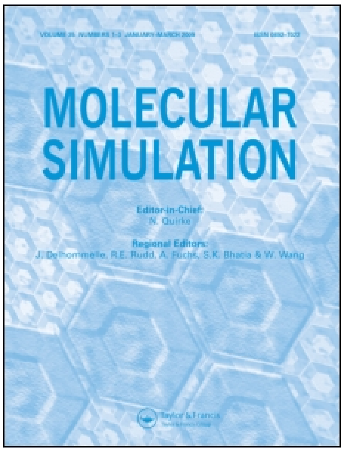

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# Ion Pairing in Confined Electrolytes

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# Ion Pairing in Confined Electrolytes

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**Equilibrium molecular dynamics has been used to investigate ion and water distributions of 0.5 M sodium chloride solutions of approximate density, 1000 kg m$^{-3}$, confined in model carbon nanotubes having radii of 0.65, 1.33 and 1.97 nm. It is observed that ion pairing can occur; its nature and location being highly dependent on pore radius. Especially notable in the smallest cylinder, where hydration is frustrated by confinement, is the formation of tightly bound ion pairs at the cylinder axis.**

*Keywords*: Electrolyte solutions; Nanotubes; Sodium chloride; Water

## INTRODUCTION

Water and electrolyte solutions in confined spaces are of great importance in biological systems (e.g. ion transport through membranes), and industrial membrane processes (e.g. desalination). In the past two decades, there has been intense and increasing research activity [1–9] in these areas. Simulation studies have contributed significantly to this effort. Much of this work has focused on very dilute electrolytes where single ions are surrounded only by water molecules, including studies of single ion transport through model cell membrane pores and studies of the hydration structure around isolated ions. Another group of simulations has used primitive models, in which there is no explicit description of the water molecules. Both approaches avoid a major difficulty for electrolytes at realistic dilutions: namely the many water molecules required for each ionic species (55:1 in a 1 M solution). Thus, a fully explicit electrolyte simulation at normal dilutions requires a very large number of particles in order to ensure a statistically sufficient number of ionic particles. However, it is arguable that, especially in confined spaces, packing and other effects may disrupt hydration shells leading to significant modifications of transport and equilibrium properties.

In this note, we report some results from a simulation study in which dilute (0.5 M) sodium chloride solutions, where both cations and anions were present simultaneously, are confined in cylindrical spaces. We wish to draw attention to some of the interesting features of equilibrium structure that can be conferred on electrolytes subjected to confinement; especially the possibility of strong ion-pairing that may occur in certain situations.

## MODEL AND SIMULATIONS

We chose graphitic nanotubes as the basic pore model type. The nanotubes were modelled as cylinders of continuum graphitic material. Physical radii are measured from the pore axis to a position at the centre of a first layer atom in the adsorbent. Three values of 0.65, 1.33 and 1.97 nm were chosen. An internal density for the electrolyte was based on a volume, estimated by choosing an internal pore radius as the position where the single particle distribution (obtained in preliminary runs) goes to zero close to the pore wall. Most runs were made with an internal density of 1000 kg m$^{-3}$. The electrolyte concentration was 0.5 M NaCl and

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all runs were carried out at 298 K. It has been demonstrated, for primitive electrolyte solutions of similar sized particles in neutral confined spaces, that there is no selective ion adsorption [10]. Although in principle, non-neutrality, due to selective adsorption, may occur when ions have different sizes even in neutral adsorbents, it would require very large numbers of particles and special simulation techniques in order to investigate this. The SPC/E model [11] was used for water, and the Na and Cl ions were modelled as singly charged particles with a 12-6 core having parameters $\varepsilon/k = 62.7\,\mathrm{K}$, and $\sigma = 0.2876\,\mathrm{nm}$ and $\sigma = 0.3785\,\mathrm{nm}$, respectively. Runs were also made with pure water at the same density as the electrolyte in order to assess the effect of ions on structure and diffusion coefficients. Each run was made with 1100 water molecules, 10 Na ions and 10 Cl ions. It was found that time step lengths of greater than 1 fs led to instability arising from reflection by the repulsive field of the wall. Run lengths were between 0.3 and 1 ns.

