Surface effects on aqueous ionic solvation: A molecular dynamics simulation study of NaCl at the air/water interface from infinite dilution to saturation

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Abstract

The concentration dependence of the behavior of the Na^+ and Cl^- ions solvated in a water slab has been investigated using molecular dynamics simulations employing a polarizable potential model. At all concentrations, the sodium ions are almost exclusively located in the interior, while the chloride anions occupy also a significant portion of the surface of the slab. This difference, which has important consequences for the atmospheric reactivity of aqueous sea-salt microparticles (microbrines), is discussed in terms of the relative sizes and polarizabilities of the two ions. The salt concentration, which has been varied from infinite dilution to saturation, has a strong effect on many physical properties, such as the ion solvation numbers and the degree of ion pairing, which are quantified separately for the interior and surface regions of the water slab.

I. INTRODUCTION

Molecular chlorine and other reactive halogen species play an important role in oxidation processes occurring in the lower marine troposphere.[1,2] Recently, unexpectedly high concentrations of Cl_2 have been measured in coastal air and a hitherto unrecognized global source of molecular chlorine has been postulated.[3] Evidence is mounting that concentrated aqueous sea-salt aerosols formed by wave action play a key role in this process.[4] Indeed, laboratory measurements have shown that Cl_2 is formed from sea-salt microparticles in the presence of ozone and UV radiation.[5] In order for the salt microparticles to be reactive, it is crucial that they are humidified above the deliquescence point.[5–7]

Typical diameters of sea-salt aerosols range from hundreds of nanometers to several micrometers.[2–3] Due to their small size and significant degree of corrugation, these microparticles have a large surface to bulk ratio. Attempts to rationalize the Cl_2 production in terms of bulk liquid phase chemistry in the interior of these aerosols has failed.[8] Experiment, kinetic modeling, and molecular dynamics (MD) simulations all consistently indicate that the observed molecular chlorine concentrations can only be explained if reactions at the air-aerosol interface dominate.[8] Ion-enhanced interactions with gases on the surfaces of the microbrines may, therefore, play a crucial role in the chemistry of the atmospheric marine boundary layer. For this reason, among others, it is of a prominent importance to simulate the physical behavior of solvated ions at the surface and in the interior of finite sized water clusters and slabs (i.e. flat water layers with two water-vacuum interfaces) at high salt concentrations.

While NaCl solvation at different concentrations in bulk solution has been intensely modeled,[9–14] much less is known about the ionic behavior at the interface between the bulk solution and air. On the other hand, solvation of Na^+ or Cl^- species in size selected water clusters has been investigated in considerable detail both theoretically[15–20] and experimentally,[21–25] albeit for systems with only a single solvated ion. It is now generally agreed that both simulations and photoelectron and IR spectroscopy measurements indicate a very different behavior of the two ionic species. Specifically, sodium ions tend to reside in the interior of water clusters, while chloride ions preferentially occupy surface positions.[15] It has been shown that the different sizes of the two ionic species and especially the much larger polarizability of the chloride are responsible for this dramatic difference in behavior.[15,20] Most recently, a comprehensive MD study of Cl^- solvation in clusters of different sizes and in a water slab[26] demonstrated that the solvation profile strongly depends on the curvature of the interface. Upon flattening the surface by moving from clusters to a slab, the chloride ion is found not only at the interface, where it exclusively resides in the small clusters, but also in the entire volume of the system.

Recently, we have reported two studies concerning this subject, an *ab initio* quantum chemical calculation of the solvation of a single NaCl molecule in small water clusters,[27] and a MD investigation of a water slab and large clusters saturated with sodium chloride (i.e. 6.1 M solutions).[8] The first paper, inspired by previous quantum chemical studies,[28–29] has shown that NaCl solvation, i.e. breaking of the ionic bond of the solute and creation of a solvent separated ion pair, occurs already in small clusters, starting from the water hexamer. The second study demonstrated that, at very high salt concentrations approaching saturation, the two ionic species behave differently from each other, both in large clusters and in a water slab. In particular, chloride is found in the entire volume of the system, including a significant portion of the interface, while sodium ions reside practically exclusively in the interior. The second paper also discusses the fact that a slab with a flat surface better mimics the atmospheric particles with micrometer sizes than clusters with typically several hundreds of water molecules.

The main goal of the present work is to study the behavior of the chloride and sodium ions, separately at the interface and in the interior of a water slab, over a broad concentration range, from infinite dilution to saturation. This is achieved by performing MD simulations with a polarizable potential model and by evaluating important physical properties such as the ion accessible surfaces, density profiles, solvation numbers, and the degree of ion pairing. Special emphasis is placed on identifying the physical characteristics of the ions that are persistently present at all concentrations, and those that are strongly concentration dependent. Finally, the main findings are presented in the context of the atmospheric reactivity of sea-salt microbrines.

The rest of the paper is organized as follows. In Section II the details concerning the systems under study and the interaction potentials are introduced. The computational methodology is briefly described in Section III. Section IV contains the results and discussion thereof and concluding remarks are presented in Section V.

