (b) Formation of rodlike micelles. (iv) and (v) are the single rodlike micelles with N pairs of ILs. Reproduced with permission from ref 107. Copyright 2015 American Chemical Society. (c) TEM image and a simulated snapshot of C12mimBr in an aqueous solution with different concentrations of ILs. Reproduced with permission from ref 101. Copyright 2013 Royal Society of Chemistry. (d) The experimental and simulated viscosities of the IL—water mixture, where the top panel is BmimAc and the bottom panel is BmimBF4. Reproduced with permission from ref 102. Copyright 2017 Wiley.
liquids \(^{109}\) (such as water, dimethyl sulfoxide, Brønsted acids, and organic electrolytes). In such a cluster system, the basic interactions include not only the Z-bond but also conventional or ionic HBs. These different HBs and Z-bonds synergistically determine the properties and functions of IL−mixture systems.

2.4. Major Challenges of Z-Bonds

Recently, researchers have extensively evaluated HBs in ILs by experiments and theoretical simulations and thereby revealed the existence of the Z-bond.\(^{8,41,65}\) This research also clarifies that the nature of the Z-bond is the coupling interactions between the HB and electrostatic interactions, which bend the HB and lead to formation of the zigzag motif. Based on the concept of the Z-bond, the specific role and unique function of ILs in several major applications can be explained well: for example, high viscosity, high thermal/chemical stability, excellent cellulose solubility, and efficient activation of the C=O bond in CO\(_2\). Hence, the proposal of the Z-bond has provided substantial support for an in-depth understanding and rational design of ILs, especially task-specific insights. However, some deficiencies in research on the Z-bond remain;\(^{110}\) in our opinion, the major challenges mainly include the following three aspects.

1. **Direct observation of Z-bonds in experiments.** One of the most intrinsic features of the Z-bond is the bent HB caused by the strong electrostatic forces between the cation and anion.\(^{11,112}\) In the context of density functional theory (DFT) and molecular dynamics (MD), researchers have simulated and analyzed the bending of HBs. However, direct observations of bent HB or Z-bonds remain unreported. Current equipment (such as Q-plus AFM) can directly obtain an image of a HB,\(^ {87}\) but such equipment does not work in IL systems because of the nonplanar structural features. Hence, developing advanced equipment that researchers can use to directly observe Z-bonds would substantially facilitate not only studies of the Z-bond but also related cutting-edge fields (including lithium-ion electrolytes, nanocatalysts, and interfacial self-assembly).

2. **Strong−weak characterization of Z-bonds.** ILs always manifest slow−fast dynamics, where the fast stage represents the Z-bond changing the interacting sites on the time scale of picoseconds. In contrast, the slow stage represents separation of the anion and cation on the time scale of nanoseconds. Such dynamics mainly result from the Z-bond, which couples the weak HB and strong electrostatic interactions. Because of the tailorable nature of ILs and because one can readily add a functional group to the ion, one can modulate the strength of the Z-bond over a large range, almost 2 orders of magnitude.\(^ {63}\) However, how to predict the strong or weak characteristics of the Z-bond from the corresponding IL structure remains unresolved. Combined machine learning, big-data analysis, and DFT calculations should be useful for determining the strong and weak features of the Z-bond.

3. **Mathematical description of coupling interactions in Z-bonds.** Because of the nonlocalized distribution of charge in the cation or anion, both the HBs and electrostatic interactions are complex and can be affected by the microenvironment around the ion. One can simplify the electrostatic interactions as the sum of the repulsive Coulombic interactions between the nuclei or electron for the donor and acceptor atom and the attractive term between the electron of one atom and the nuclei of the other atom,\(^ {93,113,114}\) but such interactions cannot account for the directional feature of Z-bonds. In other words, a more quantitative and complete description of the Z-bond is necessary. How to analyze or clarify the contribution of the HB and electrostatic interactions to the total energy of the Z-bond remains a major challenge.
Decoupling of the Z-bond, an alternative approach to analyzing the Z-bond in detail, relies on a careful design of the measurement systems and corresponding long-time-scale and large-spatial-scale simulations.

