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Communication: Nucleation rates of supersaturated aqueous NaCl using a polarizable force field

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In this work, we use molecular dynamics simulations with a polarizable force field, namely, the modified AH/BK3 model [J. Kolafa, J. Chem. Phys. **145**, 204509 (2016)], in combination with the forward flux sampling technique, to calculate the rates of homogeneous nucleation of NaCl from supersaturated aqueous solutions at 298 K and 1 bar. A non-polarizable model that reproduces the experimental equilibrium solubility {AH/TIP4P-2005 of Benavides *et al.* [J. Chem. Phys. **147**, 104501 (2017)]} is also used for comparison. Nucleation rates calculated from the polarizable force field are found to be in good agreement with experimental measurements, while the non-polarizable model severely underestimates the nucleation rates. These results, in combination with our earlier study of a different non-polarizable force field [H. Jiang *et al.*, J. Chem. Phys. **148**, 044505 (2018)], lead to the conclusion that nucleation rates are sensitive to the details of force fields, and a good representation of nucleation rates may not be feasible using available non-polarizable force fields, even if these reproduce the equilibrium salt solubility. Inclusion of polarization could be important for an accurate prediction of nucleation rates in salt solutions. *Published by AIP Publishing.* https://doi.org/10.1063/1.5053652

The formation of crystals from ionic aqueous solutions has important implications in many fields including but not limited to geochemistry[1] and atmospheric[2] and environmental[3] sciences. Despite its importance, the mechanism of this highly non-equilibrium process remains largely elusive.[4] In addition, rates of nucleation measured from experiments are often subject to large uncertainties.[5] Molecular simulations have been a useful alternative to experiments in elucidating the microscopic nucleation mechanism. Several simulation studies of the mechanism for crystallization of NaCl from aqueous solution have appeared in recent years.[6–11]

Relatively few simulation studies are available for nucleation rates because nucleation is a rare event that is hard to observe using standard molecular dynamics (MD), except at very high supersaturations. In our recent work,[12] we calculated the nucleation rates for the SPC/E water[13] and JC NaCl[14] force field using the forward flux sampling (FFS) technique,[15] a method that enhances the sampling of a rare nucleation event without introducing a biasing potential. The equilibrium salt solubility of the SPC/E+JC force field (m_{eq} = 3.7 mol/kg at 298 K and 1 bar), which defines the supersaturation S of a solution at a given concentration m, $S = m/m_{eq}$, is well established by both the chemical potential[16–20] and direct coexistence calculations.[21] It was found that the SPC/E + JC model combination significantly underestimates the nucleation rates by around 10 orders of magnitude when compared to available experimental measurements.[22,23] Using the seeding simulation technique in combination with classical nucleation theory (CNT), Zimmermann *et al.*[24] also calculated the nucleation rates of ions from the SPC/E + JC force field. However, the solubility (m_{eq}) of the JC NaCl in SPC/E water was overestimated by these authors as 5.1 mol/kg. Very recently, Zimmermann *et al.*[25] observed that such overestimation of equilibrium salt solubility leads to severe overestimation of nucleation rates. With a correct salt solubility (3.7 mol/kg), an underestimation of rates that is consistent with the forward flux sampling (FFS) calculation in Ref. 12 is achieved when using appropriate metrics for nucleus identification. Clearly, nucleation rates calculated from simulations are extremely sensitive to the solubility corresponding to the underlying force field. Given that SPC/E + JC has a lower salt solubility (3.7 mol/kg) compared to experiment (6.1 mol/kg), an interesting question is whether other models that better represent the solubility also lead to more accurate nucleation rates. Alternatively, additional physical effects, such as polarization, could also play an important role with respect to nucleation rates.

In order to address these questions, in this work, we calculate and compare the nucleation rates at ambient conditions for crystallization of NaCl at different solution supersaturations (S), from both polarizable and non-polarizable force fields that have equilibrium salt solubilities close to the experimental values. In particular, for the polarizable force field, we use AH/BK3[26] as recently modified by Kolafa,[27] termed the MAH/BK3 force field. In this model, the intermolecular interactions between ions and water are described using a Buckingham potential for van der Waals (vdW) interactions, Gaussian charges for electrostatic interactions, and Drude oscillators to represent explicitly the polarization. The original AH/BK3 force field represents satisfactorily many thermodynamic and transport properties of aqueous NaCl