II. SYSTEMS AND POTENTIALS

The aim of the present study was to mimic atmospheric sea-salt microparticles. Laboratory measurements have shown that the mechanism of Cl_2 production is the same and the yields are similar for sea-salt and rock salt aerosols.[5,8] For simplicity, we have, therefore, studied pure NaCl solutions. Aerosols with a micrometer diameter typically contain 10^{11} atoms. It is computationally impossible to simulate clusters with such a large number of particles. However, for all practical purposes the effects of the surface curvature in these aerosols can be neglected, and a slab with a flat (though corrugated) interface represents an excellent and practical computational model.[8]

We have investigated the whole salt concentration range from "infinite dilution," by which we mean a single NaCl ion pair in the whole slab, to saturation at 6.1 M with one intermediate step corresponding to a 1.2 M solution. It has been shown that, for the study of ionic solutions in a polar medium, consistently better results are being obtained by using a polarizable potential model.[13–15] As in our previous study,[8] we have employed the polarizable SPCE/POL water potential,[30] which has proven to be very successful in MD studies of NaCl solutions at different concentrations,[8–9] together with standard force field parameters for the ions.[31]

III. COMPUTATIONAL DETAILS

Molecular dynamics simulations with a polarizable potential have been performed using the AMBER 6 program package.[32] A slab of 864 water molecules was used to construct each system by replacing randomly chosen water molecules with the appropriate number of sodium and chloride ions (96 for 6.1 M, 18 for 1.2 M and 1 for infinitely dilute solution). Each slab was placed into a $30\times\ 30\ \times\ 100$ Å^3 rectangular box and three dimensional periodic boundary conditions were applied, producing slabs at least 25 Å thick with two open interfaces following equilibration. The thickness of the slabs is sufficient to achieve bulk behavior in the interior.

The simulations were run at 300 K, however, the temperature dependence of the observable quantities is very weak over a relatively broad temperature range.[8] The particle mesh Ewald method[33] was used to calculate the electrostatic energies and forces, and the van der Waals interactions and the real space part of the Ewald sum were truncated at 12 Å. A timestep of 1 fs has was employed, and the OH vibrations were frozen using the SHAKE algorithm.[34] Relatively long simulation times are required for obtaining statistically meaningful data. For all three concentrations the systems were equilibrated for at least 500 ps. The analysis is based on an additional sampling period of 500 ps for the two more concentrated slabs. A production run of1,000 ps was carried for the infinitely dilute system, but even with the additional sampling this run did not provide completely converged statistical data for the single ion pair, Therefore, some of the observables have been evaluated only for the 6.1 M and 1.2 M. Statistical quantities were computed by using the method of block averages,[35] with a block size of 50 ps.

A nanosecond simulation of the systems under study is computationally rather demanding. Using the present program, it takes several CPU weeks on a 700 MHz Linux PC. Clearly, the computational bottleneck is the evaluation of the polarizable potential, which slows down the simulation by an order of magnitude compared to a standard MD simulation with a non-polarizable force field.

IV. RESULTS AND DISCUSSION

The physical behavior of the Na^+ and Cl^- ions in the water slab can be quantified in different ways. From the point of view of the atmospheric reactivity at the air-aerosol interface, a crucial quantity is the exposed surface of the two types of ions, calculated as the ionic area accessible to typical reactive gases.[8] This ion accessible surface area is evaluated using the Lee and Richards algorithm[36] with a probe radius of 1.7 Å (size of the OH radical) over the surface of the slab. Fig. 1 depicts the percentage of the surface covered by chloride and sodium ions during the MD simulation for salt concentrations ranging from saturation to infinite dilution. For all concentrations, there is a dramatic difference between the two ions. While sodium is practically absent from the surface, chloride ions occupy a sizable fraction of the interface and, given the concentration ratio, are more exposed than an average water molecule. The two orders of magnitude difference between surface exposures of the two ionic species is due to their different physical properties. Simulations with a non-polarizable potential, where the ions differ only by size and polarity, qualitatively showed the same difference, however, the effect was about half an order of magnitude weaker.[8] Clearly, the difference in polarizabilities (0.24 vs. 3.25 Å^3) between the "hard" Na^+ ion with no valence electrons and the "soft" polarizable chloride anion plays a crucial role here.

In our previous study,[8] we have demonstrated the effect of different surface behavior of the two ions for the case of saturation. Here, we show that it is present also in more dilute systems, and that the chloride accessible surface is roughly proportional to the salt concentration ratio, dropping from 12 to 2.1 % when moving from 6.1 to 1.2 M solutions. Unfortunately, the statistics is very poor for the infinitely dilute solution with a single pair of ions, even using a doubled simulation time (see Fig. 1c). Indeed, there are long periods when the ions are absent from the surface, and it is impossible to obtain converged data concerning the surface exposure of the ions in the slab within a reasonable computational time.

Another way of quantifying the occurrence of the ions at the surface or in the bulk of the slab is to calculate density profiles along the direction perpendicular to the open surface (z-axis). from the center to the interface. In Fig. 2 we show the density profiles of the chloride and sodium ions, together with the water oxygens, for the three concentrations under study. For the numerical evaluation of the density profiles, the z-axis has been discretized to equidistant intervals of 0.2 Å . The decrease of the oxygen signal roughly correlates with the decay of the slab interface. Due to the large corrugation of the surface (as confirmed by the present and previous[8] MD simulations), however, this quantity is only orientational and much less relevant for the reactivity of the aerosols than the ion accessible surfaces discussed above. Nevertheless, we see that for all concentrations the sodium ion signal drops before that of the chloride ions, indicating more interior solvation of the former species. As may be seen in Fig. 3 depicting snapshots of the two more concentrated systems from the MD simulations, because the chloride ions are significantly larger than water molecules, they can be exposed at the interface in spite of the fact that their density profiles (which corresponds to center of mass positions) drops slightly before the oxygen signal. The surface layer, where the curves of the two ionic species significantly differ from each other is rather thick (more than 5 Å), however, this effect can be partly attributed to the corrugation of the surface (see Fig. 3). It appears from the density profiles that, in the saturated slab, a "double layer" is set up at the air/solution interface: the chloride density is enhanced relative to the sodium at the surface, while approximately one ionic diameter inside the surface the chloride density is depleted and the sodium is enhanced. Such a double layer does not appear to exist in the 1.2 M solution.

