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In situ determination of the fractal dimensions of aerosol particles

E P Emets, A E Novoselova, P P Poluektov

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Abstract. A review is given of the available in situ methods for the diagnostics of fractal aerosol aggregates, which represent loose branched structures with scaling-invariant geometric characteristics. A new method for in situ determination of the fractal dimensions of particles is proposed: it is based on an analysis of the aerodynamic behaviour of aerosol particles in electric and gravitational fields, and also on the dependence of the particle density in a cluster on the distance from the cluster centre, which is typical of fractal objects.

1. Introduction

Aerosol particles representing fractal aggregates (fractal clusters) form in many processes, both in nature (formation of clusters in clouds, coagulation of smoke particles [1], etc.) and in technological treatments (for example, in the manufacture of commercial pigments [2, 3], blanks for fibre optics [3], ceramic materials [2], laser deposition of thin films, laser welding [4], etc.). Among the many diverse systems and phenomena in the surrounding world, demonstrating increasingly clearly the fractality of all nature, fractal clusters are among the topics that attract the greatest interest of researchers.

Fractal clusters are very loose structures formed by aggregation of small solid particles. Under real conditions in a gaseous medium they represent aerosol particles, which form by aggregation of primary spherical particles, produced in the course of evaporation of a solid surface by some method, and subsequent condensation of the vapour in the course of physicochemical transformations that occur in flames in the course of combustion of some materials [3, 5-8].

E P Emets, A E Novoselova, P P Poluektov A A Bochvar All-Russia Scientific-Research Institute of Inorganic Materials, ul. Rogova 5-a, 123060 Moscow Tel. (095) 190 85 59; (095) 190 82 27 Fax. 925 59 72 (A 39); 925 28 96 (A 39)

Received 17 December 1993; revision received 12 May 1994 Uspekhi Fizicheskikh Nauk 164 (9) 959-966 (1994) Translated by A Tybulewicz Physicochemical processes which occur in solutions are responsible for the nucleation and growth of fractal clusters in liquids.

Characteristic properties of fractal aggregates (scaling invariance, self-similarity, scaling dependence of the average particle density in a cluster on its size) have been discussed many times [1, 9, 10, etc.]. The interest in the remarkable properties of fractal clusters is quite understandable. It can be attributed primarily to the fact that studies of the structure of such objects will undoubtedly be useful in the solution of a whole range of practical problems. In particular, the high specific surface of fractal aggregates facilitates their active participation in condensation processes [11], sorption phenomena [12], chemical reactions of heterogeneous catalysis and inhibition [3, 11], etc. For example, if in an adsorption system a phase boundary (interface) cannot be approximated by a two-dimensional surface, then the fractal characteristics of such a system can be used to calculate the volume occupied by the adsorbed phase in the three-dimensional Euclidean space, which in turn makes it possible to calculate the total matter in the adsorbed phase [12].

The fractal nature of aggregated systems (aerosols and colloids) is demonstrated by the somewhat unusual nature of their most important physical properties. For example, the optics of fractal aggregates has a number of special features, which combine the specifics of the optical behaviour of tiny spheres (primary particles) with the properties of large particles of dimensions comparable with the wavelength (of, for example, laser radiation). A striking illustration of the unique optical properties of fractal clusters can be, for example, the green fluorescence of aggregates observed with the naked eye when such aggregates are exposed to laser pulses of the $\lambda = 1.06 \ \mu m$ wavelength [4] or the nonlinear photomodification of silver clusters, selective in respect of the frequency and polarisation of light, which occurs when these clusters interact with laser radiation (this leads to the appearance of dips at the laser wavelengths in the absorption spectrum) [13]. The aerodynamic behaviour of aggregates with a complex irregular structure also differs considerably from the aerodynamics of compact particles with simple geometric shapes, and manifests itself, for

It follows that an aerosol of fractal nature represents a system which is interesting from the practical and purely scientific points of view. We are therefore faced with the question: what are the factors that determine the fractal growth of an aggregate and how can we control such growth and attain a result best for our practical application?