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solutions;[28] the modification introduced by Kolafa simply involves a reparameterization of the vdW interactions between cations and anions. The modification improves the model significantly with respect to its prediction of the salt melting point and solubility in water. Our choice of the non-polarizable force field is a recent model for NaCl compatible with the TIP4P-2005 water model, namely, the AH/TIP4P-2005 model.[29] In this model, ions are represented as charged Lennard-Jones particles. Charges on the Na^+ and Cl^- ions are scaled (by a factor of 0.85) in the model in order to "provide a satisfactory description of the effective ionic interactions in aqueous solutions."[29] While the salt crystal properties (e.g., lattice energy) deteriorate because of the use of scaled charges, the calculated salt solubility at ambient conditions is in excellent agreement with experiment (5.7 ± 0.3 mol/kg), making the model one of the most accurate force fields available for this property.

Nucleation rates reported in this work are calculated using the forward flux sampling (FFS) technique in combination with molecular dynamics (MD) simulations. In FFS, nucleation is sampled at a series of non-overlapping milestones defined by an order parameter (λ). Similar to Ref. 12, the order parameter is chosen as the number of ions in the largest crystalline nucleus. We distinguish ions in the solution and crystalline phases through the Steinhardt order parameter q8,[31]

$$q8(i) = \sqrt{\sum_{m=-8}^{8} |q_{8m}(i)|^2} \tag{1}$$

and

$$q_{8m}(i) = \frac{1}{N_b} \sum_{j=0}^{N_B} Y_{8m}\left(\theta(\boldsymbol{r_{ij}}), \phi(\boldsymbol{r_{ij}})\right), \tag{2}$$

where Y_{8m} is the spherical harmonics, and $\theta(\boldsymbol{r_{ij}})$ and $\phi(\boldsymbol{r_{ij}})$ are the polar and azimuthal angles associated with the vector $(\boldsymbol{r_{ij}})$ that connects the central ion (i) and one of its neighbor ions (j). The summation in Eq. (2) is over the 12 nearest neighbors of the ion i ($N_B = 12$). An ion represented by the MAH/BK3 model is considered to be part of the crystalline phase if its q8 parameter is larger than 0.45, while an AH/TIP4P-2005 ion is considered to be crystalline if its q8 parameter is larger than 0.4. In addition, two crystalline ions are considered in the same crystalline nucleus if they are separated within 0.35 nm. A very similar strategy was used by Lanaro and Patey[10] to follow the fate of early stage crystalline nuclei in aqueous NaCl solutions, and it has been shown that such criteria are insensitive to the solution concentration.[10] It is important to emphasize that nucleation rates calculated from the FFS method are not sensitive to the particular choice of an order parameter.[15] Details of the FFS approach used can be found in Ref. 12; we only briefly describe the algorithm here. The first FFS milestone is placed in the solution basin, and we subsequently placed a series of milestones with $\lambda_N > \lambda_{N-1} > \cdots > \lambda_0 = \lambda_{basin}$. The choice of milestones is given in the supplementary material. At each milestone, we collected around 100-150 crossings (except the last two-three milestones) and estimated a transition probability as the ratio between the number of trajectories that reach the next milestone and the total number of MD trajectories initialized. The calculation is iterated until at a given milestone (λ_N) the transition probability reaches (or gets very close to) 1; i.e., a crystalline nucleus that has more than λ_N ions always grows instead of shrinking back to the solution basin. The nucleation rate is calculated as the product of the initial flux (the number of trajectories that cross λ_1 from the solution basin per unit time and volume) and a cumulative transition probability. Evolution of order parameters during the progress of nucleation is jumpy; i.e., the order parameter undergoes large fluctuation and may "jump" directly to a milestone without visiting the previous milestones due to the coalescence of small sub-critical crystalline nuclei. Following the algorithm proposed by Haji-Akbari,[32] we always place a milestone away from the maximum order parameter that can be achieved from trajectories initiated from the previous milestone, and all configurations that have crossed a milestone are collected regardless of their distance to the milestone. The nucleation rates are found to be slightly underestimated (by about 2 orders of magnitude) without considering the "jumpiness" of the order parameter and only collecting configurations exactly at a milestone.

