Cambridge Centre for Computational Chemical Engineering

University of Cambridge

Department of Chemical Engineering and Biotechnology

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On the fractal dimension of soot particles

Markus Sander [1] , Robert I A Patterson [1] ,

Abhijeet Raj [1] and Markus Kraft [1]

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[1] Department of Chemical Engineering and Biotechnology
University of Cambridge
New Museums Site
Pembroke Street
Cambridge, CB2 3RA
UK
E-mail: mk306@cam.ac.uk

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Edited by
Cambridge Centre for Computational Chemical Engineering
Department of Chemical Engineering
University of Cambridge
Cambridge CB2 3RA
United Kingdom.

Fax: + 44 (0)1223 334796
E-Mail: c4e@cheng.cam.ac.uk
World Wide Web: http://www.cheng.cam.ac.uk/c4e/

Abstract

The aim of this work is to explore possible alternative explanations for the remarkably low fractal dimensions reported for soot particles by Chakrabarty et al. [Phys. Rev. Lett., 102(23):235504, 2009]. A stochastic population balance model has been developed and applied to simulate the formation of soot particles in a premixed laminar sooting flame. The model involves inception, coagulation, surface growth and condensation processes. The fractal dimension has been calculated using a double logarithmic plot of the number of primary particles against the radius of gyration and $\sqrt{LW}$ where L is the length and W the width of the projected particle. The limits of this technique are discussed by comparing fractal dimensions calculated for simulated particles.

The formation of fractal-like nanoparticles is an important process for many industrial processes. Soot nanoparticles are produced in large amounts and are dangerous for the environment and human health [8]. It is generally accepted that a soot particle is made of aggregated spherical primary particles which in turn consist of polycyclic aromatic hydrocarbons (PAHs) [2, 18]. The shape of the soot and other nano-particles is an important property, which has been widely investigated [7, 9, 10, 17] and can be described by the fractal dimension, D_f, which is usually between 1.7 and 1.9 [11, 15]. It is defined by a power law:

$$N = k_f \left(\frac{R_g}{d_p} \right)^{D_f} \tag{1}$$

where N is the number of primary particles, k_f the fractal prefactor, R_g the radius of gyration of the agglomerate and d_p the average diameter of the primary particles. The radius of gyration is defined by

$$R_g = \sqrt{\frac{\sum_{i=1}^{N} m_i r_i^2}{m_T}} \tag{2}$$

where m_T is the total mass of the soot aggregate and m_i the mass of primary particle i whose center is at a distance r_i of the center of mass.

The radius of gyration is hard to measure in an experiment, therefore other properties of the particles are used to determine the fractal dimension of a particle. Samson et al. [15] propose to use $\sqrt{LW}$ as an approximation for the radius of gyration, so that:

$$N \sim \left(\sqrt{LW} \right)^{D_f} \tag{3}$$

where L is the length and W the width of the 2D TEM image of the soot particle. Chakrabarty et al. [4] have recently reported an unexpectedly low fractal dimension of 1.2 for soot particles where the fractal dimension has been determined using relation (3). The aim of this work is to offer an alternative explanation for the unusual fractal dimensions reported by Chakrabarty et al. [4] by showing their data is consistent with simulations of particle growth carried out using a new stochastic particle model.

The model is based on a stochastic algorithm used to simulate the growth of soot particles in a premixed flame [12] and incorporates the evolution of PAHs using kinetic Monte-Carlo simulations [13, 16] involving a detailed description of the gas-phase flame chemistry proposed by Wang and Frenklach [19]. These PAHs can stick together according to a recently determined sticking probability [14]. The sticking of two PAHs is assumed to be an inception of a soot particle composed of one primary particle. The soot particles can grow by coagulating with other soot particles, by coagulating with other PAHs (condensation) and by particle gas-phase reactions. The structure of a soot particle formed from the coagulation of two smaller soot particles has been simulated by randomly rotating both colliding particles and moving one particle in a plane orthogonal to the collision direction before the coagulation.

