

# Supplementary Information

J. R. Espinosa <sup>†</sup>, J. M. Young <sup>‡</sup>, H. Jiang <sup>‡</sup>, D. Gupta <sup>‡</sup>,  
C. Vega <sup>†</sup>, E. Sanz <sup>†</sup>, P. G. Debenedetti <sup>‡</sup> and A. Z. Panagiotopoulos <sup>‡\*</sup>

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## 1 Binary Lennard-Jones Mixture

### 1.1 Chemical Potential

We calculated the chemical potential of the solid using the Einstein crystal method [1]. The uncertainty in the solid chemical potential was determined by selecting four volumes from a normal distribution about the equilibrium volume and calculating the chemical potential at each volume. Since there is a strong finite size effect on the chemical potential of a solid [2], we extrapolated the solid chemical potential to infinite size by performing simulations at 256, 500, 864 and 1372 particles.

We calculated the chemical potential of the solute using thermodynamic integration of a solute particle insertion. The integration was performed using a 15 step Legendre-Gauss quadrature. The uncertainty of the solution chemical potential was estimated by performing five independent calculations at each concentration. All of the solutions simulated consisted of 1500 particles, plus the inserted particle. The solution chemical potential was fit with the Margules activity model.

The solubility is the concentration at which the chemical potential of the solution is equal to the chemical potential of the solid, which is shown as the intersection of two curves in Figure 1. We estimated the uncertainty of the solubility from a Taylor expansion about the intersection of the curves, as explained in Nezbeda *et al.* [3]

### 1.2 Spherical Cluster

Figure 2 shows the fluctuation in the calculated solubility when inserting the spherical cluster.

Figure 3 (right) shows a snapshot of the spherical LJ crystal used in the DCM simulation for calculation of solubility.

## 2 JC/SPC/E NaCl solution

### 2.1 Spherical cluster

Figure 3 (left) shows a snapshot of spherical NaCl crystal used in the DCM simulation for calculation of solubility.

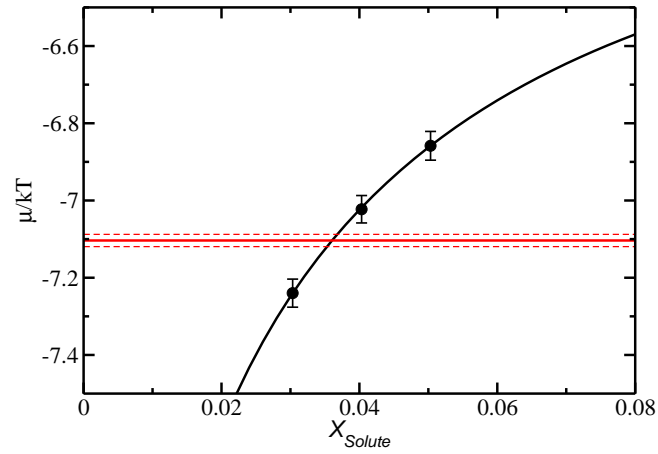


Figure 1: Chemical potential of solution (points) and solid (red line). Dashed red lines indicate the uncertainty in the chemical potential of the solid. The Margules activity model is fit to the solution chemical potential (black line).

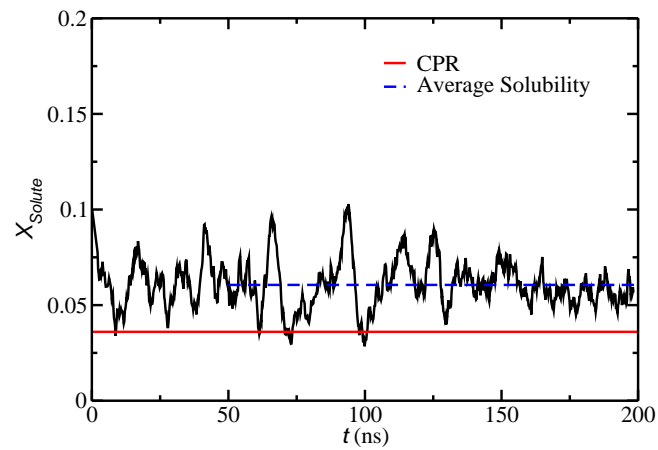


Figure 2: Calculated solubility using a spherical cluster of 7 nm of diameter. The dashed blue line indicates the average value calculated after equilibration and the red line indicates the correct solubility as obtained from the chemical potential calculations. Values shown have been averaged over blocks of 2 ns to reduce high-frequency noise.

