

Authors Response to Reviewer's Reports

"Microphysics of liquid water in sub-10 nm ultrafine aerosol particles" by Xiaohan Li and Ian C. Bourg

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Response to reviewer comments from Referee #1, 14 Nov 2022

Summary: This is a valuable and comprehensive study that models the interactions between water and typical CCN species, that include ions and organics, using molecular dynamics simulation. The most serious reservation that I have concerns Sec. 2.3 and misuse of the terms equimolecular dividing surface (at Re) and surface tension (see below). Unfortunately, Re is used in the equations, beginning with Eq. 3, instead of the "surface of tension", which should be used. This is likely to affect the calculations that follow, especially if the interfacial structure is broad. The authors should have look at this and comment. Otherwise the paper seems important and should be published. Major points, minor points, and a few typos are listed below.

Dear Dr. McGraw,

Thanks for your careful reading of our manuscript entitled "Microphysics of liquid water in sub-10 nm ultrafine aerosol particles". We highly appreciate your time and valuable suggestions. Below you will find our replies to your comments.

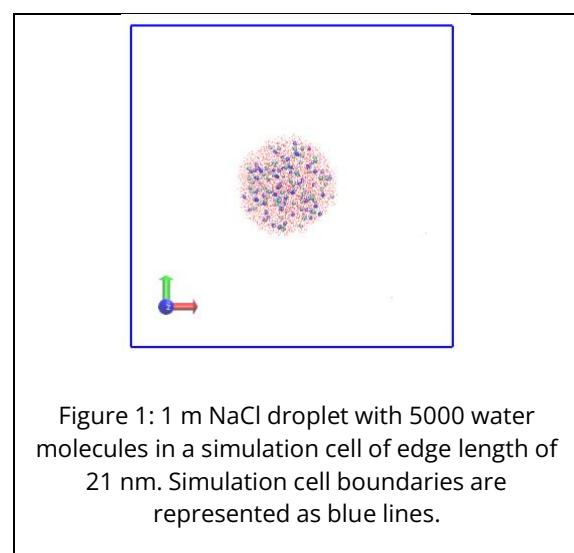
Best wishes,

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Major

Section 2.2 System prep and MD simulations: I have some points of confusion after reading this section. The first concerns the underlying model consisting of cubic cells with periodic boundary conditions and edge length exceeding the droplet diameter – a figure here would help the reader. Second, what is the advantage of periodic boundaries, with so much extra space in each cell? How is the Ewald sum applied in this model? Usually Ewald sums are applied to extended periodic structures - not to a period set of droplets with space around each one. More details here would be helpful.

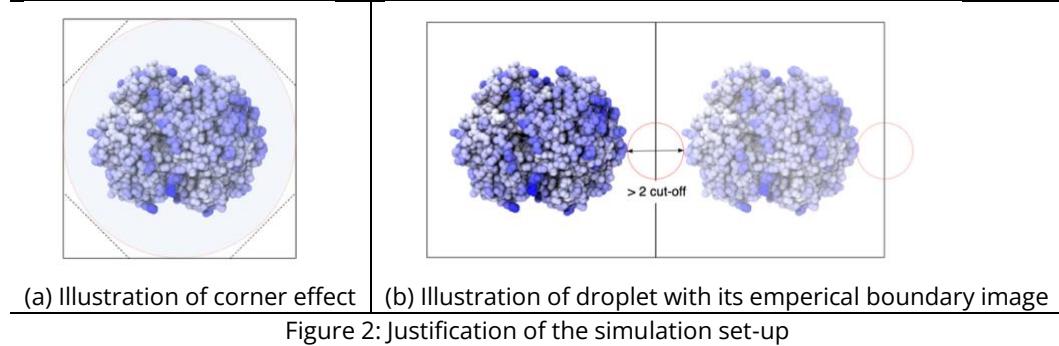
Response to question 1 (Q1): Visualization of simulation box and droplet. Thanks for your great suggestion! With regard to the illustration of our simulation cell structure, Figure 1 shows a representative simulation used in our study (specifically, of a droplet



with diameter $D \cong 6$ nm in a 21 nm simulation box). We will add this illustration to the supplementary information of our newer version manuscript.

