Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

A method for the direct measurement of surface tension of 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)

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

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 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 oxidized α-pinene were then produced, collected, and analyzed using this method. Preliminary results show that oxidized α-pinene particles formed in dry conditions have a surface tension similar to that of pure α-pinene, and 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 (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 of surface tension has not been possible. Studies on nucleation often rely on an assumption about the composition and use

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

tabulated values for bulk surface tension (Daisey and Hopke, 1993) or simply assume "physically reasonable values" (Moldanova and Ljungström, 2000). A direct method of measuring the surface tensions of particles shortly 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. 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 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 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

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. 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.

During experiments, the dry 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.

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

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 90 minutes in order to minimize changes in particle size distribution during collection.

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).

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 (Yazdanpanah et al., 2008).

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 holds:

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

$$F_{probe} = \sigma * L * \cos(\theta) \quad (1)$$

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.

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:

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

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.

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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

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.

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.

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}.

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 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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

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. Our results suggest that the surface tension of particles with a greater surfactant to water ratio is even lower, somewhere between the surface tension of pure water and the surface tension of the dry oxidized α-pinene. 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 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.

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 activation.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

Acknowledgements

The authors thank NaugaNeedles and Dr. Mehdi Yazdanpanah for supplying the tips for the atomic force microscope and assisting in developing the methods described in this paper. The authors also thank Drs. James Maneval and Ray Dagastine for their assistance.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

References

Asa-Awuku, A., Sullivan, A. P., Hennigan, C. J., Weber, R. J. and Nenes, A.: Investigation of molar volume and surfactant characteristics of water-soluble organic compounds in biomass burning aerosol, Atmos. Chem. Phys., 8, 799-812, 2008.

Asa-Awuku, A., Nenes, A., Gao, S., Flagan, R. C. and Seinfeld, J. H.: Water-soluble SOA from Alkene ozonolysis: composition and droplet activation kinetics inferences from analysis of CCN activity, Atmos. Chem. Phys., 10, 1585-1597, 2010.

Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V. M., Kondo, Y., Liao, H., Lohmann, U., Rasch, P., Satheesh, S. K., Sherwood, S., Stevens, B. and Zhang, X. Y.: Clouds and Aerosols, in: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom, 571-657, 2013.

Conant, W. C., Nenes, A. and Seinfeld, J. H.: Black carbon radiative heating effects on cloud microphysics and implications for the aerosol indirect effect 1. Extended Kohler theory, J. Geophys. Res., 107, 4604-4612, 2002.

Daisey, J. M. and Hopke, P. K.: Potential for Ion-induced Nucleation of Volatile Organic Compounds by Radon Decay in Indoor Environments, Aerosol Sci. Tech., 19, 80-93, 1993.

Duplissy, J., Gysel, M., Alfarra, M. R., Dommen, J., Metzger, A., Prevot, A. S. H., Weingartner, E., Laaksonen, A., Raatikainen, T., Good, N., Turner, S. F., McFiggans, G. and Baltensperger, U.: Cloud forming potential of secondary organic aerosol under near atmospheric conditions, Geophys. Res. Lett., 35, L03818, 2008.

Engelhart, G. J., Asa-Awuku, A., Nenes, A. and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, Atmos. Chem. Phys., 8, 3937-3949, 2008.

Facchini, M. C., Mircea, M., Fuzzi, S. and Charlson, R. J.: Cloud albedo enhancement by surface-active organic solutes in growing droplets, Nature, 401, 257-259, 1999.

Facchini, M. C., Decesari, S., Mircea, M., Fuzzi, S. and Loglio, G.: Surface tension of atmospheric wet aerosol and cloud/fog droplets in relation to their organic carbon content and chemical composition, Atmos. Environ., 34, 4853-4857, 2000.

Henning, S., Rosenørn, T., D'Anna, B., Gola, A. A., Svenningsson, B. and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, Atmos. Chem. Phys., 5, 575-582, 2005.

Huff Hartz, K. E., Rosenørn, T., Ferchak, S. R., Raymond, T. M., Bilde, M., Donahue, N. M. and Pandis, S. N.: Cloud condensation nuclei activation of monoterpene and sesquiterpene secondary organic aerosol, J. Geophys. Res., 110, D14208, 2005.

King, S. M., Rosenørn, T., Shilling, J. E., Chen, Q. and Martin, S. T.: Increased cloud activation potential of secondary organic aerosol for atmospheric mass loadings, Atmos. Chem. Phys., 9, 2959-2972, 2009.

Kiss, G., Tombácz, E. and Hansson, H.: Surface Tension Effects of Humic-Like Substances in the Aqueous Extract of Tropospheric Fine Aerosol, J. Atmos. Chem., 50, 279-294, 2005.

Köhler, H.: The nucleus in and the growth of hygroscopic droplets, Transactions of the Faraday Society, 32(2), 1152-1161, 1936.

Laaksonen, A. and McGraw, R.: Thermodynamics, gas-liquid nucleation, and size-dependent surface tension, Europhys. Lett., 35, 367-372, 1996.

