Computer Simulation of the Surface of Aqueous Ionic and Surfactant Solutions

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ABSTRACT: The surface of aqueous solutions of simple salts was not the main focus of scientific attention for a long while. Considerable interest in studying such systems has only emerged in the past two decades, following the pioneering finding that large halide ions, such as I^-, exhibit considerable surface affinity. Since then, a number of issues have been clarified; however, there are still several unresolved points (e.g., the effect of various salts on lateral water diffusion at the surface) in this respect. Computer simulation studies of the field have largely benefited from the appearance of intrinsic surface analysis methods, by which the particles staying right at the boundary of the two phases can be unambiguously identified. Considering complex ions instead of simple ones opens a number of interesting questions, both from the theoretical point of view and from that of the applications. Besides reviewing the state-of-the-art of intrinsic surface analysis methods as well as the most important advances and open questions concerning the surface of simple ionic solutions, we focus on two such systems in this Perspective, namely, the surface of aqueous mixtures of room temperature ionic liquids and that of ionic surfactants. In the case of the former systems, for which computer simulation studies have still scarcely been reported, we summarize the theoretical advances that could trigger such investigations, which might well be of importance also from the point of view of industrial applications. Computer simulation methods are, on the other hand, widely used in studies of the surface of surfactant solutions. Here we review the most important theoretical advances and issues to be addressed and discuss two areas of applications, namely, the inclusion of information gathered from such simulations in large scale atmospheric models and the better understanding of the airborne transmission of viruses, such as SARS-CoV-2.
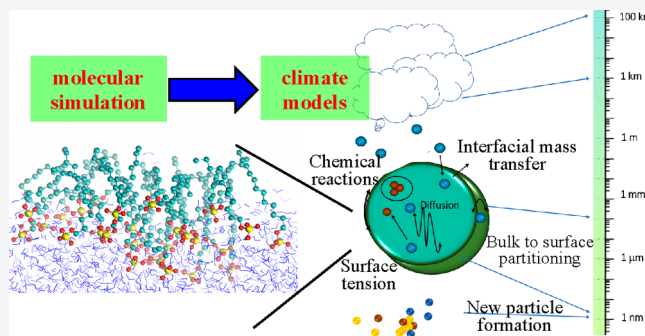
1. INTRODUCTION

Interfacial behavior of ions in their aqueous solution was thought to be one of the least interesting fields of physical chemistry in most of the previous century. Indeed, dissolved alkali halides always increase the surface tension of water,[1] and hence they are thought to be capillary inactive solutes, which are effectively repelled from the liquid surface. Issues that drew considerable scientific attention in this field, such as the Jones-Ray effect, i.e., the fact that at extreme low (i.e., around 10^{-3} M) concentration certain salts lead to a slight decrease rather than increase of the surface tension,[2] are now thought to be caused by surface active impurities rather than the salt itself.[3] The view that salts are capillary inactive solutes was rationalized by the theory of Onsager and Samaras, employing the method of image charges,[4] implying also that multivalent ions are repelled even more strongly from the liquid surface than single charged alkali halogenides. This long-standing view has been challenged at the turn of the millennium, when both experimental[5,6] and computer simulation studies[7,8] indicated the surface enrichment of large halide anions, in particular, I^-, in small droplets[5,7] as well as at macroscopic interfaces.[6,8] The theoretical background of these findings was first provided by

Levin, who improved the Onsager−Samaras theory showing that the surface propensity of the ions increases with their increasing size and polarizability.[9] These findings opened the gate for intensive investigation of the surface properties of aqueous salt solutions. However, there are still a number of challenges in understanding the surface behavior of such systems, even if they only consist of simple ions.

Furthermore, while simple multivalent ions are still not expected to be present at the liquid surface, complex ions, especially those having also a strongly polarizable or an apolar group, might well be enriched at the surface of their aqueous solutions. Such ions, bearing typically a positive charge, occur frequently in room temperature ionic liquids (RTILs). Another prominent group of ions that are accumulated at the surface of
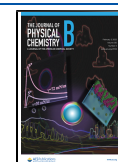
their aqueous solution is ions of amphiphilic character, i.e., surfactants.

Besides their importance in fundamental physical chemistry, the surfaces of such aqueous ionic solutions are also of great relevance from the practical point of view. Sea water droplets as well as aerosols containing ionic surfactants are abundant in the atmosphere, influencing, through condensational growth and activation as cloud condensation nuclei, the optical properties as well as the propensity of precipitation from regional to global scales.[10] Surfactants, reducing the surface tension by partitioning to the surface are also widely used in various processes of everyday life, e.g., in washing, painting, or the cosmetic or pharmaceutical industry. Interfaces containing ionic or zwitterionic amphiphiles frequently occur in biological systems as well. Eukaryotic cell membranes are built up by ionic and, mostly, zwitterionic phospholipid molecules; all interactions of the living cells, including signal transmission and transfer of molecules, involve these membranes. A particularly important example in this respect is the case of lung lining fluids. Indeed, such fluids might well influence the airborne transmission of viruses, e.g., SARS-CoV-2, through altering the surface tension and, consequently, the droplet size distribution due to the biological amphiphiles they consist of.

A broad range of industrial applications is associated with RTILs, considered to be "green" solvents due to their extremely low vapor pressure. An attractive feature of RTILs is that their physicochemical and solvation properties can be fine-tuned through the choice of the two ions. An additional degree of freedom in this respect is to mix RTILs by conventional molecular solvents. This way, the choice of the molecular solvent as well as the variation of the proportion of the two components can provide additional ways of fine-tuning the desired properties. In this respect, water is a particularly important molecular cosolvent, as its use allows avoiding other, often toxic or nonenvironmentally friendly organic molecular liquids, keeping the "green" character of the solvent unchanged.

It should finally be emphasized that in simulations of fluid interfaces, such as the liquid−vapor interface of aqueous ionic solutions, i.e., when the system is seen at atomistic resolution, the determination of the real liquid surface (i.e., the rugged, 2-dimensional covering surface of the liquid phase) is not at all a trivial task. The problem stems from the fact that, on the atomistic length scale, the liquid surface is corrugated by capillary waves.[11] The problem of finding the real, capillary wave corrugated, molecularly rough, so-called "intrinsic" liquid surface is equivalent with the task of finding the full list of the truly interfacial molecules, i.e., the ones that are located right at the boundary of the liquid and vapor phases. Unfortunately, the intrinsic liquid surface is still rather rarely determined in current interfacial simulation studies, in spite of the fact that the first such method was developed almost two decades ago,[12] since then a number of similar methods have been proposed,[13−16] some of which are even free from the assumption that the interface is macroscopically flat,[15,16] and many of these algorithms are now freely available.[17] However, it is rather evident that any meaningful computer simulation analysis of the properties of a fluid interface requires the exact identification of the interface itself as well as that of the particles pertaining to it. Thus, perspectives in the simulation of the surfaces of various aqueous ionic solutions also unavoidably imply the use of intrinsic surface analyzing methods.

In this Perspective, we review what we believe to be the most important current issues, both in fundamental physical chemistry and in its applications, in the field of computer simulation of the surface of aqueous ionic solutions. In section 2, the state-of-the-art methods used in determining the real, capillary wave corrugated liquid surface are summarized. In sections 3−5, issues in the simulations of the surface of solutions of simple ions, RTILs, and surfactants, respectively, are discussed. In the latter part, special focus is paid on implications in atmospheric chemistry and in research related to the transmission of viruses, such as the SARS-CoV-2 virus. Finally, in section 6, our most important conclusions are summarized.