Response to Q2: Justification of system set-up. Thanks for raising these questions. The simulation geometries used in our study, including periodic boundary conditions (PBCs), extra space in the simulation cell, and Ewald sum treatment of long-range interactions, are well-established settings and have been widely used in previous MD simulation studies of nano-aerosol droplets^{1,2,3,4,5}. In molecular dynamics (MD) simulations, PBCs are usually employed to preserve the thermodynamic and kinetic properties of simulated systems, such as temperature, pressure, density, and diffusivity^{6,7}. Extensive void space is needed for simulations of droplets for two main reasons: (1) to avoid potential artefacts associated with the “corner effect” in cubic simulation cells with PBCs as illustrated in Figure 2a; and (2) to avoid interactions between the droplet and its periodic images as illustrated in Figure 2b. A rule of thumb in MD simulations is that the distance between macromolecules or isolated droplets and their periodic images should equal at least twice the cut-off distance applied to pairwise interatomic interactions (cut-off = 1.2 nm in this study)⁷. In our simulations, simulated droplets were always located at least 3 nm from the simulation cell boundary (and hence > 6 nm from their periodic images). As already examined in previous studies,^{1,2,3,4,5} this should ensure that the thermodynamic and kinetic properties of the simulated droplet are not affected by their periodic images.

With regard to the particle-mesh Ewald summation used in this study, although it was originally introduced as a means to compute the energy of infinite ionic crystals, the Ewald technique is commonly used for MD simulations of non-crystalline or inhomogeneous systems.⁸ We have added a sentence to the methods section indicating that the Ewald sum treatment of long-range Coulomb interactions used in our study is commonly used in MD simulations, including in simulations of aerosol particles, and that care should be taken that it introduces artefacts that remain incompletely examined, particularly in the dynamics of charged and dipolar species. For more detail, we refer to the work of Hub et al.⁸ and Chapter 12 in Frenkel and Smit⁷.



Having called attention to Ewald sums I might point out a clever test that evaluates the accuracy of intermolecular water potentials. This by comparing the computationally relaxed structures with the 3D structure parameters and densities available for ice structures from x-ray diffraction [Morse and Rice, 1981]. For what its worth, the ST2 water potential performed quite well in the test while another did poorly.

Response to Q3: Choice of interatomic water potentials. Thanks for proposing this lovely idea. We agree that comparing with experimental results is a nice way to examine the accuracy of interatomic potentials. However, we want to point out that there are different interatomic water models for different condition (e.g. different temperature range). The ST2 water model tends to enhance tetrahedral order and has therefore frequently been used to examine water properties in the supercooled region ($T < 273$ K)^{9, 10}. However, it deviates significantly from measured water properties at ambient temperature. For example, ST2 water's density maximum at atmospheric pressure occurs at ~330 K (versus 277 K in actual water).¹¹ In contrast, the SPC/E water model predicts many properties of liquid water relatively accurately at ambient temperature (e.g.

298.15 K in our study) as already examined in previous studies. With respect to bulk properties at 298K, its radial distribution function is quite accurate, its density is within 1% of experiment, its compressibility of $4.1 \times 10^{-10} \text{ Pa}^{-1}$ is close to the experimental value of $4.5 \times 10^{-10} \text{ Pa}^{-1}$, and its dielectric constant of 70 compares well with the experimental value of 78.2.^{12,13,14} A comparison of 14 water models against synchrotron X-ray data on the atomistic-level structure of liquid water showed that the SPC/E model yields one of the most accurate predictions (about four times more accurate than the ST2 water model).¹⁵ The properties of its vapor-liquid transition are also quite good: the model is explicitly parametrized to reproduce the experimental enthalpy of vaporization, and its vapor pressure is within a factor of 2 of the experimental value.¹⁴ With regards to transport properties, its self-diffusion coefficient of about $2.5 \times 10^{-5} \text{ cm}^2/\text{s}$ compares well the experimentally measured value of $2.3 \times 10^{-5} \text{ cm}^2/\text{s}$.¹⁶ These properties lead us to believe that the SPC/E model captures sufficient water-like behavior to be useful in our study.

Section 2.3. The author's description of the Gibb's dividing surface seems to this reviewer a misrepresentation of this important concept. Specifically, the authors use of surface tension at the equimolar (equimolecular might be better in context of MD) is said to "correspond to a vanishing adsorption ... ensuring that the surface free energy per unit area so defined corresponds to the surface tension". Actually the equimolecular surface does neither! It is the dividing surface located at the "surface of tension" that has these properties. As for adsorption, the Gibbs adsorption isotherm applies only at the surface of tension. Moreover, the pressure difference across the surface of tension is the only one that appears in the standard Laplace and Kelvin relations (otherwise additional terms added to these relations are required). See [McGraw and Laaksonen, 1997] and especially the citation to Ono and Kondo, an excellent review of the subject, therein.

