

Response to community comments (CC1) by Anthony Wexler

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

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.

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

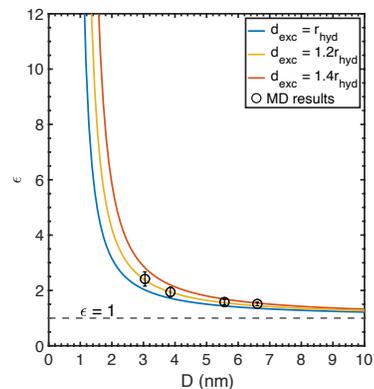


Figure 1: Predicted ϵ of NaCl droplets as a function droplet diameter D with different d_{exc}

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 that 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 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.

References

- (1) Clarke, A. D.; Owens, S. R.; Zhou, J. An Ultrafine Sea-Salt Flux from Breaking Waves: Implications for Cloud Condensation Nuclei in the Remote Marine Atmosphere. *J. Geophys. Res. Atmospheres* **2006**, *111* (D6). <https://doi.org/10.1029/2005JD006565>.
- (2) Ahlm, L.; Jones, A.; Stjern, C. W.; Muri, H.; Kravitz, B.; Kristjánsson, J. E. Marine Cloud Brightening – as Effective without Clouds. *Atmospheric Chem. Phys.* **2017**, *17* (21), 13071–13087. <https://doi.org/10.5194/acp-17-13071-2017>.
- (3) Clarke, A.; Kapustin, V.; Howell, S.; Moore, K.; Lienert, B.; Masonis, S.; Anderson, T.; Covert, D. Sea-Salt Size Distributions from Breaking Waves: Implications for Marine Aerosol Production and Optical Extinction Measurements during SEAS. *J. Atmospheric Ocean. Technol.* **2003**, *20* (10), 1362–1374. [https://doi.org/10.1175/1520-0426\(2003\)020<1362:SSDFBW>2.0.CO;2](https://doi.org/10.1175/1520-0426(2003)020<1362:SSDFBW>2.0.CO;2).
- (4) Pianezze, J.; Barthe, C.; Bielli, S.; Tulet, P.; Jullien, S.; Cambon, G.; Bousquet, O.; Claeys, M.; Cordier, E. A New Coupled Ocean-Waves-Atmosphere Model Designed for Tropical Storm Studies: Example of Tropical Cyclone Bejisa (2013–2014) in the South-West Indian Ocean. *J. Adv. Model. Earth Syst.* **2018**, *10* (3), 801–825. <https://doi.org/10.1002/2017MS001177>.
- (5) Darden, T.; York, D.; Pedersen, L. Particle Mesh Ewald: An N·log(N) Method for Ewald Sums in Large Systems. *J. Chem. Phys.* **1993**, *98* (12), 10089–10092. <https://doi.org/10.1063/1.464397>.
- (6) Shirts, M. R.; Mobley, D. L.; Chodera, J. D.; Pande, V. S. Accurate and Efficient Corrections for Missing Dispersion Interactions in Molecular Simulations. *J. Phys. Chem. B* **2007**, *111* (45), 13052–13063. <https://doi.org/10.1021/jp0735987>.
- (7) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*; Elsevier, 2001.
- (8) 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>.
- (9) Piana, S.; Lindorff-Larsen, K.; Dirks, R. M.; Salmon, J. K.; Dror, R. O.; Shaw, D. E. Evaluating the Effects of Cutoffs and Treatment of Long-Range Electrostatics in Protein Folding Simulations. *PLOS ONE* **2012**, *7* (6), e39918. <https://doi.org/10.1371/journal.pone.0039918>.
- (10) Huang, C.; Li, C.; Choi, P. Y. K.; Nandakumar, K.; Kostiuik, L. W. Effect of Cut-off Distance Used in Molecular Dynamics Simulations on Fluid Properties. *Mol. Simul.* **2010**, *36* (11), 856–864. <https://doi.org/10.1080/08927022.2010.489556>.
- (11) Sonibare, K.; Rathnayaka, L.; Zhang, L. Comparison of CHARMM and OPLS-Aa Forcefield Predictions for Components in One Model Asphalt Mixture. *Constr. Build. Mater.* **2020**, *236*, 117577. <https://doi.org/10.1016/j.conbuildmat.2019.117577>.
- (12) Joung, I. S.; Cheatham, T. E. Determination of Alkali and Halide Monovalent Ion Parameters for Use in Explicitly Solvated Biomolecular Simulations. *J. Phys. Chem. B* **2008**, *112* (30), 9020–9041. <https://doi.org/10.1021/jp8001614>.
- (13) Joung, I. S.; Cheatham, T. E. Molecular Dynamics Simulations of the Dynamic and Energetic Properties of Alkali and Halide Ions Using Water-Model-Specific Ion Parameters. *J. Phys. Chem. B* **2009**, *113* (40), 13279–13290. <https://doi.org/10.1021/jp902584c>.