2. STATE-OF-THE-ART METHODS DETERMINING THE INTRINSIC SURFACE

In analyzing the surface of a liquid phase in simulations of molecular resolution, the particles that are located right at the boundary of the two phases or, equivalently, the covering surface of the liquid phase has to be determined first. Clearly, the definition of the interfacial layer without the exact determination of the truly interfacial molecules leads to the misidentification of a number of particles either as being or not being interfacial, and hence to a systematic error of unknown magnitude of any interfacial property calculated.[13]

The first such method, called the Intrinsic Sampling Method (ISM) was proposed in the pioneering paper of Chacón and Tarazona almost two decades ago.[12] In this method, the intrinsic liquid surface is defined as the surface of minimum area that goes through an appropriately chosen set of pivot points, representing the atomic sites that are at the interface. The pivot sites are determined in a self-consistent way using an iterative procedure, controlled either by a threshold distance between the surface and new pivot sites to be added, or by a predefined desired surface density value. Having the set of pivot sites determined in each iteration step, the covering surface of the minimum area is constructed in terms of a set of Fourier components.[12,14] A big advantage of this method is the self-consistent way of determining the surface particles; however, its computational cost can be orders of magnitude larger than that of several other, more recent methods.[14]

An excellent compromise between computational cost and accuracy can be reached[14] using the Identification of the Truly Interfacial Molecules (ITIM) method.[13] In the ITIM analysis, probe spheres of a given radius are moved along a set of test lines from the bulk opposite phase toward the surface to be analyzed. The probe is stopped along each test line once it touches the first particle of the phase of interest. The particles that stop the probe at least along one test line form the surface layer,[13,14] and the covering surface can be constructed using, e.g., triangular interpolation.[18]

While both ISM and ITIM assumes the interface to be macroscopically planar, several more recent methods are even free from this assumption. Thus, the generalized version of the ITIM method (GITIM)[16] uses the concept of α-shapes and finds the α-complexes as clusters of Delaunay tetrahedra all of which have a touching sphere with a radius smaller than a predefined value. The particles located at the border of the α-complexes are regarded to be interfacial. This way, not only the (not necessarily planar) surface of one cluster (phase) but also those of several disjoint clusters (e.g., micelles) can be determined.[16] The Gaussian covering surface (GCS) method of Willard and Chandler[15] is based on defining a density field
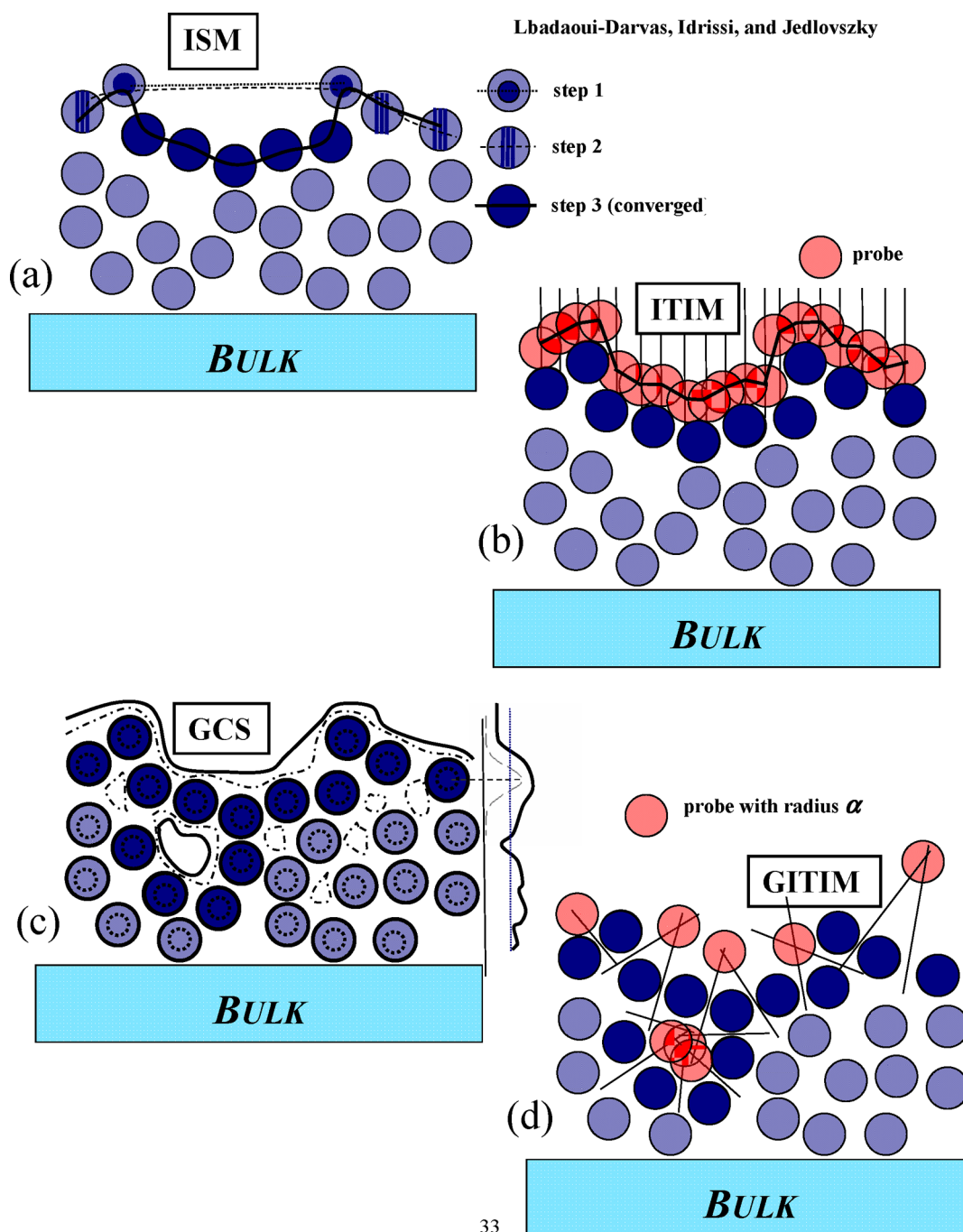
Figure 1. Schematic illustration of (a) the ISM (ref 12), (b) the ITIM (ref 13), (c) the GCS (ref 15), and (d) the GITIM (ref 16) methods.

by convolving the positions of the particles with normalized Gaussian functions. This convolution represents a coarse-graining, the length of which is given by the width of the Gaussian function. The interface is then defined as the set of spatial points corresponding to a predefined coarse grained density value.[15] A schematic illustration of these methods is shown in Figure 1.

It should be noted that all of these methods as well as all other possible ways of determining the intrinsic surface of a disordered phase contain a parameter the value of which is free to be chosen. Such a parameter is the threshold distance or desired surface density in ISM, the radius of the probe, and the threshold radius in ITIM and GITIM, respectively, and the coarse graining length in GCS. However, the use of a free

parameter is inevitable in such analyses, as it represents the length scale on which the interface is looked at.[14] It should also be emphasized that a great advantage of all of the above-discussed methods is that, having the full set of interfacial particles determined, those constructing the subsequent molecular layers can also be identified. For this purpose, simply the particles already identified to construct the surface layer (or all outer layers detected so far) have to be disregarded and the entire procedure has to be repeated.[13] It should finally be noted that a computationally very efficient Python implementation of all the above four methods are freely available[19] in the Pytim software package.[17]

3. SURFACE OF SIMPLE IONIC SOLUTIONS

3.1. Surface Affinity of Different Salts. Both experimental[6,20] and computer simulation investigations[8,21,22] of alkali halide solutions performed in the past decades revealed that certain ions, such as I⁻, are accumulated at the vicinity of the surface of their aqueous solution. It should be noted that this issue is still not settled completely, as a more recent density functional theory-based investigation led to the conclusion that, at infinite dilution, such an enrichment is only seen with respect to the subsurface region, and the potential of mean force of the I⁻ ion at the interface is roughly equal to that in the bulk aqueous phase.[23] It is also clear that the surface affinity of simple ions increases with increasing size and polarizability.[9] In other words, "soft" ions (according to the Hofmeister series), often referred to as chaotropes or structure breakers, exhibit some surface affinity, while small, "hard" ions (i.e., kosmotropes or structure makers) are effectively repelled from the liquid surface.[8,21] However, the more than 100 year old notion that all alkali halides, including also iodide salts are capillary inactive solutes, and hence they increase rather than decrease the surface tension of water has never been challenged.[1] Considering the Gibbs equation, a textbook relation between the derivative of the surface tension (γ) with respect to the bulk concentration (c) and surface excess (Γ) of the solute,[24] i.e.,

$$\Gamma = -\frac{c}{RT}\frac{d\gamma}{dc} \tag{1}$$

the capillary inactive nature of alkali halides (i.e., the fact that $d\gamma/dc > 0$) implies surface depletion even for alkali iodides. This seeming contradiction can be resolved by considering that while the concentration of the I⁻ ions is clearly higher at the vicinity of the liquid surface than in the bulk phase,[8,21,22] this enrichment affects only the first molecular layer,[22] while beyond this layer I⁻ ions have a region of depletion.[21,22] These two opposite effects result in a net negative adsorption, in accordance with the increase of the surface tension. It should also be emphasized that, due to the requirement of electroneutrality, the densities of the oppositely charged ions are equal to each other both in the bulk liquid phase and in the entire system. As a consequence, their densities have to be equal to each other also in the interfacial region, and hence the surface excess of the anions and cations also have to be equal. In other words, although the soft/hard character, and hence surface enhancement, are properties of the individual ions, surface excess, and thus also net positive or negative adsorption can meaningfully be defined for a salt rather than for its individual ions.[22] It should also be emphasized that this picture gets considerably more complex in the case of mixed salt solutions, when the requirement of electroneutrality only guarantees the equality of the surface excesses of all anions and all cations, and this is the quantity that is related to the change of the surface tension through the Gibbs equation (eq 1). In such systems, the surface excesses of the individual ions can be meaningfully defined, although it seems to be rather difficult to relate them to any experimentally accessible quantity. In addressing this issue, the modified Poisson–Boltzmann equation could be a very useful tool, as it provides a link between the density profiles or potentials of mean force of the individual ions and collective surface distributions.[3]

