Authors’ Response to the Review Comments

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Title of Paper: A Method for the Direct Measurement of surface tension of atmospherically relevant aerosol particles using Atomic Force Microscopy

Authors: A.D. Hritz, T.M. Raymond and D.D. Dutcher

Date Sent: 5/11/2016

We appreciate the time and efforts of the editors and both referees in reviewing this manuscript. We have addressed the issues indicated in the reviewer’s reports, and believe that the revised version meets the journal publication requirements. The reviewer’s efforts have led to a clearer and better manuscript.

Response to Comments from Reviewer 1

Reviewer’s comments are italicized while author responses are not. Page and line locations refer to the Markup version.

Reviewer’s Comment with Responses:

The manuscript “A method for the direct 1 measurement of surface tension of 2 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 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.

These measurements would not be possible to make on non-liquid samples. If the samples were not liquid, they could not wick up onto the nano-needle tip. To confirm that the samples were liquid upon collection as well as analysis, additional AFM measurements were made. These have been added to the paper. (p 5 1-6, p 7 12-14 and Figure 2). These measurements do indicate that the samples are liquid. To summarize, AFM images were obtained of one of the stainless steel discs before and after sampling. The image collected before sample collection shows an irregular, rough surface. The image collected after sample collection shows a smooth surface. During sample collection, the sample flowed to fill in the rough surface and leave a smooth surface.

The paper referenced by the reviewer (Virtanen et al) used a similar method of oxidizing VOCs but their VOCS were a much more complex mixture of biogenic VOCs which may be what leads to the difference in sample phase.

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 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.*

Our method is NOT a single particle method. We have added additional language (Title, p 2 5, p 5 1-6, p 9 28-29) trying to ensure that there is no confusion about this issue. Although the exact dimensions of the deposit are not known, it is certain that the width of the sample is above the nanometer range. The sample image added to confirm the sample phase (Figure 2b) shows that the sample width is at least 10 micrometers. We concur with the reviewer's point that this is likely to result in measurements that are closer to bulk measurements than single particle measurement. The purpose and strength of this method is to reduce the quantity of sample required to make these "bulk" measurements.

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 a-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 ~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 structures, such as water and a-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 a-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.*

We agree entirely with the reviewer's comments on this point. However, we do not believe that we made some of the claims to which the comments would apply. We have revised the paragraph (p 9 7-12) suggested by the reviewer to clarify this issue. The oxidized alpha-pinene system was chosen as our demonstration system because it is one of the most characterized secondary organic aerosol systems. The purpose of generating the particles at two different humidities was to demonstrate the difference in the response of the measurement method to what the reviewer correctly suggests is only likely to be a minor change in the composition of the particles. This helps demonstrate a minimal level of sensitivity. We do not claim that the change in humidity during the particle generation is directly proportional to the change in the water content of the particles. It is our hope that this method can be extended, either by us or by other researchers to investigate the surface tension of collected particles at the point of CCN activation. However, those measurements are beyond the scope of this current manuscript.

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.*

Excellent suggestion. Done!

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 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.

The Hansen reference has been added to the introduction as part of the motivation for this work

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

We have clarified the language in this section to clarify that it is not just alpha pinene but oxidized alpha pinene that was being studied.

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?

We used the statistical definition of standard error. It is calculated as the standard deviation of the sampling distribution of a statistic (s*n^-0.5) The temperature at which the bulk measurements were made (23.9 °C) has also been added (Figure 1)

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?

A paragraph describing the purpose of the check standards and clarifying the data used for comparison (the values presented in Table 1) has been added (p 8 22-27). This suggestion is quite useful as we had not previously clarified the role of the check standard.

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.

The table has been altered to reflect the supersaturation condition required for activation (Table 3). We do not mean to imply that the water content and humidities are directly proportional. We added the humidity information of our measurements and the others only to give context to our measurements.

Response to Comments from Reviewer 2

Reviewer's comments are italicized while author responses are not. Page and line locations refer to the Markup version.

The manuscript entitled: "A method for the direct measurement of surface tension of atmospherically relevant aerosol particles using atomic force microscopy" describes how to use a micro-Wilhelmy method to measure the surface tension of collected aerosol liquid in an atomic force microscope. While the manuscript is generally well-written, clear, very concise, and contains no major errors that I can tell, I wonder if it is, indeed, appropriate for publication in ACP.

From ACP's website (http://www.atmospheric-chemistry-andphysics.net/about/aims_and_scope.html), "The journal scope is focused on studies with general implications for atmospheric science rather than investigations that are primarily of local or technical interest." While there are some general implications from this study, namely, that it presents a new way to measure aerosol liquid surface tension in a direct way that uses much less sample liquid than traditional bulk methods require, the focus of this manuscript seems to be on the technical method development. The more general application of this method was to one aerosol system, oxidized alpha-pinene SOA, under dry and moderately wet conditions. The analysis was extremely short and contained no other supporting information or measurements other than a comparison to a couple prior studies in the literature that don't actually match these results or methods well at all. For better "general implications for atmospheric science," the results section needs to be developed much more extensively.

Perhaps other journals to consider submitting to would be Atmospheric Measurement Techniques or Aerosol Science & Technology. AMT's aims and scopes include "the development, intercomparison, and validation of measurement instruments and techniques of data processing and information retrieval for gases, aerosols, and clouds." AST's aims and scopes include "instrumentation for the measurement of aerosol physical, optical, chemical and biological properties." I am sure there are other appropriate journals available as well.

The authors feel that this is an issue for the editor to determine. Although Atmos. Chem. Phys. is not primarily a methods journal they are the preeminent journal in the broader topic of aerosol surface tension. And other paper like ours, method based but relating to larger issues, have regularly been published in this journal. We would consider a transfer to AMT at the editor's suggestion.

Specific comments

One major consideration the authors might also make is changing the title. The "direct measurement of ... aerosol particles" implies that the method is measuring surface tension on an individual aerosol particle; but this is not true. In reality, lots of aerosol particles are collected on a plate until there is a thin film of liquid covering the plate. In essence, this is still a bulk technique for measuring surface tension, just that this bulk is much, much smaller than traditional bulk methods (e.g. the traditional Wilhelmy plate method).

