SCANNING MOBILITY PARTICLE SIZER™ (SMPS™) SPECTROMETER NANOPARTICLE AGGREGATE MOBILITY ANALYSIS SOFTWARE MODULE

APPLICATION NOTE SMPS-002

Introduction

Urban ultrafine atmospheric aerosol and particle emissions from combustion sources such as diesel engines are typically low fractal dimension aggregates ($D_f \leq 2$) composed of spherical primary particles with diameter 5 to 50 nm. The nanoparticle aggregates are also present in several nanomaterial production processes such as manufacturing carbon black, titania and fumed silica. TSI Scanning Mobility Particle Sizer™ (SMPS™) spectrometer is commonly used to measure size distributions for these applications and more. The SMPS™ spectrometer uses electrical mobility to measure the particle size. This technique utilizes a bipolar charger to impart a known charge distribution on the aerosol sample. The particles are then classified according to their ability to traverse an electric field. The most common method of interpreting electrical mobility analysis to obtain size (in the SMPS™ spectrometer, as well as other commercially available electrical mobility analyzers), is based on a spherical particle model, including an expression for the drag coefficient over a wide range of Knudsen numbers (*Kn*) and the bipolar charging efficiency of spherical particles. While this method is appropriate for sizing spherical particles, it leads to errors in the mobility size data interpretation for aggregates, and subsequent calculations of surface area and volume (and hence mass) distributions.

A new method for analyzing mobility of nanoparticle aggregates for a limiting case of idealized aggregates ($D_f \leq 2$) has been developed (Lall and Friedlander, 2006 a) and has been recently incorporated in the Aerosol Instrument Manager® Software (version 8.0) for TSI Model 3936 series SMPS™ spectrometer. This method yields a more accurate estimate of the number, surface area and volume distributions of nanoparticle aggregates. The mobility of aggregates measured by an SMPS™ spectrometer is processed by a two module approach: *one module for the drag on the aggregates and the other for aggregate charging efficiency*. This method requires the user to input the average primary particle size of the aggregate. The average primary particle size can be measured by electron microscopy or, if available, taken from published literature. The TSI Model 3089 Nanometer Aerosol Sampler in combination with the electrostatic classifier and Differential Mobility Analyzer (DMA) can be conveniently used to collect charged particles on a microscope grid for electron microscopy. Some literature resources for information on nanoparticle aggregate characteristics are papers by Barone *et al.* (2006), Xiong and Friedlander (2001), and Park *et al.* (2004 a, b).

This application note discusses the theory of idealized aggregates, basic assumptions and implementation in the new updated Aerosol Instrument Manager® software module. We also discuss user operation of the software module and an example of analyzed data.

Note: *The software module may be used for post-processing of collected SMPS™ data, including data previously collected by older versions of Aerosol Instrument Manager® software.*

Theory

Assumptions—Limiting case of Idealized Aggregates

The nanoparticle aggregate mobility analysis software module analyzes the SMPS™ data for aggregate number, surface area and volume (mass) distributions based on certain assumptions. The basic assumptions used in the calculations are as follows:

1. Aggregates are composed of primary particles all of which have the same (known) diameter.
2. The primary particles that compose the aggregates are much smaller than the mean free path of the surrounding gas ($Kn >> 1$).
3. The total surface area of an aggregate can be obtained by summing over all primary particles in the aggregate. This is the maximum surface area which neglects the reduction due to necks between the primary particles.
4. Aggregates are "transparent", that is, (nearly) all surfaces are directly exposed to collisions with molecules of a surrounding gas. This is an acceptable approximation for aggregates with fractal dimensions less than about two.
5. Two *singly* charged particles, an aggregate and a sphere, trace the same path in the classifier if their migration velocities are equal: Both are said to have the same mobility diameter. The Brownian diffusive spread is neglected.
6. Only ultrafine aerosol particles enter the mobility analyzer. Larger particles are removed by a device (e.g., an impactor) upstream of the SMPS system.

Calculations

The nanoparticle aggregate mobility analysis method is organized into a two-module approach (as shown in Figure 1) for calculating aggregate number, surface area and volume distributions from DMA mobility data.