Another issue concerning the surface affinity of simple ions is the role of the sign of their charge in this respect. Clearly, a positive fractional charge, located on a H atom of a water molecule, can approach a negatively charged sphere closer than the fractional negative charge of a bulky water O atom can an otherwise equivalent, but positively charged sphere, as illustrated in Figure 2. In other words, due to the charge
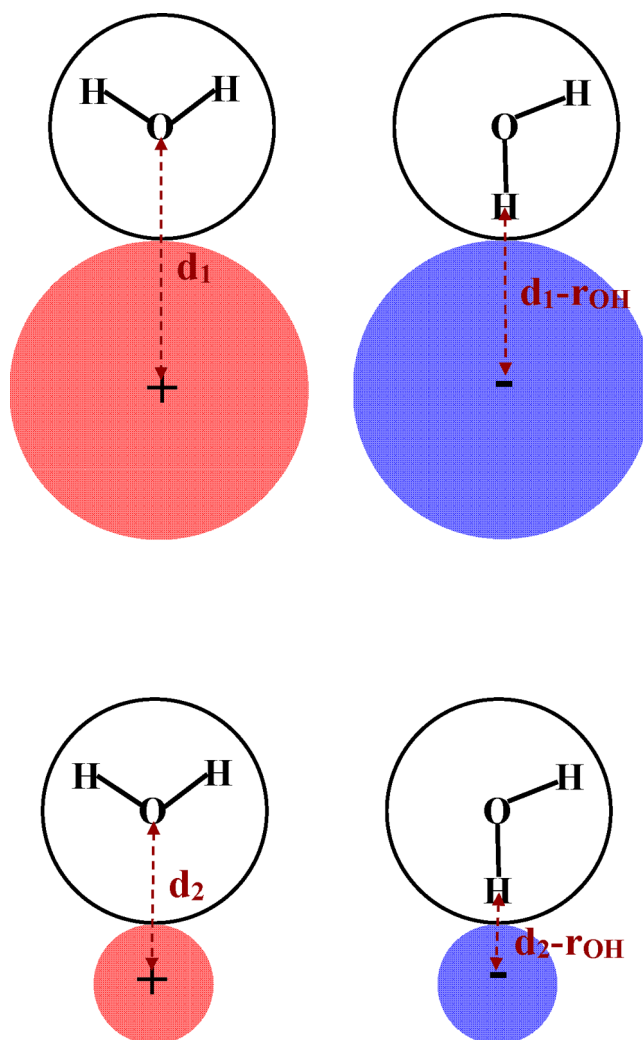
Figure 2. Schematic illustration of the difference in the hydration of a cation (pink spheres, left column) and an otherwise equivalent anion (blue spheres, right column). The ratio of the distances of the closest water fractional charge from the ion center of $d_2/(d_2 - r_{OH})$ in the case of a small pair of ions (bottom row) is considerably larger than that for a large pair of ions of $d_1/(d_1 - r_{OH})$ (top row), implying that the difference in the soft/hard character of a cation and an otherwise equivalent anion is larger for smaller ions.

asymmetry of the water molecule, anions are more strongly hydrated, (i.e., "harder"), and hence they are expected to be less surface active than cations of the same size.[22,25]

Interestingly, when simulating the aqueous solution of fictitious, charge inverted NaI (i.e., when the ions bear opposite charges than in reality), the fictitious I⁺ ion exhibited smaller surface affinity than its real, negatively charged counterpart, I⁻.[22] This surprising finding can again be understood considering that the surface behavior of a salt rather than that of its individual ions is the relevant phenomenon to be discussed. Clearly, the aforementioned difference between the hydration of (otherwise equivalent)

positive and negative ions, originating from the different distances the opposite fractional charges of a hydrating water molecule can approach them, is more pronounced for smaller ions. Thus, for smaller ions, the absolute difference of these distances of about 1 Å (i.e., the O−H bond length) corresponds to their larger *ratio*, and hence the larger difference in the electrostatic interaction (see Figure 2), as is clearly seen also from the corresponding hydration energies (see Table 4 of ref 22). As a consequence, the surface affinity of a salt is always dictated by the sign of charge of the smaller ion. For alkali halides, this is always the cation, the positive charge of which can thus also give rise to the surface affinity of a corresponding large halide anion, such as I⁻.[22] It should also be noted that the surface potential of water also plays a role in the asymmetry of the surface affinity of cations and anions,[26,27] although the ability of simple models of properly describing the surface potential is questionable.[27] To clarify the exact role of the sign of the ion charge itself plays in determining the surface affinity without the additional effect of the counterion of different size in this respect, the potentials of mean force of two oppositely charged, but otherwise equivalent, ions need to be calculated at the water−vapor interface, or the surface of the aqueous solution of a fictitious salt consisting of anions and cations that are, apart from the sign of their charge, identical with each other needs to be simulated.

Although the background of these issues has been more or less clarified in the past years, a number of questions concerning the surface behavior of the aqueous solution of various salts should be addressed in the near future. Thus, besides their size, polarizability, and sign of charge, also the chemical character of complex ions (i.e., whether they can form H-bonds with the hydrating water molecules; whether, apart from their net charge, they are hydrophobic; etc.) is related to the soft/hard character of these ions, and hence it is also expected to play an important role in their possible surface affinity. A particularly important example in this respect is the case of salts the ions of which are the constituents of zwitterions occurring in nature, such as the headgroups of biologically relevant amphiphiles. For instance, the zwitterionic head of phosphatidylcholine lipids, being the main constituents of the eukaryotic cell membranes, are built up by a tetramethylammonium (TMA) and a dimethylphosphate (DMP) ion. The large size, apolar surface, and positive charge of the TMA ion suggests considerably larger surface affinity than that of DMP, an anion that can form several H-bonds with water, which could explain the rather surprising fact that the TMA group prefers to stay in the crowded headgroup region of the lipid membrane rather than being stretched into the aqueous phase.[28] Further, in the case of alkali halides, net surface depletion of the salt was observed in all cases, mostly due to the small size and, consequently, hardness of the cations. However, the combination of I⁻ with a large complex cation of an apolar surface, such as TMA or ammonium derivatives with larger alkyl groups, would be good candidates for nonamphiphilic, yet surface active, salts.

3.2. Water Dynamics. In contrast with the structural features, very little attention has been paid to the dynamical properties of the surface of aqueous solutions of simple salts so far. The lack of such attention is a consequence of the long-standing view that simple ions are practically absent from the surface of their aqueous solution, and hence the dynamics of the surface layer is assumed to be rather similar to that in neat water. However, as it has been discussed above, this is not always the case.

