

Author Comments (Manuscript ID: acp-2010-732)

We thank Anonymous Referee #1 for the constructive and helpful comments. We here respond to the comments and revise our manuscript accordingly.

Referee #1

Interactive comment on “Amino acids in atmospheric droplets: perturbation of surface tension and critical supersaturation predicted by computer simulations” by X. Li et al.

General comments:

This paper presents molecular dynamics (MD) simulations of aqueous solutions of six amino acids. In agreement with previous observational experiments, serine, glycine, and alanine were found to increase surface tension, while valine, methionine and phenylalanine reduced surface tension. The authors conclude that (1) including the increased surface tension slightly improves the agreement between Köhler theory and recent cloud condensation nuclei (CCN) observations of serine and glycine described by Kristensson et al. (2010), and (2) that the described dependence of surface tension on droplet curvature could help improve predictions of the CCN activity of atmospheric aerosols.

MD simulations are an interesting tool that can help to explain the surface activity of hydrophobic organics in small aqueous droplets, which are difficult to investigate in the laboratory. Accordingly, the results of these simulations could be of interest to the readers of ACP. Unfortunately, I think there are major flaws with each of the conclusions mentioned above, especially the second one, and therefore I cannot recommend the manuscript as currently written for publication. The authors have not helped to explain the previous CCN experiments on amino acids in any significant way. Furthermore, the conditions of the MD simulations are very different from those of nucleating cloud droplets in the atmosphere, and thus are not relevant to the CCN activity of ambient aerosols.

Specific comments:

1. Comment: Kristensson et al. (2010) have already discussed the potential influence of surface tension on their CCN experiments. They state that “[s]ome amino acids can behave as inorganic salts and increase surface tension in aqueous solution compared to pure water”, resulting in “an increase of predicted critical supersaturation from 0.763% to 0.775% for a 40 nm diameter [glycine] particle. This brings our predicted values closer to the experimental, although the change is almost negligible.” Having essentially dismissed an increase in surface tension as an explanation, they then go on to discuss other possible reasons for the discrepancy between theory and observations. The results of these MD simulations are in agreement, and in fact predict an even smaller change in critical supersaturation ($< 0.01\%$). Although the authors admit that there is only a “slight” improvement, they still state in the abstract that their methodology “is used to improve the Köhler equation in predicting the critical water vapour supersaturation of the droplet activation.” I do not think this conclusion is justified. I disagree with this final statement in the conclusions: “[O]ur method provides the possibility of incorporating the curvature dependence of droplet surface tension in atmospheric studies, which could help to improve the accuracy of the Köhler equation in predicting the critical water vapour supersaturation of the activation process of cloud droplets.” CCN in the atmosphere have dry diameters of at least several 10s of nm, and due

to water vapor condensation are typically hundreds of nm in diameter at the point of activation. The MD simulations described here only simulate droplets with diameters less than 10 nm. Thus the curvature dependence described here is essentially irrelevant to CCN activation. In other words, it is not at all clear that the quadratic fit to such small droplets and flat surfaces can be used to interpolate to droplets that are 100s of nm in diameter; i.e., I am not convinced that the curves in Fig. 6 are accurate at values of Re^{-1} near 0.01 nm^{-1} .

Our response: We thank the referee for pointing out this. In our previous paper (Li et al., 2011) we have fitted the surface tension of pure water droplet and droplet containing GLY (glycine) molecules to a quadratic polynomial function of R_e^{-1} (inverse of droplet radius), and the resultant expression for surface tension slightly improved the supersaturation of droplet activation predicted by Köhler theory (Kristensson et al., 2010). We agree with the referee that such correction is relatively small in magnitude, and cannot fully explain the discrepancy between experimental measurements and Köhler theory. In our revised manuscript, we focus on the demonstration of the detailed mechanism of surface tension perturbation induced by the presence of amino acid molecules, and show that such an effect is closely dependent on the curvature of the surface. By regarding planar interface regarded as the limiting case of spherical interface with infinity radius or zero curvature, the surface tension show non-monotonic curvature dependence that could be fitted by a polynomial function $\sigma = c_0 + c_1 R_e^{-1} + c_2 R_e^{-2}$. We will not draw quantitative conclusion based on such fitting, instead, the curvature dependence of surface tension is roughly estimated to gain insight into the size-effect of the water droplets. It is our future goal to investigate the interfacial properties of water droplets with different amino acid concentration and composition, in order to establish a unified expression to predict the surface tension of atmospheric droplet containing amino acids, which is of great importance in understanding the role of water-soluble organic nitrogen compounds in aerosol formation and climate forcing.

2. Comment: P30920 L5: I disagree that these simulations are “representative [of] the remote marine atmospheric aerosol-cloud system.” The simulated particles are composed of single amino acids, and such particles do not exist in the ambient atmosphere. To be representative of the atmosphere, they would need to have more realistic compositions (namely, other organic compounds and well as inorganic matter).