3. FROM THE BULK TO THE INTERFACE: Z-BONDS → QUASI-LIQUIDS

When ILs approach a solid catalyst or an electrode, the features that are intrinsic to the bulk state are disrupted because of the interfacial template effect. The role of the solid interface mainly pertains to three aspects. First, the IL and solid surface can facilitate electron transfer, where the cation and anion contribute to different extents to the total Δe depending on the electronic structures of the cation, anion, and solid surface. Second, the surface atomic structure of the solid substrate is pertinent; for example, a face-centered-cubic (111) or graphite surface. The neighboring substrate environment can tune the local orientation of the supported cation or anion. Third, the surface atomic structure of the solid substrate can contribute to different extents to the total Δe depending on the structural orientation of the cation and anion. The role of the solid interface therefore mainly pertains to three aspects. First, the IL and solid surface can facilitate electron transfer (Δe), where the cation and anion contribute to different extents to the total Δe depending on the electronic structures of the cation, anion, and solid surface. Second, the surface atomic structure of the solid substrate is pertinent; for example, a face-centered-cubic (111) or graphite surface. The neighboring substrate environment can tune the local orientation of the supported cation or anion. Third, the specific functional groups that are present are pertinent (including −OH, − COOH, and −NH2). Additional HBs can form between the ILs and solid substrate and further modulate the packing structure of the interface. In summary, the surface polarization, direction, and specific adsorption to ions can synergistically affect the structure and function of interfacial ILs, in a manner that differs from that of conventional bulk ILs.

3.1. Common IL–Solid Interfacial Structure

Via advanced experiments and theoretical simulations, researchers have reported many studies on the IL–solid interface. With regard to experimental work, direct observation and measurement of the IL–solid interface is challenging in comparison with the corresponding three-dimensional bulk ILs. Common experimental techniques include AFM, scanning tunneling microscopy (STM), differential scanning calorimetry, NMR, high-resolution TEM, thermogravimetric analysis, and X-ray diffraction. In addition to direct experimental observations, researchers often use theoretical simulations to study the influence mechanism of e.g. the substrate shape, material, and applied electric field on the structures, properties, and functions of interfacial ILs. Examples of such theoretical work include quantum chemical calculations, MD simulations, coarse-grained MD simulations, Monte Carlo methods, and statistical mechanics methods. By combining experiments and theoretical simulations, researchers have conducted in-depth studies on the structures, physicochemical properties, and applications of interfacial ILs in terms of reactions, separations, and electrochemistry.

Figure 7 shows fundamental information about the IL–solid interface: for instance, the vibrational spectrum, force curve, density distribution, and orientation. At the charged surface, a dense ionic layer always forms and the orientation (parallel or vertical) depends substantially on the charge state. AFM and sum frequency generation spectroscopy are common means of representing the interfacial state of ILs. The force–distance curve in Figure 7b clearly indicates the dense distribution of ILs near the solid surface, whereas the sum frequency generation spectroscopy maps in Figure 7c indicate that the cation of 1-methyl-3-octyl-imidazolium inserts into the interfacial region once the BaF2(111) surface is covered by a graphene layer. Hence, ILs form several layer structures when the ILs approach the solid substrate, leading to density oscillations in the interfacial region. Using EmimBF4 at a graphite surface as an example, the imidazole ring in the cation preferentially adsorbs onto the surface in a parallel configuration, whereas the anion binds to the cation via the Z-bond. Because of the disruption of the liquid features of ILs, the local density at the interface is always 2–10x larger than that in the corresponding bulk IL. When one coats the functional groups onto the surface or adds an external charge to the substrate, strong HBs or electrostatic interactions can enhance the local density of the interface and the structural orientation of the cation and anion. Hence, ILs that exhibit dense packing at the interface is a remarkable feature that fundamentally differs from that of the corresponding bulk ILs.
3.2. Structural Features of Ultrathin IL Films

Because of the rearrangement of ILs in the interfacial region, solid-supported IL films (especially ultrathin films with a thickness on the scale of several nanometers) exhibit several advantages in comparison with the corresponding bulk ILs: faster diffusion, smaller amounts, and higher chemical/thermal stability. As a result, ultrathin IL films find broad use and are an active area of research in the engineering and science community. On consideration of the interfacial effect of the solid substrate and the ionic nature of ILs, the structure of the IL film should be a function of the interfacial interactions and Z-bonds within ILs.