While the diffusion of ions does not differ substantially at the vicinity of the liquid surface from that in the bulk liquid phase,[29] the effect of the ions on the surface diffusion of the water molecules is still far from being well understood. In fact, different salts affect the diffusion of water in different ways even in the bulk liquid phase.[30] Some salts, such as NaCl, NaBr, or NaI decrease, while some others, e.g., KCl or CsCl, increase the diffusion coefficient of the water molecules. Further, while its decrease is usually monotonous, an increased diffusion coefficient typically exhibits a maximum as a function of the salt concentration.[30] Although this effect was reproduced by *ab initio* molecular dynamics simulation,[31] both simple nonpolarizable[29,31−33] and polarizable models[29,32] were found to underestimate water diffusion in the presence of alkali halide salts. It was claimed that this effect is related to the charge transfer occurring both between the ion and its neighboring water molecules and also between the water molecules of the first hydration shell, and hence proper description of the water diffusion requires the use of a potential model that also includes dynamic charge transfer between the particles.[32,33]

Recently it was shown that while the diffusion coefficient of water is indeed underestimated in the presence of alkali halides, the *relative* effect of the different salts in this respect is very well captured even with a nonpolarizable potential model, at least at the moderate salt concentration of 1.3 M (see Figure 3).[29] However, neither this ratio nor even the trend of the various salts in this respect is reproduced in the surface molecular layer of these solutions (Figure 3). The excellent agreement with the experimental trend in the bulk phase suggests that the lack of this agreement at the liquid surface is not a failure of the models used, but it reflects a real physical effect triggered by the vicinity of the surface. However, the exact role of the interface in this respect is not yet understood. Clearly, this role is related to the fact that different ions are present in different concentrations in the surface layer, cations being typically practically absent from here.[22] Hence, the observed salt dependence of the surface diffusion of water is probably a combined effect of the type of the ions, in particular, that of the anion and their concentration within the surface layer (which can be rather different from that in the bulk). A thorough understanding of this phenomenon requires systematic studies in which the cation and, more importantly, the anion, the type of the model used, and in particular, the concentration of the salt is systematically varied in a wide range.

4. AQUEOUS MIXTURES OF ROOM TEMPERATURE IONIC LIQUIDS

It is well established that the physicochemical properties of pure RTILs strongly correlate with the chemical structure of the ions.[34] This correlation triggered studies of a number of different RTILs in order to establish a relationship between the ionic structure and the properties of the liquid. It was also realized later that the properties of RTILs can be fine-tuned by mixing them with a molecular solvent. In particular, RTIL/water mixtures are promising candidates to expand the application of ionic liquids in several fields, such as extraction, separation, condensation of various compounds, including polymers, and CO_2 capture.[34−36] In particular, the delicate interplay of the van der Waals, electrostatic, and H-bonding
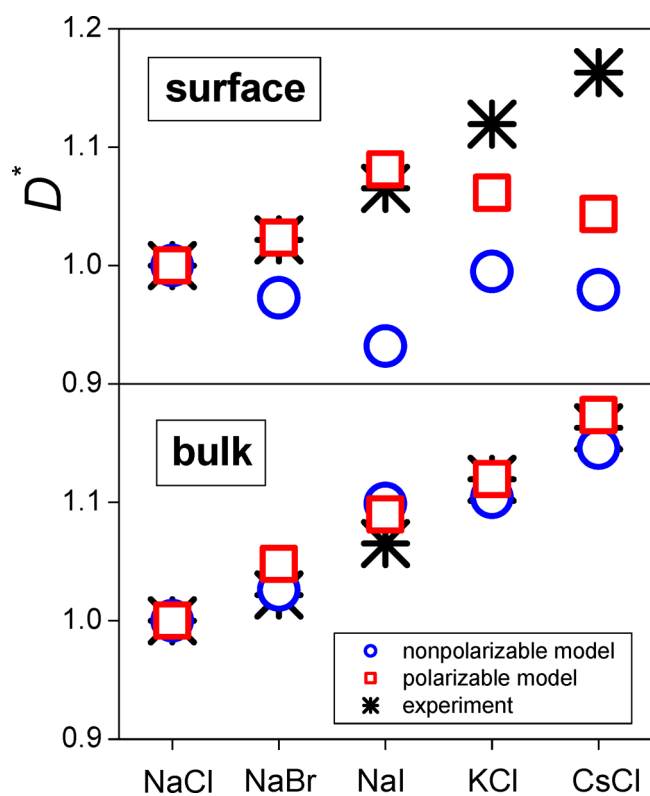
Figure 3. Lateral diffusion coefficients of the water molecules in the surface layer (top), and their 3-dimensional diffusion coefficients in the bulk liquid phase (bottom) in the presence of various salts, normalized by that in the presence of NaCl, D^*, as obtained with a nonpolarizable (blue circles) and a polarizable (red squares) potential model (ref 29). Experimental data obtained in the bulk phase (ref 30) are shown by black asterisks. All data correspond to the salt concentration of 1.3 M.

interactions brings additional complexity to these mixtures, whose nature remains a challenging area of research. As a consequence, the presence of water significantly affects the physicochemical properties, such as ion diffusion, viscosity, or surface tension, of the pure RTILs. The desire of understanding the background of these effects in terms of structure and dynamics at the molecular level has led to an increasing interest in using computer simulations when studying aqueous mixtures of RTILs. In these studies, issues such as the inhomogeneous distribution of the ions as well as the occurrence and extent of both water–water and water ion H-bonding interactions have been thoroughly investigated.[37,38] It should be noted that, unlike simple molten salts, the often asymmetric shape and large size of the ions of RTILs give rise to several technical difficulties (e.g., force field development, using proper long-range correction and slow sampling of the phase space) in the simulations.

Besides the bulk phase of aqueous RTIL mixtures, detailed investigation of the properties of the interface of these mixtures both with the vapor phase and with neat water is also of great interest, as it could also help in broadening the applications of RTILs in various fields, such as extraction or various electrochemical processes. However, in contrast with the wealth of investigations of the bulk phase properties of aqueous mixtures of RTILs, studies concerning the interface of such mixtures are rather scarce. The scarceness of studies concerning the surface of water/RTIL mixtures (as well as of

other mixtures of RTILs and molecular solvents) are likely related to two issues, which we would like to highlight here. The first of these issues is the proper combination of the existing RTIL models with those of water, while the second one is the identification of the ions and water molecules that are at the interface, determination of the distance of the particles from the interface, and thus also the definition of the spatial extent of the interface.

Probably the most important prerequisite of performing a reliable computer simulation is the proper development of the force field parameters used. In this regard, a number of force fields have been proposed for a series of RTILs in the recent years. In these force fields, the values of the van der Waals parameters have usually been adapted from widely used, general purpose force fields, such as AMBER, CHARMM, or OPLS-AA, while the fractional charges carried by the different atoms have been derived from *ab initio* calculations. There is a convergence in the literature that scaling down the net charge of the ions to values less than $\pm 1e$ is needed to obtain good reproduction of the structural and transport properties of the pure RTILs.[39] In the studies of RTIL/water mixtures, these parameters are combined with those of the commonly used water models, such as SPC, SPC/E, or TIP4P. However, although the force field parameters of both the ionic liquid and water might well be individually "good" (i.e., they reproduce the structure and dynamics of the neat ionic liquid and water, respectively), the combination of these potential models does not necessarily reproduce the structure and dynamics of their bulk mixture and its surface. For example, it has been shown that the net charge value of the ions determines, to a large extent, the miscibility of the RTIL with water when used in combination with the TIP3P, SPC/E, or TIP5P water model.[40] It should be emphasized that demixing of such systems only occurs in long enough (i.e., at least 20 ns) simulations. The miscibility of the compounds is governed by the free energy of mixing, the reproduction of which provides a rigorous test of the accuracy (and also the applicability) of the model combination, as long as all degrees of freedom of the system are properly sampled. Indeed, the sign of the free energy of mixing determines whether the mixture or the neat components correspond to a thermodynamically more stable system. Further, besides the qualitative description of the miscibility, good reproduction of the experimental free energy of mixing is a clear prerequisite for the accurate description of the microscopic structure (e.g., in terms of self-association) of the mixture in a computer simulation.

In cases where the mixing of the two components is accompanied by a slight increase of the free energy, demixing may not occur visibly on the time and length scale of the simulation.[41,42] Further, the detection of this demixing is also hampered by the use of periodic boundary conditions. However, such a demixing occurs almost instantaneously even in a computer simulation in the presence of an apolar object, such as the interface with the vapor phase. This fact makes the inappropriateness of certain model combinations, which might be used in simulations of the bulk phase without even noticing the problem, immediately evident in interfacial simulations of such mixtures, and hence limits the number of such interfacial simulations.

