Response to community comments (CC2) by Robert McGraw

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,

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

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.

Figure 1: 1 m NaCl droplet with 5000 water molecules in a simulation cell of edge length of 21 nm. Simulation cell boundaries are represented as blue lines.

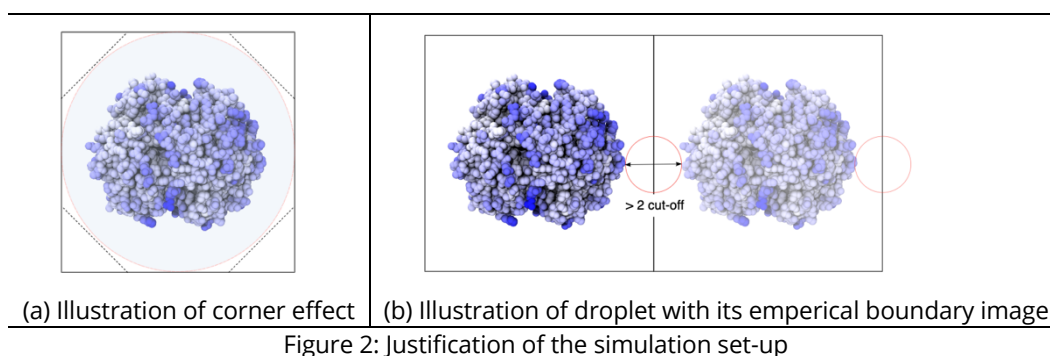**Response to question 1 (Q1): Visualization of simulation box and droplet.** Thanks for your great suggestion! With regard to the illustration of our simulation cell structure, Figure 1 shows a representative simulation used in our study (specifically, of a droplet with diameter $D \cong 6$ nm in a 21 nm simulation box). We will add this illustration to the supplementary information of our newer version manuscript.
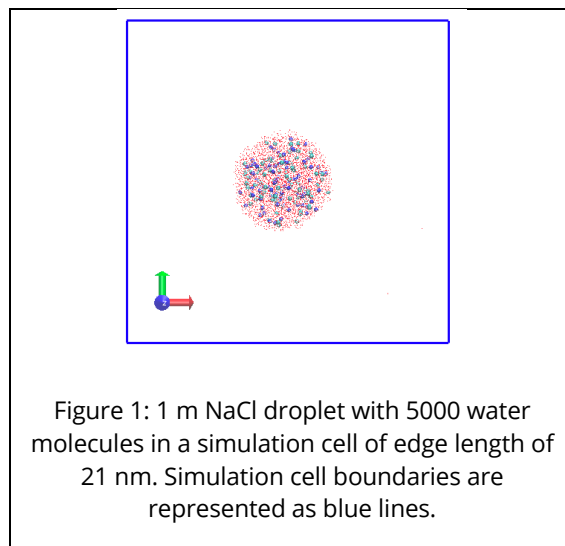
Response to Q2: Justification of system set-up. Thanks for raising these questions. The simulation geometries used in our study, including periodic boundary conditions (PBCs), extra space in the simulation cell, and Ewald sum treatment of long-range interactions, are well-established settings and have 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 Smit[7].

| (a) Illustration of corner effect | (b) Illustration of droplet with its emperical boundary image |

Figure 2: Justification of the simulation set-up

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 4.1×10^{-10} Pa^{-1} is close to the experimental value of 4.5×10^{-10} 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 2.5×10^{-5} cm^2/s compares well the experimentally measured value of 2.3×10^{-5} cm^2/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 (line134-135), 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 Re into surface tension calculation. Thanks for pointing this out. We agree that the surface tension should be rigorously calculated at the radius Rs, where the surface tension applies, instead of Re. We have modified the phrasing in our manuscript to highlight this distinction and to point out that our use of Re (instead of Rs) is an approximation justified by the following reasoning: (1) For theoretical analysis, the impact of the difference between Re and Rs 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 (Re-Rs). 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 Jhe[20] directly calculated (Re-Rs) 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, (Re-Rs) 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:

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

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 ~$\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 Rs in a traditional manner. The surface tension calculation scheme used in our study (Eq. 6- Eq. 8), which uses Re 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/m^2) of oxalic acid can be well-described by Langmuir adsorption isotherm[30] by

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

where Γ_∞ is the maximum surface excess, 1.54×10^{-6} mol/m^2; 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

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

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.