We agree with the reviewer on this point, this is not a single particle method and we never intended to imply that it was. We have added additional language (Title, p 2 5, p 5 1-6, p 9 28-29) trying to ensure that there is no confusion about this issue and to clarify that the particles were collected before analysis. This should reduce the potential for confusion about this topic.

pg 2 - line 11 : Are the results presented in this manuscript really "preliminary"? What will it take to make them final? Only final results (i.e. calibrated measurements from working instruments) should be published.

True! This has been fixed.

2 - 28 : Because this is a methods paper, it would be helpful to include equations and define each term and give the implications of each term of the equation. These include the Kelvin equation, Kohler equation (pg 3, line 6) and Raoult's Law (pg 3, line 6).

We added the full Kohler equation to the paper along with a reference that contains the other equations requested with more information about their derivation.

3 - 1 : What do you mean by "tabulated values"? Also, the literature review on surface tension measurements should be expanded - certainly there are more than two papers that talk about surface tension values with regards to nucleation?

We have added more detail about how the values cited above were tabulated. We also added additional references that talk about surface tension values with regards to nucleation.

3 - 3 : Is "shortly after nucleation" referring to a time issue or a particle size issue?

We have clarified this language.

3 - 12 : What does "good" mean? What basis do you have for making the "good initial assumption" claim? This phrase is confusing, especially given the next sentence which says the surface tension is reduced by 10-15%.

The "good" in this case referred to reasonable choice for the initial surface tensions assumptions in system models. We have changed it to "reasonable" to avoid any confusion.

4 - 6, 7 : Define "clean" air. What filters/scrubbers do you use? Is the air from a cylinder or compressed air line?

Details of our compressed air system have been added.

4 - 25-26 : This is the same basic sentence as pg 5, lines 4-5.

The sentence with repeated information has been eliminated.

5 - 20 : To be clear, are you paraphrasing this method in the next few paragraphs? You should make it clear that the reader does or does not need to read the Yazdanpanah et al., 2008 paper.

We leave this decision to the reader of the paper. We summarize the most important aspects of Yazdanpanah's paper, especially the parts that apply to our research. However, we'd never advise against reading the other paper for more detail if a reader so wished.

5 - 29 : Is there a citation for equation 1?

A citation that contains the equation along with additional derivation information has been added.

6 - 3 : Is there an image that can be used to demonstrate the contact angle? Perhaps this can be included in a supplemental section.

We are not aware of a photograph showing this angle. (We also can’t tell if the reviewer is requesting an actual photograph or just a schematic. If the schematic is what is being suggested, we can add that but without that clarification we will wait.)

6 - 10 : Explain better what capillary length means in the context of this measurement technique. Perhaps include an equation. This explanation is important to justify use of equation 2 as the basis for the technique.

A reference has been added that contains more information about capillary lengths.

6 - 23 : I do not understand this calibration method. It sounds like you are pushing the needle into a hard surface and deflecting the needle. But it must be the case that the needle actually stays rigid and the deflection comes where the needle is connected to something else that measures force. Perhaps a figure describing this process with some actual images would be helpful. Also, if what I have described is how the calibration is done, then how do you relate deflection to force?

The reviewer’s understanding is correct. It is not that the needle is deflecting but the cantilever (which is part of the AFM tip) that flexes as the nano-needle is pushed into a hard surface. The calibration of deflection sensitivity is a common procedure among AFM users. A reference to the manufacturer of our instrument (with associated manuals) has been added though this reference might not be relevant to users of different brands of AFMs.

7 - 3 : What is a "thermal tune" and how exactly is it done?

A thermal tune is used to determine the spring constant of an individual AFM tip. Each manufacturer of AFMs has implemented this tune somewhat differently. A reference to a white paper on our instrument’s manufacturer method has been added. Similarly to the previous comment, this is a common procedure and a detailed description of how to do it on one instrument is not necessarily pertinent to the use of another instrument.

7 - 15 : There is no mention of a "check standard" until later, which can be confusing when first looking at Figure 3. Also, where is the hard, steel surface used for calibration?

This is an excellent point, noted by both reviewers. We have added information defining the purpose and our use of a check standard in this system. The thermal tune and deflection calibration are included in figure 4 (the old figure 3) in the first step. Without these calibrations, the Force (F in step 1) cannot be measured accurately.

8 - 13-14 : What modifications? Explain in much greater detail what you mean by this sentence.

We are suggesting a potential important extension of this methodology in this sentence. Until the experiment has actually been done, we hesitate to suggest exactly how the particle generation and collection methodologies should be modified. We have removed the word "minor" from the description as that was an assumption on our part the veracity of which has not been confirmed yet.

8 - 32 : Use of "particles at activation" implies measurement of individual small droplets - this is not true with these current methods. Can these "modification" (list them) actually get to measuring surface tension of individual droplets?

We are in complete agreement with the reviewer about the limitations of this technique. It is not a single particle technique and it is unlikely (though perhaps not impossible) that it will ever be modified for single particle measurements.

Table 1 : The term "reasonably close" is subjective and should be avoided. What temperature were your measurements taken at? Did you only take two measurements per solution? I think measurements should usually be done at least three times and then averaged. For these compounds, are there any temperature-dependent models of surface tension that you could use to better compare to your measurements at whatever temperature your measurements were taken at?

Unfortunately, the literature values referenced in this table did not all contain information about the purity of the chemicals being tested. Our measurements were all made at 23.9 °C. This information has been added to this table. However, it is not possible to accurately model a complete correction to our measurements without the previously mentioned missing information. We agree with the reviewer that increasing the number of measurements can decrease the uncertainty associated with a measurement. However, it may not reduce to total error depending on the source of the error. The two sets of measurements that were made are in statistical agreement (0.2 and 1.5% relative error). The utility of making additional measurements at this point would be questionable due to the time offset between the original measurements and any potential current measurements.

Table 3 : Which measurements are approximated versus measured? I can make a guess, but this should be much clearer in the table. In the caption, the last two sentences look like analysis, which should go in the body of the manuscript rather than in the caption. Where does the surface tension value of 27.5 come from? I can't find it on Table 2 anywhere. Also, Table 3 should have uncertainties next to each surface tension value.