Our present chloride density profile at infinite dilution roughly correlates with the corresponding result of a recent MD simulation of a single chloride ion in a slightly smaller water slab.[26] However, we stress again that the ion signals get progressively more noisy upon decreasing the concentration due to the inferior statistics in more diluted slabs. We conclude that the density profiles support the conclusions drawn from the ion accessible surfaces, namely, that at all concentrations sodium ions are essentially located in the bulk, while chloride ions are present both in the interior and on the surface of the slab. The observation that at infinite dilution chloride is present in the whole slab volume, in contrast to the situation in finite sized clusters where the Cl^- ion strongly favors the interface,[15,20] has been made recently.[26] The present study extends this picture to the whole concentration range, and in the presence of the Na^+ counterions.

It has long been recognized that the basic assumption of the simple Debye-Hückel model of electrolytes, namely, that the ions are perfectly separated from each other by the polar solvent molecules is not valid at higher salt concentrations.[11] In Figs. 4 and 5, this is demonstrated on the pairing of Cl^- and Na^+ ions for 6.1 and 1.2 M slabs separately for the surface and the interior as a function of simulation time. The dividing line has been drawn at the distance of 14 Å for 6.1 M or 11 Å for 1.2 M solution from the center of the slab based on the positions of the decaying region of the oxygen density profiles (see Fig. 2). On one hand this defines a relatively thick surface layer, which improves the statistics there. On the other hand, slightly more ions of both types now appear at the interface than in the previous discussion based on ion accessible surfaces. Clearly, it is difficult to unambiguously define an interfacial region in terms of distances for corrugated surfaces. A Na^+–Cl^- pair is considered to be paired (unpaired) if the interionic distance is smaller (larger) than 3.7 Å . This value corresponds to the barrier on the potential of mean force between the two ions, which separates the contact from the solvent-separated ion pair in bulk water at infinite dilution.[9] We do not display here the results for the case of infinite dilution, where the ions are practically always unpaired and, therefore, the corresponding signals in Figs. 4 and 5 would simply be the base line. We see, however, that already at 1.2 M about 5 % of the ions are paired and at saturation ion pairing is actually the dominant process.

In the context of the present study, the most interesting result drawn from Fig. 4 is the different degree of Cl^- ion pairing with Na^+ at the surface compared to the interior of the slab. While at 1.2 M this difference is small (5.0 vs. 5.5 %), at saturation 75 % of the chloride ions are paired in the bulk while only 54 % at the interface. This indicates that in concentrated aerosols there is a significant amount of (more reactive) unpaired chlorides, which is in accord with the proposed atmospheric reactivity at the interface.[8] Interestingly, the numbers concerning ion pairing for the sodium ion differ from those for chloride, and also the difference between the interior and the surface is much less pronounced for Na^+. The difference between the numbers for the two ionic species is explained by a frequent formation of Na^+–Cl^-–Na^+ metastable aggregates, which are indeed observed, especially close to the interface, during our simulations.

Figures 6 and 7 display the water solvation numbers for the two ions as a function of simulation time, again separately for the surface and the interior of the 1.2 and 6.1 M slabs. We have considered a water molecule as solvating the Cl^- (Na^+) ion when the ion-oxygen distance is smaller than 3.8 (3.1) Å which are values corresponding to the minima on the ion-oxygen radial distribution functions.[9] We do not present the corresponding results at infinite dilution for two reasons. First, since the single Cl^- or Na^+ ion is either in the interior or at the interface, the curves would necessarily be discontinuous. Second, as discussed above, due to poor ion statistics the signals are noisy even for very long simulation times. Nevertheless, we have verified that within statistical error the average solvation numbers for infinite dilution agree with the previously reported values of 6.0 for Cl^- and 5.8 for Na^+.[9]

An important observation is that the water solvation numbers drop strongly with increasing concentration. This is clearly due to ion pairing which causes that nearly one water is "lost" from the solvation shell (as defined in the previous paragraph) at 1.2 M concentration, and another is lost at saturation. A notable result is that the solvation numbers are consistently slightly smaller at the interface than in the interior. For Cl^- at saturation this difference is larger than the statistical uncertainty. Note, that this difference arises despite the fact that more unpaired chlorides (with a potentially larger solvation number) reside at the surface of the concentrated slab than in the interior (see Fig. 4). Thes results further support our previous claim based on ion accessible surfaces (see Fig. 1) that a significant fraction of the chloride ions is exposed at the interface of a concentrated NaCl solution.