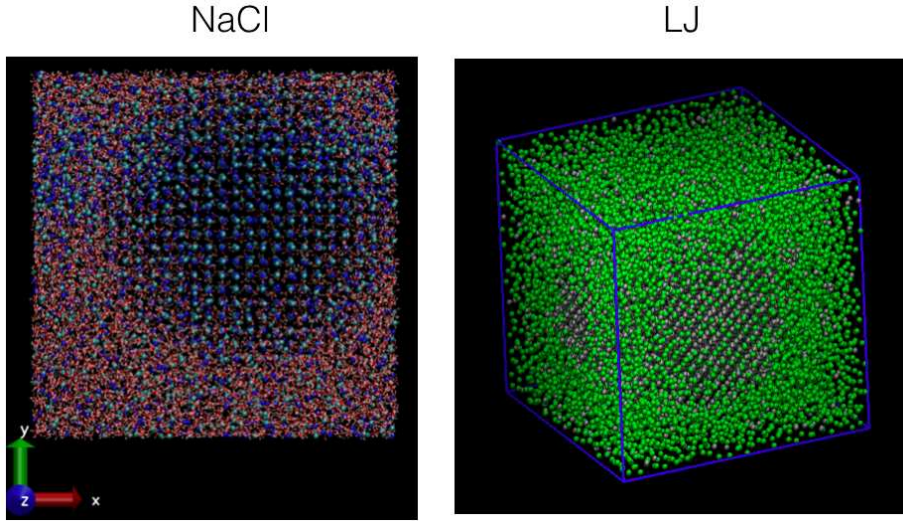


Figure 3: On the left side, a snapshot of the ionic NaCl crystal cluster formed by 7230 ions and surrounded by a solution composed by 9230 water molecules at a concentration of 7.3 m. On the right side, snapshot of the LJ seed cluster formed by 4537 particles and surrounded by a solvent composed by 9668 particles with a concentration of 0.1 mole fraction.

Figure 4 shows the concentration in the solution as a function of time for a simulation using the spherical NaCl crystal. The green line is the concentration obtained using the  $q_4$  local order parameter ( $m_{NaCl,approx}$ ). For the last 200 nanoseconds, in which the equilibrium was reached, the density profile criterion gave a solubility of 5.4 m which is much higher than the 3.7 m obtained by CPR estimations.

## 2.2 Net ionic density charge profiles

In this section, we show the different net ionic charge density profiles that we have obtained for the 4 different crystal orientations studied ( $(100)$ ,  $(1\bar{1}0)$ ,  $(111)$  and  $(22\bar{1})$ ) in this work. All of these systems belong to case E (see Main text Table II), having between 2880 to 3034 ions in the crystal slab depending on the crystal face and 1620 water molecules forming the solution. The initial concentration of the solution for these systems was about 4 mol/kg, but these profiles have been obtained once the simulations reached the equilibrium, typically from 800 ns to 1000 ns. As can be seen in Fig. 5, panels (a), (b), and (c) show electroneutrality both in the crystal and the solution, and charges on the interfaces due to the adsorption and desorption of ions. Panel (d) is a special case: it is the plane  $(111)$  which has negative and positive peaks in the crystal slab due to the fact that planes are composed of just one type of ion. Although it is more difficult to see, in this case there are still charged interfaces.

We have also studied if there was any effect on the charge profile with different system sizes. In Figure 6 we have plotted the net ionic density charge profile for case A (see main text Table II), the smallest system studied which was composed of a crystal slab of 512 ions and a solution of 810 water molecules.

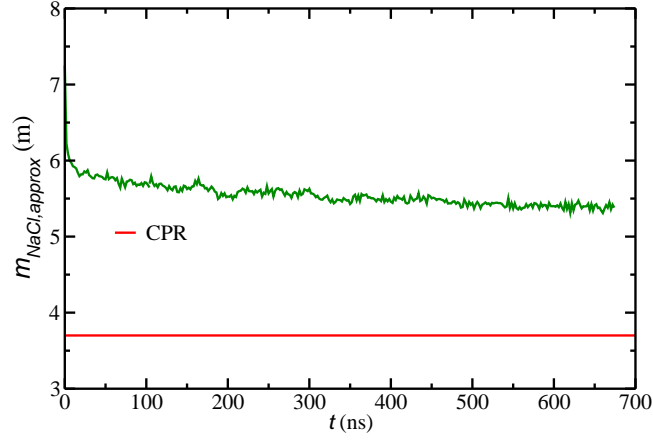


Figure 4: Solution concentration as a function of time for the NaCl cluster (green line). The CPR estimation is indicated in red.