The values from our experiments are all measured. The values from Engelhart et al, Huff Hartz et al and Prenni et al are all provided to give context to our values. It demonstrates that our surface tension values for particles generated in dry conditions are similar to the bulk un-oxidized liquid while our surface tension values for the particle generated in wet conditions are more similar to those used and published by the authors cited above. We have changed the formatting of this table to indicate which value were measured by us in the hope of reducing any potential confusion.

Technical corrections

A careful proofread of the entire manuscript should be done – there are several places where no space exists between words and several places where multiple spaces exist between words.

We have reviewed our manuscript and hope that we caught and corrected these typographical errors.

pg 2 - line 17 : Do not need this line; this information is in the citation.

We do not agree that all potential readers of this manuscript will recognize the reference. So we would prefer to provide the information more directly even if it is technically repetitious.

2 - 30 : What is "this type"? Be more clear and specific.

We have clarified the language in this line to be clear that we are discussing the surface tension of particles near activation conditions. This should be clearer and more specific.

3 - 23 : I am not sure ACP's convention, but should references be moved to the end of the sentence? This isn't the only sentence in the manuscript written this way, but this one first caught my attention as one where the reference could be moved to the end without sacrificing any meaning.

Several of the references have been moved for the references that we deemed would not lose meaning with said change.

6 - 26-27 : This is an unnecessary detail.

We wish to be clear that the calibration constant (slope) is automatically applied by the instrument operating software and not post-applied in our calculation.

7 - 22 : Fix "a an average"

Done!

8 - 10 : What is "This"?

Clarified!

A method for the direct measurement of surface tension of collected atmospherically relevant aerosol particles using atomic force microscopy

A. D. Hritz, T. M. Raymond, and D. D. Dutcher

{Bucknell University, Lewisburg, Pennsylvania}

Correspondence to: D. D. Dutcher (dabrina.dutcher@bucknell.edu)

Abstract

Accurate estimates of particle surface tension are required for models concerning atmospheric aerosol nucleation and activation. However, it is difficult to collect sufficiently large volumes of atmospheric aerosol for use in typical instruments that measure surface tension, such as goniometers or Wilhelmy plates. In this work, a method that measures, *ex situ*, the surface tension of collected liquid nanoparticles using atomic force microscopy is presented. A film of particles is collected via impaction and is probed using nanoneedle tips with the atomic force microscope. This micro-Wilhelmy method allows for direct measurements of surface tension of small amounts of sample.

This method was verified using liquids whose surface tensions were known. Particles of ozone oxidized α-pinene, a well characterized system, were then produced, collected, and analyzed using this method to demonstrate its applicability for liquid aerosol samples. ~~Preliminary r~~It was determined~~esults show~~ that oxidized α-pinene particles formed in dry conditions have a surface tension similar to that of pure α-pinene, and oxidized α-pinene particles particles formed in wet conditions have a surface tension that is significantly higher.

1 Introduction

According to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, clouds and aerosols contribute the largest uncertainty to understanding changes in climate (Boucher et al., 2013). Aerosols affect the climate directly by reflecting or absorbing solar radiation, and indirectly when they form cloud particles (Boucher et al., 2013). A major difficulty in modeling particle nucleation and aerosol activation lies in determining physical properties of particles on the nanoscale without precise knowledge about chemical composition.

Recent studies in particle nucleation and cloud droplet activation have used various methods to estimate particle surface tension, which is a very important parameter in modeling both processes (Sorjamaa et al. 2004, Prisle et al. 2010. Laaksonen and McGraw, 1996; Moldanova and Ljungström, 2000; Wex et al., 2009; Petters et al., 2009; Duplissy et al., 2008; Kiss et al., 2005). Particle nucleation is described by the Kelvin equation (Laaksonen and McGraw, 1996), which requires knowledge about surface tension of the nucleating particle (Laaksonen and McGraw, 1996; Schmelzer et al., 1996). Not surprisingly, direct measurement ~~of this type~~

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Comment [DDD1]: http://www.atmos-chem-phys.net/15/6337/2015/acp-15-6337-2015.html of the surface tension of particles near activation state conditions has not been possible. Studies on nucleation often rely on an assumption about the composition and use ~~tabulated~~ complied values for bulk surface tension including values extrapolated from other phases, estimated or interprelated from similar compounds (Daisey and Hopke, 1993) or simply assume “physically reasonable values“ (Moldanova and Ljungström, 2000). Hansen et al (2015) demonstrated the magnitude of the error that can occur when commonly made assumptions about surface tensions are used in models. A direct method of measuring the surface tensions of particles ~~shortly~~ immediately after nucleation is preferable to these assumptions and would likely reduce the error in particle nucleation models.

Köhler theory is used to predict the properties of activating cloud condensation nuclei (Köhler, 1936). The Köhler equation balances the Kelvin effect with Raoult’s Law in order to describe particle activation. The Kohler equation applies equilibrium thermodynamics to describe the process in which water vapor condenses to form liquid droplets.

$$\ln\left(\frac{p_w(D_p)}{p^0}\right) = \frac{4M_w\sigma_w}{RT\rho_w D_p} - \frac{6n_s M_w}{\pi\rho_w D_p^3} \qquad (1)$$

where, T=absolute temperature, R=ideal gas constant, p_w=droplet water vapor pressure, p_0=saturation vapor pressure over a flat surface, σ_w=droplet surface tension, ρ_w=denisty of pure water, n_s=moles of solute, M_w=molecular weight of water, D_p=droplet diamter (Köhler, H., 1936. The nucleus in and the growth of hygroscopic droplets. Trans.Faraday Soc., 32, 1152–1161). Thus, similar problems arise in specifying physical properties used in the Kelvin term of the Köhler equation. To date, there has been little consistency between assumptions used for the activated particles‘ surface tensions. Many researchers (Prenni et al., 2007; Petters and Kreidenweis, 2007; Huff Hartz et al., 2005; Conant et al., 2002) have assumed that, at activation, the particles consist mainly of water, so a surface tension for pure water was used. Though this is a ~~good~~ reasonable initial assumption, it neglects the depressive effect of organic surfactants on the activating particles‘ surface tensions (Kiss et al., 2005; Facchini et al., 1999). It is now generally agreed upon that, for most activating particles with these surfactants, the surface tension is reduced by about 10-15% (Facchini et al., 2000; Engelhart et al., 2008; Awa-Awuku et al., 2010; King et al., 2009). Several methods have been used to predict this surface tension reduction. Some researchers have collected particles and diluted them so as to allow for a direct measurement using conventional instruments (Asa-Awuku et al., 2008; Moore et al., 2008; Schwier et al., 2013; Henning et al., 2005). These values were then extrapolated back to the initial concentration by fitting them to a Szyskowski-Langmuir