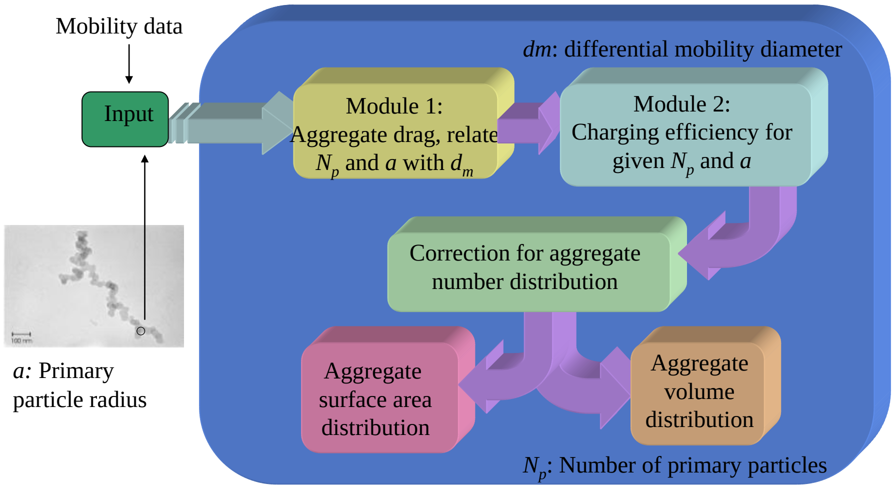

Figure 1. Two module approach for nanoparticle aggregate mobility analysis. Courtesy: Lall, *et al., 2006 c*

Module 1: Aggregate Drag

Consider an aggregate composed of N_p particles of radius a and a spherical particle of diameter d_m, both with unit charge. If the two have same migration velocity, then by equating the drag forces, we get

$$\frac{d_m}{C(d_m)} = \frac{c^* N_p a^2}{3\pi\lambda} \qquad (1)$$

Where, C is the slip correction, c^* is the dimensionless drag force and λ is the mean free path of the gas. The value of c^* is 6.62 (Chan and Dahneke, 1981) for aggregates oriented parallel to the direction of motion relative to gas and 9.17 (Dahneke, 1982) for aggregates oriented perpendicular to the direction of motion. The method holds well for $N_p > 10$. For aggregates with $D_f \leq 2$, using equation 1, the number of primary particles in an aggregate with primary particle size in the free molecular regime can be related to the diameter of a sphere even in the transition regime ($Kn \sim 1$).

Module 2: Charging Efficiency

The charging efficiency is the fraction of the particles of a given size that have a certain number of charges at equilibrium. The fraction of spheres and aggregates that assume unit charge after bipolar charging in general differ. Expressions for calculating the charge distributions are needed for both. The bipolar charging efficiency of spheres used in the Aerosol Instrument Manager software is given by the Fuchs charge distribution. The charging efficiency of aggregates, η_{agg}, (Wen *et al.*, 1984) is given as:

$$\eta_{agg} = \frac{e}{\left(\pi D_{qe} kT\right)^{\frac{1}{2}}} \exp\left[-\frac{\left(n_p - \bar{n}_p\right)^2 e^2}{D_{qe} kT}\right] \qquad (2)$$

Where,

n_p is the number of elementary charges

$\bar{n}_p$ is the median charge number

e is the electronic charge

k is the Boltzmann's constant

T is the absolute temperature

D_{qe} is the charging equivalent diameter ($N_p \geq 10$)

$$D_{qe} = \frac{2aN_p}{\ln(2N_p)} \qquad (3)$$

The median charge number is given by the following equation:

$$\bar{n}_p = \frac{D_{qe} kT}{2e^2} \ln\left(\frac{N_+ Z_+}{N_- Z_-}\right) \qquad (4)$$

Where,

N_+ / N_- is the ion concentration ratio

Z_+ / Z_- is the ion mobility ratio, For air, this ratio is usually taken to be 1.4/1.6

From equations 1 to 4, the charge distribution for aggregates can be determined as a function of the mobility diameter.

Number, surface and volume distribution of aggregates

Only a fraction of the charged particles pass through the DMA. The true number of spheres or aggregates is obtained by correcting for their charging efficiencies. For a given number of spheres or aggregates that are detected at the exit from the DMA per unit volume, the true number concentrations of aggregates and spheres will differ because of different charging efficiencies. The algorithm used to calculate the number distribution of aggregates (n_{agg}) from DMA mobility data is identical to the one used for spheres except aggregate charge distribution described in equation 2 is used instead of Fuchs charge distribution. Wang and Flagan (1990) describes in detail the data inversion algorithm used in the Aerosol Instrument Manager® software to derive number based size distributions.