The Z-bond between the cation and anion modulate the geometrical arrangement of the IL film, where the various Z-bond sites and direction can provide a more readily tailored design and function. Through multiscale simulations from DFT to MD, researchers have recently evaluated the Z-bond within IL subunits. Using EmimPF$_6$ on a graphite surface as an example (Figure 8a–c), researchers proposed four subunits constructed by the cation–anion pair. The difference between the subunits is mainly the number of ILs and the relative orientation of the neighboring cations. As grown from specific subunits, one can obtain a two-dimensional (2D) monolayer (Figure 8d–f). Via physical vapor deposition and STM, researchers have prepared 2D ordered IL films (including 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide (BMPTf$_2$N) on the surface of Ag(111) and 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imide on the surface of Au(111)) and 2D disordered IL films such as BMPTf$_2$N@Cu(111). Furthermore, by changing the solid substrate, temperature, and external electrical field, one can modulate the extent of ordering of the ultrathin film.

In addition to ultrathin IL films on a solid surface, researchers can also prepare a film via placing ILs inside a nanoscale cavity constructed by using flexible 2D materials (including graphene, MoS$_2$, hexagonal BN). Layer spacing is one of the most powerful strategies to modulate ILs. For example, when the layer spacing decreases to the nanoscale, the ionic arrangement, liquid state, and cation–anion correlations exhibit obvious differences from those of the corresponding bulk state. The density distribution, entropy, free energy, and vibrational spectra reveal that confined ILs undergo a transition from a liquid to a partially solid to a fully solid (Figure 9). Via X-ray scattering, researchers determined the TFSI–TFSI pair near the surface...
and partial disruption of the Coulombic ordering of bulk IL.\(^{115}\) MD simulations of confined ILs also indicate that the Z-bond in ILs couples substantially with the graphene wall, imparting monotonic behavior to the entropy, vibrational information, electric conductivity, and ionicity in accordance with the layer spacing.\(^{156,158}\) ILs with strong Z-bonds always exhibit high affinity to the solid surface and vice versa. The good hydrophilicity of ILs to the solid readily enhances the local density and modulates the orientation of the ILs near the surface. Furthermore, the Z-bonds and wall surface can facilitate substantial charge transfer, leading to reconstruction of the interfacial ionic structure. These unique interfacial structures can impart ILs with substantially different properties in comparison with the corresponding bulk ILs; for example, a high separation selectivity for CO\(_2/\)CH\(_4\),\(^{159}\) an abnormally enhanced fraction of free ions in confined ILs,\(^{158}\) and a nonmonotonic relationship between the entropy and confined size of ILs.\(^{40,156}\)

As discussed in previous paragraphs, ultrathin IL films (whether surface-supported or confined) exhibit substantial differences in comparison with conventional bulk ILs, mainly in terms of three aspects: (a) one can more readily modulate the structure because of the reduction of the number of Z-bonds per ion, (b) the structure can be substantially ordered, dependent on the interfacial properties of the solid substrate or 2D wall materials, and (c) the phase state is more complex than the liquid nature of bulk ILs (and can be partially liquid, partially solid, or even fully solid).

### 3.3. Z-Bonds Impart Unique Properties and Functions to Interfacial ILs

Within interfacial ILs, there are several basic interactions that one rarely finds to coexist in a single-material system (including Coulombic, solvophobic, \(π−π\), vdW, and Z-bond interactions).\(^{8,61}\) These coupled interactions enable interfacial ILs to establish many unique structures and microenvironments as discussed in previous paragraphs, which are active areas of multidisciplinary research (including material phase transitions, highly selective gas separations, and high reactive activity of the catalyst).\(^{46,133,141,159−163}\)

One can form self-assembled, ordered, ultrathin IL structures (Figure 8) that can modulate the electron distribution in ILs and expose the gas adsorption sites of ILs and finally improve the reaction and separation efficiencies.\(^{164}\) Furthermore, interfacial ILs can increase the high melting point and enhance the thermal stability of ILs. Hence, the unique structural features of ultrathin IL structures may reduce the amount of ILs needed for a given application and further strengthen the intrinsic advantages of ILs, which is pertinent to engineering applications of ILs.