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isotherm. Occasionally, surface tensions for the particles have been back-calculated using Köhler Theory Analysis when all other parameters are known or estimated (Asa-Awuku et al., 2010; Engelhart et al., 2008). Others (Raymond and Pandis, 2002; Kiss et al., 2005) have prepared solutions mimicking the bulk chemical composition of aerosol particles and directly measured their surface tensions. However, none of these methods directly measures the surface tension of the actual particles in question.

Yazdanpanah (Yazdanpanah et al., 2008) has developed a method to measure the surface tension of small (~200 nm in diameter) droplets and films using constant-diameter nanoneedle tips on the atomic force microscope. In this work, we will show how his method has been adapted to accurately measure the surface tensions of collected atmospheric aerosols.

2 Experimental Methods

2.1 Particle Generation

In this project, oxidized α-pinene particles were generated in a 1 m^3 polytetrafluoroethylene (PTFE) smog chamber (Fig. 1). Particles were formed in either “dry“ (<5% RH) or “wet“ (67% RH) conditions. To generate the “dry“ conditions, the chamber was flushed with clean, dry air for several hours. Compressed air was cleaned using a TSI 3074B filtered air supply. To generate the “wet“ conditions, clean air was bubbled through water at 2 liters per minute (LPM), filtered, and sent to the smog chamber. The chamber was flushed with this humid air stream until a maximum relative humidity was reached. Relative humidity was measured using a Vaisala HM337 Humidity and Temperature Transmitter. Neither the water content of the particles, nor the surface tensions of the particles generated under dry and wet conditions are likely to be be directly porpotional to the relative humidities (Jonsson et al 2007).

During experiments, the dry, cleaned, air stream was sent into the smog chamber at 2 LPM. This air stream could be diverted either through a sample port or through an ozone generator (Poseidon Ozone Generator by Ozotech) in series with a HEPA filter before entering the chamber. An outlet port from the chamber could be connected either to a scanning mobility particle sizer (a 3080 TSI Differential Mobility Analyzer in series with the 3775 TSI Condensation Particle Counter) or a cascade impactor (I-1L Cascade impactor by PIXE).

Experiments were only conducted when the initial particle concentration in the smog chamber was below 100 particles/cm^3, as measured by the scanning mobility particle sizer (SMPS).

At the start of each experiment, ozone was added to the smog chamber. If particle counts in the smog chamber remained low after about five minutes, indicating a chamber free of oxidizible volatile organic compounds, 5 µL of liquid α-pinene (97% pure, Acros Organics) was then injected into a sample port, where it was vaporized and carried into the smog chamber. Ozone and α-pinene were added in a roughly 1:1 molar ratio; the high starting concentrations were necessary so that an adequate particle volume would form for collection later. The resulting oxidized α-pinene particles were allowed to age in the chamber for 90 minutes. The ozone-alpha-pinene system was sellected because it is one of the more, if not the most, characterized SOA systems. Speciation and chemical characterization results from similar systems have been reported by various researchers (e.g. Yu et al (1999), Jang and Kamens (1999), Tu et al 2016 and Praplan et al (2015))

During the aging process, particle size distribution data was collected with the SMPS. The SMPS sample flowrate was 0.3 LPM and the sheath flowrate used on the Differential Mobility Analyzer (DMA) was 3 LPM. These settings allowed for collection of particle size distribution data over the range of 15 to 660 nm. The low sampling flowrate ensured that the smog chamber operated under positive pressure. The size of the oxidized α-pinene particles followed a log-normal distribution whose center shifted to larger sizes over time. In the period where particles aged, the modal diameter increased from around 120 to 200 nm. The most significant changes in particle size distribution occurred in the first hour after the α-pinene was introduced to the smog chamber. ~~Particles were left to age for~~ The 90 minutes aging period ~~in order to~~ensured ~~minimize~~ minimal changes in particle size distribution during collection. A schematic of the experimental set-up is shown in Figure 1.

2.2 Particle Collection

Ninety minutes after α-pinene was introduced to the smog chamber, the outlet of the chamber was switched to feed to the cascade impactor. The second smallest stage (L2) was used to collect the particles on a cleaned steel disk. The 50% aerodynamic cutoff diameter for this stage at 4 LPM was 40 nm. After 90 minutes a visible particle film had collected on the disk. Immediately after collection, the sample disk was analyzed using atomic force microscopy

(AFM). The particles deposit in a circular region ~6 mm in diamter on the steel disc. The steel disc before and after sample collection was imaged using a ScanAsyst and PeakForce Tapping-mode AFM microscopy. These images are displayed in Figure 2a and 2b. These images show that the steel puck is very rough. After sampling the surface is smoother indicating that the sample flowed and filled in the roughness. Two traces, centered vertically and horizontally, from each image are shown in Figure 2c.

2.3 Sample Analysis

A Veeco Multimode V Atomic Force Microscope (AFM) and NaugaNeedle NN-HAR-FM60 probes were used to analyze the particle film collected on the disk. The probes consist of a flat, flexible cantilever, and a nanoneedle mounted normally to the cantilever at its end. The Ga-Ag nanoneedles are shaped as cylinders on the order of 100 nm in diameter and 10 µm in length. A micro-Wilhelmy method ~~was used to measure surface tensions~~developed by ~~(~~Yazdanpanah et al., 2008~~)~~, described below, was then used to measure the surface tension of the samples..

The sample was analyzed with the AFM in force mode. In this mode, the AFM's piezoelectric transducers push the sample film up to and away from the probe with high precision. The downward force exerted on the probe was recorded by the AFM as a function of its location relative to the film's surface. A force curve obtained with the AFM is presented in Fig. 2.

