

## ***Interactive comment on “A method for the direct measurement of surface tension of atmospherically relevant aerosol particles using atomic force microscopy” by A. D. Hritz et al.***

**Anonymous Referee #1**

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The manuscript “A method for the direct measurement of surface tension of atmospherically relevant aerosol particles using atomic force microscopy” by A. D. Hritz et al. presents a new method for measurement of surface tension for collected liquid nanoparticles using atomic force microscopy. Particle surface tension is a crucial parameter in aerosol thermodynamics and cloud microphysics, but has so far remained an elusive property, due to the lack of experimental methods for single nano-particle surface tension measurements, and the challenges involved in capturing the composition dependent thermodynamic properties of complex chemical mixtures representative of atmospheric aerosols. The method presented here represents one important step towards this goal, enabling direct measurements on much smaller amounts of sample

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material, and thus readily applicable to a much wider range of aerosol samples from both laboratory and field measurements than was previously possible.

The manuscript is well-written in clear language with a logic structure and a refreshingly compact presentation. I recommend publishing after addressing three major points, and a few minor issues, as detailed below.

Major points:

1) The authors state in the abstract that the method applies to liquid nano-particles. I am missing a discussion of the actual phase-state of the samples. Are they really all liquid? What are the experimental conditions? It was shown by Virtanen et al. (Nature 467, 824-7, 2010) that chamber generated aerosol of very similar compositions to those sampled here are solid.

2) It is crucially important in the context of nano-particle surface tension to distinguish between the actual surface tension of a single particle and that of a bulk sample comprising a collection of many nano-particles. What are the dimensions of the sampled systems in the presented set-up, i.e. how thick and wide are the collected films on the impactor? Even if one dimension is in the nano-meter range, unless all of them are, chances are that the surface tension will still correspond to that of a much larger macroscopic sample – as the results present here indeed show. Is there any effect of the substrate onto which the sample is collected? Would there be, for certain film thicknesses?

The reason for the importance of this distinction is that interactions between surface area/bulk volume ratio and surfactant bulk/surface partitioning may change the surface tension in aqueous surfactant solutions depending on solution dimensions. This has been predicted from aerosol process models based on Gibbs adsorption theory (see e.g. Prisle et al., Atmos. Chem. Phys., 10, 5663–5683, 2010 and Prisle et al., Atmos. Chem. Phys., 11, 4073–4083, 2011), but not verified by direct measurement, as proper experimental methods are still lacking. It is still of great interest to know the surface

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tension of systems with representative chemical compositions, however, as made feasible with the method presented here, since even such information is also still sorely lacking for proper cloud micro-physic modelling.

3) A major concern is that for the results to be applicable in a wider context, they must be accompanied by more detailed or specific chemical information. Surface tension, especially for aqueous surfactants, is a highly non-linear function of composition, for one part due to the non-isotropic nature of the solutions inherent from the surface activity of the organics. Although I understand that such chemical characterization may be beyond the scope of this work, the authors could more carefully distinguish the different systems they are studying and comparing.

First, actual organic composition differences between  $\alpha$ -pinene and its oxidation products may indeed cause differences in surface tension of the purely organic phases, and it is indeed plausible that the more oxidized mixtures could have higher surface tensions due to more polar intermolecular interactions. But without any chemical information to facilitate comparison to thermodynamic modelling, or corresponding measurements with conventional methods on samples comprising similar mixtures of oxidation products, it is difficult to arrive at a firm validation of the method presented.

Second, the high-RH oxidation products are likely different than those formed at dry conditions (e.g. Jonsson et al., *J. Aerosol Sci.*, 38, 843–852, 2007), but again the authors do not comment on the chemical composition or perform parallel conventional measurements, so it is difficult to evaluate the source of the change in surface tension. I would furthermore strongly doubt that the WATER content of these organic mixtures conditioned at  $\sim 65\%$  RH is more than a minor fraction of the particle mass and therefore these particles are essentially highly dilute water solutions in organic solvent. The properties of such mixtures are not immediately comparable to those of dilute aqueous solutions of even the exact same organics (see e.g. a conceptual mixing diagram in Prisle et al., 37, L01802, 2010). This is again due to the highly non-linear variation of thermodynamic properties with composition, for mixtures of molecules with different

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structures, such as water and  $\alpha$ -pinene and its oxidation products. Specifically, additive surface tensions generally apply most readily for mixtures of components with very similar molecular structures, unlike those where oxidized functionalities or water molecules are introduced to organics. The dilute aqueous organic solutions are representative of the  $\alpha$ -pinene oxidation products at the point of CCN activation, as referenced with e.g. Engelhart et al. (*Atmos. Chem. Phys.*, 8, 3937–3949, 2008). I therefore suggest a revision of the discussion, in particular in the paragraph p. 8, l. 3-15, where these differences in sample composition and the implications for the thermodynamic origins of surface tension is taken more closely into account.

Minor comments:

p. 2, l. 26-27: It may be useful to add references to the methods using detailed Gibbs adsorption thermodynamics for evaluating surface tension during cloud activation, e.g. Sorjamaa et al. *Atmos. Chem. Phys.*, 4, 2107–2117, 2004 and previously mentioned Prisle et al., *Atmos. Chem. Phys.*, 10, 5663–5683, 2010.

p. 3, l. 14-16: In connection to the point above, there are a number of studies showing that particles containing strong organic surfactants display cloud activation properties consistent with the surface tension of pure water. This of course does not prove that the droplet surface tensions are in fact identical to that of pure water. Still, there is a convention of using the (counterintuitive) surface tension value of pure water for applications in cloud modelling. Furthermore, several process-level studies have firmly demonstrated that using bulk surface tension values can lead to great over-estimations of particle CCN activity, recently e.g. Hansen et al. *Atmos. Chem. Phys.*, 15, 14071-14089, 2015. These points do not imply that direct measurements of droplet surface tension is not of great interest, on the contrary, it will be a most valuable addition to the field to be able to determine the actual in situ droplet surface tension. As the authors note, none of the existing methods “directly measures the surface tension of the actual particles in question” (p. 3, l. 25-26). Furthermore, both the methods calculating surface tensions from Gibbs adsorption theory, and those applying back-calculation

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from observed cloud activation, rely on assumptions of droplet properties in addition to surface tension, which have also not been verified by direct and specific measurement.

p. 7, l. 29: The particles measured by e.g. Engelhart are also the  $\alpha$ -pinene oxidation products.

Table 1: How is the “standard error” defined? Is it e.g. taken as the standard deviation or twice that quantity? What temperature were the present measurements made at?

Table 2: I think it would be useful to clarify further what the functions of the standard and check standard, respectively, are. Specifically, what is the relationship between the surface tension of these standards (why is it not given in the table directly, or why is there not an explicit reference to where the values are found elsewhere in the manuscript) and the sample surface tensions?

Table 3: The RH is not 100% at activation. These particles require supersaturated conditions for CCN activation. Note that the water content for mixtures conditioned at these different humidities is by no means implicit.

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