The surface area distribution (A_{agg}) with respect to the mobility diameter can be obtained from number distribution for aggregates from the expression:

$$A_{agg}(d_m) = n_{agg}(d_m) N_p(d_m) 4\pi a^2 \qquad (5)$$

Similarly, the volume distribution (V_{agg}) with respect to the mobility diameter can be obtained from the expression:

$$V_{agg}(d_m) = n_{agg}(d_m) N_p(d_m) \left(4\pi a^3 / 3\right) \qquad (6)$$

The theory of idealized aggregates has been experimentally verified by Lall *et al.* (2006 b).

Software Operation

The nanoparticle aggregate mobility analysis module is a part of the Aerosol Instrument Manager® software for Model 3936 series SMPS™ spectrometer. The user may select the nanoparticle aggregate mobility analysis by checking the appropriate box in the physical parameters tab of the software. The physical parameters tab is located in the "Properties" section under both the File and Run menus. This may be done either before or after data collection. To revert back to spherical analysis method, the user needs to uncheck the box. This type of user interface facilitates comparison of both types of data—data obtained with spherical model as well as the data analyzed by nanoparticle aggregate model.

Once the check box is checked, the user needs to input primary particle diameter (in units of nanometers) of the aggregate; the default value is set to 10 nm. The user may also select the aggregate orientation (parallel or random with respect to the electric field). By default the software is set for parallel orientation. All electrically conducting aggregates tend to align parallel to the electric field due to the interaction of the induced dipole with the field (Stober, Boose, & Prodi, 1974). Diesel exhaust, ambient particles as well as most other ultrafine particles are conductive, and thus have parallel orientation.

The nanoparticle aggregate mobility analysis software module may be used for post-processing of previously collected SMPS™ data, including data previously collected by older versions of Aerosol Instrument Manager® software. It simply provides an alternative processing of the same primary data.

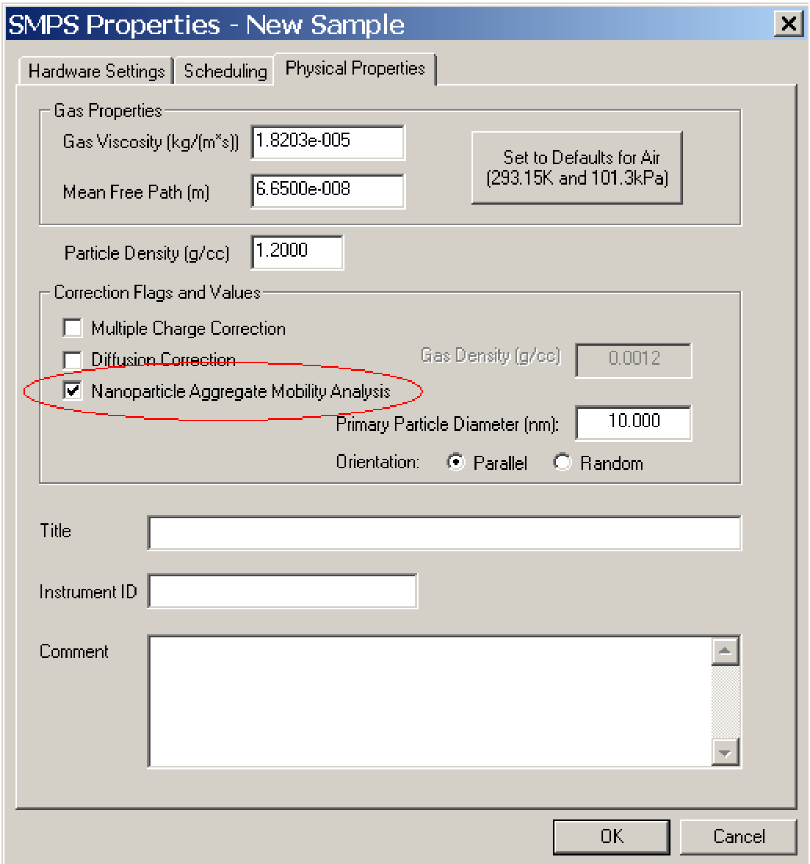

Figure 2. Physical properties tab of the Aerosol Instrument Manager® software showing the nanoparticle aggregate mobility analysis module user interface.