In Fig. 2, the curve in blue illustrates the force exerted on the probe as it approaches and touches the sample surface. The curve in red illustrates the force exerted on the probe as it is pulled from the sample. If it is assumed that only forces related to the surface tension of the liquid film are exerted on the probe, then equation ~~1~~ 2 holds:

$$F_{probe} = \sigma * L * \cos(\theta) \qquad (\cancel{1}2)$$

where σ is the surface tension of the sample, L is the wetted perimeter of the tip, and θ is the contact angle between the fluid and the tip. For a more complete derivation of this equation see

Comment [DDD2]: **1Measurement of Wetting Properties of Individual Boron Nitride Nanotubes with the Wilhelmy Method Using a Nanotube-Based Force Sensor**
Kyungsuk Yum **and** Min-Feng Yu *
Department of Mechanical and Industrial Engineering, University of Illinois at Urbana-Champaign, 1206 West Green Street, Urbana, Illinois 61801
Nano Lett., **2006**, *6* (2), pp 329–333
DOI: 10.1021/nl052084l

Because the nanoneedle has a cylindrical geometry, the wetted perimeter, L, is constant during all force measurements. This can be seen by the near-constant negative force exerted on the probe when it is initially retracting out of the sample. The increase in the downward force before the nanoneedle is completely pulled from the sample is attributed to a decrease in the contact angle. At the point the sample breaks away from the nanoneedle, the contact angle is zero. When this angle is zero and the needle is smaller than the capillary length (Uddin et al., 2011), equation 2 holds:

$$\sigma = \frac{F_{probe}}{L} \qquad (2)$$

For this project, equation 2 was used, using the force reading at the point the nanoneedle broke from the sample. This corresponds to point 5 in Figure ~~2~~3. The magnitude of the force at the break-away step suggests that the collected sample is liquid rather than a glassy or amorphous solid observed for some oxidized VOC systems.

Comment [DDD3]: http://pubs.rsc.org/en/Content/ArticleLanding/1975/F1/f197501919#!divAbstract

Several aspects of the AFM system were calibrated daily before the collected α-pinene particles were analyzed, typically during particle collection. Because the AFM directly measures deflection of the cantilever, a force exerted on the nanoneedle could only be obtained after calibrating the cantilever's deflection and determining its spring constant. In the AFM, a laser is reflected off of the cantilever into a photodetector; cantilever deflection is measured by movement of the laser on the photodetector. To calibrate this measurement, the probe was gently pushed into a hard, steel surface. The slope of the force curve when the probe is in contact with the surface indicates the observed cantilever deflection from the photodetector (y-axis of the force curve) versus the actual distance the surface is moving the cantilever (x-axis of the force curve). This slope was entered into the AFM's operating program.

Comment [DDD4]: add bruker.com reference

The spring constant of the tip was found using a thermal tune. The thermal tune is a common method to calculate spring constant using measurements of the cantilever's response to thermal noise (Serry, 2010). The native Veeco software was used to perform the thermal tune. After these calibrations, the AFM will produce force curves that relate force and distance accurately.

Comment [DDD5]: http://www.bruker.co.jp/axs/nano/imgs/pdf/AN090.pdf

In order to calculate surface tension from force data, the wetted perimeter of the nanoneedle also had to be obtained. This was done by obtaining force curves of liquid standards and using equation 2 to back-calculate the wetted perimeter given force and surface tension information. Two liquid standards were used: 90% pure oleic acid (Sigma-Aldrich) and 97% pure, non-oxidized liquid α-pinene. The surface tensions of these two standards were measured using a Wilhelmy plate (Sigma 703D, KSV Instruments Ltd.); results are shown in Table 1. Measurements for the standards yielded lower values compared to the literature for pure oleic acid and α-pinene. Because the standards were not completely pure, this was not unexpected, and surface tension values obtained from the Wilhelmy plate were used.

A summary of the steps used to calibrate and analyze samples on the AFM is shown in Figure ~~3~~4.

3 Results and Discussion

Surface tension data was obtained for oxidized α-pinene particles. The AFM’s measurements and calculated values are presented in Table 2. Both“dry“ oxidized α-pinene particles and “wet“ oxidized α-pinene particles were analyzed. The mean surface tension of “dry“ oxidized α-pinene particles was found to be 27.5 dyn cm^{-1} at 23 degrees C, with~~ a~~ an average uncertainty of 1.1 dyn cm^{-1}. This is similar to the surface tension of pure α-pinene as reported in the literature (Daisey and Hopke, 1993) and measured with our Wilhelmy plate. The mean surface tension of “wet“ oxidized α-pinene particles was found to be 44.4 dyn cm^{-1} at 23 degrees C, with an uncertaintyof 2.4 dyn cm^{-1}.

The results presented in Table 2 include a set of standards which were done for every set of measurements. The purpose of this standard was to allow the determination of the perimeter of the nano-needle. For the first set of reported measurements a check standard was also added to verify that the perimeter measurement was correct. This check standard is not required for each set of measurements. The surface tensions measured here were compared to the surface tensions of our standards measured and presented in Table 1.

Table 3 compares the mean surface tensions of oxidized α-pinene particles measured in this study with published estimates for the surface tension of activating, oxidized α-pinene particles (Engelhart et al., 2008; Huff Hartz et al., 2005; Prenni et al., 2007). Our results suggest that the surface tension of dry oxidized α-pinene particles is not very different from the surface tension of its VOC precursor. It is also apparent that the surface tension of oxidized α-pinene particles formed in more humid conditions had a higher surface tension than oxidized α-pinene particles formed in dry conditions.

