Nanometer Scale Particulate Defining Particle Diameter

Model 3757

Application Note 3757-002 (A4)

Introduction

Below 2 nm, the concept of particle size becomes complex. In aerosol science, sub-micrometer particles are often sized by measuring their electrical mobility diameter. In other disciplines such as chemistry or physics, it is common to measure the mass of a molecule or particle and calculate its corresponding mass/volume/geometric diameter. As aerosol measurement instrumentation technology is pushed to smaller particle sizes, it is now possible to measure molecules and clusters. As a result, it is necessary to consider the definition of particle diameter when describing the size of the particles measured.

Definition of Electrical Mobility Diameter

Particle mobility is defined as the relative ease of producing steady motion for an aerosol particle (Hinds, 1999). Electrical mobility is the velocity of a charged particle in an electric field of unit strength. The equation for calculating electrical mobility was determined by Millikan's oil drop experiments and can be derived by balancing the viscous drag force (Stokes' drag force) on a particle with the electrostatic force on a particle, assuming the particle is spherical. Equation 1 is known as the Millikan model:

$$Z = \frac{V_{TE}}{E} = \frac{neC_c}{3\pi\eta d_e}$$ **Equation 1**

Where:

- Z = Electrical mobility of the particle
- V_{TE} = Terminal electrostatic velocity of the particle
- E = Strength of the electric field
- n = Number of charges per particle
- e = Elementary unit of charge
- C_c = Cunningham slip factor (dependent on particle diameter)
- η = Viscosity of surrounding gas
- d_e = Electrical mobility diameter of the particle

The electrical mobility, Z, can be measured using a Scanning Mobility Particle Sizer™ (SMPS™) spectrometer and assuming the particle is singly charged, can be solved for electrical mobility diameter as in Equation 2.

$$d_e = \frac{neC_c}{3\pi\eta Z}$$ **Equation 2**

Definition of Mass Diameter

Mass, volumetric, or geometric diameter all refer to the same parameter. To follow the nomenclature used by Tammet, throughout this document we will refer to this parameter as "mass diameter."

The mass diameter is determined by: measuring the mass of a particle, and then assuming the particle is spherical with a known density, ρ. The mass diameter can then be calculated using Equation 3.

$$d_m = \left(\frac{6m}{\pi\rho}\right)^{\frac{1}{3}}$$ **Equation 3**

Where:

d_m = mass diameter (also known as geometric, or volume diameter)
m = Mass of the particle
ρ = Particle density

Discrepancies between Mass and Electrical Mobility Diameter

The Millikan equation is applicable when the size of ambient gas molecules is negligible as it assumes that particles and gas molecules collide elastically. However, as particle sizes approach the size of gas molecules the collisions are no longer elastic (Tammet, 1995).

To account for the departure from elastic collisions as particle size approaches the size of gas molecules, Tammet proposed replacing the particle diameter, d_e in Equation 1 with the collision distance, 2δ, calculated using Equation 4.

$$\delta = \frac{d_m + h + d_g}{2}$$ **Equation 4**

Where:

δ = Half of the collision distance
d_g = Diameter of the surrounding gas molecules
h = "Extra distance" accounting for effects such as Van der Waals forces and other effects not considered, determined empirically.

Tammet's modified Millikan equation is simplified by combining d_g and h into a single empirically derived term, the effective gas diameter, D_g.

NOTE: Literature refers to the new term as simply d_g; however, to avoid confusion with d_g in Equation 4, here we will refer to this updated term (d_g+h) as D_g.

This updated form of the Millikan equation is referred to as the constant-updated Millikan model:

$$Z = f_M(p, T, d_m + D_g) = \frac{neC_c}{3\pi\eta(d_m + D_g)}$$ **Equation 5**

Where:

p = Pressure
T = Temperature
D_g = Effective diameter of gas molecules (determined empirically)

Using Equation 1 and Equation 5 d_e and d_m can be correlated as in Equation 6.

$$d_e = d_m + D_g$$ **Equation 6**

Ku et al. (2009) empirically solved for D_g using a variety of materials and determined the effective gas diameter to be 0.300 nm. Larriba et al. (2011) confirmed that the effective gas diameter of 0.3 nm is accurate to within 1% over the size range of 1.4 nm to 3 nm (mass diameter).

Implications for TSI® Model 3757 Nano Enhancer

The TSI® Model 3757 builds on the success of its predecessor, the 3757 which was originally developed in conjunction with the University of Minnesota based on the work of Iida et al. (2009). It uses diethylene glycol to initiate the particle growth on sub 2 nm particles. When paired with a conventional CPC, the Model 3757 has a 50% detection efficiency (D_{50}) at 1.4 nm electrical mobility diameter, corresponding to a mass diameter of 1.1 nm using Equation 6 as shown in Equation 7.

$$d_m = d_e - D_g = 1.4\ nm - 0.3\ nm = 1.1\ nm$$ **Equation 7**

References

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