On the basis of the concept of a heterogeneous catalyst, Riisager et al.\(^{165}\) confined ILs to the pore structure of a porous matrix to form a supported IL-phase catalyst, which helped to overcome the main disadvantages of ILs (such as high viscosity, slow gas diffusion, and high cost). For example, one can restrict EmimBr into mesoporous silica to form an EmimBr@mSiO\(_2\) catalyst, which activates otherwise stable CO\(_2\) and efficiently catalyzes CO\(_2\) conversion to produce dimethyl carbonate. The turnover frequency of the EmimBr@SiO\(_2\) catalyst reached 112.6 h\(^{−1}\), which is almost 1.7 times that of the corresponding bulk ILs under the same reaction conditions.\(^{166}\) The high catalytic activity of confined ILs is attributable to the large proportion of mesopores, good dispersion of EmimBr, and high exposure of the Si–OH groups. One can enhance the catalytic performance of supported noble-metal catalysts by simply depositing an IL film on the top.\(^{167,168}\) An ultrathin BmimBF\(_4\) film forms a complex with a single-atom catalyst due to strong electrostatic interactions (Figure 10a). The film restrained the diffusion and migration of the single-atom catalyst, decreased the probability of polymerization, and enhanced the stability of the catalyst.\(^{169}\)

**Figure 10.** (a) Illustration of a thin BmimBF\(_4\) film stabilizing a single-atom catalyst. The bottom panels are the conversion and selectivity of C\(_2\)H\(_4\) using the catalyst with and without ILs. Reproduced with permission from ref 160. Copyright 2019 Cell Press. (b) TEM images of an individual ChZnCl\(_3\)@SWNT after annealing in a vacuum for 6 h at 200, 300, and 400 °C, where ChZnCl\(_3\) refers to the zinc-containing quaternary ammonium-based IL [Me\(_4\)NC\(_3\)H\(_2\)OH][ZnCl\(_4\)]. Reproduced with permission from ref 133. Copyright 2009 American Chemical Society. (c) The confined EmimBF\(_4\) for high-efficient gas separation. Reproduced with permission from ref 159. Copyright 2018 American Chemical Society.
With regard to interfacial ILs, the liquid-to-solid phase transition differs from that of traditional ILs. By combining high-resolution TEM, X-ray diffraction, and differential scanning calorimetry (Figure 10b), Wu et al. found that the melting point of 1-hexyl-3-methylimidazolium bromide confined in carbon nanotubes (CNTs) with a diameter of 10 nm increased ca. 100 K in comparison with that of bulk ILs. Theoretical simulations indicated that disordered bulk BmimBF4 adopts an ordered microcrystal structure, inducing an abnormal enhancement of the melting point. Furthermore, the melting point of confined EmimPF6 further increases with a decreasing radius of the CNT. By confinement of ILs in a 2D nanochannel constructed from graphene, the ILs are preferentially in a partial liquid state rather than a pure solid state as the interlayer spacing decreases to 0.75 nm.

Interfacial ILs can also enable exposure to specific molecules and exhibit high performance in gas separation. On the basis of the Gibbs free energy, imidazole ILs confined in porous solid materials can efficiently adsorb CO2 and exhibit a high CO2/CH4 selectivity, as confirmed by experiments and simulations. Furthermore, one can confine ILs into 2D materials (e.g., graphene oxide, MoS2, BN, and MXene) to form solid-supported IL membranes, which can efficiently capture CO2 from a mixture of CH4, H2, N2, and CO2 (Figure 10c). The high performance of confined ILs is mainly attributable to ILs being able to assemble into a relatively ordered structure on the surface of 2D materials to provide additional adsorption sites to CO2 in comparison with unconfined ILs and enhance the gas separation selectivity.

Interfacial ILs can also enhance the performance of many other processes; for instance, lithium-ion battery electrolytes, the power density of supercapacitors, and single-atom stabilizers. The unique properties and functions of interfacial ILs is closely related to the interfacial structures, interactions, and Z-bonds within ILs. The strong interfacial interactions can facilitate adsorption of more ILs and tune the corresponding strength of the Z-bonds between the cations and anions. Furthermore, interfacial ILs exhibit an abundance of activation sites; this abundance can enhance the uptake of a given reactant or target molecule. In other words, coupling of the Z-bonds and interfacial interactions impart ILs with unique properties and facilitate promising applications in reactions, separations, and electrochemistry.

