Computing the coexistence lines of the sodium chloride–water mixture

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NaCl aqueous solutions are ubiquitous. They can crystallize into ice, NaCl or $NaCl{\cdot}H_2O$. These crystallization transitions have important implications in geology, cryopreservation, or atmospheric science.

Computer simulations can help understand the crystallization of these solids, which requires a detailed knowledge of the equilibrium phase diagram. We use molecular simulations in which we put at contact the solution with the solid of interest to determine points of the solid-solution coexistence lines. We follow two different approaches, one in which we narrow down the melting temperature for a given concentration [1], and another one in which we equilibrate the concentration for a given temperature [2], obtaining consistent results. The phase diagram thus calculated for the selected model (TIP4P/2005 for water molecules and Joung-Cheatham for the ions) correctly predicts coexistence between the solution and ice.

We were only able to determine $NaCl{\cdot}H_2O$-solution coexistence points at higher temperatures and concentrations than in the experiment [3], so we could not establish a direct comparison in this case. On the other hand, the model underestimates the concentration of the solution in equilibrium with the NaCl solid. Our results, alongside other literature evidence, seem to indicate that ion-ion interactions are too strong in the model. Our work is a good starting point for the improvement of the potential model and for the study of the nucleation kinetics of the solid phases involved in the phase diagram [4].

REFERENCES

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