It is assumed a soot particle

$$P = P(p_1, p_2, ..., p_n) \tag{4}$$

is composed of primary particles p_i which in turn are composed of PAHs,

$$p_i = p_i(PAH_1, PAH_2, ..., PAH_m) \quad i = 1, ..., n \tag{5}$$

where m is the number of PAHs in the i th primary particle p. The gas-phase species concentration and temperature profile have been calculated using PREMIX [6, 19]. An important property of the model is the collision rate for particles and PAHs which is calculated using the free molecular coagulation kernel:

$$K^{fm}(i,j) \propto \left(\frac{1}{m(i)} + \frac{1}{m(j)}\right)^{\frac{1}{2}} (d_c(i) + d_c(j))^2 \tag{6}$$

where $d_c(i)$ and $d_c(j)$ are the collision diameters of the colliding PAHs or particles P; $m(i)$ and $m(j)$ are the corresponding masses. The collision diameter of PAHs is calculated as

$$d_c^{PAH} = d_A \sqrt{\frac{2n_c}{3}} \tag{7}$$

where $d_A = 1.395\sqrt{3}$Å for a single aromatic ring and n_c is the number of carbon atoms in the PAH [5]. The collision diameter of a particle P is assumed to be the arithmetic mean of its volume V and its surface area A equivalent diameters

$$d_c^{part} = \left(\frac{3V}{4\pi}\right)^{\frac{1}{3}} + \left(\frac{A}{4\pi}\right)^{\frac{1}{2}}. \tag{8}$$

The particles interact according to the rates for different processes: particle inception, coagulation, condensation and surface growth:

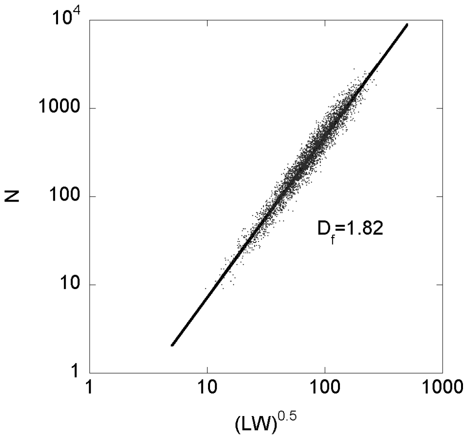
1. Inception: It is assumed that the successful collision of two PAHs creates a spherical soot particle P consisting of one primary particle p with the mass of the two colliding PAHs [1]:
$$PAH_1 + PAH_2 \rightarrow P(p_1). \tag{9}$$
The volume is calculated assuming a soot mass density of 1.8 g/cm^3. The collision efficiency is taken from [14].

2. Coagulation: Two colliding particles do not change shape, but stick together creating a bigger particle containing the primary particles of the two colliding particles:
$$P(p_1, ..., p_m) + P(p_1, ..., p_n) \longrightarrow P(p_1, ..., p_{n+m}). \tag{10}$$

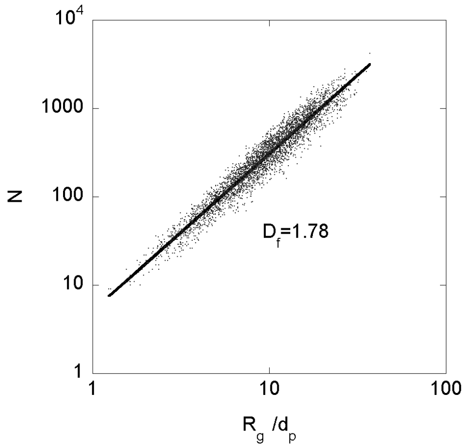
3. Condensation: The coagulation of a PAH with a particle is implemented by adding this PAH to a randomly chosen primary particle within the particle.

4. Particle gas-phase growth: The reaction of a soot particle with the gas-phase is incorporated by calculating the evolution of each PAH in a soot particle using a kinetic Monte-Carlo algorithm [13].