For the MAH/BK3 force field, we calculated its electrolyte and crystal chemical potentials, and obtained the solubility as the salt concentration where the two chemical potentials are the same. It is essential to have an accurate determination of solubility in order to interpret the nucleation rates from simulations, as the difference between the chemical potential at a certain concentration and that at the equilibrium solubility defines the driving force of nucleation. The electrolyte chemical potential is calculated as the change of Gibbs free energy associated with inserting a pair of ions into the solution, and the free energy is obtained via a thermodynamic integration process by slowly turning on the interactions between the inserted ion pair and the solution. The crystal chemical potential was obtained using the Einstein crystal method where the Helmholtz free energy difference between the rock-salt crystal and the ideal Einstein crystal (as the reference of free energy calculation) is calculated from a thermodynamic integration process. Further details on the algorithm of chemical potential calculation can be found in Ref. 28. Details of the MD simulations performed in this work are provided in the supplementary material.

The equilibrium solubility of the MAH/BK3 force field was determined to be 5.0 ± 0.1 mol/kg, as shown in Fig. 1. Direct coexistence simulations from Kolafa[27] obtained the solubility of the MAH/BK3 force field as 3.7 mol/kg, while Monte Carlo simulations in the osmotic ensemble (OEMC) gave a solubility of 4.7 mol/kg,[33] which is more consistent with our calculation. It is a known issue that direct coexistence simulations suffer from system size effects and may not yield sufficiently accurate estimations of salt solubility.[21] The solubility of the AH/TIP4P-2005 model is 5.7 ± 0.3 mol/kg, a value determined from the chemical potentials of ions in Ref. 29.

As shown in Fig. 1, the electrolyte chemical potential first increases and starts to plateau at a concentration around 16.0 mol/kg, where the derivative of the chemical potential with respect to salt concentration is zero. Such behavior indicates that the solution has reached a limit of stability (spinodal) and the phase separation may follow a spinodal decomposition process different from the nucleation/growth scheme. The

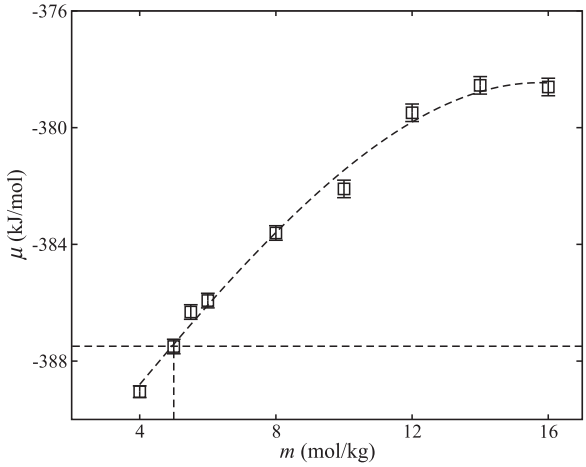

FIG. 1. Chemical potential (μ) of ions in the solution (symbols) and crystal (horizontal line) phases from the MAH/BK3 force field at 298 K and 1 bar. The curved dashed line is a polynomial fit to the simulation data.

mechanism of crystallization at and beyond the spinodal is discussed in a separate manuscript.[30]

With the salt solubility of the MAH/BK3 (and AH/TIP4P-2005) force fields determined from the electrolyte and crystal chemical potentials, nucleation rates at 298 K and 1 bar calculated from the FFS technique in MD simulations can be expressed as a function of solution supersaturation ($S = m/m_{eq}$) and compared to experimental measurements. Figure 2 shows this comparison, including also nucleation rates for the non-polarizable SPC/E + JC model from Ref. 12. As shown in Fig. 2, the nucleation rate from the MAH/BK3 force field at S = 2.46 (salt concentration of 12.3 mol/kg) is in very good agreement with the experimental data.[23] Considering that the MAH/BK3 force field was parameterized only against equilibrium thermodynamic properties (e.g., hydration free energies), the accurate prediction of nucleation rate, a non-equilibrium kinetic property, is remarkable. It is noted that the nucleation rate as a function of supersaturation from the MAH/BK3 and SPC/E + JC force fields has a different slope, especially at