One of these factors is the probability of the sticking together of primary particles, which unavoidably differs from unity in real physical systems and is governed by the aggregation conditions (for example, by the ambient atmosphere) and influences the rate of formation of an aggregate, its density, and fractal dimension.

On the other hand, the fractal characteristics of a cluster are governed not only by the probability of aggregation of the particles, but also by the aggregation mechanism. Under real conditions the fractal growth frequently takes place under the simultaneous action of several mechanisms [3, 11]. It is natural to assume that aggregates with the desired morphology and properties can be obtained if we identify the conditions stimulating predominance of one of these mechanisms.

A liquid containing fractal aggregates can readily be converted to the aerosol state by, for example, its atomisation. When particles aggregate in a solution, the aggregate growth can again be controlled (by altering the acidity or chemical composition of the solution) and, consequently, the fractal structure can be controlled and after atomisation (and drying) the appropriate fractal structures can be obtained.

These circumstances justify the unusually great current interest in the search for the methods of experimental diagnostics of the fractal structure of aerosols. The aim of the present paper is to review these methods.

2. In situ methods for determination of the fractal dimensions of aerosol aggregates

One of the most popular methods for experimental investigation of the fractal nature of real clusters in a two-dimensional space is an analysis of their electronmicroscopic images, which yield the following dependences: (a) the mass of a fractal aggregate (the number of particles N in the aggregate) on its size R:

$$N(R) \propto R^D , \qquad (2.1)$$

where D is the fractal dimension of the aggregate; (b) the correlation function C(r) on the distance r

$$C(r) = \operatorname{const} r^{-(d_{\rm E}-D)},$$

$$C(r) = \frac{1}{N} \sum_{i} \rho(r_i) \rho(r_i + r),$$
(2.2)

where $d_{\rm E}$ is the dimension of the space containing the cluster; N is the number of identical regions into which the image of a cluster is split; *i* is the sequential number labelling such a region; $\rho(r)$ is the density equal to unity at the point occupied by a cluster and zero at the point which is not so occupied.

Electron-microscopic analysis can be used to determine the fractal dimensions also of a three-dimensional cluster if its optical thickness is small (very loose clusters with low fractal dimensions). In this case the fractal dimension can be found accurately [9]. However, in an analysis of real aerosol systems in three-dimensional space it would be much more convenient to use in situ methods, which are attractive because of their speed and have clear advantages over electron microscopy in that a subjective error introduced by an investigator and the deformation of an object preparatory to experiments is considerably less.

The method of determining of the fractal dimensions from the results of the scattering of radiation (which may be x rays, neutrons, or light) by a fractal structure is popular and very effective. The method is based on the angular dependence of the intensity of the scattered radiation $I_M(q)$ on the structure factor $S_M(q)$ [15–17]:

$$I_M(q) = M^2 S_M(q) , (2.3)$$

where M is the mass of a cluster, which has the following scaling properties if $qR_G \gg 1$:

$$S_M(qR_G) = \begin{cases} 1 - \frac{1}{3} (qR_G)^2, & qR_G \ll 1, \\ (qR_G)^{-D}, & qR_G \gg 1, \end{cases}$$
(2.4)

where \underline{R}_G is the radius of gyration of the cluster; $R_G = (\overline{R}^2)^{0.5}$ (*R* is the distance from the particle in a cluster to its centre of mass); *q* is the modulus of the scattering vector given by

$$q=2\pi\lambda^{-1}\sin\frac{\theta}{2}\,.$$

(Here, λ is the wavelength of the selected radiation and θ is the scattering angle.)

When different types of radiation are combined and thus q is varied, an unusually wide range of cluster sizes can be covered. It should be noted that if $q > r_0^{-1}$ (r_0 is the size of primary particles from which any aggregate is formed), it is possible to determine the fractal dimension of the surface of the primary particles, since in this range the intensity of the radiation scattered by a particle varies in accordance with the law $I(q) = q^{-6+D_s}$, where D_s is the fractal dimension of the surface of the primary particles [3]. The power exponent of -4 (corresponding to $D_s = 2$) is evidence of a smooth surface, but if the particle surface is rough the value of the power exponent lies between -3 and -4 [3, 18].