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

Reference

(1) Chowdhary, J.; Ladanyi, B. M. Molecular Dynamics Simulation of Aerosol-OT Reverse Micelles. *J. Phys. Chem. B* **2009**, *113* (45), 15029–15039.
(2) Karadima, K. S.; Mavrantzas, V. G.; Pandis, S. N. Insights into the Morphology of Multicomponent Organic and Inorganic Aerosols from Molecular Dynamics Simulations. *Atmospheric Chem. Phys.* **2019**, *19* (8), 5571–5587.
(3) Sun, L.; Hede, T.; Tu, Y.; Leck, C.; Ågren, H. Combined Effect of Glycine and Sea Salt on Aerosol Cloud Droplet Activation Predicted by Molecular Dynamics Simulations. *J. Phys. Chem. A* **2013**, *117* (41), 10746–10752.
(4) Julin, J.; Shiraiwa, M.; Miles, R. E.; Reid, J. P.; Pöschl, U.; Riipinen, I. Mass Accommodation of Water: Bridging the Gap between Molecular Dynamics Simulations and Kinetic Condensation Models. *J. Phys. Chem. A* **2013**, *117* (2), 410–420.
(5) Bahadur, R.; Russell, L. M. Effect of Surface Tension from MD Simulations on Size-Dependent Deliquescence of NaCl Nanoparticles. *Aerosol Sci. Technol.* **2008**, *42* (5), 369–376.
(6) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High Performance Molecular Simulations through Multi-Level Parallelism from Laptops to Supercomputers. *SoftwareX* **2015**, *1*, 19–25.
(7) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Elsevier, 2001.
(8) *Quantifying Artifacts in Ewald Simulations of Inhomogeneous Systems with a Net Charge | Journal of Chemical Theory and Computation*. https://pubs.acs.org/doi/full/10.1021/ct400626b (accessed 2022-11-14).
(9) *Low-temperature fluid-phase behavior of ST2 water: The Journal of Chemical Physics: Vol 131, No 10*. https://aip.scitation.org/doi/10.1063/1.3229892 (accessed 2022-11-14).
(10) *Two-state thermodynamics of the ST2 model for supercooled water: The Journal of Chemical Physics: Vol 140, No 10*. https://aip.scitation.org/doi/10.1063/1.4867287 (accessed 2022-11-14).
(11) Harrington, S.; Poole, P. H.; Sciortino, F.; Stanley, H. E. Equation of State of Supercooled Water Simulated Using the Extended Simple Point Charge Intermolecular Potential. *J. Chem. Phys.* **1997**, *107* (18), 7443–7450. https://doi.org/10.1063/1.474982.
(12) Vega, C.; McBride, C.; Sanz, E.; Abascal, J. L. F. Radial Distribution Functions and Densities for the SPC/E, TIP4P and TIP5P Models for Liquid Water and Ices Ih, Ic, II, III, IV, V, VI, VII, VIII, IX, XI and XII. *Phys. Chem. Chem. Phys.* **2005**, *7* (7), 1450–1456. https://doi.org/10.1039/B418934E.
(13) Mark, P.; Nilsson, L. Structure and Dynamics of the TIP3P, SPC, and SPC/E Water Models at 298 K. *J. Phys. Chem. A* **2001**, *105* (43), 9954–9960. https://doi.org/10.1021/jp003020w.
(14) Varilly, P.; Chandler, D. Water Evaporation: A Transition Path Sampling Study. *J. Phys. Chem. B* **2013**, *117* (5), 1419–1428.

(15) *Water structure as a function of temperature from X-ray scattering experiments and ab initio molecular dynamics - Physical Chemistry Chemical Physics (RSC Publishing)*. https://pubs.rsc.org/en/content/articlelanding/2003/cp/b301481a (accessed 2022-11-17).

(16) Tsimpanogiannis, I. N.; Moultos, O. A.; Franco, L. F. M.; Spera, M. B. de M.; Erdős, M.; Economou, I. G. Self-Diffusion Coefficient of Bulk and Confined Water: A Critical Review of Classical Molecular Simulation Studies. *Mol. Simul.* **2019**, *45* (4–5), 425–453. https://doi.org/10.1080/08927022.2018.1511903.