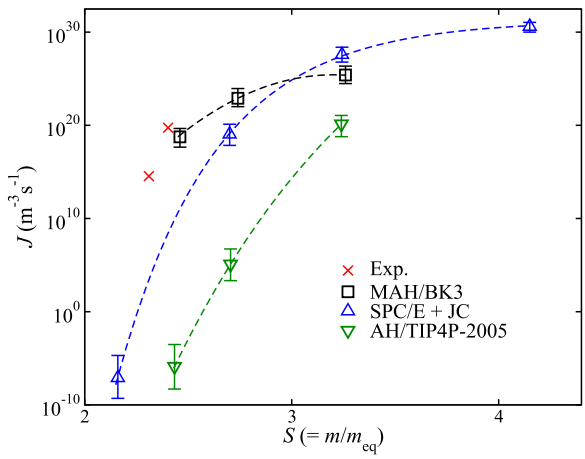

FIG. 2. Nucleation rates (J) of ions at different supersaturation (S) from the polarizable MAH/BK3, AH/TIP4P-2005, and SPC/E + JC models. The experimental data are from Refs. 22 and 23, and the nucleation rates from the SPC/E + JC models are from Ref. 12. The dashed lines are only guide to the eye.

supersaturations around and above 3. For the MAH/BK3 force field, at S above 3 (concentration more than 15.0 mol/kg), the solution is close to the spinodal (see Fig. 1) and the nucleation mechanism may have changed from nucleation/growth to a mechanism that in its initial stage involves spinodal decomposition. For the SPC/E + JC force field, the system reaches the spinodal at higher supersaturation (around 4 or 15.0 mol/kg) possibly due to the lower equilibrium solubility (see the supplementary material for the electrolyte chemical potential of the SPC/E + JC force field). In a separate study,[30] we found that the spinodal corresponds to a liquid/liquid phase separation rather than solution/crystal spinodal decomposition. Beyond the spinodal, the system phase separates into a solution phase and a more dense "liquid salt" phase, and crystallization of ions occurs after the liquid/liquid phase separation. Because of the high computational cost, we are not able to extend the calculation for the MAH/BK3 force field to lower supersaturations. The AH/TIP4P-2005 force field significantly underestimates the nucleation rates by almost 25 orders of magnitude, and its prediction of nucleation rates is not improved relative to the non-polarizable SPC/E + JC force field, despite the fact that the AH/TIP4P-2005 force field has a much better representation of equilibrium salt solubility than the SPC/E + JC force field. It is worth mentioning that due to the more accurate representation of the equilibrium salt solubility (m_{eq}), at the same supersaturation (S), the actual salt concentrations (m) of the MAH/BK3 and AH/TIP4P-2005 solutions are both higher than that of the solution represented by the SPC/E + JC force field. Thus, the better prediction of the nucleation rates from the polarizable force field compared to the non-polarizable SPC/E + JC models is not because the MAH/BK3 solution is at a higher salt concentration than the SPC/E + JC solution at a given supersaturation. In order to understand the different nucleation rates from the three force fields, we show in Fig. 3 the nucleation rate, in terms of $\ln(J)$, as a function of $1/\Delta\mu^2$, following the procedure in Ref. 24. The difference of chemical potentials between the solution and crystal phases was interpolated from the data in Fig. 1 (Fig. S2 in the supplementary material) for the MAH/BK3 (SPC/E + JC) force field and extrapolated from the chemical potential data reported in Fig. 9 of Ref. 29 for the AH/TIP4P-2005 force field. Assuming that CNT is valid, $\ln(J)$ correlates linearly with $1/\Delta\mu^2$, and the slope is $-16\pi\gamma^3/(3\rho^2 k_b T)$ where γ is the interfacial tension and ρ is the crystal density. The intercept is $\ln A$, where A is a kinetic factor. As shown in Fig. 3, $\ln(J)$ is indeed linear with $1/\Delta\mu^2$, suggesting that CNT may be valid for the nucleation of ions in supersaturated solutions. The interfacial tensions of the MAH/BK3, SPC/E + JC, and AH/TIP4P-2005 force fields extracted from the slope of the linear functions are 68 ± 7, 97 ± 5, and 144 ± 4 mN/m, respectively. The experimental estimation of interfacial tension is 87 mN/m,[22] a value not necessarily free of error. The kinetic factors of the MAH/BK3, SPC/E + JC, and AH/TIP4P-2005 force fields extracted from the intercept of the linear functions are $10^{42\pm7}$, $10^{45\pm4}$, and $10^{39\pm3}$ m^{-3} s^{-1}, respectively, consistent with each other within the statistical uncertainty. The kinetic factor is a measure of collision frequency and can be viewed as the upper limit of the nucleation rate. The values obtained in the present work are also consistent with the upper bound of the nucleation