V. CONCLUSIONS

MD simulations with a polarizable potential of water slabs with NaCl concentrations ranging from infinite dilution to saturation have been performed. These systems serve primarily as models of atmospheric sea-salt microbrines that have recently been implicated in the production of molecular chlorine in the marine boundary layer.[4–5] Our finding that at all concentrations the chloride anions occupy the whole volume of the slab, including a significant fraction of the interface, while the sodium ions reside practically only in the interior, strongly supports the proposed surface mechanism of the reaction of Cl^- with reactive atmospheric gases (primarily OH and O_3) towards Cl_2.[8]

The surface vs. interior ion solvation has been quantified both via ion accessible surfaces and density profiles. Due to a large degree of surface corrugation, the latter quantity is probably less representative. Nevertheless, both support the findings discussed in the above paragraph. Other physical measurables such as solvation numbers and the degree of ion pairing have been evaluated for different concentrations. While negligible at lower concentrations, ion pairing becomes dominant at saturation. Also, the water solvation number drops by roughly 20% for both ions when moving from 1.2 to 6.1 M solutions. For chloride, there is a sizable difference between the surface and the interior for both of these quantities, the Cl^- ions at the interface being less paired and having a smaller solvation number.

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VI. FIGURE CAPTIONS

Fig.1: Fractional accessible surface area of the Na^+ and Cl^- ions for water slabs with NaCl concentrations of (a) 6.1 M (saturation), (b) 1.2 M, and (c) infinite dilution. Average values and their standard deviations are reported in the legend.

Fig.2: Density profiles of sodium, chloride and water oxygen atoms in water slabs with NaCl concentrations of (a) 6.1 M (saturation), (b) 1.2 M, and (c) infinite dilution. The z coordinate is measured from the center of the slab in the direction perpendicular to the open surfaces, and the profiles have been symmetrized by averaging over the two halves of the slab.

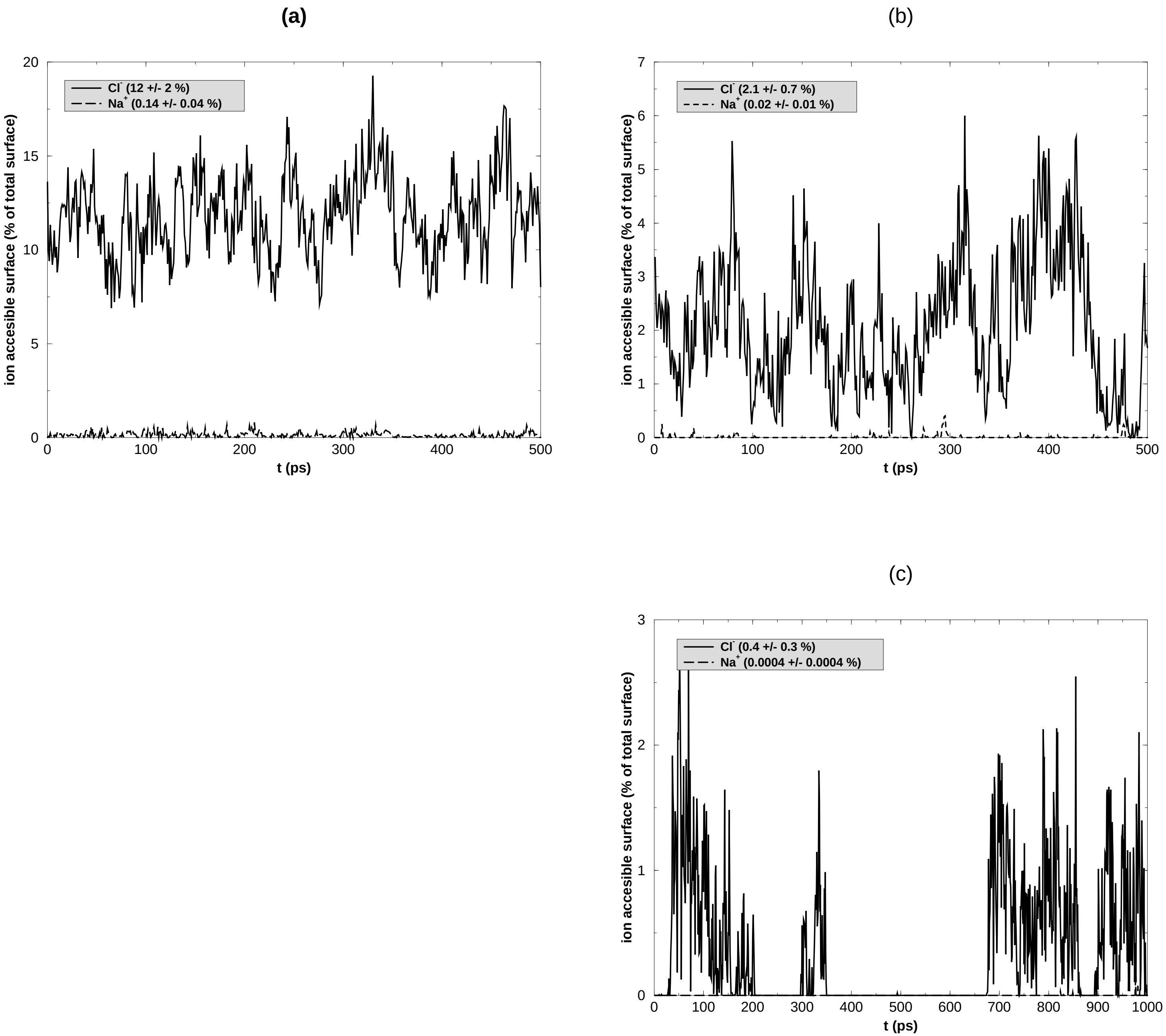
Fig.3: Snapshots from MD simulations of (a) the 6.1 M slab, and (b) the 1.2 M slab. The vertical direction is the direction of the inhomogeneity, z. The water molecules are drawn in the ball-and-stick representation, the chloride are the larger, lighter spheres, and the sodium ions are the smaller, darker spheres.