Note: *Nanoparticle aggregate mobility analysis software module was designed and validated for use with the Model 3080 Classifier Platform only.*

Example

Figures 3a-c depict the comparison of number, surface area and volume based mobility diameter distributions, respectively, of diesel exhaust aggregates. The DMA calibration based on spherical particles is compared with the nanoparticle aggregate model based analysis using Aerosol Instrument Manager® software. This example shows that the spherical model under estimates the surface area and greatly over estimates the volume (hence, mass) concentrations of diesel nanoparticle chain aggregates. The total number concentration based on aggregate model was found to be in good agreement with that measured directly by a CPC (Lall *et al.,* 2006 c).

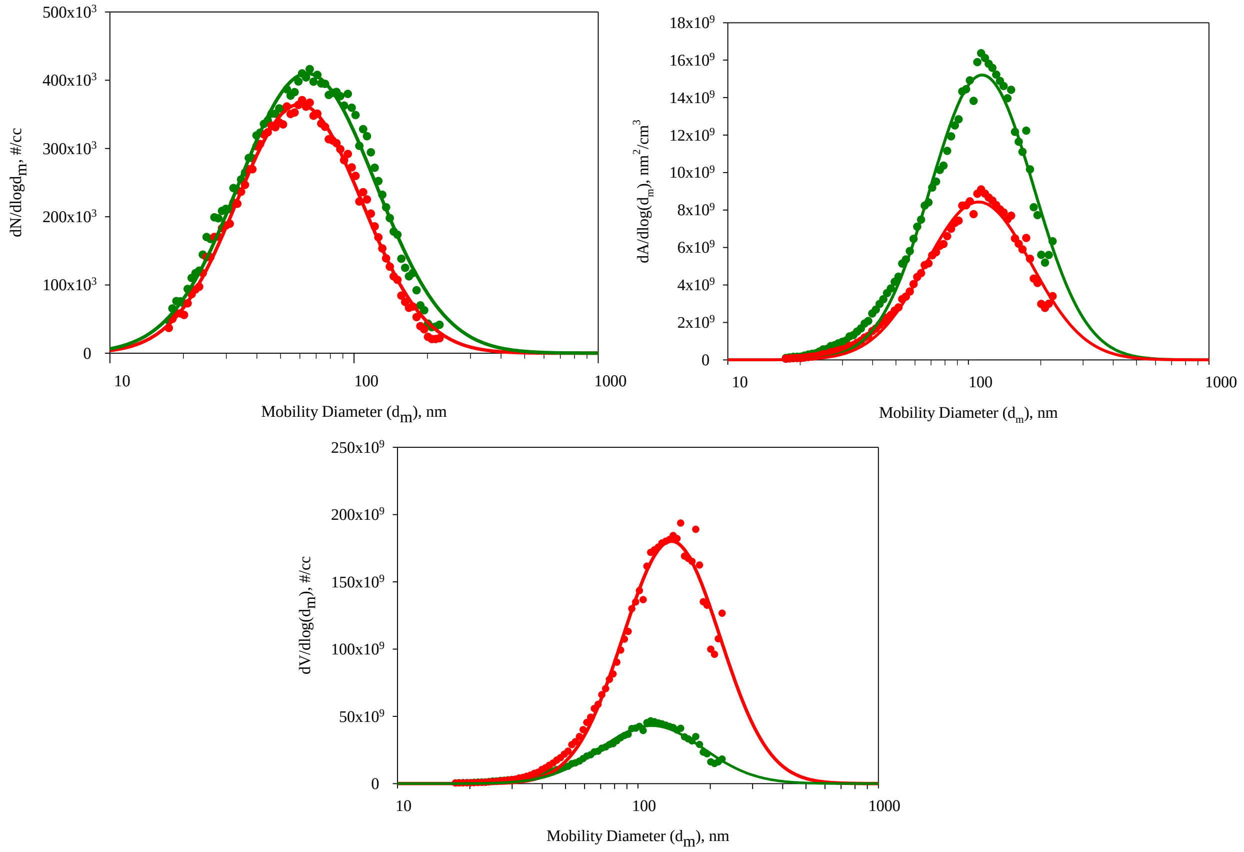

Figure 3. Aggregate distribution functions based on standard calibration for spheres (Red) compared with the distributions based on the idealized aggregate theory (Green). Primary particle diameter = 17 nm, aggregate orientation: parallel to the electric field. (a) Number Distributions, (b) Surface area distributions and (c) Volume distributions. Courtesy: Lall *et al.,* 2006 c.