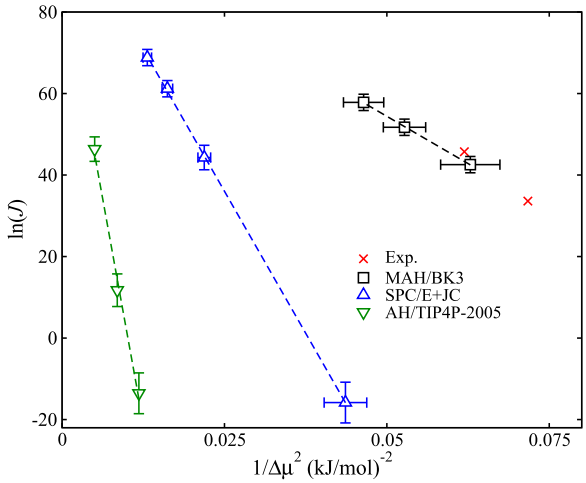

FIG. 3. Nucleation rates ($\ln(J)$) as a function of $1/\Delta\mu^2$ from the polarizable MAH/BK3, AH/TIP4P-2005, and SPC/E + JC models. Dashed lines are linear fitting to simulation data. The uncertainty in $\Delta\mu$ for the AH/TIP4P-2005 force field is not estimated as the chemical potential is extrapolated from the original data in Ref. 29.

rate determined from the lifetime of solvent-separated ions in Ref. 24 (10^{41} m^{-3} s^{-1}). Therefore, the difference in nucleation rates from the three force fields may be attributed to the difference in their representation of solution/crystal interfacial tensions. While the use of scaling charges in the AH/TIP4P-2005 force field leads to a satisfactory calculation for properties of the solution phase, the interfacial tension is significantly overestimated leading to severe underestimation of nucleation rates.

At supersaturation (S) around 2.4, the size of the critical crystalline nucleus, which has a 50% chance of shrinking back to the solution basin, is 146 for the AH/TIP4P-2005 force field, much larger than that of the MAH/BK3 force field, 52. The size of critical nuclei at different supersaturations is also provided in the supplementary material.

The structure of crystalline nuclei can be analyzed from configurations collected at FFS milestones. Our analysis in Ref. 12 shows that, for the non-polarizable SPC/E + JC force field, the nuclei have a rock-salt (FCC) type structure, even for very small nuclei at the early stage of nucleation. The observation also holds here for the polarizable MAH/BK3 and non-polarizable AH/TIP4P-2005 force fields: crystalline nuclei collected at FFS milestones resemble the thermodynamically stable rock salt crystal rather than the less stable wurtzite crystal. A snapshot that shows the structure of a typical crystalline nucleus is provided in the supplementary material for the MAH/BK3 force field, and a AH/TIP4P-2005 crystalline nucleus has a similar structure, thus not shown. It is believed that, at least at relatively low supersaturation, the mechanism of the ion nucleation predicted from the three force fields is consistent with classical nucleation theory, in which the ions form the thermodynamically stable solid in one step. For a solution at sufficiently high concentration that is close to (or passes) the spinodal, the nucleation mechanism may involve liquid/liquid phase separation. The details of the nucleation mechanism at and beyond the spinodal is discussed in a separated study.[30]

In summary, we used forward flux sampling and MD simulations to calculate the nucleation rates of supersaturated NaCl solutions from the polarizable MAH/BK3 and non-polarizable AH/TIP4P-2005 force field. The calculated nucleation rates are found to be sensitive to the details of force fields. With the explicit inclusion of polarization, the MAH/BK3 force field yields nucleation rates that are in close agreement with experimental measurements. The success of the polarizable force field is not simply related to its relatively accurate representation of the equilibrium salt solubility, which is used as the reference to establish solution supersaturation. Despite its almost perfect representation of salt solubility, the AH/TIP4P-2005 force fields show more severe underestimation of nucleation rates than the non-polarizable SPC/E + JC force field, which underestimates the equilibrium salt solubility. The implicit handling of polarization by scaling ion charges, though it certainly improves the performance of a force field for solution phase properties, appears to be inappropriate if the nucleation rate is a property of interest. Since the effect of polarization is important for an electrolyte solution, the explicit handing of polarization (e.g., the use of Drude oscillators) may deserve to be considered during the development of force fields in order to achieve a simultaneous representation of equilibrium thermodynamic properties and nucleation rates.

See the supplementary material for the details of MD simulations, choice of milestones and transition probability of the FFS calculation, a snapshot for a crystalline nucleus from the MAH/BK3 force field, and the electrolyte chemical potential of the SPC/E + JC force fields.

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