### 3.4. New Era of Precise Liquid Regulation: Quasi-Liquids

When an IL contacts a solid surface, the intrinsic Z-bond network is disrupted and the solid surface can modulate the structure of the IL. When one places ILs at a solid-liquid interface, on an ultrathin film, or in a nanoconfined space, the IL structure changes dramatically. The main features of interfacial ILs are as follows. (1) The density of interfacial ILs is always smaller than that of the corresponding bulk ILs, ranging from 2× to even 10× depending on the coupling between the ILs and solid substrate. (2) The arrangements of the cations and anions exhibit regular patterns or an ordered structure due to the directionality of the Z-bond: for example, a linear chain in the inner space of a CNT and quadrilateral packing on the surface of Au(111). (3) One can readily modulate the Z-bond network and structure of interfacial ILs via the external conditions, including the ionic species, temperature, and electric field. Consequently, the unique, tailorable, functional interfacial IL structure is pertinent to applications in cutting-edge fields in chemical engineering, chemistry, materials, and energy.
In addition to ILs, other liquids (including water, organic solvent, and even gases) can exhibit similarly unique behaviors under specific conditions.\textsuperscript{174−176} Examples are as follows: formation of 2D-ordered ice on a solid surface,\textsuperscript{174} an ordered monolayer of perylenetetracarboxylic dianhydride exhibiting hybrid magnetism/superconductivity,\textsuperscript{176} water confined in a protein channel,\textsuperscript{177} where water cannot flow freely but undergoes transport across the channel in a single chain of water molecules, and CO\textsubscript{2} in an electrochemical system, where CO\textsubscript{2} molecules near the electrode surface preferentially undergo a hopping diffusive rather than free-diffusive mechanism.\textsuperscript{178} In general, such a unique interfacial liquid structure consists of a partially ordered structure and exhibits the properties of both a solid and liquid. In such a system, several basic interactions and phase structures are present. However, the characteristics of this kind of surface or interfacial liquid or gas cannot be simply described by traditional solid, liquid, or gas theory.\textsuperscript{179,180} Their structure, dynamics, and transport properties are intermediate to those of a solid and liquid. To account for the nature of the specific interfacial system, we term this intermediate state a quasi-liquid.\textsuperscript{181,182}

From our recent studies, we propose that the main structural features of a quasi-liquid are as follows (Figure 11) (1) At the electronic level, molecules or ions undergo substantial charge transfer with the substrate: i.e., the internal interaction in the bulk liquid couples with the interface, leading to a liquid that readily self-assembles at the interface. (2) A quasi-liquid exhibits an intermediate degree of ordering, which differs from the long-range order of a crystal and the short-range order of a liquid. (3) The thickness of a quasi-liquid may be only several nanometers or only a few molecules or ions, such as a 2D IL\textsuperscript{183} supported by a metal or a molten water layer on an ice surface.\textsuperscript{178}

Focusing on ILs, one can understand the quasi-liquid state as the outcome of coupling among the surface structures, solid interactions, and Z-bonds in ILs. The high viscosity and thermal/chemical stability facilitate the use of ILs in constructing specific interfacial structures, which one can also modulate over a wide range of temperatures or electrical fields. Furthermore, the tailorable nature of the ions can lead to many promising functions of IL-based quasi-liquids. For example, placing an IL-based quasi-liquid with a regular or ordered arrangement on a catalyst surface can substantially improve the stability and selectivity of catalysts.\textsuperscript{184} Confining ILs into 2D materials facilitates the preparation of new types of electrodes that can enable the fabrication of ultrafast ion transfer channels for electrolytes and facilitate the development of new batteries with ultrafast charging dynamics.\textsuperscript{179} One can also use a quasi-liquid with high permeability and selectivity for CO\textsubscript{2} capture and conversion, to enable atmospheric carbon reduction and utilization.

This series of major potential applications, based on the concept of the quasi-liquid, will provide theoretical and technical support for new opportunities in the context of emerging strategic industries (such as renewable energy, new materials, life and health, electronic information, and artificial intelligence).

