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A simple semi-empirical model for effective density measurements of fractal aggregates

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ABSTRACT

Effective density measurements are used extensively to convert submicron particle sizes based on a particle's mobility diameter into mass. Measurements of the effective density also provide information concerning the particle morphology. For example, the effective density curves of fractal aggregates reveal a scaling factor that seems to correlate with the fractal dimension of the particles. The present paper proposes a simple semi-empirical model that permits the quantitative interpretation of these measurements to determine parameters such as the fractal dimension, the primary particle size, and the bulk density of an aggregate particle. The proposed model is based on the assumption that the hydrodynamic drag force of an aggregate is proportional to the drag force applied to isolated primary spheres and to the number of primary spheres in the aggregate at power α. The model was applied to soot particles produced by either a spark discharge (PALAS GFG1000) or by combustion (miniCAST 5206)—both mechanisms enable the generation of aggregates or agglomerates with very different primary sphere diameters. The proposed model showed a good fit for all of the effective density measurements obtained in this study; the α parameter was driven by the aggregate fractal dimension and by the Knudsen number that was determined based on the primary particle diameter. Finally, for a known primary particle diameter, the fractal dimension and the bulk density were determined successfully with the proposed model.

1. Introduction

The effective density (ρ_{eff}) of a particle is defined as the ratio of its mass to the volume of a sphere whose diameter is the mobility equivalent diameter. The first ρ_{eff} measurements of submicron aerosols where achieved by coupling a differential mobility analyzer (DMA) with an electrical low pressure impactor (ELPI) in a serial configuration (Maricq & Xu, 2004; Van Gulijk, Marijnissen, Makkee, Moulijn, & Schmidt-Ott, 2004; Virtanen, Ristimäki, & Keskinen, 2004). Recently, measuring techniques have been improved by coupling a DMA with either an aerosol particle mass analyzer (APM) or a centrifugal particle mass analyzer (CPMA) (Charvet, Bau, Paez Coy, Bémer, & Thomas, 2014; Durdina et al., 2014; Lee, Chang, Ogi, Iskandar, & Okuyama, 2011; Johnson, Symonds, & Olfert, 2013; McMurry, Wang, Park, & Ehara, 2002; Olfert, Reavell, Rushton, & Collings, 2006; Rissler et al., 2013).

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For spherical and non-porous particles, ρ_{eff} corresponds to the particle "bulk" density because, in this case, the mobility diameter corresponds to the geometrical diameter. The effective density ρ_{eff} is size-dependent (DeCarlo, Slowik, Worsnop, Davidovits, & Jimenez, 2004; Maricq & Xu, 2004) for non-spherical particles such as soot particles characterized by a ramified structure: ρ_{eff} decreases when the particle size increases. This behavior correlates with the shape factor concept (DeCarlo et al., 2004). For cases in which a power-law relationship exists between the mass and the size of the particle (mobility diameter in this case), ρ_{eff} exhibits a linear behavior in a log–log representation with the slope expected to be equal to D_f-3, where D_f is the fractal dimension (Virtanen et al., 2004; Van Gulijk et al., 2004).

For fractal aggregates, ρ_{eff} measurements were used initially to determine the fractal dimension in order to characterize the particle morphology. Compared with transmission electron microscopy (TEM), this *in-line* method is advantageous because it does not require sampling of the particles on TEM grids. Such an *in-line* approach also avoids the time-consuming and tedious image analysis that results from the use of 2D–3D correction laws. Nevertheless, various studies have demonstrated that the fractal dimensions obtained with this method either become size dependent (DeCarlo et al., 2004) or are consistently larger than those determined through TEM analysis (Park, Kittelson, & McMurry, 2004). This discrepancy occurs because the fractal law is based on a relationship between the particle mass and a *geometrical* size parameter (e.g., the gyration radius) whereas the mobility diameter also depends on the particle morphology and on thermodynamical considerations (i.e., the flow regime) (Schmid, Karg, Hagen, Whitefield, & Ferron, 2007; Sorensen, 2011). To avoid misinterpretation, recent papers investigating the measured slope in a log–log plot no longer refer to the fractal dimension but instead use the term "scaling exponent" (Sorensen, 2011). Nevertheless, its interpretation remains essentially qualitative.