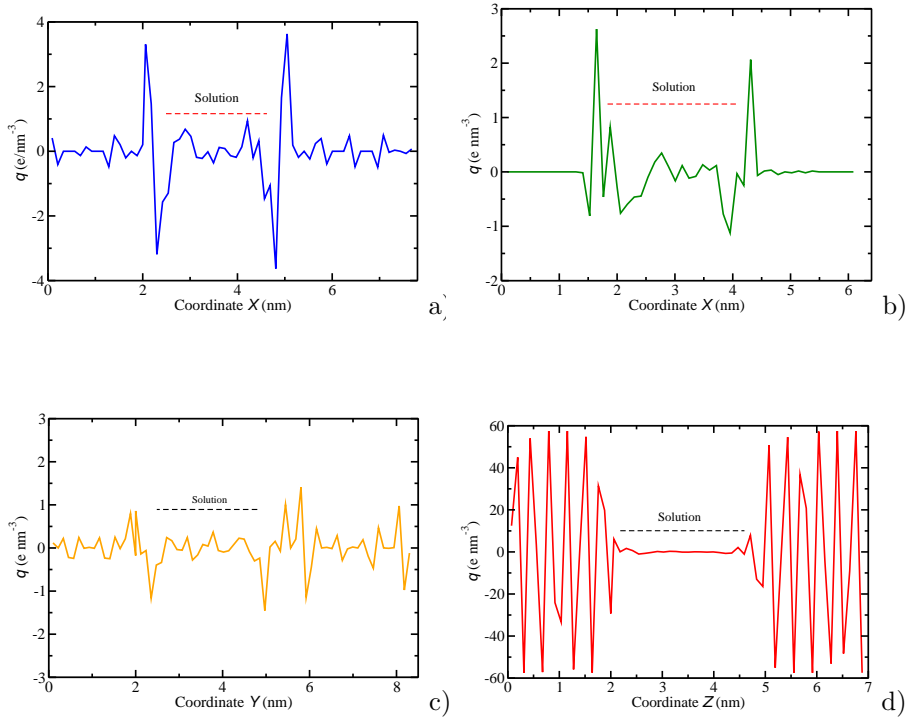


Figure 5: Net ionic charge density profiles for the 4 different crystal orientations studied corresponding to a system size E (see Main text Table II) a) Plane (100). b) Plane (110). c) Plane (221). d) Plane (111).

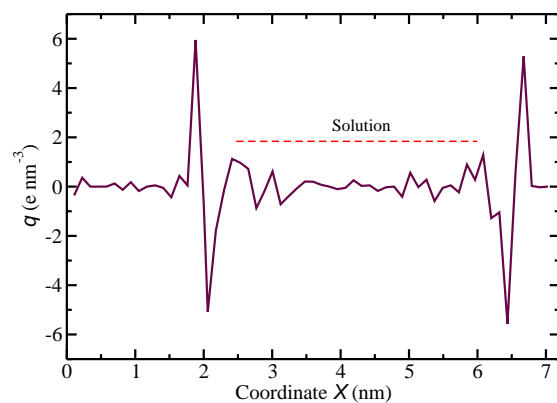


Figure 6: Net ionic density charge profile for a system composed by 810 water molecules and 512 ions in the crystal slab, exposing the plane 100 to the solution.

As it can be seen the profile is very similar to the one shown in Fig. 5 a) except for that it seems that peaks for the net charge density increase when the width of the crystal slab decreases.

## References

- [1] C. Vega, E. Sanz, J. L. F. Abascal, and E. G. Noya *Journal of Physics: Condensed Matter*, vol. 20, 2008.
- [2] J. M. Polson, E. Trizac, S. Pronk, and D. Frenkel *The Journal of Chemical Physics*, vol. 112, no. 12, p. 5339, 2000.
- [3] I. Nezbeda, F. Moučka, and W. R. Smith *Molecular Physics*, vol. 114, pp. 1665–1690, 2016.