Fig.4: Ion pairing of the Cl^- species at the interface and in the interior for water slabs with NaCl concentrations of (a) 6.1 M (saturation) and (b) 1.2 M. Average values and their standard deviations are reported in the legend

Fig.5: Ion pairing of the Na^+ species at the interface and in the interior for water slabs with NaCl concentrations of (a) 6.1 M (saturation) and (b) 1.2 M. Average values and their standard deviations are reported in the legend

Fig.6: Solvation numbers of the Cl^- species at the interface and in the interior for water slabs with NaCl concentrations of (a) 6.1 M (saturation) and (b) 1.2 M. Average values and their standard deviations are reported in the legend

Fig.7: Solvation numbers of the Na^+ species at the interface and in the interior for water slabs with NaCl concentrations of (a) 6.1 M (saturation) and (b) 1.2 M. Average values and their standard deviations are reported in the legend



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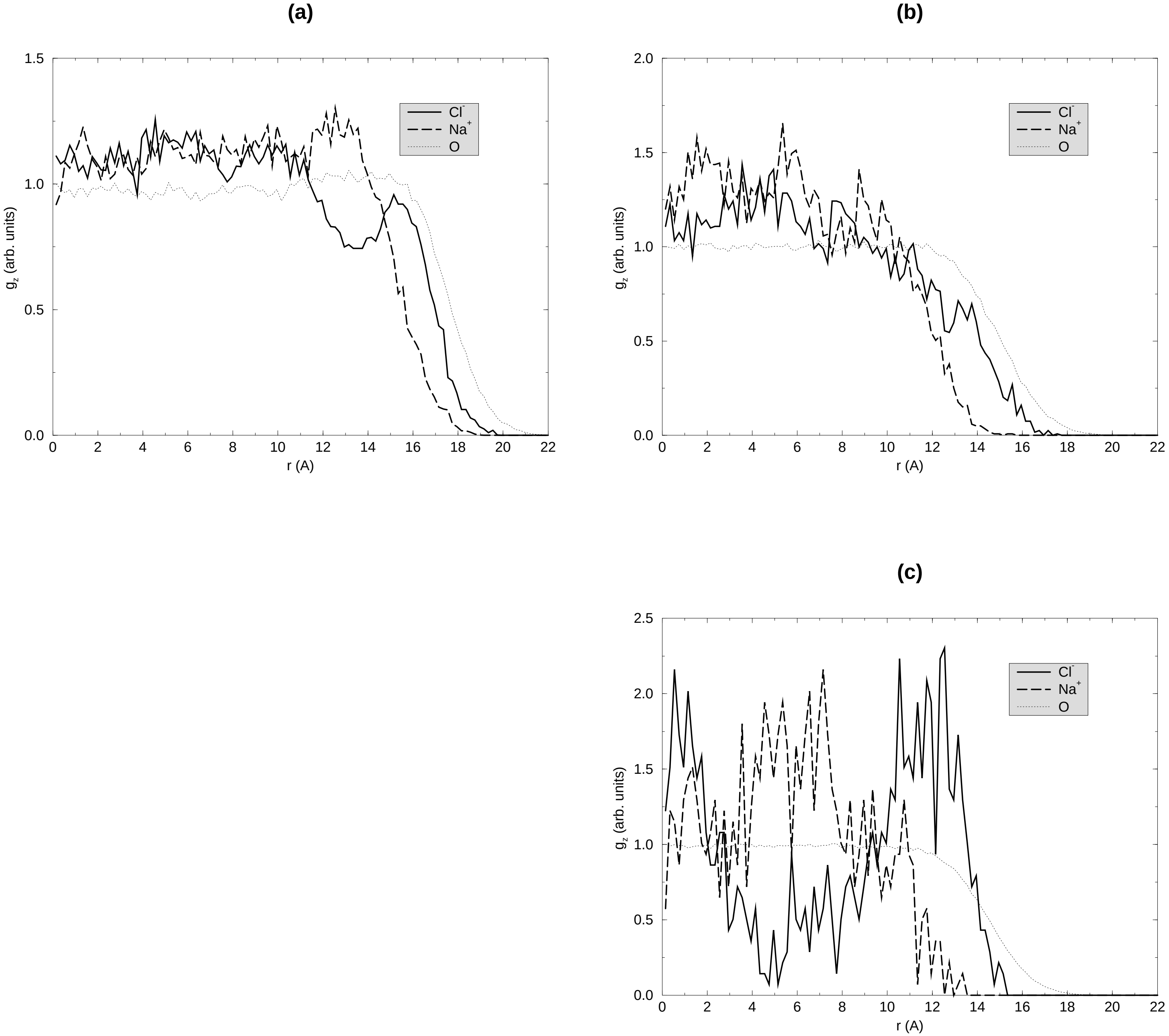

