

Interactive comment on “Glycine in aerosol water droplets: a critical assessment of Köhler theory by predicting surface tension from molecular dynamics simulations” by X. Li et al.

Anonymous Referee #2

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General comments

The authors perform molecular dynamics (MD) simulations of water and water-glycine droplets to determine the curvature dependence of surface tension. The obtained surface tension is then used in Köhler theory to calculate critical supersaturations and the results are compared to recent measurements. Such a study is justified because the amino acids may act as cloud condensation nuclei in marine areas. This work parallels to a previous work by the authors (Li et al., 2010) where cis-pinonic acid-water clusters were studied. In the present paper the same simulation methods are used but the rigid SPC/E water model is replaced by a semi-flexible SPC/E model. I find the paper well

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written, interesting, and relevant to atmospheric sciences. The methods and argumentation are scientifically sound. I can recommend publication after the authors consider the following items and correct some misprints.

Specific comments

1) If surface tension is needed in a thermodynamic theory (like Köhler theory), it is preferable to use a thermodynamically defined surface tension. Unfortunately, surface tension for spherical interfaces is not a uniquely defined quantity. A good choice is the surface tension related to the surface of tension. Then the relevant thermodynamic machinery, that is Laplace equation, Gibbs adsorption equation, etc., is valid. Equation 9 would give this surface tension, if a) R_e were the radius of the surface of tension R_s and b) W corresponded to the true thermodynamic free energy barrier to nucleation. In eq. 9 neither case is true. R_e is the radius of the equimolar surface and W is calculated using the Irving-Kirkwood pressure tensor, which results in wrong energy barrier (see ten Wolde and Frenkel, J. Chem. Phys. 109, 9901 (1998)). Unfortunately, it is very difficult to obtain R_s and the correct energy barrier from MD simulations, and therefore the approximations in the paper are acceptable, especially as the clusters are quite large ($N > 750$). The authors should nevertheless highlight the fact that only an approximation of a thermodynamic cluster surface tension is obtained.

2) The curvature-corrected surface tension brings the critical supersaturations a bit closer to the experimental values. Nevertheless, I think it would be best to mention in the conclusions or in the end of section 4 that there are probably other factors causing the discrepancy in addition of surface tension (Kristensson et al., 2010).

3) On page 4 there are discussion on previous simulation studies of droplets. The authors might want to add the following recent papers to the references list: B. J. Block et al., J. Chem. Phys. 133, 154702 (2010) and J. Julin et al, J. Chem. Phys. 133, 044704 (2010).

4) The density profiles from planar and spherical simulations are fitted to hyperbolic

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tangent function. Some authors prefer error function. Have the authors checked if fitting to an error function form would change the results? I find it conceivable that the location of equimolar surface might be affected.

Technical corrections

5) The caption of Table 4 is erroneous.

6) Page 23176, equation 9: the exponent of R_e is 2, not 3.

7) Page 23178, line 24: radius number densities of water -> radial number densities of water.

8) Page 23182, the beginning of line 9: are -> where.

9) In several places in the text: Alejandre, not Alejandrea. Irving, not Ivring (also in the captions of figs. 2 and 4). Zakharov, not Zakharova (also in the references list).

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