It is obvious that some difficulty can be expected in an analysis of a polydisperse sample, which may contain clusters corresponding to the two limiting cases $(qR_G \ge 1, qR_G \ll 1)$, as well as clusters which are intermediate in respect of this condition. The total intensity of the radiation scattered by a polydisperse sample is [17]

$$I(q) = \sum N(M) M^2 S_M(q) , \qquad (2.5)$$

where N(M) is the number of clusters of mass M in the scattering region. However, a theoretical analysis of this problem has led to the conclusion [19] that interpretation of the scattering experiments (in the case of diffusion-limited aggregation) is possible without information on the distribution of the cluster masses in the sample being analysed. The angular dependence of the scattered-

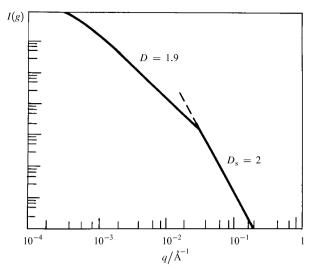


Figure 1. Results of an investigation of fumed silica particles (M-5) by the method of scattering of light and neutrons (D W Schaefer, 1991).

radiation intensity is practically identical to that in the case of monodisperse clusters, with the exception of small differences in the intermediate (crossover) range when $qR_{\rm G} \sim 1$.

The great capabilities of the scattered-radiation method have been illustrated strikingly by Schaefer and his colleagues, who have investigated the structure of fumed silica aggregates [3, 6] and of condensed silica polymers [20, 21]. Fig. 1 shows the results of the scattering of light and neutrons by fumed silica particles (M-5 sample). We can distinguish here two power-law dependences with a change from one to the other at $q \sim 0.01 \text{ Å}^{-1}$. The slopes of these dependences for $q < 0.01 \text{ Å}^{-1}$ and $q > 0.01 \text{ Å}^{-1}$ yield the mass fractal dimension ($D = 1.9 \pm 0.1$) and the fractal dimension of the particle surfaces ($D_s = 2$, dense surfaces of primary particles).

The methods of scattering of x rays, light, or neutrons and electron-microscopic analysis have been regarded as the main means for the experimental determination of the fractal dimensions of aerosol and colloidal aggregates. However, there is a whole range of in situ methods for determination of the fractal dimensions and many of these have been developed for specific tasks (such as the study of modification of the structure of silver aggregates during heating [14, 22] or the scaling behaviour of physical properties of aggregates in the hydrodynamic regime and in the free-molecule regime [23]). A characteristic feature of these methods is their utilisation of the aerodynamics of fractal aggregates.

The aerodynamic behaviour of aerosols of complex irregular shape has been treated as the behaviour of systems composed of ideal spherical particles and only some corrections have been made to allow for the influence of the shape or empirically determined size equivalents. However, this approach gives only very rough estimates of the aerodynamic characteristics of aerosols with the fractal structure. The aerodynamics of such objects is currently treated in terms of the fractal geometry employing the recently obtained [24-26] relationships between the density, fractal dimension of a cluster, and its traditional geometric characteristics (aerodynamic, geometric, volume-equivalent and mass-equivalent diameters, and

surface area). Some definitions must be introduced before we consider some of these methods.

The aerodynamic diameter of a particle is the diameter of a particle whose density is $\rho_{\omega} = 1 \text{ g cm}^{-3}$ and which has the same sedimentation rate as the particle in question.

The volume equivalent diameter is the diameter of a spherical particle with the same volume as the particle under investigation.

The geometric diameter of a particle is the diameter of a sphere which describes this particle.

The dependence $N \propto R^{D}$ makes it possible to determine readily the relationship between these characteristics for a fractal particle. For example, the aerodynamic d_{ae} and geometric d_{ge} diameters of a cluster are related by the fractal dimension as follows [25]:

$$d_{\rm ae} = d_0 (\rho_0 \rho_{\omega}^{-1})^{1/2} (d_{\rm ge} d_0^{-1})^{(D-1)/2} , \qquad (2.6)$$

where d_0 and ρ_0 are the diameter and density of the primary particles.