The other issue concerns the definition of the interfacial layer in such a simulation. In the early studies of RTIL interfaces, reported before the availability of the wealth of intrinsic surface analyzing methods (as discussed in section 2),

the surface of the liquid was either defined in a nonintrinsic way (e.g., through the region in which the density drops from 90% to 10% of its bulk phase value in a slab parallel with the Gibbs dividing surface or simply by taking a slab of given width along the interface normal),[40,43] or the analyses were limited to profiles along the interface normal axis.[44,45] In the first case, the fact that the liquid surface is corrugated by thermal capillary waves[11] is neglected. This arbitrary definition of the "interfacial" and "bulk" liquid domains poses significant problems when one wants to compare different results from the literature with the aim of rationalizing them in a single framework. Further, this treatment makes the relevance of any comparison with experimental data questionable, since surface sensitive experiments probe, by definition, only the truly interfacial molecules, while the nonintrinsic treatment of the interface in a computer simulation results in the misidentification of the molecules as being or not being interfacial, and the resulting erroneous set of interfacial molecules probed leads to a systematic error of any of the calculated interfacial properties. Limiting the analyses to profiles along the interface normal, on the other hand, is free from such a systematic error; however, it limits the properties of the interface accessible by such calculations.

The importance of using an intrinsic method to detect the surface of a RTIL or its mixture with a molecular solvent is further enhanced by the typically rather large size of the cation. Using intrinsic surface analysis could enable one to determine the composition of the surface layer as well as that of the subsequent ones, to address the question how broad is the surface region (in terms of, e.g., molecular layers), i.e., where the properties of the liquid are altered by the vicinity of the interface, and to analyze the lateral clustering, relative arrangement, and surface orientation of the various particles at the liquid surface. Further, applying the intrinsic analysis to chemical groups rather than molecules would allow the determination of the polar/apolar character or charge density of the liquid surface, also in comparison with the bulk liquid phase, and to address the issue how these properties are related to the thermodynamic quantities (e.g., surface tension) that characterize the system. The need of using intrinsic analysis in the simulation studies of the surface of RTILs and their mixtures with molecular solvents started to be realized in the past decade, leading to several pioneering studies in this respect.[46−48] We believe that proper assessment of the combination of existing potential models of RTILs and water (or other molecular solvent) in order to find those that can properly describe the miscibility of these compounds, and the use of intrinsic surface analyzing methods will lead to a large number of interfacial simulation studies of such mixtures in the near future.

5. SOLUTIONS OF SURFACTANTS

Amphiphilic molecules, consisting of both hydrophobic and hydrophilic moieties, often called surfactants, constitute a special group of water-soluble compounds, as their concentration is strongly enhanced at the surface of their aqueous solution. The hydrophilic part of the surfactants often contains charged groups, neutralized either by simple counterions in the solution (anionic or cationic surfactants) or by an oppositely charged group that still belongs to the surfactant molecule (zwitterionic surfactants). The surface of aqueous surfactant solutions represents thus a special group of charged aqueous surfaces, since, unlike the majority of simple (e.g., alkali halide) salts, ionic surfactants are strongly accumulated at the surface. Surfactant solutions are omnipresent in products of the hygiene and personal care industry; they are responsible for optimizing the surface tension in biological fluids (bile salts) and membranes (lung lining fluids, cell membranes) and are crucial to maintain the proper functioning of living organisms. Less well-known is the fact that surfactants are present in large concentrations in the Earth's atmosphere,[49,50] and their partitioning between the gas phase and aerosol particles has a non-negligible, yet to date little understood, effect on cloud optical properties, which is related to the surface tension of the resulting cloud droplets. A new and burning question concerning surfactants in biological systems is how they impact properties of respiratory droplets, responsible for airborne transmission of viruses, such as SARS-CoV-2.

In the following subsections we describe major theoretical questions that are important for exploring these fields, where the use of intrinsic surface analysis has already led to a breakthrough in our understanding of the molecular level theory of surface activity. We then showcase recent pivotal results of applied research and collect perspectives of potentially important future directions in these fields.

5.1. Issues Concerning Simple Surfactant Solutions. In surfactant solutions, the tendency of thermodynamically stable systems to minimize their surface tension results in the preferential adsorption of the surfactants at the interface and, hence, in the positive surface excess of these compounds. Surface excess can be accessed by surface tension measurements through the Gibbs equation of adsorption (eq 1)[24] and can also directly be measured by various surface sensitive experimental techniques (e.g., X-ray or neutron reflectivity, X-ray photoelectron, sum frequency generation spectroscopy, etc.). Having the surface excess already measured, adsorption isotherms are relatively easy to obtain from routine experiments. The interpretation of adsorption isotherms has led to many historical discoveries, such as the existence of critical micellar or critical aggregation concentrations.[51−53] However, to unambiguously interpret the observed isotherms, it is crucial to gain a molecular resolution insight into the structural and dynamical properties driving the adsorption process, and this is nearly uniquely possible from molecular simulations coupled to intrinsic surface analysis.

5.1.1. Theoretical Models of Surface Adsorption Challenged by Simulations. Existing thermodynamic or statistical mechanical models, which are often used to describe surfactant effects in atmospheric chemistry or biophysics, are built on the adsorption isotherms that estimate the surface excess as a function of the bulk concentration. The surface excess is then converted to surface tension or surface pressure from corresponding equations of state. As it has recently been summarized,[54] such models typically contain the following assumptions: (i) the surface layer is infinitely thin or, at most, it has a fixed and constant width; (ii) the adsorption sites are fixed (with the clear exception of the Volmer model, which also accounts for diffusion within the adsorbed layer); (iii) at low surface coverage, adsorbed surfactant molecules do not interact with each other (i.e., gas-like adsorption); (iv) the hydrophobic interaction between the surfactant tails is neglected or, at most, is integrated in the headgroup interaction as a small perturbation;[55,56] and finally, (v) the adsorption of polymers consists of the partitioning of monomer segments between the bulk liquid phase and its surface. The validity of these modeling assumptions for
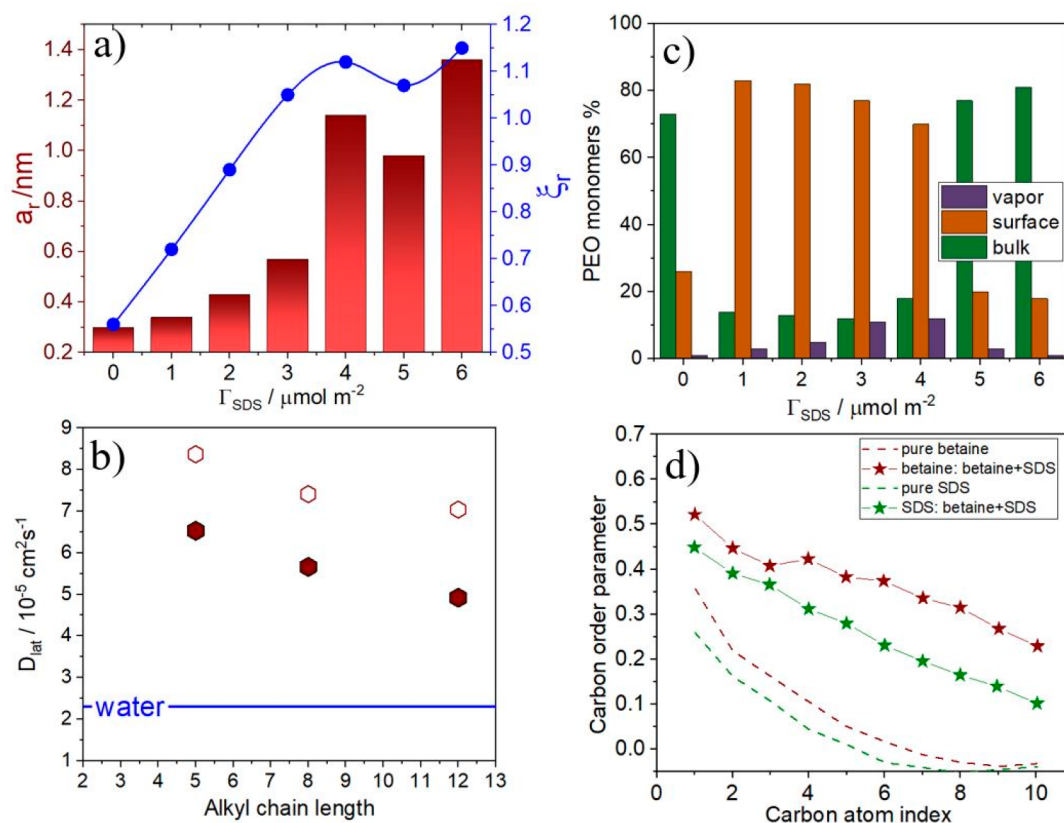
Figure 4. (a) Frequency (blue line) and amplitude (bars) parameters of the surface roughness (ref 13) in mixed adsorption layers containing PEO and SDS at varying ratios (ref 63). Scales on the left and right of the panel refer to the amplitude and frequency parameters, respectively. (b) 2D diffusion coefficients in adsorption layers of long chained 1-alkanols at the air water interface as a function of the alkyl chain length. Open and filled symbols correspond to the surface concentrations of 1 and 4 μmol/m^2, respectively, while the horizontal blue line indicates the self-diffusion coefficient of water (ref 64). (c) The distribution of polymer segments in mixed PEO/SDS adsorption layers as a function of the SDS surface concentration (ref 63). (d) Order parameters of the different carbon atoms in neat and mixed monolayers of ionic surfactants (SDS and betaine) (Adapted with permission from Figure 8a of ref 61. Copyright 2017 American Chemical Society).