These results appear to be in agreement with current theory. It is generally believed that the surface tension of an activating oxidized α-pinene particle is slightly lower than that of pure water, at 61.7 dyn cm^{-1} (Engelhart et al., 2008). This is due to the depressive effect of organic surfactants in the droplets. The results from our particle generated at the higher of two humidities~~Our results~~ suggest that the surface tension ~~of particles with a greater surfactant to water ratio is even lower, somewhere~~is between the surface tension of pure water and the surface tension of the dry oxidized α-pinene. This relationship is unlikely to be directly linear given that additive surface tensions only apply to chemicals with similar properties which water and the organics produced from the oxidation of alpha-pinene are not. Furthermore, the surface tension of the dry oxidized α-pinene particles was found to be similar to the surface tension of pure α-pinene. This similarity in properties may be due to their similar structures. Now that a method suitable for the direct measurement of particle surface tension has been established, direct measurements of particles with several other moisture contents should be taken to examine the precise relationship between surface tension and moisture content in a particle. With ~~minor~~ modifications to the particle generation technique, this method can be used to experimentally measure the surface tension of activating particles.

4 Conclusions

A method was developed to measure the surface tension of collected liquid aerosol particles using atomic force microscopy. Particles are impacted on a clean surface until a film is formed, then probed with a clean tip in an atomic force microscope. This method minimizes processing of the particles and therefore reduces the risk of sample contamination. The method was verified and calibrated using standard liquids whose surface tensions were in the range of the sample specimens. The standard liquid surface tensions were checked with a Wilhelmy plate. This method does not measure single particle surface tension but does dramatically reduce the required amount of material required to make such measurements.

Relatively dry, oxidized α-pinene particles were found to have a surface tension similar to that of pure liquid α-pinene. Oxidized α-pinene particles with higher moisture content were found to have a surface tension significantly higher than that of pure α-pinene, but lower than current assumptions for the surface tension of activating oxidized α-pinene particles. These preliminary results are consistent with the assumption of surface tension depression currently used to approximate the surface tension of activating aerosol particles. With ~~simple~~ modifications to the particle generation technique, this method can be used to experimentally measure the surface tension of particles ~~at~~ closer to activation conditions.

Acknowledgements

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Table 1. Surface tension of bulk liquids used for standardization, measured by the Wilhelmy plate at 23.9 degrees C. Averages reported as “average +/- standard ~~error~~error (s/$\sqrt{n}$).” Pure oleic acid has a surface tension of 32.79 dyn/cm at 20 degrees C (Chumpitaz et al., 1999), and pure α-pinene has a surface tension of 26.0 dyn/cm at 25 degrees C (Daisey and Hopkey, 1993). Measured values on Wilhelmy plate are ~~reasonably~~ close to reported values, considering differences in purity and temperature.

Component	Surface Tension (dyn/cm)
Oleic Acid (90% purity)	29.47
	29.53
Average	**29.50±0.03**
α-pinene (97% purity)	25.75
	25.36
Average	**25.6±0.2**

Table 2. Measured and calculated values obtained during three experiments. In the first experiment, α-pinene was used as the standard, oleic acid was used as a check standard, and the oxidized α-pinene particles were generated in dry conditions. In the second experiment, oleic acid was used as the standard, there was no check standard, and the oxidized α-pinene particles were generated in dry conditions. In the third experiment, α-pinene was used as the standard, there was no check standard, and the oxidized α-pinene particles were generated in wet conditions.

	Standard		Check Standard		Sample Oxidized α-pinene particles	
Experimental conditions	Measured Maximum Force(nN)	Calculated Wetted Tip Perimeter (nm)	Measured Maximum Force(nN)	Calculated Wetted Tip Perimeter (nm)	Measured Maximum Force(nN)	Calculated Surface Tension (dyn/cm)
-Particles generated					10.1	26.8
at <10% RH	9.7	377.0	11.0	373.8	10.3	27.4
-Standard: α-pinene	9.6	373.8	10.9	370.7	10.2	27.0
(97% purity)	9.7	377.0	10.8	364.4	11.4	30.2
-Check Standard: Oleic					10.5	27.8
Acid (90% purity)						
Average		**375.9±1.1**		**369.7±2.8**		**27.8±0.6**
-Particles generated						
at <10% RH	11.7	395.8			10.8	27.2
-Standard: Oleic Acid	11.8	399.0			10.6	26.7
(90% purity)	11.7	395.8			10.6	26.8
-Check Standard: None						
Average		**369.9±1.0**				**26.9±0.2**
-Particles generated					21.4	43.3
at 67% RH	12.7	496.4			21.2	42.9
-Standard: α-pinene	12.5	490.1			20.6	41.8
(97% purity)	12.6	493.2			22.8	46.3
-Check Standard: None					23.4	47.5
Average		**493.2±1.8**				**44.4±1.1**

Table 3. Measured and approximated surface tensions of α-pinene particles. Bulk α-pinene and dry, oxidized α-pinene particles have a similar surface tension. Wet α-pinene particles have a higher surface tension. Our measurements are shown in italicized font, other values are given for context.

RH at particle creation (%)	Surface tension (dyn/cm)	Description, Source
n/a	**25.6**	Pure α-pinene, bulk This experiment; Wilhelmy plate
<10	***27.5***	*Oxidized α-pinene particles* *This experiment; AFM measurements*
67	***44.4***	*Oxidized α-pinene particles* *This experiment; AFM measurements*
≥100 (Activation)	**61.7**	Oxidized α-pinene particles, assume depressed surface tension of pure water Engelhart et al., 2008
≥100 (Activation)	**72.5**	Oxidized α-pinene particles, assume surface tension of pure water Huff Hartz et al., 2005; Prenni et al., 2007