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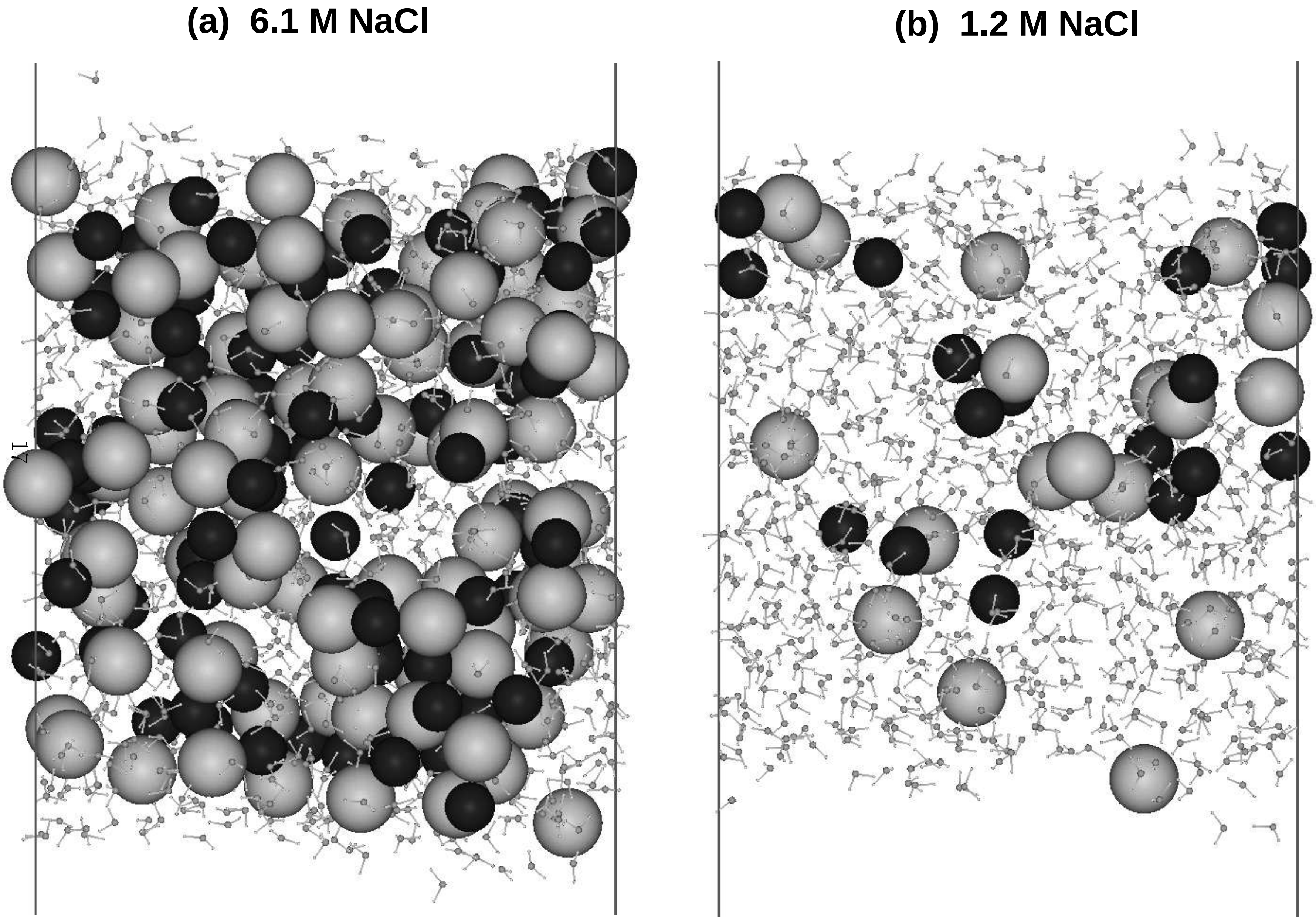

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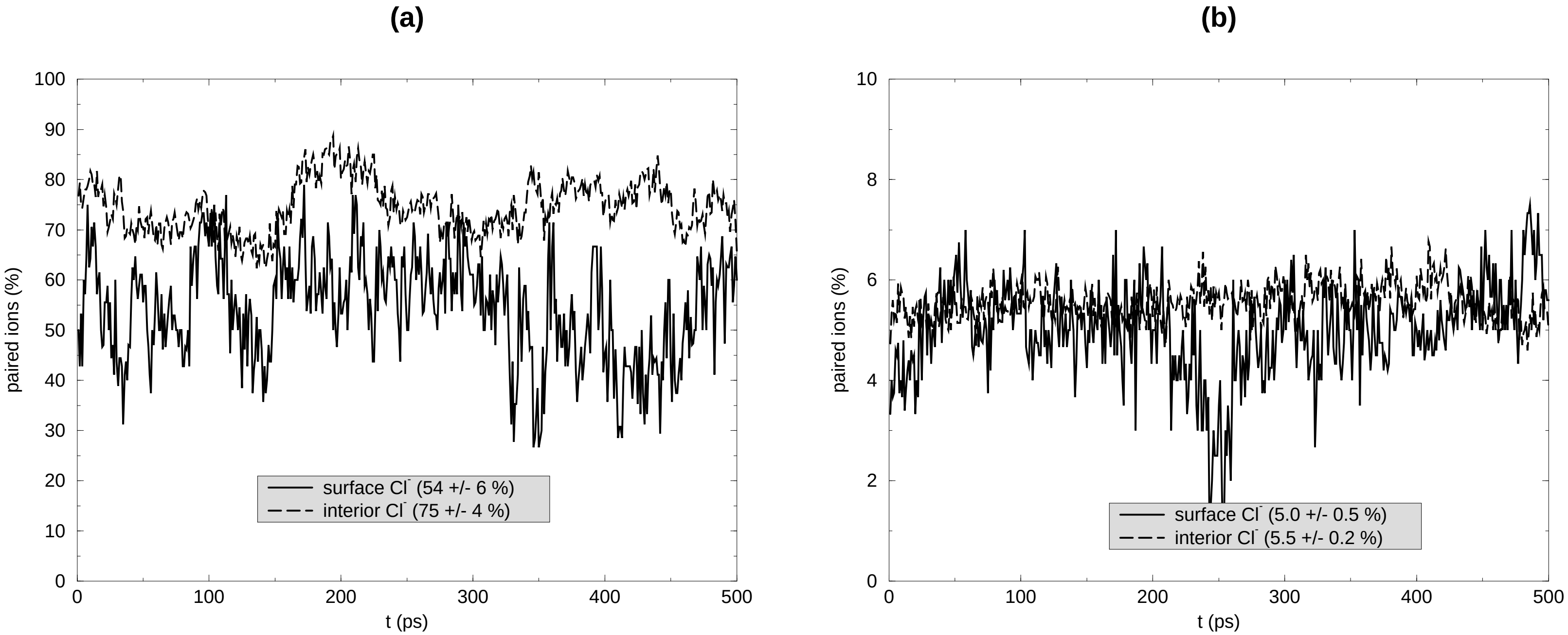