Moldanova, J. and Ljungström, E.: Modelling of Particle Formation From NO3 Oxidation of Selected Monoterpenes, J. Aerosol Sci., 31, 1317-1333, 2000.

Moore, R. H., Ingall, E. D., Sorooshian, A. and Nenes, A.: Molar mass, surface tension, and droplet growth kinetics of marine organics from measurements of CCN activity, Geophys. Res. Lett., 35, 2008.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961-1971, 2007.

Petters, M. D., Wex, H., Carrico, C. M., Hallbauer, E., Massling, A., McMeeking, G. R., Poulain, L., Wu, Z., Kreidenweis, S. M. and Stratmann, F.: Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol- Part 2: Theoretical approaches, Atmos. Chem. Phys., 9, 3999-4009, 2009.

Prenni, A. J., Petters, M. D., Kreidenweis, S. M., DeMott, P. J. and Ziemann, P. J.: Cloud droplet activation of secondary organic aerosol, J. Geophys. Res., 112, D10223, 2007.

Raymond, T. M. and Pandis, S. N.: Cloud activation of single-component organic aerosol particles, J. Geophys. Res., 107, 4787-4794, 2002.

Schmelzer, J. W. P., Gutzow, I. and Schmelzer Jr., J.: Curvature-Dependent Surface Tension and Nucleation Theory, J. Colloid Interf. Sci., 178, 657-665, 1996.

Schwier, A. N., Viglione, G. A., Li, Z. and McNeill, V. F.: Modeling the surface tension of complex, reactive organic-inorganic mixtures, Atmos. Chem. Phys. Discuss., 13, 549-580, 2013.

Serry, F. M.: Improving the Accuracy of AFM Force Measurements: The Thermal Tune Solution to the Cantilever Spring Constant Problem, 2010.

Uddin, M. H., Tan, S. Y. and Dagastine, R. R.: Novel Characterization of Microdrops and Microbubbles in Emulsions and Foams Using Atomic Force Microscopy, Langmuir, 27, 2536-2544, 2011.

Wex, H., Petters, M. D., Carrico, C. M., Hallbauer, E., Massling, A., McMeeking, G. R., Poulain, L., Wu, Z., Kreidenweis, S. M. and Stratmann, F.: Towards closing the gap between hygroscopic growth and activation for secondary organic aerosol: Part 1- Evidence from measurements, Atmos. Chem. Phys., 9, 3987-3997, 2009.

Yazdanpanah, M. M., Hosseini, M., Pabba, S., Berry, S. M., Dobrokhotov, V. V., Safir, A., Keynton, R. S. and Cohn, R. W.: Micro-Wilhelmy and Related Liquid Property Measurements Using Constant-Diameter Nanoneedle-Tipped Atomic Force Microscope Probes, Langmuir, 24, 13753-13764, 2008.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

Table 1. Surface tension of bulk liquids used for standardization, measured by the Wilhelmy plate. Averages reported as "average +/- standard error." 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**

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

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**

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

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.

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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

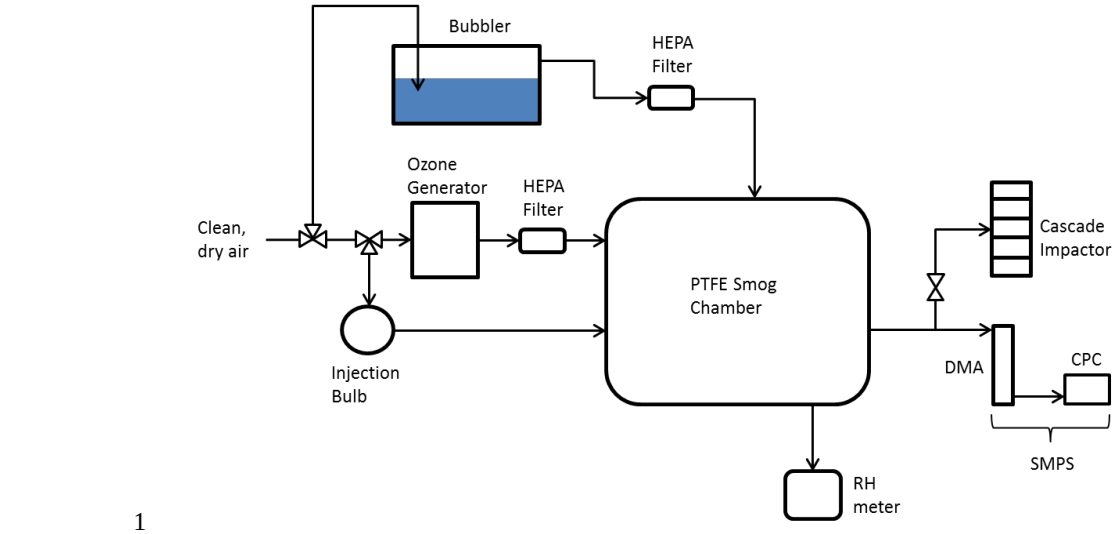

Figure 1. Experimental setup used to generate and collect oxidized α-pinene particles. The smog chamber is initially flushed with dry or wet air. Once the relative humidity in the chamber is established, particles are generated in the smog chamber by mixing α-pinene and ozone. Resulting particles are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