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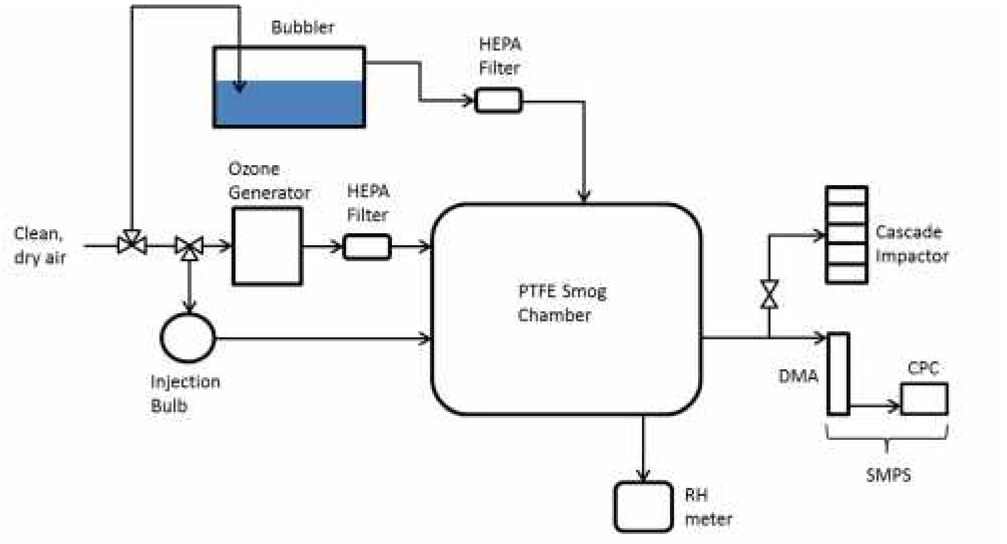
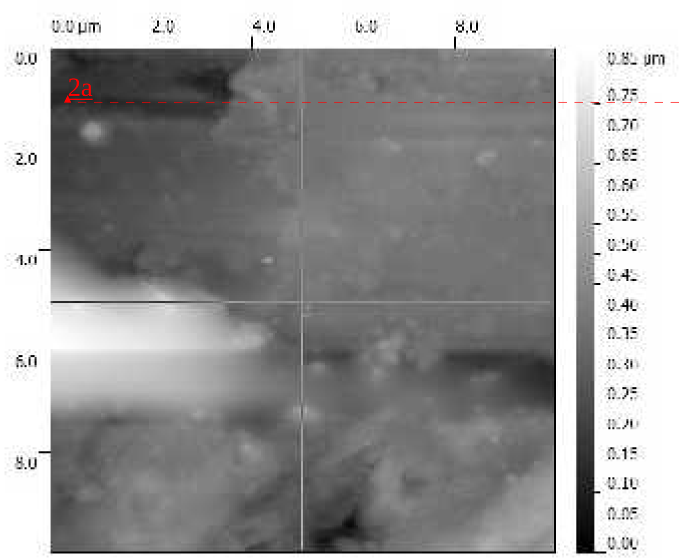


Figure 1. Experimental setup used to generate and collect oxidized α-pinene particles. The smog chamber is initially flushed with dry or wet air. Once the relative humidity in the chamber is established, particles are generated in the smog chamber by mixing α-pinene and ozone. Resulting particles are either analyzed with the SMPS or sampled using the cascade impactor.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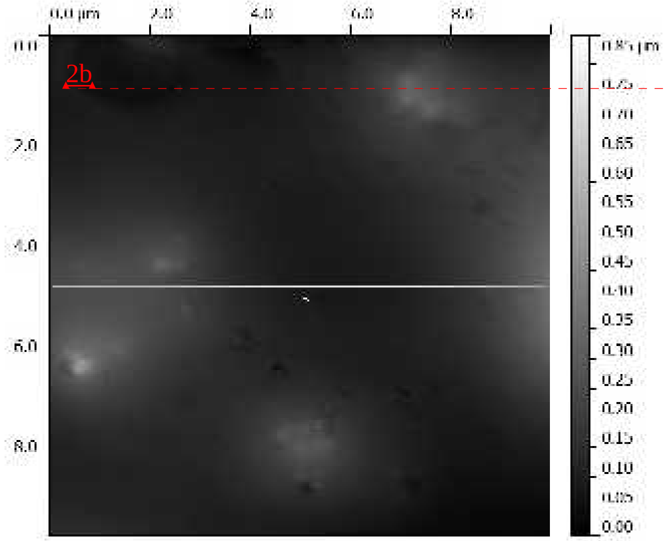
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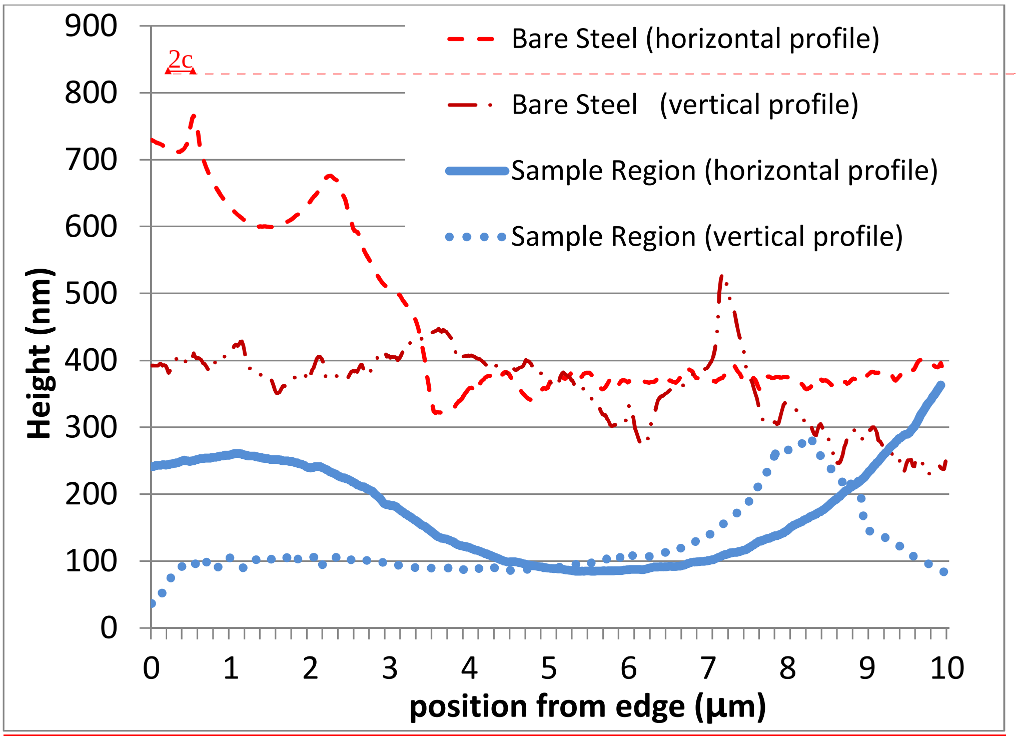

Figures 2a-c. Figure 2a shows an AFM surface scan of cleaned (no sample) puck. The surface is rough at this microscopic level. Figure 2b shows an AFM scan of the same puck after sampling. This image was collected in the sample deposit region. It shows that the roughness gets filled in by the sample. Figure 2c shows the centered vertical and horizontal traces from these analysis. Significant roughness is observed on the steel that is not observed on the collected sample. This indicates that the sample could flow, i.e. had liquid characteristics at the time of sampling.