The volume-equivalent diameter of a cluster d_{ve} can be expressed in terms of the geometric diameter d_{ge} as follows:

$$d_{\rm ve} = d_0 (d_{\rm ge} d_0^{-1})^{D/3} , \qquad (2.7)$$

and in terms of the aerodynamic diameter:

$$d_{\rm ve} = d_0 [(\rho_{\omega} \rho_0^{-1})^{1/2} d_{\rm ae} d_0^{-1}]^{2D/3(D-1)} .$$
(2.8)

The aerodynamic diameter d_{ae} can be defined as follows:

$$d_{\rm ae}^2 = 18 V_{\rm sed} \, \mu g^{-1} \; ,$$

where μ is the dynamic viscosity of air [27].

Hence, the rate of sedimentation of a fractal aggregate is

$$V_{\rm sed} = \frac{\rho_0 g d_0^2}{18\mu} \left(d_{\rm ge} d_0^{-1} \right)^{D-1} \,. \tag{2.9}$$

The relationships (2.6)-(2.9) can be used in experimental determination of the fractal dimension *D*. For example, Eqn (2.8) gives a straight line in logarithmic coordinates and its slope is $1.5(1-D^{-1})$:

$$\log d_{\rm ae} = 1.5(1 - D^{-1})\log d_{\rm ve} + C , \qquad (2.10)$$

where C is a constant. Information on d_{ae} can be obtained, for example, from the results of a sedimentation analysis and d_{ve} from the number of clusters, measured with the aid of a condensation nucleus counter, and the total mass concentration of particles in a given volume of air [26].

Schmidt-Ott and his colleagues have carried out a fractal analysis of silver particle aggregates and have also used the dependence $N \propto R^{D}$. Their experiments, carried out in 1988-1990 [14, 22, 23, 28], varied in respect of the methods used and the apparatus employed. However, they were all based on the general idea of the behaviour of a fractal particle in the presence of gravity and electric fields. The investigated aerosol was passed through a charge neutraliser and then through a differential mobility analyser (DMA), where a fraction with the same aggregate mobility in an electric field was selected from the total flow. The volume rate of flow of the aerosol, which in this case determined the charge distribution of the aggregate [14], had to be selected so that the probability that the aggregate has not one but several elementary charges was low. In this case the aggregates with the same electric mobility, all of which have the same charge (1e) had in fact the same size. After selection by passage through the DMA gap the fate of

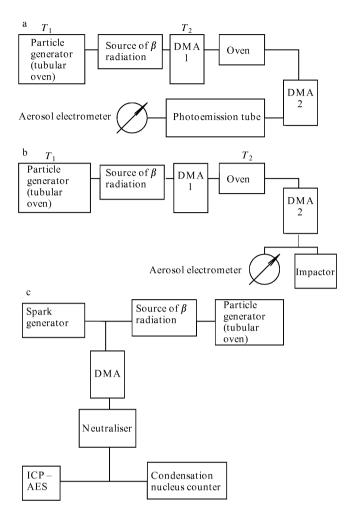


Figure 2. Diagrams of the apparatus used in various experiments intended to determine the fractal dimensions of silver particle aggregates (A Schmidt-Ott, 1988–1990).

the silver aggregates was determined by the specifics of a given experiment.

In the first of these experiments (Fig. 2a) the aggregates were heated in a tubular oven to a temperature T [14]. The heating destroyed the aggregates and produced closepacked clusters with the fractal dimension $D_{cl} = d_E = 3$. (Similar destruction of the fractal structure in the formation of compact nonfractal clusters occurs also during growth of aggregates formed in a plane when certain substances are burnt. The temperatures at which this growth occurs are sufficiently high to melt individual aggregates. The compact nature of the new formations is governed by the action of the surface tension forces [3].) In the case of close-packed clusters of size R_{cl} the number of primary particles can be described by $N_{cl} \propto R_{cl}^3$. Consequently, the fractal dimension of the initial aggregates can be found from the relationship

$$Rr_0^{-1} = a(R_{cl}r_0^{-1})^{3/D} , \qquad (2.11)$$

where R is the size of the original aggregate and a is a constant.

