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Bivariate population dynamics simulation of fractal aerosol aggregate coagulation and restructuring

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Abstract

In the present work a previously developed model of fractal aggregates evolution from an initial morphology (as described by their fractal dimension) towards to that defined by the prevailing coagulation mechanism is extended in two directions. Firstly a new constitutive law for the fractal dimension of the aggregate resulting from a coagulation event is generalized and secondly a restructuring mechanism is added to the population balance model. Several techniques from detailed Monte Carlo simulations to simple monodisperse (in both volume and fractal dimension) approximations are employed for the solution of the corresponding bivariate coagulation equation. The parametric evolution of the fractal dimension of aggregates for the case of Brownian coagulation in the continuum regime is studied and the results indicate that the existence of restructuring makes the evolution dynamics of the fractal dimension distribution of the aggregate population much richer than in the case of simple coagulation examined previously. As an application of the present approach, the morphological data of Xiong and Friedlander [(2001) Morphological properties of atmospheric aerosol aggregates. Proceedings of the National Academy of Sciences of USA, 98, 11851–11856] on atmospheric aggregates are examined and are shown to be consistent with a combined coagulation–restructuring process.

Keywords: Fractal; Aggregates; Coagulation; Restructuring; Aerosol

1. Introduction

Aggregate morphology has an important effect on the transport, optical, thermal and mechanical properties of aerosol particles and hence on the way that such particles impact the environment and public health (e.g. soot aggregate effects on climate and the human body), on the way such particles are measured in particle instrumentation as well as on the way such particles affect the properties of end products where they might be incorporated (e.g. pigments, fillers, electronic and catalyst particles). The morphology of aggregates consisting of a number n of smaller primary spherules of typical size α, is often characterized in terms of their fractal dimension D defined by

$$n = k\left(\frac{R}{\alpha}\right)^{D} \tag{1}$$

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where R is the aggregate radius. The prefactor k has a weak dependence on D (Naumann, 2003) but in many studies including the present it is taken as a constant.

Fractal aggregates are typically products of combustion processes and their "size" (e.g. as measured by their electrical mobility diameter) is typically less than 500 nm. The aggregate size distribution, is governed by the combined action of several phenomena (e.g. nucleation, vapor phase growth, coagulation, restructuring, deposition/collection processes). In principle, particle interactions can and will occur between particles of different morphologies (as described by their fractal dimension), either due to different histories of the respective particle populations (e.g. in an internal combustion engine cylinder, a turbulent combustor or in the atmosphere) or due to deliberate mixing of different particle populations, e.g. in an aerosol reactor. This in general will lead to a distribution of particle morphologies for the same particle size as demonstrated by Xiong and Friedlander (2001). These authors have measured employing electron microscopy and image analysis the fractal dimension and aggregate size (expressed by the number of primary particles) of different atmospheric aggregates and concluded that "... simulations of aggregate dynamics should take into account the distribution of D as well as aggregate size".

For a long time the general population balance equation (Friedlander, 1977) originating from Smoluchowski's description of the coagulation process has served as the main tool for the mesoscopic (mean field) simulation of particle population dynamics in several scientific disciplines (industrial and atmospheric aerosols, colloid science, polymer science, crystallization, powder technology, etc.). The main feature of this approach is that particles are described by only one variable (i.e. their size). When applied to fractal aggregates, the general population balance equation until very recently (Kostoglou and Konstandopoulos, 2001) was typically employed with a modified coagulation kernel that included a pre-specified fractal dimension for the entire aggregate population. The need for more advanced and realistic description of particulate processes in combination with the advent of computing power has made possible during the last 15 years the development of several models where particles are described by more than one variable, referred to as multivariate population dynamics. The additional to particle size variables depend on the specific particle and process characteristics simulated.

A bivariate description of particle population dynamics can be written in the form:

$$\begin{aligned}\frac{\partial f(x,p,t)}{\partial t} = \frac{1}{2}\int_{p_2}\int_{p_1}\int_0^\infty\int_0^\infty K(x_1,x_2,p_1,p_2)\delta(x-c_x(x_1,x_2))\delta(p-c_p(p_1,p_2,x_1,x_2))\\ \times f(x_1,p_1,t)f(x_2,p_2,t)\,\mathrm{d}x_1\,\mathrm{d}x_2\,\mathrm{d}p_1\,\mathrm{d}p_2\\ - f(x,p,t)\int_{p_1}\int_0^\infty K(x,x_1,p,p_1)f(x_1,p_1,t)\,\mathrm{d}x_1\,\mathrm{d}p_1 - \frac{\partial G(x,p)f(x,p,t)}{\partial p},\end{aligned} \tag{2}$$

where $f(x,p,t)$ is the probability density function for the number concentration of particles (described by their volume x and a second variable p), $K(x_1,x_2,p_1,p_2)$ is the coagulation rate between a particle with properties x_1, p_1 and a particle with properties x_2, p_2, δ is the Dirac delta function and the functions c_x, c_p are the values of x and p for the new particle resulting from the coagulation event. Particle volume conservation requires that $c_x(x_1,x_2)=x_1+x_2$. The function $G(x,p)$ provides the rate of any additional mechanism (independent from coagulation) which may affect the evolution of the second variable, p.

Important applications of Eq. (2) are found in the field of aerosol reaction engineering. In this case variable p is taken to be the aggregate surface area and the function $G(x,p)$ accounts for the phenomenon of sintering. Initially, it had been assumed that the coagulation kernel does not depend on the aggregate surface area. In this case the particle size distribution remains the same with the one resulting from the univariate coagulation equation and the bivariate equation was employed to provide the (one-way coupled) evolution of the particle surface area (Koch and Friedlander, 1990; Rosner and Yu, 2001; Tandon and Rosner, 1999). In more recent studies (Rosner and Pyykonen, 2002) two-way coupling between coagulation and sintering has been employed. Equation (2) has been also recently used for the simulation of powder aggregation via capillary forces (Biggs et al., 2003). Variable p in this case was taken to be the water content of the aggregate, which in turn determines the aggregation efficiency. In this application the function $G(x,p)$ describes condensation/evaporation processes on the aggregate. Other examples of the use of Eq. (2) are in the flocculation of paramagnetic particles where variable p is the particle magnetic susceptibility (Tsouris et al., 1995) and in the coalescence of emulsions where variable p is the particle surface potential (Hall et al., 1991).