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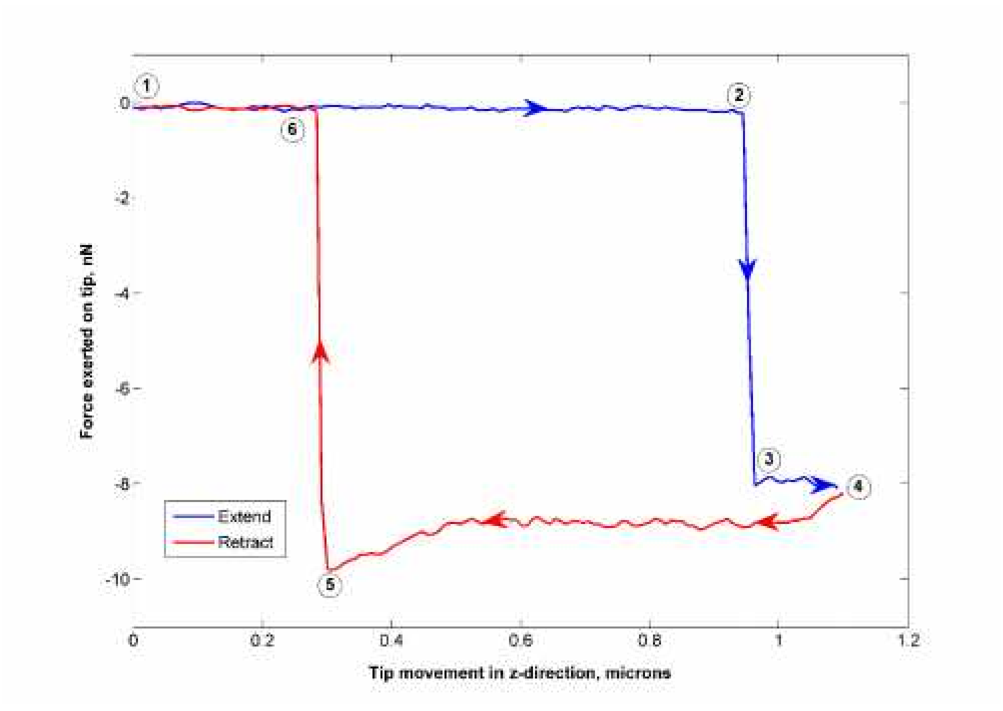

Figure ~~2~~3. A typical force curve obtained using NaugaNeedle NN-HAR-FM60 probes and an atomic force microscope. The blue line indicates the probe approaching the sample, and the red line indicates the probe retracting from the sample. At point 1, the nanoneedle is approximately 1 micron from the surface of the liquid sample. At point 2, the nanoneedle is just above the surface of the liquid. At point 3, the nanoneedle has touched the liquid, which wicks up and exerts a downward force on the probe. At point 4, the nanoneedle begins to pull out of the liquid. At point 5, the liquid is just about to break from the end of the nanoneedle, and the contact angle of the liquid-needle interface approaches zero. At point 6, the nanoneedle has pulled out of the liquid sample. The probe retracts back to point 1.

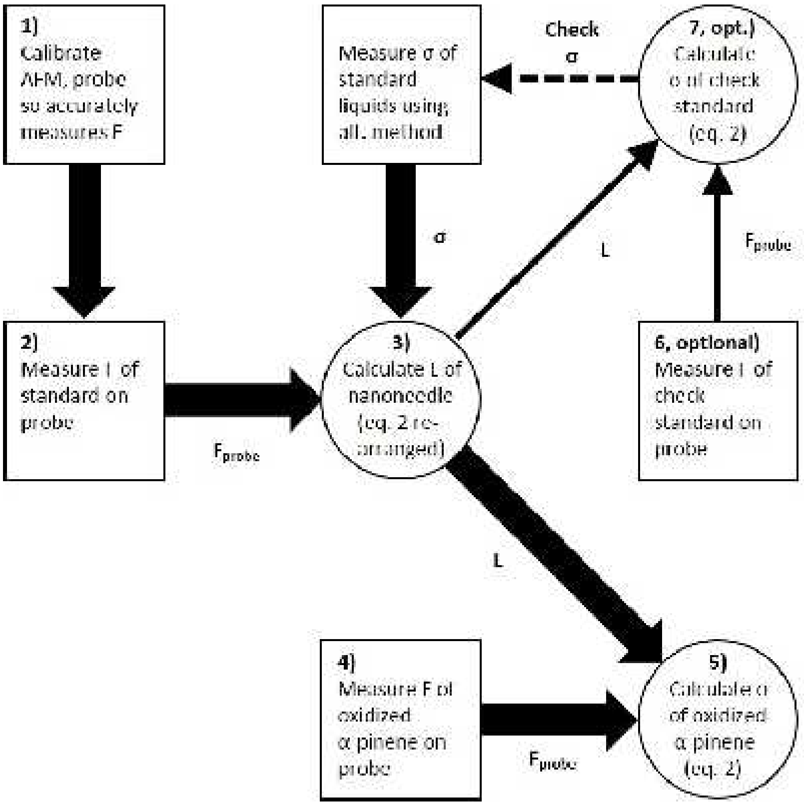

Figure ~~3~~4. Procedure used to determine the surface tension of oxidized α-pinene particles using the AFM. The cantilever's spring constant was determined (step 1), which allowed the AFM to obtain force curves. Force curves of a liquid standard were obtained (step 2), and the nanoneedle's wetted perimeter was calculated with equation 2 given the standard's known surface tension (step 3). Force curves of the oxidized α -pinene sample were obtained (step 4), and its surface tension was calculated with equation 2 given the nanoneedle's wetted perimeter (step 5). For initial tests, a check standard was used to verify the validity of the wetted perimeter and sample surface tension calculations (optional steps 6-7).b