The structural changes caused by heating can be determined with the aid of a second DMA and photoemission tube and an aerosol electrometer placed beyond the tube (Fig. 2a). The fractal dimension of the aerosol

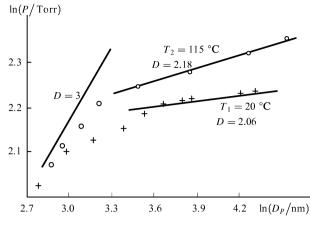


Figure 3. Results of a fractal analysis of silver particle aggregates, carried out with the aid of a low-pressure impactor.

aggregates, formed from primary silver particles of \sim 7.5 nm size, was found experimentally to be 2.18.

In the experiments described in Refs [22, 29] a part of the aerosol leaving the second DMA was passed through a low-pressure impactor (Fig. 2b). The fractal dimension of the aggregates was found by plotting the dependence $d_P^{D-2} \propto P^2$, obtained by Schmidt-Ott for fractal particles (d_p) is the mobility equivalent parameter and P is the pressure during impacting of particles). For a densely packed cluster its mass M obeys $M \propto d_P^3$ and the pressure is $P \propto d_P^{0/5}$. The experimental data on the impacting of particles, heated to $T_2 = 220$ °C and of practically spherical shape, yield the dependence $d_P \propto (P + 3.11)$. The pressure correction constant allows fro the nonideal profile of the velocities inside the impactor aperture and for deviations from the incompressibility of the stream. The results of two other experiments $(T_2 = 20 \text{ °C} \text{ and}$ $T_2 = 115$ °C) are presented in Fig. 3. In both cases the fractal dimension D was close to 3 for small aggregates; in the case of large aggregates the slope of a straight line $\ln P = D \ln d_P + C$ and, consequently, D increased with the temperature T_2 (D = 2.06 for $T_2 = 20$ °C, but D = 2.18for $T_2 = 115$ °C). Obviously, the method which made it possible to detect the change in the fractal structure of particles during heating would be very attractive for the analysis of the evolution of the particles and could be used successfully in, for example, investiga-tions of the structure of atmospheric aerosol particles.

In the next experiment (2c) the parameter N in the dependence $N \propto R^D$ was determined with the aid of a plasma atomic-emission spectrometer (ICP-AES) to which a fraction of the aerosol was directed after it passed through a charge neutraliser [28]. The aggregates were introduced into the plasma at a temperature above 6000 K and this caused atomisation of the aggregates. The atoms and ions that formed gave rise to specific emission spectra and the signal intensity in these spectra was proportional to the number of atoms. A condensation nucleus counter yielded the concentration of the aggregates in the fraction that left the DMA, so that normalisation of the results of the ICP-AES analysis to this fraction made it possible to determine the mass per aggregate. The fractal dimension of the silver aggregates depended on the method used to generate them. When a spark discharge between silver electrodes was used for this purpose, the subsequent condensation produced

Method of formation of primary particles	Diameter of primary particles/nm	Fractal dimensionality of aggregates	Ref.
Evaporation – condensation	7.5	$2.18(T_2 = 20 \ ^{\circ}\text{C})$	[14]
Evaporation – condensation	15.0	$2.06(T_2 = 20 \ ^{\circ}\text{C})$ $2.18(T_2 = 115 \ ^{\circ}\text{C})$	[22]
Spark generator	6.0	2.19 ± 0.16 ($T_2 = 20$ °C)	[28]
Evaporation – condensation	18.0	2.60 ± 0.17 $(T_2 = 20 \ ^{\circ}\text{C})$	[28]

Table 1. Fractal dimensions of silver aggregates

aggregates with $D = 2.19 \pm 0.16$, whereas the traditional heating in a tubular oven and condensation gave aggregates with $D = 2.60 \pm 0.17$.

The fractal dimensions of the silver aggregates obtained in these experiments are listed in Table 1.