Summary and Conclusions

A new method for nanoparticle aggregate mobility analysis for a limiting case of idealized aggregates ($D_f \leq 2$) has been developed. This method provides a more accurate estimate of number, surface area and volume (hence, mass) distributions of nanoparticle aggregates. The nanoparticle aggregate mobility analysis method has been recently incorporated in the Aerosol Instrument Manager® Software for TSI Model 3936 series SMPS™ spectrometer. The software module may be used for post-processing of collected SMPS™ data, including data previously collected by older versions of Aerosol Instrument Manager® software. The updated Aerosol Instrument Manager® software (version 8.0) will be available starting October 1, 2006. Existing SMPS customers may upgrade their Aerosol Instrument Manager® software with the new nanoparticle aggregate mobility analysis module for a nominal fee.

Note: *The nanoparticle aggregate mobility analysis software module is compatible with all (new and old) TSI model 3936 series component SMPS™ systems, however, cannot be used with TSI Model 3034 single box SMPS™ systems.*

References

Barone, T. Lall, A. A. Zhu, Y., Yu. R., and Friedlander, S. K. (2006) Inertial Deposition of Nanoparticle Chain Aggregates: Theory and Comparison with Impactor Data for Ultrafine Atmospheric Aerosols. J. Nanoparticle Res. DOI: 10.1007/s11051-006-9128-z. *In press*.

Chan, P., and Dahneke, B. (1981). Free-molecule Drag on Straight Chains of Uniform Spheres. *J. Appl. Phys.* **52**, 3106.

Dahneke, B. (1982). Viscous resistance of straight-chain aggregates of uniform spheres. *Aerosol Sci. and Technol.,* ***1,*** 179*.*

Lall, A. A. and Friedlander, S. K. (2006 a) On-line Measurement of Ultrafine Aggregate Surface Area and Volume Distributions by Electrical Mobility Analysis: I. Theoretical Analysis. *J. Aerosol Sci.* **27**, 260.

Lall, A. A., Seipenbusch, M., Rong, W. and Friedlander, S. K. (2006 b) On-line Measurement of Ultrafine Aggregate Surface Area and Volume Distributions by Electrical Mobility Analysis: II. Comparison of Theory and Measurements. *J. Aerosol Sci.* **27**, 272.

Lall, A.A., Robertson W.H., Sahay K. and Friedlander, S.K. (2006 c) New interpretation of DMA data that makes realistic characterization of diesel emission possible: Theory of idealized aggregates. Poster presentation at 10th ETH-Conference on Combustion Generated Nanoparticles August 21–23, 2006 at ETH Zentrum, Zurich, Switzerland.

Park, K., Kittelson, D. B., McMurry, P. H. (2004a) Structural Properties of Diesel Exhaust Particles Measured by Transmission Electron Microscopy (TEM): Relationships to Particle Mass and Mobility. *Aerosol Sci. Technol*. **38**, 881.

Park, K., Kittelson, D. B., Zachariah, M. R. and McMurry, P. H. (2004b) Measurement of Inherent Material Density of Nanoparticle Agglomerates*. J. Nanopart. Res.* **6**, 267.

Stöber, W., Boose, C., and Prodi, V. (1974). Über die Orientierung und den dynamischen Formfaktor von kettenförmigen Aerosolteilchen in Ladungsspektrometern. *Water, Air and Soil Pollution*, ***3***, 493.

Wang, S. C. and Flagan, R. C. (1990). Scanning Electrical Mobility Spectrometer. *Aerosol Sci. and Technol.* **13**, 230.

Wen, H. Y., Reischl, G. P., and Kasper, G. (1984). Bipolar diffusion charging of fibrous aerosol particles—I. Charging theory. *J. Aerosol Sci.*, **15**, 89.

Xiong, C., and Friedlander, S. K. (2001) Morphological Properties of Atmospheric Aerosol Aggregates. *Proc. Natl. Acad. Sci.,* U.S.A **98,** *11851.*

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