Our response: We thank the referee for pointing out this. We agree with the referee that the water-soluble carbonaceous content of the marine aerosol is much more complex than the group of six DFAAs selected in this study. However, in order to use MD simulations to investigate DFAAs in nanoaerosol particles representative of the marine environment, we first need a basic understanding concerning the molecular properties and behaviour of the most abundant DFAAs. One drawback with modelling a system made up by both organic and inorganic constituents is that the combined effect increases the difficulties in interpreting the results. Without a reference system, these types of mixtures would be much harder to understand and it would certainly be difficult to distinguish between a number of molecular interactions without the basic and thorough understanding of the behaviour of each individual constituent. Therefore, in this work we seek to benchmark the role of the main amino acid themselves, and see how their inherent differences in chemical structure and properties alter the droplet distribution and surface tension. Such

variability is important to establish for the well defined single component systems before addressing more complex amino acids-containing clusters, mixed either with different salt ions or with mixtures of different amino acids, or both. In the revised manuscript the statement has been rewritten as “... six types of amino acids that are relevant to the remote marine atmospheric aerosol-cloud system ...”

3. Comment: P30922 L24: The laboratory experiments of Leck & Bigg (1999) demonstrated that the oxidation products of L-methionine could nucleate new particles.

Our response: We thank the referee and have corrected this point.

4. Comment: P30925 L20-21: Mopper & Zika (1987) report maximum amino acid concentrations in rainwater of 15 μM ; to claim that the concentration of 0.56 M used in this study is “a bit high compared with the typical values in marine rain” is misleading. It is higher by a factor of approximately 40,000. Regardless, it is not clear why marine rain concentrations are relevant here; it is the presumably higher concentration at the point of activation (long before raindrops form) that is relevant.

Our response: We thank the referee for this point. We agree with the referee that the comparison between amino acid concentrations in rainwater and our simulated droplets is to some extent misleading, and have revised the manuscript by addressing the concentration at the point of activation. According to Köhler equation, a dry glycine particle with diameter of 50 nm has a critical diameter of 262 nm at the point of activation, at which the concentration of glycine is 0.15 mol L^{-1} . The other amino acids have larger concentration at the point of activation (ranging from 0.17 mol L^{-1} to 0.29 mol L^{-1}). In the study by Kristensson et al. (2010) particles containing amino acids were studied with a minimum diameter of 40 nm and a maximum concentration of 0.3 M. Even higher concentrations would be probable for smaller particles. Therefore our selected concentration of 0.56 mol L^{-1} is on the same order of magnitude and relevant to droplet activation in the atmosphere.

5. Comment: P30925 L23-24: “we therefore increased slightly the number of amino acids...” Increased slightly compared to what? As written this implies it is increased slightly compared to typical marine rain concentrations, but as noted above this is quite a bit more than a slight increase.

Our response: We thank the referee for this point. In our response to comment No. 4 we have shown that the amino acid concentration in our simulated droplets is slightly larger than the concentration at the point of activation. In the revised manuscript we state that “The applied concentration of amino acids in the droplet in this study (0.56 mol L^{-1}) is slightly elevated compared with the concentration used in Kristensson et al. (2010).” The slightly increased number of amino acid molecules is expected to diminish statistical error in molecular dynamics simulations.

6. Comment: P30930 L2: “[T]herefore VAL is expected to increase the surface tension of the

droplet.” Doesn’t this contradict the results from Table 1, which show that VAL decreases the surface tension of the droplet relative to that of pure water? Please clarify.

Our response: We thank the referee for this point. In the original text we indicated that VAL will increase the surface tension of droplet by comparing the $P_N(r)$ curves between droplet containing VAL and pure water droplet. In the revised manuscript the different effects of VAL on planar and spherical interfaces have been elaborated. It is shown in Table 1 that VAL is able to decrease the surface tension of the planar liquid-gas interface, in qualitative agreement with experimental observations. In fact, we have found that the presence of hydrophobic amino acid like VAL gives rise to a stronger enhancement in Lennard-Jones repulsion than Coulomb attraction, and in turn puts different impact on the surface tension of planar and spherical interfaces. As shown in the figure below (Fig. 7 in revised manuscript), a pair of repulsive forces parallel to the planar surface contribute positively to $(P_{xx}+P_{yy})/2$, i.e. the tangential component of the pressure tensor P_T . However, there is no contribution to P_{zz} , namely the normal component of pressure tensor P_N , as shown in Table 1. According to Eq. (1), the surface tension of the planar interface is diminished. Differently, the same repulsive interaction is divided into two contributions to both normal component $P_N(r)$ and tangential component $P_T(r)$, since the interacting force \mathbf{f}_{ij} crosses the spherical slice near surface with a certain intersecting angle. In other words, $P_N(r)$ is increased while $P_T(r)$ is decreased in the surface region. The balance between $P_N(r)$ and $P_T(r)$, which is closely dependent on the curvature of droplet surface, determines the variation of surface tension (increase or decrease). This explains why the presence of hydrophobic amino acid like VAL, MET and PHE diminishes surface tension of planar interface while enhances surface tension of spherical interface with diameter of 6–7 nm. Naturally, such an effect is closely dependent on the curvature of the surface; it can be inferred that $P_N(r)$ and $P_T(r)$ could be balanced at some larger diameter so that the influence of hydrophobic amino acids on surface tension vanishes.