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

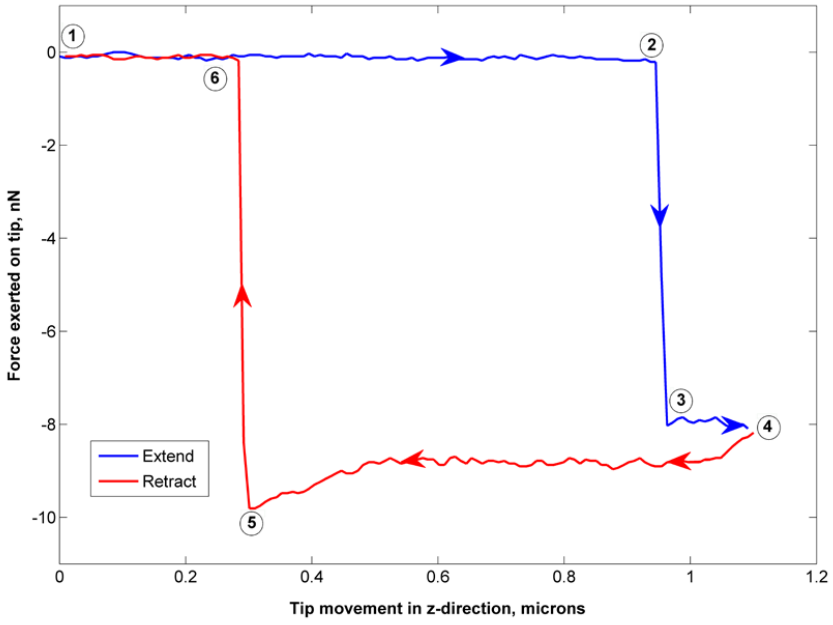

Figure 2. A typical force curve obtained using NaugaNeedle NN-HAR-FM60 probes and an atomic force microscope. The blue line indicates the probe approaching the sample, and the red line indicates the probe retracting from the sample. At point 1, the nanoneedle is approximately 1 micron from the surface 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.

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-35, 2016
Manuscript under review for journal Atmos. Chem. Phys.
Published: 19 January 2016

Atmospheric Chemistry and Physics Discussions

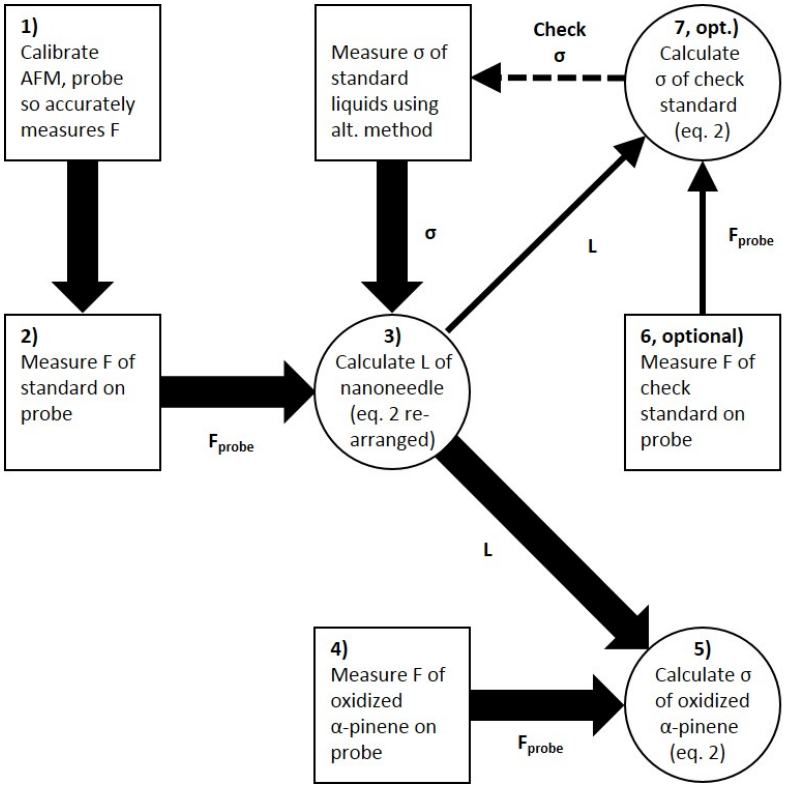

Figure 3. Procedure used to determine the surface tension of oxidized α-pinene particles using the AFM. The cantilever's spring constant was determined (step 1), which allowed the AFM to obtain force curves. Force curves of a liquid standard were obtained (step 2), and the nanoneedle's wetted perimeter 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).