multicomponent surfactant mixtures, found, for instance, in atmospheric particles or industrial products, has to be carefully checked. In such mixtures, the delicate interplay of the intermolecular interactions between the surfactants (and often also the counterions) may result in scenarios where the surface excess cannot be trivially predicted from the bulk concentration. Instead, competitive and synergistic effects are expected depending on the concentration and the chemical nature of the surfactants. To implement these effects in more sophisticated adsorption models, it is crucial to understand the underlying molecular scale driving forces.

Molecular simulation, combined with intrinsic surface analysis can be used to study structural and dynamical properties of mixed adsorption layers at various surface coverages. This approach has the additional advantage that particles pertaining to any number of consecutive molecular layers can be identified, providing thus depth concentration profiles, similar to those obtained from, e.g., X-ray photoelectron spectra, for any component by simply calculating its concentration in the individual layers.[57] It should be emphasized that in the case of aqueous surfactant solutions, where the solute and solvent molecules differ considerably in size, the surface layer as well as the subsequent subsurface layers should be defined in terms of (non-H) atoms rather than of molecules.[57] Additionally, atomistic scale structural and dynamic properties, such as lifetimes, preferred orientations,

clustering, or ordering of the surface layers, the total surface tension and the individual contributions coming from different molecules or moieties[58,59] can be obtained from such simulations selectively for the surface, subsurface, and bulk-like layers. These results can serve as starting points to refine the aforementioned set of assumptions of the adsorption models.

Although molecular simulations can, in principle, generate the full partitioning process, including micelle formation in the bulk, attainable system sizes and computational power usually limit counting statistics and make brute force equilibrium atomistic simulations very inefficient. As a consequence, such simulations usually neglect the presence of surfactants in the bulk phase (due to finite size effects) and hence cannot be adapted to directly observe the thermodynamics of adsorption and surface to bulk partitioning. Instead, coarse graining or free energy methods might be utilized to predict thermodynamic state functions, such as the free energy or the excess chemical potential. A recent method uses thermodynamic integration to estimate the surface excess chemical potential from the free energy difference of exchanging a surfactant molecule with an equivalent volume of solvent both at the surface and in the bulk.[60] The combination of this method with intrinsic surface analysis provides a powerful tool to understand the effect of surface properties on the corresponding thermodynamic state functions.[61]

Both equilibrium simulations and thermodynamic integration have already yielded very important insights to the adsorption of surfactants, which can directly validate or question the model assumptions discussed above. Thus, the finding that the charged headgroup of adsorbed ionic surfactants can penetrate 6−8 molecular layers deep into the aqueous phase, pulling 3−4 tail C atoms also there,[57] clearly invalidated the long-standing view that the adsorption layer is infinitely thin and gave rise to the development of more sophisticated adsorption models.[62] Further, the waviness of the liquid surface, resulting from capillary wave fluctuations, challenges the assumption that the adsorption layer has a fixed width and can be confined into a rectangular space. This is best demonstrated by observing the amplitude and frequency parameters[13] describing the roughness of the liquid/vapor interface. Figure 4a shows these data for mixed solutions of poly(ethylene oxide) (PEO) and sodium dodecyl sulfate (SDS) as a function of the SDS surface concentration.[63] Further, non-negligible two-dimensional diffusion coefficients along the macroscopic plane of the interface have been estimated both for ionic and nonionic surfactants[64] (see Figure 3b), suggesting that while fixed adsorption site models (e.g., Langmuir, Frumkin) might still be successful in describing surfactant adsorption, models with mobile adsorption sites (such as that of Volmer) provide a better description of the dynamics within the adsorbed layer.

The assumption of gas-like adsorption is challenged by simulations of PEO/SDS mixed adsorption layers on aqueous surfaces,[63] which revealed strongly enhanced surface adsorption of the polymer in the presence of SDS at low concentrations, as compared to that in the lack of SDS, due to favorable lateral interactions between the polymer and the ionic surfactants (see Figure 3c). It is worth noting that the synergistic effect between the polymer and the ionic surfactant, invoked by lateral interactions at low surface coverages, is overcompensated by the stronger surface activity of the latter at high coverages. Thus, at high SDS surface concentrations, competitive adsorption results in the expulsion of the polymer, being the weaker surfactant, from the adsorption layer.[63] Further, the partitioning of the PEO monomer segments between the surface, the bulk liquid, and the vapor phase also revealed the surprising presence of a non-negligible fraction of polymer segments in the vapor phase both in the lack[65] and in the presence[63] of SDS, in a clear contrast with classical theories of polymer adsorption, which assume that monomer segments are distributed solely among portions adsorbed at the surface and bulk phase loops.

The widely assumed negligible effect of tail interaction on adsorption has also been recently challenged by computer simulations of mixed layers containing anionic (SDS) and cationic (C12-betaine) or zwitterionic (cocamidopropyl betaine) surfactants in several surface concentrations.[61] Figure 3d shows the deuterium order parameter of the carbon atoms in the alkyl chains of pure and mixed SDS and C12-betaine surfactant layers.[61] Increased order is observed in mixed surfactants as a result of electrostatic interactions between the oppositely charged headgroups, resulting in more tightly packed surface layers compared to the pure surfactants, and hence synergistic adsorption. While the degree of surface tension reduction due to headgroup interactions (tight packing) can be described by thermodynamic models that do not include explicit interactions between the hydrophobic tails,[56] they cannot predict that the presence of heteroatoms in

the alkyl chain (the N and O atoms in cocamidopropyl betaine) can cancel this synergistic effect by reducing close packing and increasing the translational entropy of the adsorption layer.[61]

5.1.2. Total Surface Tension and Surface Tension Contributions. In statistical thermodynamics, the surface tension is defined as the integral of the difference between the lateral (p_L) and normal (p_N) contributions of the pressure tensor along the surface normal direction, z, i.e.,

$$\gamma = \int_{-\infty}^{\infty} [p_N - p_L(z)] \, dz \tag{2}$$

where p_N is constant along the axis z due to the requirement of the mechanical stability of the system. In a periodic system of size L, consisting of two equivalent surfaces, eq 2 can be rewritten using the volume average of the pressure tensor as $\gamma = L(p_N - p_L)/2$. The elements of the pressure tensor can easily be calculated from MD simulations as

$$p_{\alpha\beta} = \frac{1}{V}\left(\sum_i m_i v_i^\alpha v_i^\beta + \left\langle \sum_{ij} f_{ij}^\alpha \int_{C_{ij}} \delta(\mathbf{r} - \mathbf{s}) \, ds^\beta \right\rangle \right) \tag{3}$$