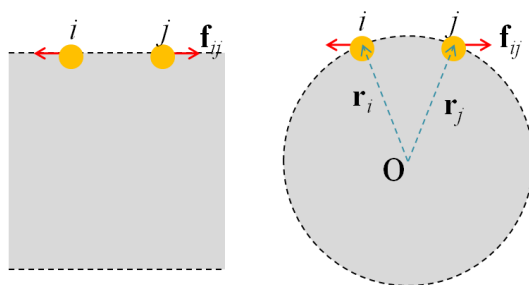


Fig. 7. Different effects of a pair of repulsive force on the surface tension of planar and spherical interfaces. Here i and j denotes the two interacting particles, \mathbf{f}_{ij} is the force exerted on particle j , O denotes center of mass of droplet, and \mathbf{r}_i and \mathbf{r}_j are the $O \rightarrow i$ and $O \rightarrow j$ vectors, respectively.

7. Comment: Figure 2 – Why are the results at the two air-water surfaces (at ~3.5 and ~6.2 nm) different?

Our response: We thank the referee for this point. In our simulation the initial structure of a water slab was constructed by first randomly inserting amino acid molecules (like PHE) into a cubic simulation box and then enlarging the box in z -direction to create two planar liquid-gas interfaces

(top and bottom). During equilibration the PHE molecules are concentrated on the interface, and there chances for these molecules to become asymmetrically distributed on the two surfaces. In other words, the number of PHE molecules on the two planar liquid-air interfaces could be different, resulting in different height in the density curve (e.g. at ~3.5 and ~6.2 nm). Nonetheless, the computed surface tension for the planar interface is obtained as an average over two interfaces, therefore the influence arising from an inhomogeneous distribution of the PHE molecules will be averaged out. Considering the fact that the surface tension of the planar interface is linearly dependent on the amino acid concentration, plain average will give the correct result of surface tension. In the revised manuscript the density profiles have been averaged over two planar interfaces in order to keep consistent with the computed surface tension results.

8. Comment: Figure 6 – Unfortunately the limitation of the MD simulations is on display here. The authors present results for a flat surface ($R_e^{-1} = 0$ nm), but the largest droplet presented has a diameter of ~ 6 nm ($R_e^{-1} = 0.3$ nm). This is much too small to be relevant for atmospheric CCN activation, which typically occurs when droplets are at least several hundred nm in diameter. The most important question in my mind is, “at what maximum diameter is the surface tension of a droplet enhanced relative to a flat surface?” Unfortunately, the MD simulations described in this manuscript are not able to answer this question.

Our response: We thank the referee for this point. Currently the size of droplets studied by all-atom molecular dynamics simulation is mostly limited within 10 nm, however, it is possible to estimate the surface tension of droplets with larger diameters by fitting and extrapolating the available data via a polynomial function of R_e^{-1} . By fitting to quadratic polynomial function $\sigma = c_0 + c_1 R_e^{-1} + c_2 R_e^{-2}$ we found that the intersections between the curves for pure water droplet and droplets containing hydrophobic amino acids appear in the region of $R_e = 40$ – 200 nm, in other words, the diameter of droplet is between 80 and 400 nm. Therefore, at typical activation point where the diameter of droplet is on the order of several hundred nm, the influence of hydrophobic amino acids on surface tension is expected to be very small, and it might be reasonable to neglect the effects of these amino acids, as inferred in our response to comment No. 6. Still, it should be noted that the surface tension of droplets with diameter of several hundred nm is slightly enhanced comparing with that of planar interface, due to the previously mentioned quadratic dependence on the droplet curvature.

9. Comment: Figure 7 – This figure suggests that the influence of the surface activity of amino acids on their CCN properties is at most minor, and likely negligible.

Our response: We thank the referee for this point. We agree with the referee that the correction arising from surface activity of amino acids is small in magnitude, and cannot fully explain the discrepancy between experimental measurements and Köhler theory. In our revised manuscript we are not drawing quantitative conclusion on supersaturation predicted by Köhler theory; instead, we focus on the interaction between the amino acids and water molecules and discuss in detail their influences on the surface tension, especially the origin of their different effects on planar and spherical interfaces.

10. Comment: Technical corrections:

P30920 L26: should be “help determine” – along with meteorological variables such as updraft speed.

P30921 L13: should be “making them reflect” (grammar)

P30923-4: Equations 1 and 2 use variables which are not defined.

Our response: We thank the referee and have corrected these points.