The idea of obtaining information on the morphology of fractal particles from their behaviour in an electric field has been used also in one further method for in situ determination of the fractal dimensions of aerosol particles [7, 26]. An electric field E, balancing out the gravitational forces acting on a particle, was generated in a classical Millikan cell. When the particle charge was altered (by ultraviolet radiation) by a definite amount (for example, by 1e), the particle began to move at a velocity V which could be measured. Since

$$eE = 6\pi\mu r_{ae}V$$
, $Nmg = 6\pi\mu r_{ae}V_{ts}$,

where $N = (r_{\rm ac}/r_0)^D$ is the number of primary particles of mass m which compose a cluster and V_{ts} is the velocity at which the particle settles when E = 0, the fractal dimension D can be determined from the slope of the straight line

$$\log V_{\rm ts} = \log P + (D-1)\log(EV^{-1}), \qquad (2.12)$$

where $P = (r_{ac}/r_0)^D mg e^{D-1}/(6\pi\mu)^D$. Colbeck et al. [26] assumed that $N = (r_{ac}/r_0)^D$, although the classical formula of Mandelbrot $N = (r/r_0)^D$ [10] gives N for a cluster not in terms of its aerodynamic but its geometric radius. A possible variant of this method is shown in Fig. 4.

All these variants of experimental determination of Drely on the scaling dependence between the size of an aggregate and the number of particles in it: $N \propto R^{D}$. A

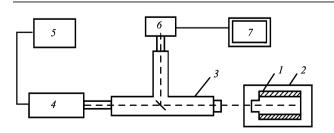


Figure 4. Apparatus used in determination of fractal dimensions of (1) modified Millikan cell; aggregates (I Colbeck, 1992): (3) telescope with a beam splitter; (2) insulating chamber; (4) photomultiplier; (5) computer; (6) video camera; (7) monitor.

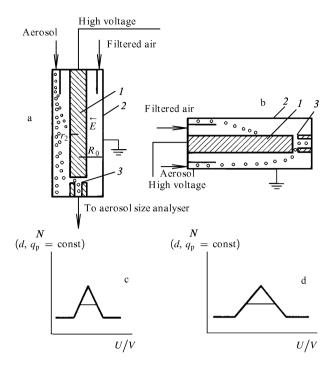


Figure 5. Schematic representation of the paths of particles in a differential mobility analyser of aerosols and the analyser transfer function: (a, c) vertically oriented analyser; (b, d) horizontally oriented analyser. (1) Inner electrode; (2) outer electrode; (3) sampling slit.

different dependence, of the density of an aggregate on its size given by $\rho \propto R^{-D}$, can be used for the same purpose.

Let us consider in greater detail the original in situ method for the diagnostics of fractal aerosol aggregates based on the remarkable property of the fractals described by the above dependence (it should be pointed out that this method, in contrast to those known earlier, requires direct determination of the size of an aggregate in the course of an experiment). As in the previously discussed method [14, 22, 23, 26, 28] for the determination of D, the information on the fractal properties of the investigated aerosol is deduced from the aerodynamic behaviour of the aerosol in gravitational and electric fields.

The density of the particle matter is determined from an analysis of the degree of deformation of the transfer function of a horizontal DMA, relative to the transfer function of a vertical DMA [30]. A mobility analyser is a cylindrical capacitor (Fig. 5). In the upper part of this capacitor a very thin cylindrical jet of an aerosol is formed along the inner wall of the outer electrode and a stream of pure filtered air occupies the rest of the space between the DMA electrodes. The DMA is constructed to ensure laminar flow of the aerosol and air from top to bottom without mutual mixing. If there is a potential difference between the DMA electrodes, charged aerosol particles (and their fraction is usually sufficiently high [31]) are also set in radial motion. In the case of the vertical DMA, this motion is governed by Stokes and Coulomb forces:

$$3\pi\mu \ \frac{\mathrm{d}R}{\mathrm{d}t} = -\frac{Uq_{\mathrm{p}}}{R \left[\ln \left(R_2/R_1\right)\right] d_{\mathrm{ge}}}, \qquad (2.13a)$$

$$R_1 < R < R_2$$
, $t > 0$, $R(t = 0) = R_2$, (2.13b)

where U is the voltage applied between the DMA electrodes; q_p is the charge of a particle; R_2 is the radius of the inner electrode of the DMA; d_{ge} is the diameter of a particle.