and are available as built-in options in many of the commonly used software packages. In eq 3, indices α and β run over the spatial directions, while i and j are over the particles, m and v denote the mass and velocity of the particles, respectively, V is the total volume of the system, δ is the Kronecker symbol, the integral is performed over the C_{ij} open path connecting particles i and j, parametrized by the vector $\mathbf{s}$, and the brackets $\langle \cdots \rangle$ denote ensemble averaging. The first term of this equation represents the kinetic, while the second term the virial (or excess) contribution to the pressure. Assuming that the average kinetic energy of the particles is the same along all space-fixed axes, the surface tension can also be accessed using the elements of the virial tensor, Ξ, instead of the pressure tensor, i.e., $\gamma = L(\Xi_N - \Xi_L)/2$. Although the virial route has the advantage that it only requires molecular coordinates to be saved in the trajectory while for the pressure route velocities are also needed, the underlying assumption is not always true, which might lead to erroneous surface tension values.[66] Namely, the equipartition theorem states that the average of the *total* energy of the particles (i.e., the sum of their potential and kinetic energies) rather than the kinetic energy itself is distributed evenly along all spatial directions. Therefore, in an inhomogeneous environment, such as a liquid surface, where the potential energy of the particles coming from the direction of the interface normal is different from those in lateral directions, the equality of the kinetic terms is only guaranteed in the absence of constraints. In the presence of constraints (i.e., for rigid molecules), on the other hand, the difference of the mean kinetic energies in the lateral and normal directions to the surface gives rise to an ideal gas contribution of the surface tension, which is about 15% in the case of water.[66] Although it seems to be a rather technical point, it does have relevance for real systems. Indeed, considering that the first excited (bending) state of a water molecule corresponds to about $8k_B T$ activation energy at room temperature, molecules of ambient water can well be assumed to be rigid particles.

A great advantage of using the pressure route is that the lateral pressure can be distributed among the interacting sites in a simulation, allowing the calculation of the surface tension contribution of the individual sites or molecules through eq
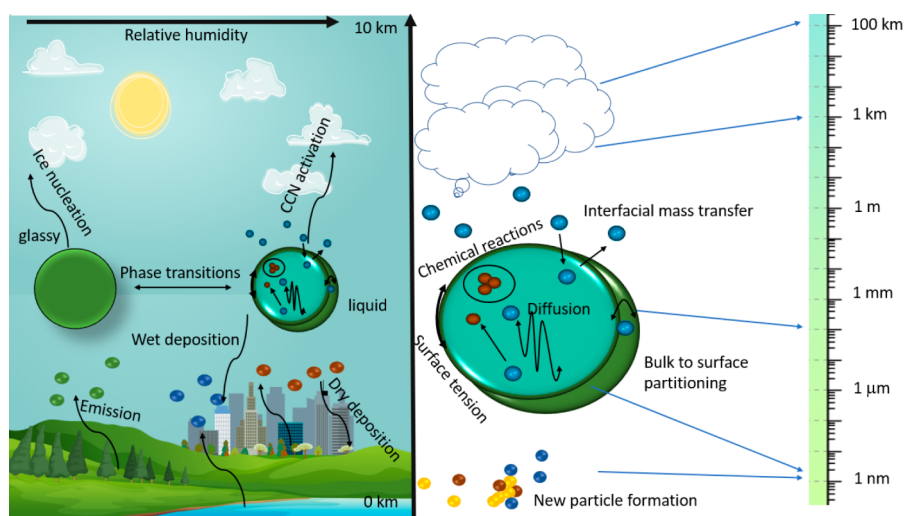
Figure 5. Schematic representation of the role of processes occurring at the surface of aerosol particles with their impact on cloud formation with corresponding humidity, heights above the surface, and spatial scales.

2.[67] This freely available[68] method has recently been applied to aqueous surfaces containing ionic surfactants, revealing the crucial role of the counterions in this respect, as they can contribute to the surface tension with values, either positive or negative, that are several times higher in magnitude than the surface tension itself.[58,59] This huge contribution is largely compensated by the charged headgroups of the surfactants and the interfacial water molecules. Although it is clear that the sign of the counterion charge has a large effect on their surface tension contribution (and, hence, indirectly also on those of the headgroups and water molecules)[58,59] and the size and polarity (i.e., "hardness") of the counterion is also related to the surface tension,[59,69] the exact relation between the properties of the counterions and the surface tension contribution they give is far from being well understood. Therefore, we expect a number of studies in the near future aiming at clarifying this relation. Further, this method is expected to be applied to a number of more complicated surfactant solutions, such as multicomponent mixtures of different surfactants, including cationic, anionic, and zwitterionic ones, and to those consisting also surface active polymers, that are present in realistic systems.

5.2. Atmospheric Implications. Atmospheric aerosols, i.e., nanoparticles suspended in the air, affect the climate both directly, via absorbing and scattering solar radiation, and indirectly, via their interactions with the surrounding vapor phase that lead to their growth and activation as cloud droplets. The indirect effect of aerosols, i.e., aerosol–cloud interactions, has been persistently and repeatedly identified by the International Panel on Climate Change as the most uncertain contributions in climate models.[70] Aerosol–cloud interactions mainly consist of microphysical processes that compete for the initial aerosol population, and whose interplay determines the properties of cloud droplets. Many of these processes, summarized in Figure 5 together with their large-scale consequences on cloud properties, involve the surface of the particles. Climate models, whose resolution is on the range of kilometers in space and hours in time, cannot explicitly include aerosol microphysical processes. Nevertheless, aerosol number concentrations and size distributions are necessary input parameters to predict radiative properties as well as

precipitation propensity and type. Consequently, these values are taken from models of varying complexity.

The most elaborate of such models are direct aerosol simulations, which predict the desired concentrations and size distributions by combining thermodynamics[71] and kinetic processes of the growth.[72] Typical input parameters of such models include the surface tension, the mass accommodation coefficient that describes the kinetics of condensational growth by collisions with vapor phase molecules, or the contact angle that serves as a proxy to the interfacial free energy and is often used to model droplet condensation near insoluble surfaces via the classical nucleation theory. Very surprisingly, not even the most elaborate of these models takes the corrugation of the surface of these droplets into account but describes the surface as a series of predefined rectangular slabs.[73]

Ionic surfactants comprise a non-negligible fraction of the atmospheric particulate matter. For instance, humic like substances are abundant in rural environments, while other ionic and biological surfactants are contained in sea spray aerosols.[49,50] By reducing the surface tension of the aerosol droplets, these molecules directly affect the resulting cloud droplet sizes and concentrations. The Köhler theory relates the onset size and supersaturation (i.e., vapor pressure of water) at which a particle activates as a cloud droplet (i.e., beyond which it experiences unconstrained growth by condensation of water vapor) both to the surface curvature (Kelvin effect) and to the amount of solute (Raoult effect). In simple terms, any component that lowers the surface tension will favor cloud condensation nuclei activation at lower vapor pressures. Köhler calculations are performed using surface tensions taken from macroscopic measurements, despite the recent discovery that the surface tension of micro- and nanodroplets of aqueous surfactant solutions are significantly different from the corresponding macroscopic values.[74] The fact that using these values instead of macroscopic ones have improved predictions of Köhler curves suggests that a better understanding of the surface tension of nanodroplets, for instance using molecular simulations and intrinsic surface analysis, could improve existing aerosol models. Additionally, the complex interfaces of mixed surfactants have been reported to cause strongly reduced surface tensions in atmospheric aerosols.[75] This effect has, however, not been unambiguously

attributed either to synergistic interactions or to the presence of biological surfactants yet, and thus it needs to be studies in detail.

For liquid aerosol particles, the kinetics of condensational growth (i.e., water uptake) is mostly determined by the rate at which water molecules cross the particle–vapor interface. The measure of interfacial transfer rates is the mass accommodation coefficient, i.e., the ratio of water uptake events and the total number of collisions. Mass accommodation coefficients larger that 0.01 do not affect droplet number concentrations; however, any value below that results in hindered water uptake, thus increased supersaturation of water and, consequently, increased cloud droplet concentration in the full height range of the troposphere.[76] While such low values are globally not representative, it has been shown from molecular simulations[77] that self-organized monolayers of nonionic surfactants can lead to mass accommodation coefficients as low as 10^{-4}, which are potentially important locally or regionally in places where the surfactant concentrations are high in aerosol particles. The reduced mass accommodation coefficient is due to the free energy barrier introduced by the presence of a tightly packed layer of alkyl chains. The effect of ionic surfactants and their mixtures is so far unknown, and intrinsic surface analysis connected with enhanced sampling molecular simulations to reveal free energy profiles are clearly adequate tools to complement experimental observations and improve modeling assumptions.