Response to Q4: Description of Gibbs dividing surface. Thank you very much for pointing this out. Actually, the description in our manuscript that "*The density profile was used to locate the equimolar (Gibbs) dividing surface, which corresponds to a vanishing adsorption in a one-component system, ensuring that the surface free energy per unit area so defined corresponds to the surface tension*" was quoted from Lau et al.¹⁷ We agree, however, that the equimolar surface and the surface of tension are different, and the sentence "*the surface free energy per unit area so defined corresponds to the surface tension*" is not appropriate. Therefore, we will correct our description of equimolar dividing surface (line 134-135), as suggested, to "*The density profile was used to locate the equimolar dividing surface, which corresponds to a vanishing adsorption in a one-component system.*".

Related: Eq. 7 is similar to the equation developed by Gibbs for the work to form a capillary drop from vapor. This formula can be applied even to droplets having a broadened interfacial region - provided the radius at the surface of tension is used.

Response to Q5: Discussion of using equimolar radius R_e into surface tension calculation. Thanks for pointing this out. We agree that the surface tension should be rigorously calculated at the radius R_s , where the surface tension applies, instead of R_e . We have modified the phrasing in our manuscript to highlight this distinction and to point out that our use of R_e (instead of R_s) is an approximation justified by the following reasoning: (1) For theoretical analysis, the impact of the difference between R_e and R_s on the σ calculation is small in most of our simulated systems. The Tolman length δ can be approximated as a measurement of the difference between $(R_e - R_s)$. Previous studies, including MD simulations, theoretical analysis, and experimental measurement, have reported δ values range from -0.1 to 0.2 nm for liquid water systems (e.g. water droplets, bubbles, water cavitation in minerals and water with hydrophobic solute).^{18,19,20,21,22,23,24,25} Among these studies, Kim and Jhe²⁰ directly calculated $(R_e - R_s)$ from MD simulations of pure water droplet with radii ranging from 0.5 to 1.5 nm. Their results show that for nanodroplets with radii larger than 0.9 nm, $(R_e - R_s)$ is in the range of [-0.05, 0.05] nm. Our results in Section 3.4 similarly show that δ is very small (~ 0.06 nm). The sensitivity of Eq. 7 to the choice of R value should be given by the expression:

$$f_{err} = \frac{d\sigma}{dR} (R_s - R_e) = -\frac{2R^{-3}}{R^{-2}} (R_s - R_e) = -\frac{2}{R} (R_s - R_e)$$

For $(R_s - R_e) < 0.06$ nm, which is the case in our study, the maximum error introduced by the use of R_e in σ calculation is less than 8% for droplets with $N_w > 500$. We have added a sentence to our manuscript noting this potential source of systematic error and, also, noting that it is commensurate with the statistical error of our predicted σ values (as shown by our reported error bars of $\sim\pm 8\%$). (2) In MD simulation practice, as noted in our manuscript, the droplets simulated here do not have a perfectly spherical shape. As a result, it is impossible to accurately determine the surface tension surface R_s in a traditional manner. The surface tension calculation scheme used in our study (Eq. 6- Eq. 8), which uses R_e for approximation, is widely used in previous MD simulation studies for nano-droplet surface tension calculation^{26,27,3,28,29}. Finally, as will be shown in our next paper, the surface tension values calculated in our study are consistent with experimental measurements on the dependence of droplet surface tension dependence on organic concentration.

Finally, a couple of comments on the “validity of the Kelvin and Kohler theory at droplet sizes larger than 4nm under moderate salinities and organic loadings and the need to account for ion-concentration enhancement in sub-10nm particles” mentioned in the Abstract. This is an important theme that runs through and adds value to the paper. With respect to the Kelvin relation this has been confirmed for the Kelvin (pure water) and Kelvin-Thomson (ionic solution) relations [Winkler et al., 2012]. For Kohler theory, on the other hand, this is unlikely to be the case for organics. The latter tend to partition between the bulk and surface phases, whereas the standard Kohler and kappa-Kohler models pertain only to fully water-soluble species. A recent extension of Kohler theory, based on analysis of droplet stability, takes into account the partitioning of both water-soluble and surface-active species in a unified way for applications to cloud activation [McGraw and Wang, 2021].

