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

Report on acp-2010-732 Glycine in Aerosol Water Droplets: A Critical Assessment of Köhler Theory by Predicting Surface Tension from Molecular Dynamics Simulations by X. Li et al.

The submitted contains a molecular dynamics investigation of the curvature dependence of surface tension of aerosols with glycine and using Köhler's theory. In Köhler's theory the nucleation is governed by two (driving) terms, a Kelvin (surface tension) term and a bulk Raoult therm.

1. Comment: The main reason why I cannot recommend the work for publication is that the authors own data demonstrate that one cannot use Köhler's theory for an aerosol with Glycine. The reason is simply that the mixture do not follow Raoult's (ideal mixture) law but instead of Henry's. This can be seen by compare the density profiles in Figure 3 (Glycine) with the profiles of (pure) water in Figure 1 (The author have omitted the profile of water with Glycine!). I do not know whether this crucial shortcoming can be healed.

Our response: We thank the referee for pointing out this. As we know, Henry's law describes the fact that the partial pressure of the solvated gas is proportional to its concentration. In our opinion, Henry's law should not be used in our study, since glycine is not a gas and the partial pressure of the solute is not meaningful. On the other hand, Raoult's law describes the solute-induced perturbation on the vapor pressure of the solvent, which is water in our study. Rauolt's law relates the vapor pressure of the solution and molar concentration of the solvent, the former being an important quantity in atmospheric processes. Traditional Rauolt's law is valid for ideal mixtures; however, the non-ideality can be taken into account by using water activity instead of the molar concentration of water. In our study, we use the same formula of Köhler's equation as in the papers by Bilde and Svenningsson (Tellus, 56B, 128–134, 2004), Rosenørn et al. (Atmos. Environ., 40, 1794–1802, 2006), and Kristensson et al. (J. Phys. Chem. A, 114, 379–386, 2010)

$$s \equiv \frac{p}{p_0} = a_w \exp\left(\frac{4M_w\sigma}{RT\rho D_p}\right)$$

which has been proved to predict critical supersaturation very close to experimental measurements (Kristensson et al., J. Phys. Chem. A, 114, 379–386, 2010). Therefore, our data can be used in Köhler's equation to study the effects of glycine on critical supersaturation. For better illustration we also modified Fig. 3 to include the radial number densities of water molecules in the droplets

containing glycine, as shown below.



Fig. 3. Radial number densities of glycine and water molecules in systems 7–10.

2. Comment: I have some other critical comments: From where comes Eq. 4? It is not a trivial problem to handle the effect of long range forces in gas-liquid interfaces. See e.g. a resent published article J. Chem. Phys. 130, 054703 (2009), but there are many other, which show that although the forces are weak- the net effect for a semi infinite continuum is (very) important. Well you might argue that you indeed have taken this effect into account by Eq.4, but it looks fundamentally wrong: The (effective) energy parameter ε_{ij} between different species is not an arithmetic mean, but a geometric ("Lorentz-Berthelot", due to that it is a mean of Boltzmann factors)?

Our response: We thank the referee for pointing out this. We agree that the computation of long-range corrections to surface tension of liquid/gas interface is non-trivial and requires careful treatment. In our calculation, we followed the paper by Blokhuis et al. (Mol. Phys., 85, 665–669, 1995) to incorporate the dispersion correction to surface tension. Our idea is to obtain average $\varepsilon\sigma^6$ of the mixture and then to use the averaged $\varepsilon\sigma^6$ in the computation of the dispersion correction. Here $\varepsilon\sigma^6$ is related to the dispersion term of the Lennard-Jones potential function ($E_{disp} = -4\varepsilon\sigma^6 / r^6$). Since the Lennard-Jones potential is pair-additive, it is reasonable to calculate the average $\varepsilon\sigma^6$ of the mixture as the arithmetic average over all interacting Lennard-Jones pairs, as in Eq. (4). This treatment is the same as the dispersion correction formula in the manual of the GROMACS program package (van der Spoel, et al., Gromacs User Manual version 4.0, www.gromacs.org, 2005). The parameter ε_{ij} itself is determined as a geometric average of the individual parameters ε_i and ε_{ij} according to the definition of the force field, and such a geometric average does not relate

to Eq. (4) in our manuscript.

3. Comment: The interpretation of the stress profiles (Figure 2 and Figure 4) and the conclusion drawn from them is not "well founded". Only the net effect of the difference of the stress is well defined and give the thermodynamic effect. The problem is discuss in Proc. Roy. Soc. A 379, 231 (1982).

Our response: We thank the referee for this. We have modified Fig. 4 to include the net effect of glycine on the $P_N(r)$ curve of water droplet. Here $\Delta P_N(r)$ is equal to the difference between the $P_N(r)$ values of the glycine-containing droplet and the pure water droplet. It can be seen that the presence of glycine molecules has an undulate effect on the $P_N(r)$ curve. Although glycine molecules mainly reside in the bulk of the droplet, a small influence can be found in the surface region of the $P_N(r)$ curve. Inside the droplet where glycine molecules assemble, the value of $\Delta P_N(r)$ goes negative and therefore tends to reduce the surface tension. As the droplet size increases, the $\Delta P_N(r)$ curve becomes closer to zero inside the droplet and preserves the positive peak at the surface. This explains the trend of the change of the glycine-induced surface tension in droplets with different sizes.



Fig. 4. Normal component of Irving-Kirkwood pressure tensor and $\Delta P_N(r)$ curves in systems 7–10.