However, if the analyser is horizontal, gravity plays a role in the radial motion of the particles:

$$3\pi\mu d_{\rm gc} \frac{\mathrm{d}R}{\mathrm{d}t} = -\frac{Uq_{\rm p}}{R\ln(R_2/R_1)} + Mg\,\cos\alpha\,,\qquad(2.14)$$

where α is the angle between the direction of the electric field and the gravitational field.

This the particle paths affects in an obvious manner: particles of a given size moving from top to bottom follow paths different from those of identical particles moving from bottom to top towards the central electrode (see Fig. 5).

The transfer function representing the dependences of the number of particles with a given size and charge (for example, $d_{ge} = 1 \ \mu m$, $q_p = 1e$), which have passed through the sample-selecting DMA slit, on the voltage between the electrodes are therefore different for the horizontal and vertical DMAs [other conditions being equal] and the magnitude of this difference (or the degree of deformation of the transfer function) depends significantly on the density of the aerosol particle material.[†] The density ρ of the aerosol particle material is related to the degree of deformation of the transfer function [32]:

$$\delta = 4\pi \rho g (d_{\rm gc})^2 R_2 Lz \left(9Q\mu\right)^{-1} , \qquad (2.15)$$

$$\delta = 2(A' - A), \quad 1 \le \frac{A'}{A} \le \frac{6}{5},$$
 (2.16)

$$\delta = \frac{A^4}{4} + \frac{1}{4} \left(8AA' - 8A^2 - A'^2 \right)^{1/2}, \quad \frac{6}{5} \le \frac{A'}{A} \le 2, \quad (2.17)$$

$$\delta = \frac{A'}{2}, \quad 2 \leqslant \frac{A'}{A} \leqslant \infty , \qquad (2.18)$$

where L is the length of the working volume of the DMA; Q is the volume rate of flow of air through the DMA; z is the dimensionless coefficient governed by the DMA geometry; A and A' are the half-widths of the transfer functions of vertical and horizontal DMAs, respectively.

It follows that if the density of the particles belonging to different size fractions is determined and the dependence $\rho(d) = \operatorname{const} r^{d_{\rm E}-D}$ for the fractal structures is employed, the fractal dimensions of the investigated particles can be found. The method was tested on particles of polystyrene latex and on sodium chloride and calcium nitrate aerosols, formed by atomisation of their aqueous solutions and subsequent drying (block diagram of the apparatus used in this method is shown in Fig. 6).

The latex particles were spherical and of constant density, since they did not have a fractal structure. Fig. 7 shows the experimentally determined pattern of the deformation of the transfer function of a horizontal DMA, compared with the corresponding function of a vertical DMA when these functions were determined in a study of the polystyrene latex particles with a diameter

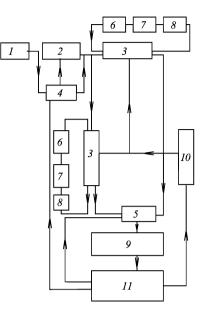


Figure 6. Block diagram of a universal aerosol analyser: (1) sampling device; (2) particle charge neutraliser; (3) differential mobility analysers; (4, 5) aerosol flow switching unit; (6) flow meters; (7) filter; (8) micro-pumps; (9) laser aerosol-size analyser; (10) controlled high-voltage supply unit; (11) automated system for the control of measurement and data analysis methods.

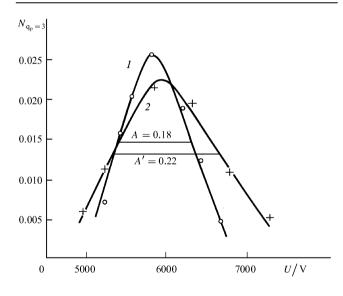


Figure 7. Typical experimental deformation of the transfer function of a DMA: (1) vertical DMA; (2) horizontal DMA. The experiments were carried out on particles of polystyrene latex ($d = 1.05 \mu$ m).