4. OPPORTUNITIES AND FUTURE CHALLENGES OF Z-BONDS AND QUASI-LIQUIDS

The common nature of the Z-bond and quasi-liquid is the coupling interaction, where the first term represents the coupling between the HB and electrostatic interactions and the latter term represents the coupling between the Z-bond and solid structure/interaction. The nature of the coupling can further affect the specific geometry and strength of the Z-bond or the local ion arrangement and function of the quasi-liquid. Physically, understanding the Z-bond and quasi-liquid from the basic interactions or units is the key point: for instance, clarifying the quantitative contributions of the HB and electrostatic interactions to the Z-bond in various ILs, understanding the manner in which one can modulate the quasi-liquid on the basis of the polarization of the IL on the solid surface, and constructing new preparation methods for Z-bonds and quasi-liquids based on force and the material unit. Hence, a basic understanding of the Z-bond and quasi-liquid is essential for the rational design and development of IL-based applications.

To clarify the formation, evolution, and operation of Z-bonds and quasi-liquids (clearly and quantitatively), crucial questions remain of how to obtain details and information about IL bonding and structure \textit{in situ} and in real time. In our opinion, the potential challenges and opportunities in the context of Z-bonds and quasi-liquids of ILs are as follows.

1. \textit{Precise simulations of ILs near the interface}. High-precision and long-time-scale simulations are important for the design of ILs, especially quasi-liquid systems. Common force fields for the ILs are the molecular force field\textsuperscript{185,186,187,188,189,190} and some polarizable force fields.\textsuperscript{181} Although one can use such simulations to study the intrinsic bulk phase properties of ILs, obtaining an accurate description of the charge polarization and orientation of ILs on the solid surface remains challenging, especially for metal catalysts or charged electrode systems. For long-duration simulations, most current methods reduce the number of atoms in the simulation system and thereby sacrifice accuracy, such as in the united atomic strategy\textsuperscript{156} and coarse-grained MD simulations.\textsuperscript{182} How to improve the computational efficiency while ensuring the accuracy of the force field is a key challenge. It is essential to develop new technologies on the basis of DFT calculations and machine learning\textsuperscript{181,182,183,184} to construct a high-accuracy force field of the IL–solid interface. Furthermore, researchers should develop new simulation programs or software based on quantum calculations or graphics processing unit technology, to enable high-precision and long-duration simulations.

2. \textit{Ultrafast spectroscopy to detect the dynamics of forming/breaking Z-bonds}. Currently, researchers mainly study the kinetic processes of forming and breaking HBs by spectroscopic methods (including IR and NMR). Examples include the following: nonideality and ionic clusters in ILs have been thoroughly studied by IR spectroscopy,\textsuperscript{184} Tokmakoff et al. revealed the unique vibration potential of the HF system in water and differentiated hydrogen bonding from chemical bonding via femtosecond IR technology,\textsuperscript{185} and Hunger et al. reported that the time scale of the vibrational spectrum of the N–H bond in \( \text{[C}_6\text{H}_4\text{NH}_2\text{]}\text{[NO}_3\text{]} \) ranges from femtoseconds to picoseconds, indicating the Z-bond-induced complex movement of ions.\textsuperscript{186} How to quickly detect the disruption of the Z-bond or the separation of cation–anion pairs remains a major challenge. The IL system features slow–fast dynamics, indicating that the time scale of the HB disruption is on the order of picoseconds whereas that of cation–anion separation is on the order of nanoseconds.\textsuperscript{186} However, at present,
femtosecond infrared data of ILs remain limited; researchers have not used such experiments to obtain a universal law for the Z-bond (and thus distill the corresponding essence and theory) or used such results to facilitate practical chemical applications. Therefore, it is essential to develop the femtosecond infrared technique to reveal the dynamics of the Z-bond, provide a key reference for an in-depth understanding of the nanostructure in ILs, and guide the functional modulation of ILs in the context of chemical applications.