The fractal dimension of 4000 simulated particles has been calculated using Eq. (1) and relation (3) for a premixed laminar flame described in [14]. The radius of gyration of each particle has been determined using Eq. (2). The length and the width of the particle



(a)



(b)

Figure 1: *Double logarithmic plot of $\sqrt{LW}$ and R_g against the number of primary particles N.*

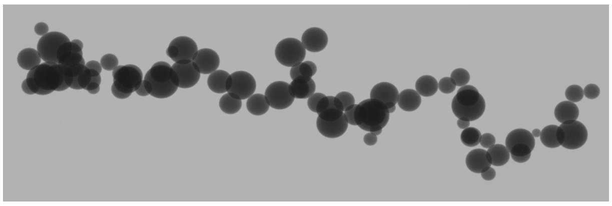
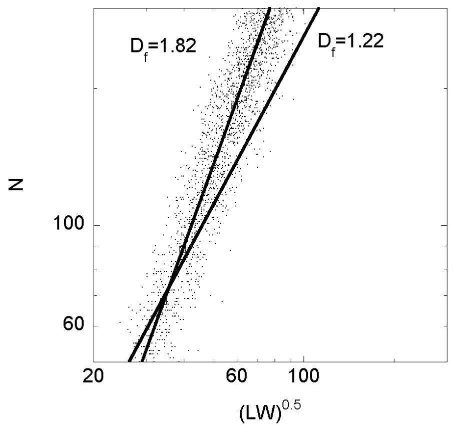


Figure 2: *A TEM-style image of a simulated particle with a fractal dimension of 1.42.*

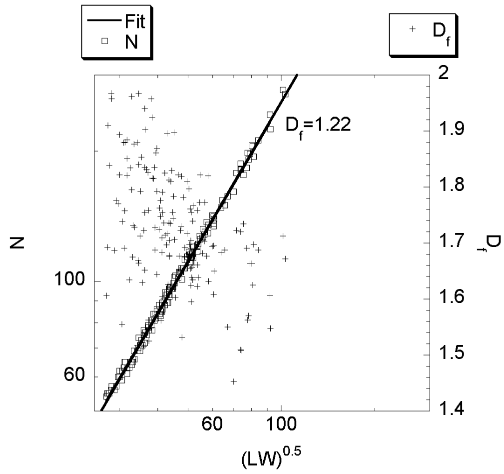
has been evaluated by rotating the particle such that the primary which is farthest away from the center of mass lies on the x axis and the center of mass has been shifted to the origin of the coordinate system. It is then projected into the x-y plane and the surrounding rectangle parallel to the x and y axis determines the particle's length L and width W. A double logarithmic plot of $\sqrt{LW}$ against the number of primary particles N of the soot particles reveals a fractal dimension of 1.82 (FIG. 1(a)). A fractal dimension of 1.78 has been determined using the radius of gyration (FIG. 1(b)). The corresponding fractal prefactor k_f is equal to 1.49. The fractal dimension is slightly larger using $\sqrt{LW}$, which has also been observed by Samson et al. [15].

The fractal dimension has also been calculated for each individual particle using Eq. (1). The distribution is almost exactly a Gaussian with mean 1.78 and standard deviation 0.1. The lowest observed fractal dimension is 1.42. This particle is shown in FIG. 2. Note that in the simulation the particles are formed by random coagulation without any force that aligns the particles.