 $d_{\rm ge} = 1.05 \pm 0.05 \,\mu$ m and with a charge 3*e*. Similar measurements had been carried out earlier on latex particles of size $d_{\rm ge} = 0.80$, 1.18, and 1.51 μ m, which made it possible to plot the dependence shown in Fig. 8. The density of the latex particles belonging to different size fractions was the same, within the limits of experimental error, and its numerical value agreed well with the tabulated data: $\rho = 10 \pm 0.1 \,\mathrm{g \ cm^{-3}}$.

A similar absence of the dependence of the density of the particle material on the particle size was observed also for the sodium chloride aerosol (Fig. 8). However, in the case of aerosol formed by atomisation of the $Ca(NO_3)_2$ salt

[†]An analysis of the transfer function of a vertical DMA has been investigated sufficiently thoroughly, both theoretically and experimentally, [32]. It has been found that the transfer function of the vertical mobility analyser is independent of the parameters of the particles being analysed and is nearly triangular with a relative half-width of the order of 10% - 15%.

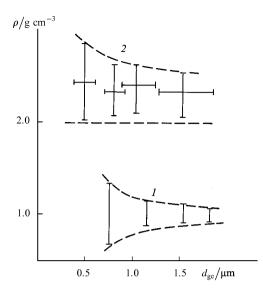


Figure 8. Density of particles belonging to different size fractions: (1) polystyrene latex; (2) sodium chloride.

solution there was a considerable reduction in the particle density when the size fraction was increased: the dependence was typical of fractal objects. An analysis of the dependence $\rho = \rho(d_{ge})$ showed (Fig. 9) that for the $Ca(NO_3)_2$ salt particles the result was $d_{\rm E} - D = 1.2 \pm 0.3$. The fractal dimension of a cluster was in this case $D = 1.8 \pm 0.3$, which was closest to the value $D = 1.77 \pm 0.03$ found for the clusters aggregating in accordance with the cluster-cluster model [1]. Although there are no published reports of the fractal properties of clusters formed by drying of salt solution droplets, these results are a concrete illustration of the self-evident feasibility of applying this method to the study of the fractal structure of aerosol particles. The method is highly sensitive (in the adopted form it can be applied to clusters with sizes from 0.3 μ m to 10 μ m); it is also highly accurate and fast. The measurement process can be fully automated.

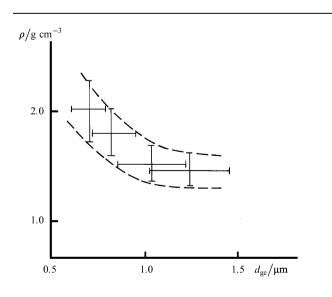


Figure 9. Density of calcium nitrate particles.

3. Conclusions

Fractal clusters consisting of a large number of bound macroscopic particles (of size much less than the size of a cluster) have a characteristic branched structure and a number of properties distinguishing fractals as a whole (scaling invariance, self-similarity, dependence of the density on the aggregate size). The search for possible ways of experimental determination of the fractal dimension (which is the principal characteristic of a cluster in terms of the fractal geometry) is a very topical and interesting task. The experimental diagnostics of a fractal aerosol can be performed by a variety of diverse methods and, in particular, this can be done in situ. The in situ methods are attractive because of their speed and the absence of mechanical effects on an object. They are based on the known scaling relationships between the number of particles in a cluster, their average density in the cluster, and the cluster size. Among these methods the most powerful is that based on the scattering of radiation by the fractal material. In spite of some complications encountered in a theoretical description of fractal aggregates by this method (because of the 'finite size effect', the structure factor depends on the mass distribution of clusters), the method is widely used in practice. Some of the other methods rely on the aerodynamic behaviour of fractal aerosol particles in gravitational and electric fields. They are very simple in practice and are designed to analyse a polydisperse sample. It should be pointed out that these in situ methods for the diagnostics of fractal clusters are correct only when the process of generation of aggregates is such that we can definitely say that the aggregates are composed of primary particles of the same size and that there is only one fractal growth mechanism, because otherwise the averaging of the fractal dimensions may be too rough.

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