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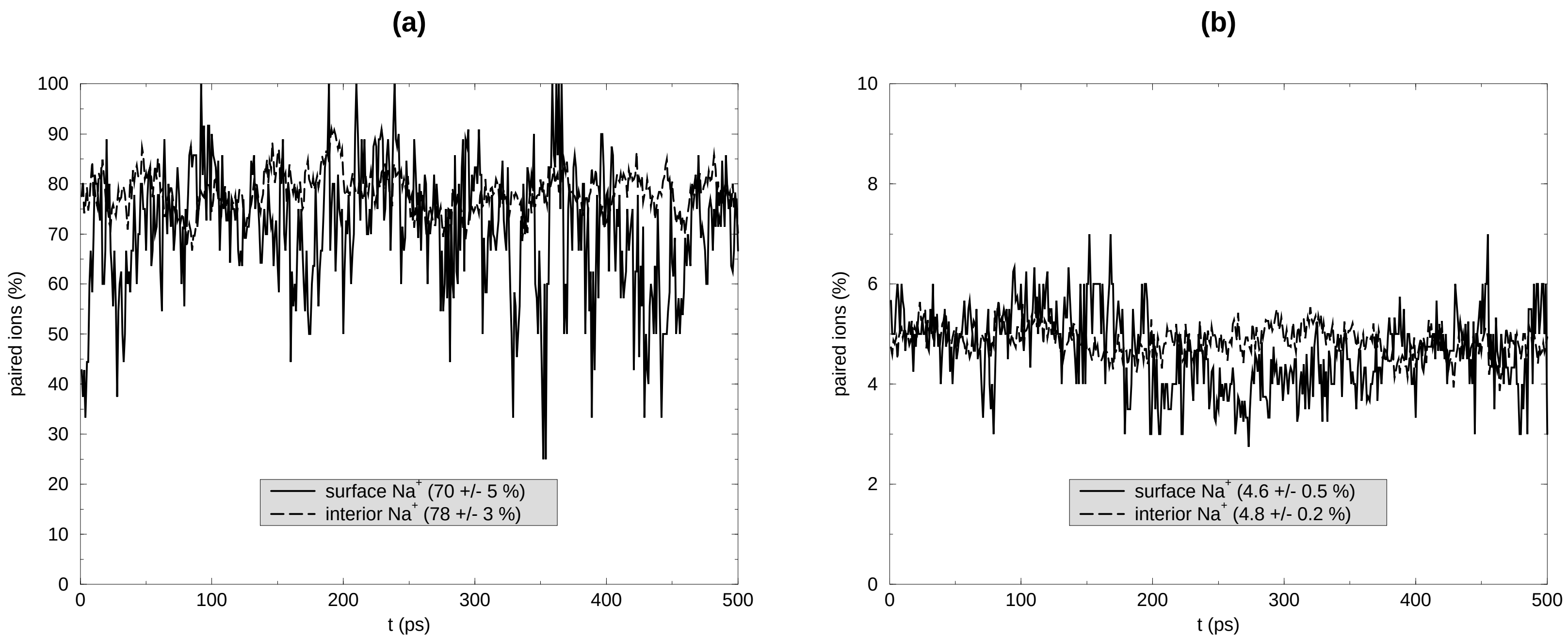