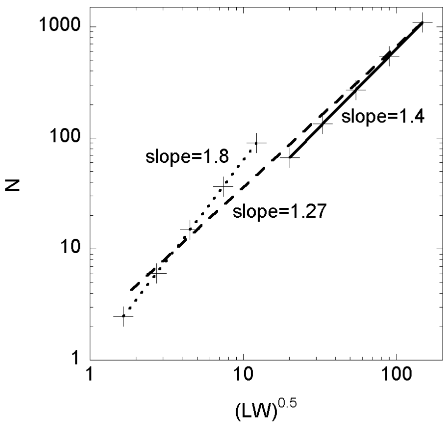
Chakrabarty et al. [4] reported soot particles with the unusually low fractal dimension of 1.2. However, the fractal dimension has only been determined by fitting a straight line into the double logarithmic plot of $\sqrt{LW}$ against the number of primaries N. The range of N in this fit was between approximately 40 and 300 primary particles for the particle



(a)



(b)



(c)

Figure 3: *(a) The particles of our simulation with a number of primary particles between 50 and 300. It is possible to select a subset of particles with an apparent fractal dimension of 1.22. (b)The dependence of the fractal dimension of the particles in the subset from their size is the reason for the apparent low fractal dimension. (c) A fictitious ensemble consisting of five particles with a fractal dimension of 1.8 and five with 1.4. The resulting fractal dimension would be 1.27.*

ensemble where they obtained a fractal dimension of 1.2. We want to present an explanation for the surprisingly low fractal dimension.

FIG. 3(a) presents the simulated particles which have a number of primary particles in the range of 40 to 300. A line with a slope of 1.22 has been placed in the ensemble such that the line is close to the line with a slope of 1.82 in the region of the small particles. The line is clearly far away from the original line with a slope of 1.82 for the large particles, however there are particles close to this line over the entire range. The particles close to this line (FIG. 3(b)) are a subset of the entire particle population that have an apparent fractal dimension of 1.22 using relation (3) despite the fact that no simulated particle has such a low fractal dimension. The average of the fractal dimension of the individual particles calculated with Eq. (1) is 1.73. The reason for the apparent low fractal dimension is a dependency of the fractal dimension on the size of the particles. The crosses in FIG. 3(b) show the individual fractal dimension of the particles calculated using Eq. (1). It is obvious that the distribution of the fractal dimension is not independent of the number of primary particles. The larger the particles are the narrower the distribution and the lower the average fractal dimension. This is due to the fact that the selected subset of particles is close to the line with a slope of 1.8 for the smaller particles whereas the larger particles are further away from the 1.8 line. In summary, the particles with an apparent fractal dimension of 1.22 change their fractal dimension from about 1.8 for the small particles to about 1.6 for the large particles. Fitting a straight line in such a fashion underestimates the fractal dimension.

The same point is illustrated in FIG. 3(c). Two groups of five particles have been generated. The five smallest particles have a fractal dimension of 1.8 and the five largest particles 1.4. However fitting a straight line to the entire 10 particles reveals a fractal dimension of 1.27.

Certainly our subset has been selected by forcing an apparent fractal dimension of 1.22. We propose that the selection technique of Chakrabarty et al. [3] selects just such a particle ensemble. The technique they have been using assumes that elongated particles with a low fractal dimension are more likely to be double charged. For smaller particles the distance between the charges is not going to vary much even for particles with different fractal dimensions. It is therefore more likely that the resolution of the double charge method with respect to fractal dimension is higher for larger particles where the distance between two charges can be much larger for varying fractal dimensions. It is even indicated by Chakrabarty et al. [4] that their separation method does not work for particles with a mobility diameter smaller then 200 nm. This would imply that the efficiency of selecting the most elongated particles increases with their size and hence the average fractal dimension decreases.

It seems therefore possible that the very low fractal dimensions observed by Chakrabarty et al. [4] can be explained entirely by sampling and process effects. The comparison of our calculated TEM in FIG. 2 with the TEM sample in FIG. 3 in [4] reveals a very similar structure and supports our argument.

In conclusion we have introduced a stochastic particle model including particle inception, coagulation, condensation and surface growth to calculate the fractal dimension of soot particles. It has been demonstrated that using a double logarithmic plot of $\sqrt{LW}$ against the number of primary particles N can be used to calculate the fractal dimension as long as the average fractal dimension is independent of the size of the particles. This is of course not necessarily the case due to either the way the measurements are taken or because of an intrinsic relationship between the fractal dimension of a particle and its size.

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