Response to Q6: Discussion about the concept of organic solubility at nanoscale. Thanks for the nice comments. We agree that the standard Köhler and κ - Köhler theory were developed for water-soluble organics. However, we would point out that “water-soluble species” is a concept that is well-defined for bulk solutions but not for sub-10 nm droplet, because of the surface partitioning of organic molecules. For example, oxalic acid ($C_2H_2O_4$), is often defined as water-soluble species (solubility in water 118g/L at 25 °C). Experimental studies have shown that the surface excess Γ (mol/m²) of oxalic acid can be well-described by Langmuir adsorption isotherm³⁰ by

$$\Gamma = \frac{\Gamma_\infty C}{b + C}$$

where Γ_∞ is the maximum surface excess, 1.54×10^{-6} mol/m²; b is the inverse Langmuir adsorption constant, 1.67 mol/L; and C is the bulk solute concentration (mol/L). For a droplet with diameter $D = 10$ nm and with $C = 1$ mol/L, the organic mass ratio of the interfacial and in the droplet can be estimated as

$$\frac{m_{surface}}{m_{bulk}} = \frac{4\pi\Gamma(D/2)^2}{4\pi/3(D/2)^3C} = 0.35$$

As can be seen from the above derivation, in sub-10 nm nanodroplet, the surface partitioning of “water-soluble organic species” is non-negligible anymore. In our study, we compare our simulation results for PML-water clusters with Köhler theory to examine how water activity deviates from Köhler theory predictions under “water-soluble-organic-species” assumption, because this has not previously been examined (to the best of our knowledge). As noted in our manuscript, at low organic loading and droplet larger than 4 nm, the water activity results calculated from our study match the Köhler theory prediction. This is why we are saying that Köhler theory seems valid at moderate organic surface loadings.

McGraw, R. and A. Laaksonen (1997), J. Chem. Phys. 106, 5284-5287.

Morse, M. D. and S. A. Rice (1981), J. Chem. Phys. 74, 6514-6516.

Winkler, P. M., et. al. (2012), *Phys. Rev. Letts.* **108**, 085701.

McGraw, R. and J. Wang (2021), *J. Chem. Phys.* **154**, 024707; doi: 10.1063/5.0031436

Response to Q7: Comments on the references. We really appreciate your recommendations of these references. In particular, we think the papers by McGraw, R. and A. Laaksonen (1997) and McGraw, R. and J. Wang (2021) are highly relevant and helpful to our studies. We will cite these papers in our discussion and conclusion.

Minor points and typos:

Eq. 9 (previously just below Eq. 5) rho_0 was used, which I assume is the density at the center of the drop. Why the switch to rho_w, which I assume is the bulk density of water? I don't see these symbols defined.

The switch from molecular units, kT, to molar units, RT, in equation 9 and back to kT in Eq. 10 can be avoided using consistent units.

Line 777. The correct authorciting should be to Lewis and Schwartz, 2004. Same in line 102: change Lewis et. al. to Lewis and Schwartz, 2004.

Response to Q8: Comments of minor points. Thank you so much for these corrections. We will update our newest manuscript accordingly.

Reference

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Response to reviewer comments from Referee #2, 1 Dec 2022

The authors present a theoretical study of nanoparticle morphology and gas/droplet partitioning behavior of water using systems consisting of sodium chloride, water, and pimelic acid. The authors discover several parameters - sphericity and fractional surface coverage - that aptly describe chemical morphology as a function of composition and size regimes and variation in mass accommodation coefficients. The authors also report a threshold for the validity of continuum theories. The paper is well-written and is of interest to the Atmospheric Chemistry and Physics community, and is recommended for publication after the following general comments have been addressed.

Dear Reviewer,

Thanks for your careful reading of our manuscript entitled "**Microphysics of liquid water in sub-10 nm ultrafine aerosol particles**". We highly appreciate your time and valuable suggestions. Below you will find our replies to your comments.

Best wishes,

Xiaohan Li & Ian C. Bourg
Department of Civil and Environmental Engineering, Princeton University

As the authors note in Section 3.4, classical water models are known to have biases in errors in reproducing experimental surface tensions - though with SPC/E having one of the smallest errors (Vega and de Miguel, 2007). Additionally, a study (Lbadaoui-Darvas and Takahama, 2019) suggest that carboxylic acid-water dynamics are not well captured in equilibrium MD simulations and lead to deviations in predictions of water activity even above 0.95. On the other hand, the water activity calculations seem to suggest that the simulation results are in good agreement - with observations - is this due to canceling of errors (e.g., with molar volume) or the relatively small magnitude of the error in surface tension by these models?