5.3. Biosurfactants and Their Effect on Airborne Viral Transmission. Biological surfactants constituting membranes that form the barrier between the intra- and extracellular space in living organisms have long been in the forefront of scientific research. Their interactions with other molecules, such as drugs, oxidants, or nanoparticles have been extensively studied by molecular simulations. One of the most recent works implements the intrinsic coordinate, using the GCS method,[15] to study the free energy profile of the transfer of a C_{60} fullerene into a phospholipid membrane.[78] Lung lining fluids (LLFs), comprising a special group of biosurfactants, form a monolayer along the respiratory tract. LLFs consist of a mixture of ionic surfactants, proteins and cholesterol, the interaction of which with inhaled material, such as nitrous gases or nanoparticles (in particular, soot) has been extensively studied by molecular simulations.[79]

In relation to the SARS-CoV-2 pandemic, studies of airborne transmission of viruses lived their renaissance in the past two years.[80] While coughing, speaking, or breathing, a population of respiratory droplets of polydisperse size distribution is ejected through the nose or the mouth. Respiratory droplets are, in fact, aqueous solutions of LLFs, salts, and acids that envelope viruses ejected by an infected person. How long the exhaled viruses remain suspended in the air and where they deposit along the respiratory tract of those who are in contact with the infected person are crucial questions of virus transmission and are clearly related to the size of these droplets.[81] The viability of the pathogen, on the other hand, is a function of external humidity and of the composition (ionic strength) and the pH of the droplet.[82] Droplet size is partly determined by the mode of ejection, which is by now well-known: coughing or sneezing results in much larger droplets than normal speech or breathing. However, an equally important factor in this respect is the composition of the surfactant coating of the droplet, which fine-tunes the surface tension. The composition of the droplets

is a complex function of both the condition of the patient, and of the external conditions, such as humidity. The exchange (condensation and evaporation) of water vapor and nitric acid (HNO_3) between the particle and the atmosphere is particularly important in this respect, because it moderates the viability of the pathogen. A recent study has shown, for instance, that the Φ6 bacteriophage is inactivated both in moderately acidic and basic solutions.[82] It is suggested that while the droplet size is mainly determined by the composition of the surfactant coating, the viability as a function of humidity and pH depends on the identity of the pathogen.

Experimental observation of real droplets often raises ethical issues concerning the use of biological fluids from living patients, which makes computer simulation methods extremely important in studying this question. In particular, detailed analysis of the dependence of the surface tension on the composition of LLF, the uptake or evaporation of water and HNO_3 through the LLF monolayer, and the interactions of LLF with viruses can be envisaged using computer simulations. Such simulations (in particular, coarse grained or machine learning molecular dynamics) together with intrinsic surface analysis could be used to retrieve surface tension contributions and to anchor free energy profiles that describe the uptake of relevant molecules.

6. CONCLUSIONS AND OUTLOOK

Computer simulation investigation of the surface of aqueous solutions of simple salts has become the focus of scientific interest in the past two decades. While this interest was triggered by the pioneering finding that certain simple ions, e.g., I^-, can be accumulated at the surface of their aqueous solutions,[5–8] meaningful analysis of the structural and dynamical properties of such surfaces was enabled by the development of various intrinsic surface analysis methods,[12–16] which have become easily accessible by now.[17]

Studies in this field have led to the clarification of a number of issues concerning these systems, among which we stress here that surface enhancement, at least in the thermodynamic sense, can be meaningfully discussed for salts rather than for their anions and cations separately, and also that, besides their size and polarity, the sign of charge of the the ions is related to their surface affinity. Namely, due to the charge asymmetry of the hydrating water molecules, cations are softer and thus exhibit stronger surface affinity than otherwise equivalent anions.[22] This effect could be unambiguously demonstrated by simulating the surface of the aqueous solution of two fictitious ions that are identical with each other apart from the sign of their charge or calculating the potential of mean force of these ions at the water-vapor interface. An important question still to be understood in this respect is the exact relation between the type of the dissolved salt and the lateral diffusion of water at the surface, a property determined by the delicate interplay of the dynamic charge transfer within the first hydration shell, the distortion of this shell at the vicinity of the surface, and the concentration of the two ions within the surface layer.[29]

The chemical composition of complex ions brings an additional degree of freedom to this phenomenon. An interesting question here is whether there are truly (i.e., also in the thermodynamic sense) surface active water-soluble salts, consisting of nonamphiphilic ions. Tetramethylammonium iodide seems to be a good candidate in this respect. Moreover, HCl and HBr, although technically not being salts, are known to be surface active electrolytes, as they induce a decrease of

the surface tension of water.[83] Understanding the origin of this surface active behavior could shed some additional light to our knowledge about the behavior of simple ions at aqueous interfaces. Considering the difficulties in modeling the cation, we expect this issue to be addressed by *ab initio*-based simulation methods. Investigation of the ion pairs at the surface of their aqueous solutions of high concentration is also an area of active research. Further, understanding the surface behavior of tetramethylammonium dimethylphosphate, a salt consisting of the charged groups of the zwitterionic head of phospholipid molecules as individual ions would be a question of great importance, as it could shed light also to the behavior of the phosphatidylcholine headgroups in the membranes of living cells.

Once at least one of the two ions consists of a hydrophobic and a hydrophilic moiety, the salt immediately exhibits strong surface adsorption. Here we have discussed questions concerning two such groups of salts, namely, RTILs and ionic surfactants. The computer simulation investigation of the surface of aqueous mixtures of RTILs has been long hindered by two factors, i.e., the lack of using intrinsic surface analysis methods and the possible incompatibility of the RTIL and water potential models employed. While well-established intrinsic surface analysis methods are now readily available,[17] a thorough assessment of the combination of existing RTIL force fields and conventionally used water models, preferably against experimental free energy of mixing (or simply miscibility) data, is an urgent task to be done to open the way to computer simulation studies of such interfaces.

The surface of aqueous surfactant solutions has widely been studied by computer simulation methods in the past decades. These studies, in particular, when combined with intrinsic surface analysis, have challenged long-standing assumptions in adsorption models (e.g., the concept of infinitely thin or constant width adsorption layers, fixed adsorption sites, gas-like adsorption, etc.) and have led to the refinement of these models. Here we have pointed out an area of great importance of such a refinement, namely, understanding the effect of surfactant mixtures on the surface tension of small droplets. This question has important practical consequences concerning several urgent issues. Thus, such droplets are abundant in the atmosphere, and their activity as cloud condensation nuclei, a factor that influences the optical properties as well as propensity of precipitation on, at least, regional scales, depends sensitively on their surface tension. Further, droplets of lung lining fluids, ejected to the air by coughing, sneezing, or simply speaking, being the career of various human viruses, e.g., SARS-CoV-2, also consist of such surfactant mixtures. The size distribution of the droplets, depending sensitively on the surface tension, directly influences the effectivity of the transmission of these viruses and hence their virulence.

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Notes

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Abdenacer Idrissi received his M.Sc. in Physics from the University of Mohammed I (Oujda, Morocco) and his Ph.D. in Physical Chemistry from the University of Lille (France), where he is a Professor of Chemistry and Physics at the present time. His research interest is focused on the understanding of the structure and dynamics of fluids including ionic liquids and supercritical fluids and the combination of an array of spectroscopic technics (IR, Raman, neutron scattering, time-resolved spectroscopy) with molecular dynamics simulation.

Pál Jedlovszky obtained his Ph.D. in 1996 at the Hungarian Academy of Sciences under the supervision of Prof. Gábor Pálinkás. He was a postdoctoral fellow at the University of Trento (Italy) and Mount Sinai School of Medicine (New York). He started his independent research career at the ELTE University (Budapest, Hungary). In 2009, he joined to the Department of Chemistry of the Eszterházy Károly University (Eger, Hungary), where he became Professor of Chemistry in 2010 and Head of the Department in 2016. In the early years of his research career, he studied structural and thermodynamic properties of bulk molecular liquids. Later, his research interest has moved toward interfacial systems; it is currently focused on issues concerning the determination of the intrinsic surface of liquid phases, molecular level structural and dynamical properties of liquid–vapor and liquid–liquid interfaces of various binary mixtures and solutions, adsorption and reactivity at solid surfaces, and understanding the molecular level mechanism of anesthesia.

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