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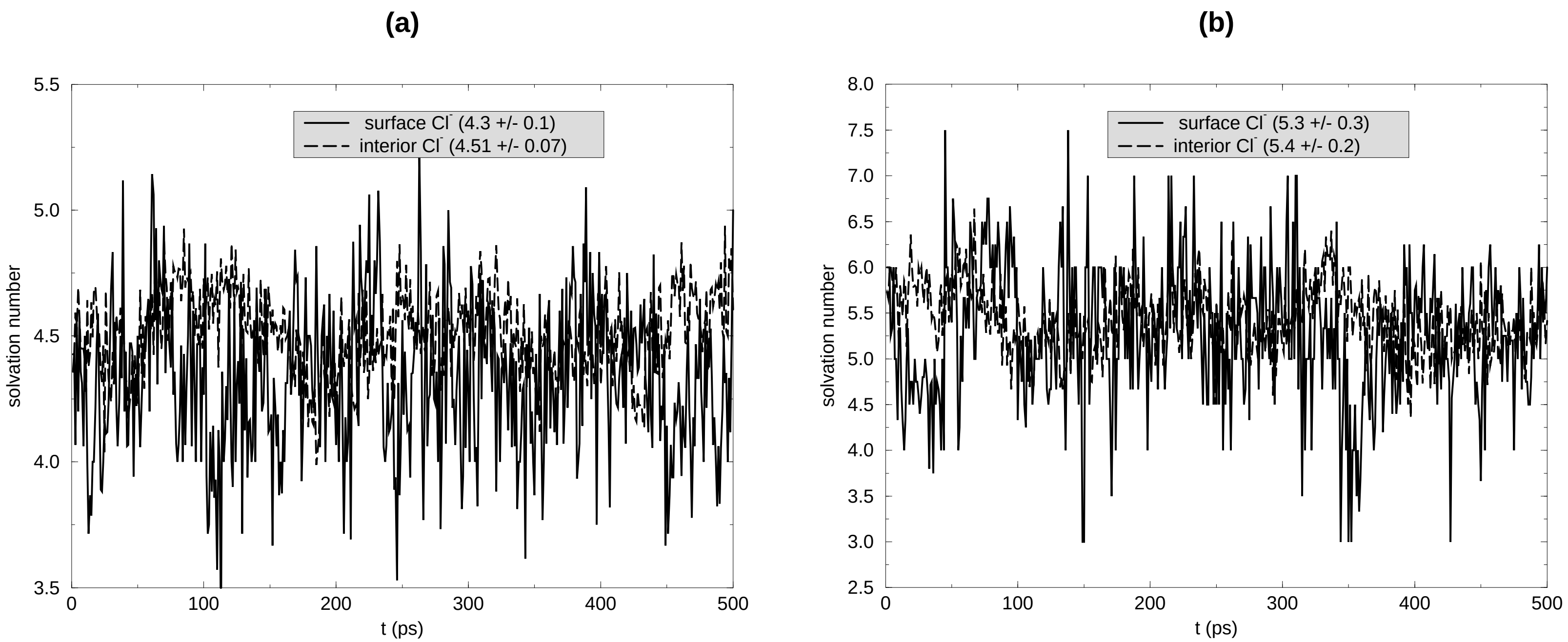

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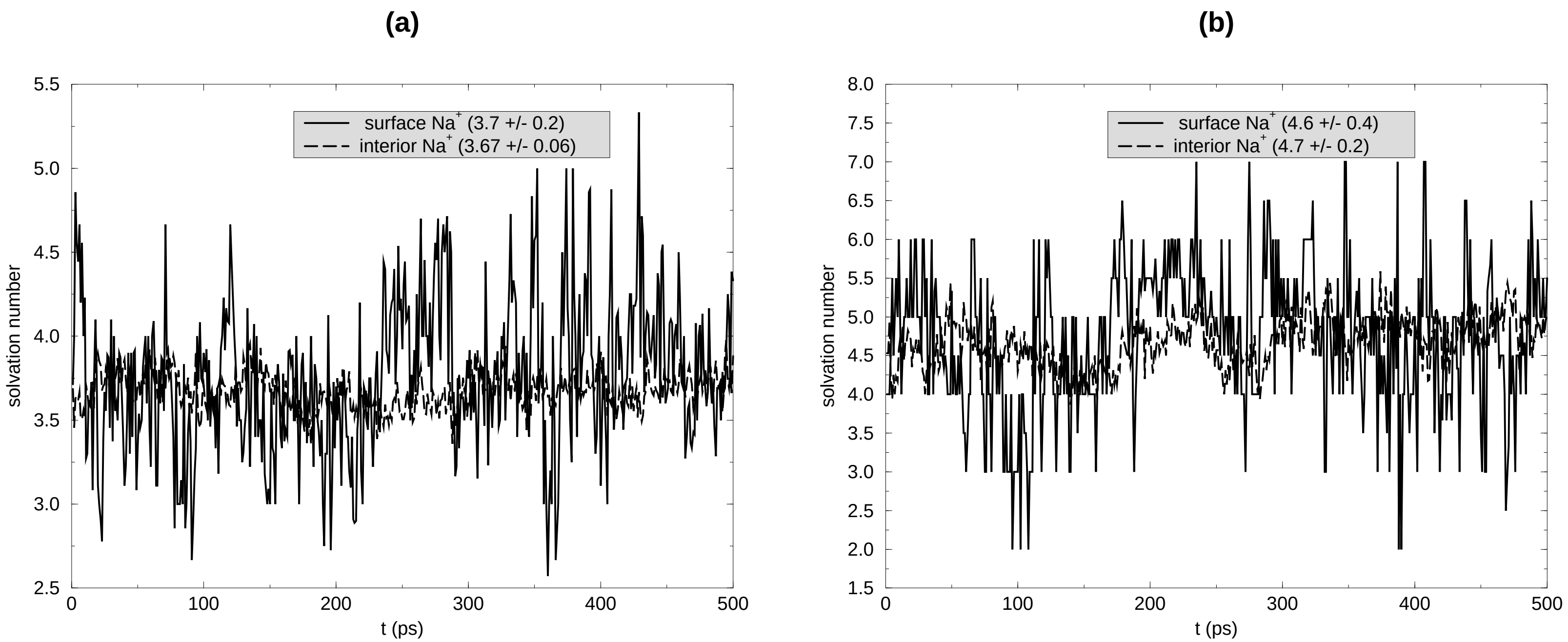

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