Response to question 1 (Q1): Discussion about the water activity results. Thanks for raising this question. First of all, we would like to point out that the calculations of water activity (a_w) in dicarboxylic acid-water systems carried out by Lbadaoui-Darvas and Takahama¹ differ from those reported in our manuscript in several important ways: (1) we use different interatomic models to simulate carboxylic-acid-water systems; more precisely, we use the OPLS-AA model for dicarboxylic acid and the SPC/E model for water, whereas they used the OPLS-UA model for dicarboxylic acid and the TIP4P model for water; (2) our systems include a water-air interface, where dicarboxylic acid molecules preferentially accumulate relative to bulk liquid water, whereas they simulate organics in bulk liquid water; and (3) we calculated water activity using two different methods (umbrella sampling and the vapor-liquid coexistence method), whereas they calculated water activity using a third method (from the derivative of chemical potential vs. solute mole fraction, where the chemical potential was inferred from structural results). Therefore, differences between our water activity predictions are not unexpected.

More importantly, the calculations reported by Lbadaoui-Darvas and Takahama exclusively evaluate the Raoult effect in bulk aqueous solutions (i.e., the decrease in water activity associated with the organic solute). They find

that this effect is underestimated by their MD simulations, with a resulting error in predicted water activity of up to about 5%. Our simulations, however, quantify the overall impact of both the Raoult and Kelvin effects in nano-scale droplets. Unfortunately, we cannot precisely quantify the Raoult effect, for two reasons: (1) the Kelvin effect is much larger than the Raoult effect in our simulated systems (the expected Kelvin enhancement is up to ~250%; the expected Raoult inhibition is only up to ~10%), and (2) the bulk aqueous concentration of dicarboxylic acid in our systems is not well defined, because we study nanoscale droplets with significant organic accumulation at the interface, not bulk aqueous solutions.

We agree that SPC/E water model used in our study should underestimate the Kelvin effect, because it somewhat underestimates water surface tension (although less than most other water models, as noted by the reviewer). In our comparison with the Kelvin equation and Köhler theory, we account for this discrepancy by using the surface tension of SPC/E water, instead of that of real water, to obtain Kelvin/Köhler theory predictions of water activity.

Many of the conclusions summarize the effect of "organic loadings" but the simulations use a specific type of organic, namely pimelic acid. Many studies on the other hand suggest the importance of alcohols in marine aerosols (e.g., Russell et al., 2010). Is there reason that the authors can justify broadening the conclusion from a particular "organic acid" to "organics" generally? Other abundant dicarboxylic acids (e.g., oxalic acid) may also exhibit different bulk/surface partitioning behavior than demarcated by the sphericity factor. The main question is whether parts of the manuscript should be more clear in what is meant by "organic loading" in this work.

Response to question 2 (Q2): The choice of organic species and clarification of organic loading. Thank you for raising this important point. We justify our usage of pimelic acid (PML) as a representative of general aerosol organic compounds due to the following reasons: (1) organic species with 6 or 7 carbon and 3 or 4 oxygen atoms are important in organic aerosols: for example, online and offline spectrometer measurements of PM_{2.5} in Beijing by Zheng et al. (2021)² revealed that the carbon number of organic species in organic aerosols was distributed from 2 to 20, with the highest abundance observed for C6-C7 species, and that organics most commonly contained 3 or 4 oxygen atoms. This finding is also validated by measurements above temperate and boreal forests, where the molecular weight of organic species was predominantly in the range of 150-200 g mol⁻¹ (for reference, the molecular weight of PML is 160 g mol⁻¹).³ Furthermore, C3-C11 dicarboxylic acid (DA) species have been shown to be important contributors to total organic aerosol mass and can contribute ~50% of the total DA mass both in urban and rural areas.^{4,5} (2) As noted in our manuscript, the O/C ratio of PML (0.57) lies near the midpoint of the range commonly observed for aerosol organic materials (0.2 to 1.0) and near the value below which liquid-liquid phase separation is commonly observed in aerosol particles (~ 0.7 to 0.8 for organic-salt-water aerosols, ~ 0.6 for organic-water aerosols). Therefore, we believe PML has the potential to mimic the properties of key organic substances in nano-aerosol droplets. However, we agree that a variety of other organic species, including alcohols, other dicarboxylic acids, etc, are also present in aerosols, and that their behavior and impact on aerosol properties may differ from those evidenced for pimelic acid in our simulations (although some generality of our results is suggested, for example, by the consistency of our predicted water accommodation coefficients with values observed in other studies with different organic species, see Figure 6 in our manuscript). To clarify this, we plan to add the following paragraph to our conclusion section:

"Finally, we reiterate that our simulations use a highly simplified proxy for aerosol organic matter as a single compound (PML). This compound was selected for its similarity to the compounds most abundantly observed in organic aerosols in terms of molecular weight (Thornton et al., 2020), number of C atoms (Zheng et al., 2021), O:C ratio (Song et al., 2018, Zheng et al., 2021), and functional groups (Zhao et al., 2018, Wang et al., 2022). Although the use of such an idealized proxy facilitates our effort to evaluate the sensitivity of aerosol properties to organic loading, future studies should examine whether our predictions can be generalized to other organic compounds (or mixtures of organic compounds) abundantly found in organic aerosols, such as alcohols or other dicarboxylic acids."

References:

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Response to community comment #1, 03 Oct 2022

Summary

This is a comprehensive study of the thermodynamics of nanoscale aerosol particles presenting some unintuitive but well explained results. There are some shortcomings in the work that need to be addressed before it is ready for publication.

Dear Professor Wexler,

Thanks for your careful reading of our manuscript entitled "***Microphysics of liquid water in sub-10 nm ultrafine aerosol particles***". We highly appreciate your time and valuable suggestions. Below you will find our replies to your comments.

Best wishes,

Xiaohan Li & Ian C. Bourg
Department of Civil and Environmental Engineering, Princeton University

Major comments

L13: Relevance to sea spray particles is questionable since (a) particles this small are likely composed primarily of sea surface organics and (b) the physical processes that generated sea spray are not able to generate particles in the ~10nm size range.

Response: Thanks for raising these questions. We agree that sea salt particles are likely to contain organic compounds. However, salt dissolved in seawater, also is a non-negligible component in these particles. Our simulations examine the impact of dissolved salts and organics separately, which cannot reveal salt-organic interactions but facilitates the examination of the impact of each compound. With regard to particle size, previous studies have shown that atmospherically relevant sea salt particles have sizes as small as 10 nm^{1,2,3}, and recent climate models have employed a mode in the range of 1-10 nm diameter to better characterize the impact of ultrafine sea salt aerosol on cloud formation and climates⁴.

L125: what are the implications of a 1.2 nm cut-off for Coulombic and VDW interactions? 1.2 nm is much larger than these molecules and ions and monopole-dipole interactions could be significant. What is the justification for this cut-off.

Response: Thanks for proposing this great question. Here is our response to your questions:

1. **Justification of the cut-off scheme in MD simulations:** The most computationally expensive part of an MD simulation is generally the calculation of nonbonded forces, including both electrostatic and van der Waals interactions, which act between all pairs of atoms. A general approach to reduce the cost of this computation is to treat electrostatic and van der Waals (VDW) interactions using a well-established cut-off scheme, whereby (1) atom-atom pairwise interactions are explicitly computed within the cut-off distance (i.e., 1.2 nm in our simulation); (2) atom-atom pairwise interactions beyond the cut-off distance is calculated using a reaction-field method combined with shifting or switching functions. Specifically, for electrostatic interactions, we use the particle mesh Ewald sum treatment⁵ to divide the

interactions into a short-range contribution (distance less than 1.2 nm), and a long-range contribution (distance beyond 1.2 nm). The short-range contribution is calculated in real space, whereas the long-range contribution is calculated using a Fourier transform. While such Ewald methods involve a cutoff distance, the choice of cutoff acts to shift the computational burden between the short-range (real space) and long-range (reciprocal space) calculations, without limiting the accuracy of the calculated forces. For VDW interactions, we accurately characterized the VDW interactions within the 1.2 nm cut-off distance and applied a tail-correction to account for the missing dispersion interactions due to VDW cut-off⁶. In conclusion, all VDW and electrostatic interactions (even beyond the short range cutoff) are accounted for in our simulations.