## RESULTS

The single particle distributions for water are shown in Fig. 1. There is a well-ordered layer of water at the wall; in the 1.97 nm pore this ordering extended to the second and third layer, and there is an annular layer and a fairly well-defined ordering of water at the pore centre in the 0.65 nm pore. At the intermediate pore size (radius 1.33 nm), very little ordering of the water occurs beyond the wall layer. At all radii, hydrogen faces outwards towards the wall. These distributions are characteristic of water in confined spaces.

The ion distributions normal to the wall, and those along the axis, are shown in Figs. 2 and 3, respectively. There is a tendency for the ionic components to cluster axially, especially in the two smaller pores. This structure in the single particle distributions in Fig. 3 can be regarded as evidence of very long-lived ionic clusters. Clearly in the limit of infinite time the distributions in Fig. 3 should tend to unity. However, the most dramatic differences are seen in the distributions normal to the wall. At the smallest radius (0.65 nm), both ions are concentrated close to the cylinder axis. Figure 2 shows that there is also a strong correlation between the positions of the positive and negative ions in the axial direction. These distributions provide statistical evidence for ion pairing in these pores. Figure 4 shows a snapshot from a simulation in the cylinder with $R = 0.65\,\mathrm{nm}$, where a centrally located ion pair can be clearly seen.

For the other two radii examined, the distribution of ions normal to the wall (Fig. 2) is quite different. At $R = 1.33\,\mathrm{nm}$, there is a more uniform distribution of ions over the pore radius, although positive and negative ions tend to form layers with the chloride ion more concentrated towards the wall. Positive and negative ion positions tend to be de-correlated normal to the wall, despite the tendency to axial clustering. By contrast, the largest pore size shows a strongly localised structure for the ions normal to the wall, with complete absence of ions in a central core of radius 0.4 nm, and the negative ions form two concentric layers with maxima at 0.7 and 1.3 nm from the centre. The sodium ions are more diffusely distributed over the radius range from 0.4 to 1.8 nm. Positive and negative positions show some degree of correlation in both normal and axial directions, but this is much weaker than for $R = 0.65\,\mathrm{nm}$.

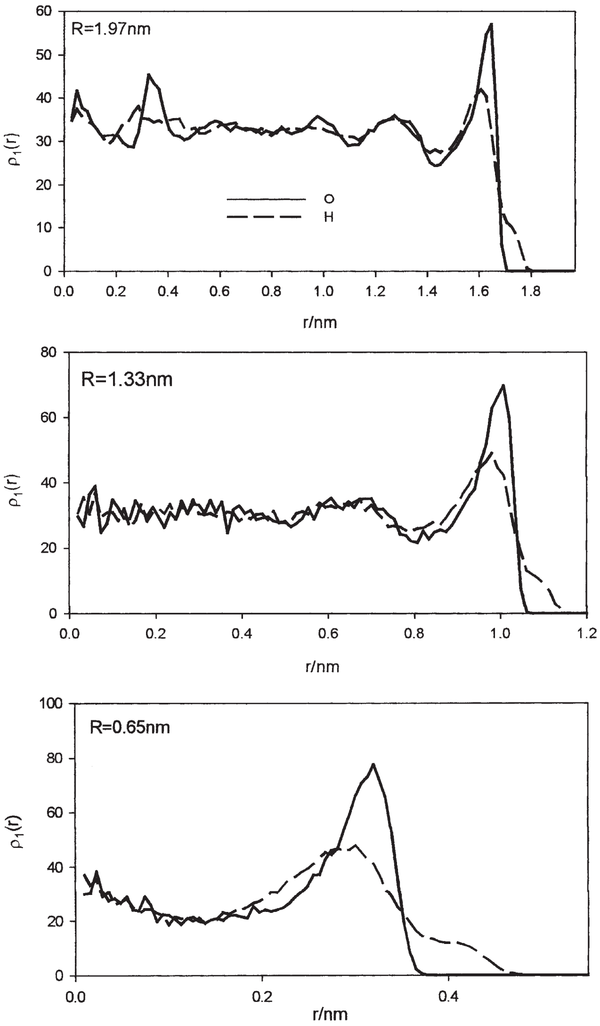

FIGURE 1 Single particle distributions for oxygen and hydrogen atoms in water normal to the wall.