(3) In situ and real-time observation techniques on IL-based quasi-liquids. Unambiguous observations of the ion arrangement and Z-bond orientation on a solid surface is the basis of structural analyses of quasi-liquid systems. For example, researchers used AFM and STM to identify striped and hexagonal subunits in monolayer ILs on the Au (111) surface and a combination of STM experiments and theoretical simulations to study the transition of monolayer ILs from an ordered checkerboard to a disordered glass state. However, most current studies of ILs are static because of the high viscosity and complex ionic structure of ILs, in which it is difficult to capture the dynamic structural evolution or properties of IL-based quasi-liquids. Hence, it is meaningful and necessary to design equipment for in situ and real-time studies of the dynamic behavior of ILs on a solid surface, which requires the participation of researchers from diverse disciplines, especially in the context of instrument research, development, and design.

(4) Effect of solvent and interfacial environments on Z-bonds. The microenvironment of ILs (including solvent and interface) substantially influences the Z-bond structure and energy. Different solvents (such as water, organics, or even IL solvents) can have completely different effects on Z-bonds. The solvent molecule can obtain electrons from the donor ion of Z-bonds or lose electrons to the acceptor of Z-bonds and thus affect the contribution of the electrostatic interaction to the total Z-bond and modulate the bond strength. Furthermore, a surface with a nanoscale structure or functional groups exhibits different charge polarizations, which also affects the correlation strength between the Z-bond donor and receptor. However, a quantitative understanding of the effect of the solvent and interface on the geometry and energy of the Z-bond remains unavailable. Such a bottleneck is mainly because of the complexity and diversity of the structures and properties of the IL, solvent, and solid substrate. Hence, future research should evaluate a typical and well-defined solvent and interface to systematically study the response of the Z-bond, which will substantially affect the rational design of ILs and enhance the application prospects of ILs.

(5) Response prediction of Z-bonds and quasi-liquids in a multifield system. In practical applications of ILs, multiple physical fields are often present concomitantly, for example, in heterogeneous catalysis, the electrostatic, temperature, and reactive species/generated species concentration fields are always present on the surface of the catalyst. Hence, revealing the effect of coupling these fields on the structure and function of the Z-bond and quasi-liquid is pertinent to practical applications of ILs. In this regard, developing new simulations and experimental methods to study the behavior of ILs under the coupling of multiple fields quantitatively and systematically remains a high priority.

Generally, the diversity and complexity of an IL structure are not only foundational to developing broad applications but are also major obstacles to research. At present, researchers have synthesized more than 4000 types of ILs and reported more than 140000 properties, which constitutes an especially large data set. How to collect and analyze this information remains a major challenge. In the future, combining current big-data mining and machine learning with the basic data of ILs obtained from advanced experiments and multiscale simulations, researchers should work on high-throughput design screening to directly predict IL function from the corresponding structure. In principle, the overall objective of IL research should focus on typical industrial applications. With progress in the aforementioned aspects, researchers will obtain a new understanding of Z-bonds and quasi-liquids and new ideas for the applications of ILs. Future applications of ILs not only will be in separations, catalysis, and electrochemistry but will also extend to other cutting-edge fields (e.g., smart materials and devices, DNA analysis, cell membrane protein extraction, and drug synthesis).

5. CONCLUSION

In this Perspective, we summarized the recent developments and future challenges of two basic concepts of ILs: the Z-bond and the quasi-liquid. First, we discussed the definition, characteristics, properties, and functions of Z-bonds in ILs and explained that the scientific nature of the Z-bond is a coupling between traditional HB bonds and electrostatic interactions. Second, we comprehensively discussed the origin, structural features, and potential functions of quasi-liquids and revealed that the concept of the quasi-liquid mainly corresponds to the coupling of various interactions within interfacial ILs (including the Z-bond, vdW interactions, and solid–surface interactions). Finally, we discussed the current research on Z-bonds and quasi-liquids in terms of research methods, scientific connotations, and main applications. As discussed elsewhere in this perspective, ILs are common in many research fields (such as the chemical industry, chemistry, materials, information, medicine, and aerospace). The multidisciplinary nature of ILs indicates that such research on Z-bonds and quasi-liquids is best completed by multidisciplinary collaborations, which will facilitate the fundamental–applied iterative development of ILs. In summary, by focusing on the Z-bond and quasi-liquid in ILs, researchers can not only deepen the scientific understanding of ILs but also provide supports for the rational design of ILs in practical applications.

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Notes
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