(17) Lau, G. V.; Ford, I. J.; Hunt, P. A.; Müller, E. A.; Jackson, G. Surface Thermodynamics of Planar, Cylindrical, and Spherical Vapour-Liquid Interfaces of Water. *J. Chem. Phys.* **2015**, *142* (11), 114701.

(18) Min, S. H.; Berkowitz, M. L. Bubbles in Water under Stretch-Induced Cavitation. *J. Chem. Phys.* **2019**, *150* (5), 054501. https://doi.org/10.1063/1.5079735.

(19) Wilhelmsen, Ø.; Bedeaux, D.; Reguera, D. Communication: Tolman Length and Rigidity Constants of Water and Their Role in Nucleation. *J. Chem. Phys.* **2015**, *142* (17), 171103.

(20) Kim, Qh.; Jhe, W. Interfacial Thermodynamics of Spherical Nanodroplets: Molecular Understanding of Surface Tension via a Hydrogen Bond Network. *Nanoscale* **2020**, *12* (36), 18701–18709. https://doi.org/10.1039/D0NR04533K.

(21) Burian, S.; Isaiev, M.; Termentzidis, K.; Sysoev, V.; Bulavin, L. Size Dependence of the Surface Tension of a Free Surface of an Isotropic Fluid. *Phys. Rev. E* **2017**, *95* (6), 062801. https://doi.org/10.1103/PhysRevE.95.062801.

(22) Menzl, G.; Gonzalez, M. A.; Geiger, P.; Caupin, F.; Abascal, J. L. F.; Valeriani, C.; Dellago, C. Molecular Mechanism for Cavitation in Water under Tension. *Proc. Natl. Acad. Sci.* **2016**, *113* (48), 13582–13587. https://doi.org/10.1073/pnas.1608421113.

(23) Azouzi, M. E. M.; Ramboz, C.; Lenain, J.-F.; Caupin, F. A Coherent Picture of Water at Extreme Negative Pressure. *Nat. Phys.* **2013**, *9* (1), 38–41. https://doi.org/10.1038/nphys2475.

(24) Joswiak, M. N.; Duff, N.; Doherty, M. F.; Peters, B. Size-Dependent Surface Free Energy and Tolman-Corrected Droplet Nucleation of TIP4P/2005 Water. *J. Phys. Chem. Lett.* **2013**, *4* (24), 4267–4272. https://doi.org/10.1021/jz402226p.

(25) *The spontaneous curvature of the water-hydrophobe interface: The Journal of Chemical Physics: Vol 137, No 13*. https://aip.scitation.org/doi/full/10.1063/1.4755753 (accessed 2022-08-26).

(26) Li, X.; Hede, T.; Tu, Y.; Leck, C.; Ågren, H. Surface-Active Cis-Pinonic Acid in Atmospheric Droplets: A Molecular Dynamics Study. *J. Phys. Chem. Lett.* **2010**, *1* (4), 769–773.

(27) Zhao, Z.; Kong, K.; Wang, S.; Zhou, Y.; Cheng, D.; Wang, W.; Zeng, X. C.; Li, H. Understanding Hygroscopic Nucleation of Sulfate Aerosols: Combination of Molecular Dynamics Simulation with Classical Nucleation Theory. *J. Phys. Chem. Lett.* **2019**, *10* (5), 1126–1132.

(28) Li, X.; Hede, T.; Tu, Y.; Leck, C.; Ågren, H. Cloud Droplet Activation Mechanisms of Amino Acid Aerosol Particles: Insight from Molecular Dynamics Simulations. *Tellus B Chem. Phys. Meteorol.* **2013**, *65* (1), 20476.

(29) Zakharov, V. V.; Brodskaya, E. N.; Laaksonen, A. Surface Tension of Water Droplets: A Molecular Dynamics Study of Model and Size Dependencies. *J. Chem. Phys.* **1997**, *107* (24), 10675–10683.

(30) Aumann, E.; Hildemann, L.; Tabazadeh, A. Measuring and Modeling the Composition and Temperature-Dependence of Surface Tension for Organic Solutions. *Atmos. Environ.* **2010**, *44* (3), 329–337.