These differences in structure and ordering of the aqueous and ionic components have their origin in the facility with which particles of different sizes can pack into a confined space of a given width. This in turn affects the ability of the water molecules to form

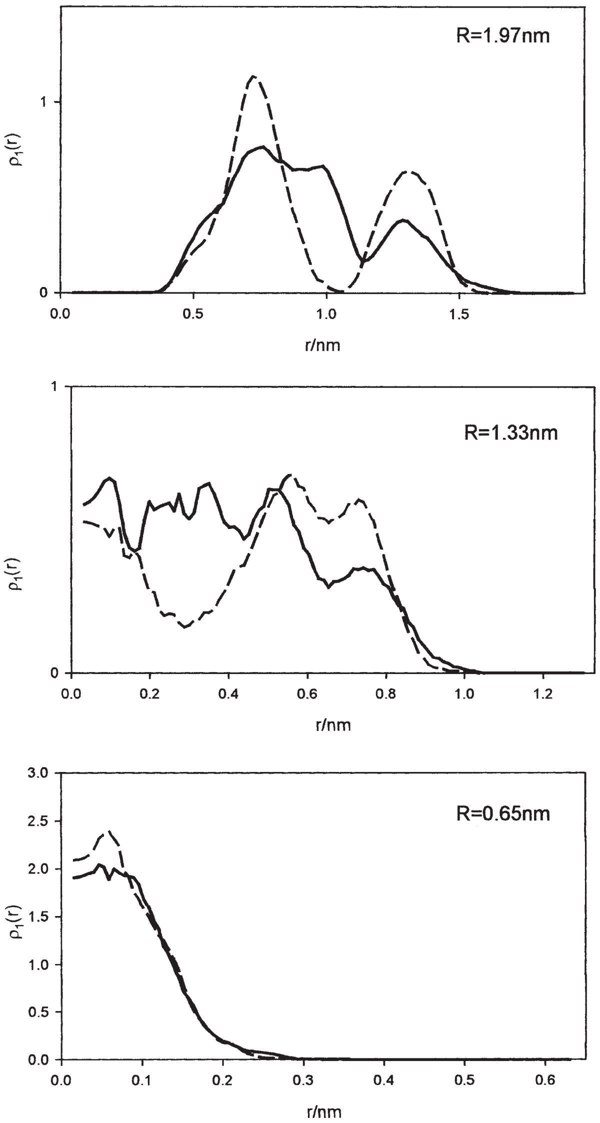

FIGURE 2 Single particle distributions for sodium and chloride ions normal to the wall. The full lines are smoothed functions, indicating the overall trends. The points and dotted lines are the raw data.

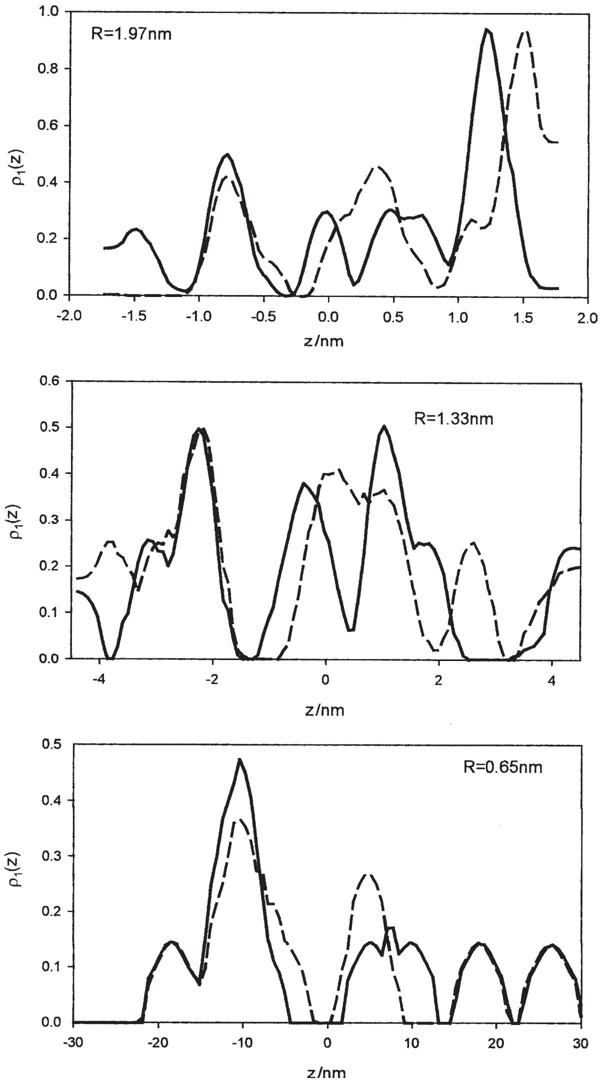

FIGURE 3 Single particle distributions for sodium and chloride ions parallel to the cylinder axis. Lines and symbols as in Fig. 2.