Additionally, ρ_{eff} measurements can be used to link the mobility diameter to a corresponding mass. In fact, if ρ_{eff} is known, number-based size distributions expressed in the form of a mobility diameter can be converted to mass concentrations, which make it possible to evaluate mass emission factors and other data. Nevertheless, effective density curves seem to be considerably material-dependent. In the case of soot particles, whose morphology remains essentially the same irrespective of the fuel and the combustion facility, ρ_{eff} curves can present very differing trends. Consequently, it is impossible to systematize mass interpretations based on size distributions. On the other hand, the variability of ρ_{eff} curves suggests that effective density measurements could provide valuable information. This idea is supported by Mamakos, Khalek, Giannelli, and Spears (2013) who conclude from their analysis "the generally overlooked absolute value of the effective density may actually contain more valuable information on particle morphology than the widely employed mass-mobility exponent".

In the interest of continuously improving the quantitative interpretation of soot particle ρ_{eff} measurements, the present study measured the effective density of carbonaceous nanoparticle aggregates generated by miniCAST and spark discharge generators GFG1000. The selected set points of these systems allowed us to generate aggregates with a well-characterized morphology and a controlled quantity of organic compounds. Specifically, we considered diameters ranging from 7 nm to 36 nm for the primary particles that form these aggregates/agglomerates. The semi-empirical model proposed in this paper—which describes the relationship between the mobility diameter D_m and the number of primary spheres per aggregate N_p—showed a good fit with our measurements. The fitting procedure used with the effective density data allowed us to evaluate the aggregate bulk density as well as a new power-law parameter discussed in the following. This approach could potentially provide a foundation for a more quantitative interpretation of ρ_{eff} measurements because empirical unification relies on physical parameters such as the particle primary diameter D_p, the bulk density ρ_{pp}, and the mass fractal dimension D_f.

2. Experimental apparatus and ρ_{eff} measurements

This study used four particle sources to generate aerosols of nanoparticles. To validate the technique, we chose diethyl phthalate (DEP) and polystyrene latex spheres (PSL) because their airborne dispersion (with a TSI 3076 collision-type atomizer and a TSI 3062 diffusion dryer) generates spherical nanoparticles with a well-known bulk density ($\rho_{DEP} = 980\ \text{kg/m}^3$ and $\rho_{PSL} = 1050\ \text{kg/m}^3$). Two apparatuses were used to generate aggregates of nanoparticles: A PALAS GFG 1000 equipped with pure graphite electrodes produced amorphous particles made of very small primary spheres ($D_p = 7$ nm) whose bulk density is estimated at 2000 kg/m^3 (Schnaiter et al., 2003). Soot particles were generated with a miniCAST 5206 commercial burner (Jing Ltd.). Based on a propane-air diffusion flame quenched by a nitrogen flux, this device is capable of producing a very stable and repeatable flux of particles, allowing us to control the size and composition of generated soot particles. We selected four operating conditions (Table 1). For miniCAST soot, the primary particle size distribution was determined through automated image analysis described in Bescond et al. (2014). We considered the diameter of the average-mass primary particle D_p (the particle size whose mass multiplied by the total number of primary particles is equal to the total mass). This diameter is calculated based on the count median diameter and the geometric standard deviation according to the Hatch–Choate equation. A classical analysis of threshold TEM images was used to determine the fractal properties of CAST soot particles (Brasil, Farias, & Carvalho, 1999; Köylü, Faeth, Farias, & Carvalho, 1995; Ouf, Yon, Ausset, Coppalle, & Maillé, 2010). The count median diameter and the geometric standard deviation of the primary particles composing the GFG1000 agglomerates are reported in Table 1; these values were originally determined by Thomas, Ouf, Gensdarmes, Bourrous, and Bouilloux (2014) and Wentzel, Gorzawski, Naumann, Saathoff, and Weinbruch (2003). Because very few fractal analyses are found in the literature for these particles and because observations with high-resolution transmission electronic microscopy are impaired by an inadequate resolution for such amorphous particles, we