



EGUsphere, referee comment RC1
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Comment on egusphere-2022-826

Robert McGraw (Referee)

Referee comment on "Microphysics of liquid water in sub-10 μ m ultrafine aerosol particles" by Xiaohan Li and Ian C. Bourg, EGU sphere,
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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 R_e) and surface tension (see below). Unfortunately, R_e 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.

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.

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.

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.

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.

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].

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

Minor points and typos:

Eq. 9 (previously just below Eq. 5) ρ_0 was used, which I assume is the density at the

center of the drop. Why the switch to ρ_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.