hydration shells around the ions. An analogous phenomenon occurs in adsorbate structures in confined spaces, where "packing transitions" can be observed in plots of density against pore width at a constant pressure [12]. An approximate calculation (assuming a shell of water, one molecule thick, around each ion) gives hydrated diameters for $Na^+$ and $Cl^-$ as 1.04 and 1.14 nm, respectively. In the narrowest pore, the available diameter between the strongly repulsive parts of the ion-wall potential is approximately 1.0 nm. In this pore, electrostatic energy from close proximity of the paired ions compensates for the poor hydration and for repulsive forces from the pore wall consequently ion pairing occurs at the centre of the pore.

FIGURE 4 Spontaneous formation of an ion pair: Na (black) and Chloride (white) in a confined aqueous environment at 298 K ($R = 65$ nm, 0.5 M).

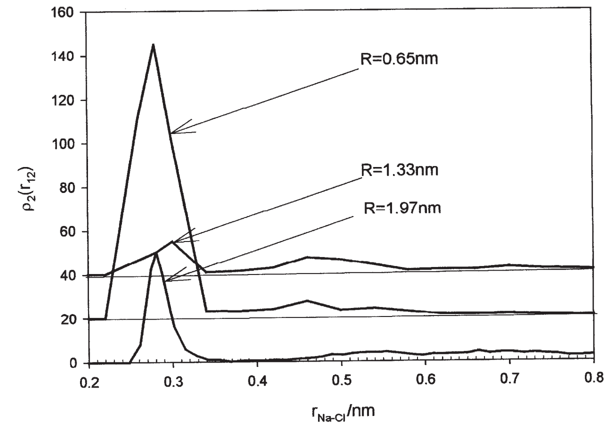

FIGURE 5 Pair distribution functions for Na–Cl in nanotubes of different radius.

In the largest pore, ($R = 1.97$ nm) there are two well-defined annuli of Cl ions. However, snapshots and the axial distributions suggest that these do not exist as contingent layers, but tend to be staggered at alternate positions along the pore length. The sodium ions occupy intermediate locations between the chloride ions, and their normal distribution (Fig. 2) shows two unresolved annuli towards the centre of the pore. Ion pairing occurs within these annuli, as is evident from the intense Na–Cl peak in the pair distribution (Fig. 5). The smaller cylinder, with $R = 1.33$ nm, favours packing of Cl-ions along the pore axis, and here there is evidence, from the axial distributions and from snapshots, of ion-pairing in this region. However, the first peak of the sodium to chloride pair distributions in Fig. 5 is much weaker than for the larger or smaller pores, and there is relatively more structure in the second and third Na–Cl neighbours than is seen in the other pores.

## CONCLUSION

We have shown that strong ion-pairing can occur in confined NaCl solutions at moderate electrolyte concentrations. In the smallest cylinders investigated here, (physical radius 0.65 nm) ions are strongly paired along the pore axis. At a larger pore size ($R = 1.97$ nm), where two annular layers of ions can form, there is evidence that ions tend to pair within the annuli. However, ion-pairing was weak in cylinders having an intermediate radius ($R = 1.33$ nm). The effect of packing on hydration structure is the central mechanism in operation; in analogy to the packing transitions observed in adsorbates, which also depend on the structures available to the packed fluid [12]. The relative sizes of the ions should also be a significant factor. It is clear that the interplay of the repulsive constraints due to confinement, and strong electrostatic interactions, engenders a complex parameter space, and it is not possible to draw many general conclusions at this stage. Similarly, different geometries (e.g. slit-shaped pores, or linked spherical spaces), and densities, may lead to quantitatively different results. In a future publication, we shall discuss the transport properties of these confined electrolytes.

### *Acknowledgements*

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