2. **Justification of the cut-off choice 1.2 nm:** A rule of thumb in determining the cut-off distance in MD simulations is that the cutoff should be larger than 2.5σ (σ is the distance corresponding to the minimum of the VDW pairwise interaction: 0.3166 nm for interactions between two O atoms in H₂O, 0.35 nm for C atoms in organic molecules) to accurately characterize the pairwise VDW interactions, but less than half of the simulation cell length to reduce the computation burden and maintain the accuracy of the Ewald summation⁷. There have been extensive studies discussing the choice of cut-off for the interatomic interaction potential models of water, salts, and organic compounds^{8,9,10,11,12}. These studies have shown that at ambient temperature, MD simulations using a real space cutoff of 1.2 nm with a particle mesh Ewald sum treatment of long-range Coulomb interactions, can accurately characterize the dynamics, structures, and energetic properties of systems related to those examined in our study compared with experiments.

Equation 1: How is the interfacial width parameter determined? How sensitive are the results to changes in its value? What value was used?

Response: Thanks for this great question! The first hydration shell radii (r_{hyd}) of alkali cations Li⁺, Na⁺, and K⁺ are 0.279, 0.318, and 0.359 nm, respectively, as reported by Joung and Cheatham¹³. The interfacial width parameter (exclusion width d_{exc}) was determined following two steps: (1) from the ion density profile relative to the Gibbs dividing interface (Appendix Figure A2e), we can see that the distance where Na⁺ density reaches the well-mixed density 1m, ranges from 0.3 to 0.5 nm for all simulated droplets, which provides estimates of the upper and lower bounds of d_{exc} ; (2) we tested different values of the ion exclusion width and calculated the corresponding ion concentration enhancement factor and, then, compared the calculated results with our MD simulation results. Our results show that setting d_{exc} to $1.2r_{hyd}$, yielded the best match to our MD simulation results. The sensitivity of ϵ values of NaCl droplets to d_{exc} are illustrated in Figure 1 on the right. We will add this analysis to the Appendix section in the next version of our manuscript.

L450-480: This is the opposite trend to what I expected. Since NaCl is concentrated in the core of the particle due to exclusion from the surface, that should lower the water activity in the particle relative to that in the bulk at the same NaCl concentration. The opposite trend is observed. More discussion about this discrepancy is needed.

Response: Thanks for pointing this out. As noted in our Manuscript L455, water activity can be expressed as

$$a_w = x_w \exp \frac{2\sigma V_m}{RT r}$$

According to this equation, water activity a_w is influenced by two properties: (1) salt concentration, through the term x_w (water mole fraction), and (2) droplet curvature ($1/r$) through the term $\exp \frac{2\sigma V_m}{RT r}$, which originates from the Kelvin effect. For the salty droplets studied here, the size dependence of a_w is dominated by the Kelvin

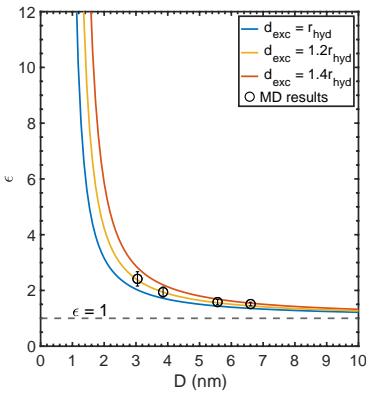


Figure 3: Predicted ϵ of NaCl droplets as a function droplet diameter D with different d_{exc}

effect term: as droplet size r decreases, $1/r$ increases, $\exp \frac{2\sigma V_m}{RT r}$ increases, and a_w increases. The ion concentration enhancement in smaller droplets, acts in the opposite direction, but its impact is comparatively smaller. As noted in our manuscript, under the ideal solution assumption that underlies Köhler theory, 2 m NaCl droplet should have $x_w = 0.93$, whereas our result shows that nano-droplets considered in this study have an effective water mole fraction of $x_w = 0.86 \pm 0.02$, which indicates that the impact of NaCl on the activity of water is rough twice as large as predicted by Raoult's law. This discrepancy between our results compared with theoretical Köhler theory predictions comes from the ion concentration enhancement in the core of small droplets.

Minor comments

Equation 2: What are N_w and N_{org} ?

Equation 6: what are P_k and P_U ?

L174: vapor pressure of the bulk water?

L269: different numbers of water molecules

L299: diminished

L333: dividing

Response: Thanks for your suggestions! We have updated the text accordingly in our newest manuscript.

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