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1.1 Introduction

Aerosol science studies the properties of particles suspended in air or other gases, or even in vacuum, and the behavior of collections of such particles. A collection of aerosol particles is referred to as an aerosol, although the particles may be suspended in some other gaseous medium, not just air. The term cosmosol is used for a collection of particles suspended in vacuum. Although attempts to give a strict definition of aerosol have appeared from time to time, to date no commonly acceptable and concise definition of an aerosol exists. In my opinion, it is better not to make any attempts in this direction, especially because intuitively it is clear what an aerosol is. For example, it is clear that birds or airplanes are not aerosol particles. On the other hand, smoke from cigarettes, fumes from chimneys, dust raised by the wind, and so on, are aerosols. Hence, there are some essential features that allow us to distinguish between aerosols and other objects suspended in the gas phase. There are at least two such features: (i) aerosol particles can exist beyond the aerosol for a sufficiently long time; and (ii) an aerosol can be described in terms of the concentration of aerosol particles, or, better, the concentration field. From this point of view, it is clear why birds are not aerosols. Interestingly, clouds are also not aerosols! Of course, we can introduce the concentration of cloud droplets. But if we isolate a cloud particle, it will immediately evaporate. The cloud creates a specially designed environment inside it - the humidity and the temperature fields - the conditions in which a water droplet does not evaporate during a long time.

Aerosols are divided into two classes, namely *primary aerosols* and *secondary aerosols*, according to the mechanisms of their origination. Primary aerosol particles result, for example, from fragmentation processes or combustion, and appear in the carrier gas as already well-shaped objects. Of course, their shape can change because of a number of physico-chemical processes such as humidification, gas-particle reactions, coagulation, and so on. Secondary aerosol particles appear in the carrier gas from "nothing" as a result of gas-to-particle conversion. For example, such aerosols regularly form in the Earth's atmosphere and play a key role in a number

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of global processes such as the formation of clouds. They serve as the centers for heterogeneous nucleation of water vapor. No aerosols – no clouds! One can imagine how our planet would look without secondary aerosol particles.

Primary and secondary aerosols are characterized by the size, shape, and chemical content of the aerosol particles. As for the shape, one normally assumes that the particles are spheres. Of course, this assumption is an idealization necessary for simplification of the mathematical problems related to the behavior of aerosol particles. There are very many aerosols comprising irregularly shaped particles. The non-sphericity of particles creates many problems. There exist also agglomerates of particles, which in some cases reveal fractal properties. We shall return to the methods for their description later on.

There are a number of classifications of particles with respect to their size. For example, if the particles are much smaller than the molecular mean free path, they are referred to as "fine" particles. This size range stretches from 1 to 10 nm under normal conditions. But from the point of view of aerosol optics, these particles are not small if the wavelength of the incident light is comparable with their size. This is the reason why such very convenient and commonly accepted classifications cannot compete with natural classifications based on the comparison of the particle size with a characteristic size that comes up each time when one solves a concrete physical problem.

1.2

Aerosol Phenomenology

1.2.1

Basic Dimensionless Criteria

It is convenient to characterize aerosols by dimensionless criteria. The most commonly used in the area of aerosol science are listed below. Each of these criteria contains the particle size *a*. In what follows we consider spherical particles of radius *a*.

1.2.1.1 Reynolds Number

The Reynolds number Re is introduced as follows:

$$Re = \frac{ua}{v}$$
(1.1)

Here v is the *kinematic viscosity* of the carrier gas and u is the particle velocity with respect to the carrier gas. Small and large Re correspond to laminar or turbulent motion of the particle, respectively.

1.2.1.2 Stokes Number

The Stokes number Stk characterizes the role of inertial effects:

$$Stk = \frac{2a^2u}{9\nu L} \tag{1.2}$$

Here L is the characteristic length of the flow. The Stokes number Stk is seen to increase on increasing the particle size.

1.2.1.3 Knudsen Number

The Knudsen number Kn characterizes the discreteness of the carrier gas:

$$Kn = \frac{l}{a}$$
(1.3)

Here l is the mean free path of the molecules of the carrier gas,

$$l = \frac{1}{\sqrt{2}\,\sigma^2 N} \tag{1.4}$$

 σ is the size of a carrier gas molecule, and N is the molecular number concentration. If a foreign molecule moves toward the aerosol particle, then Kn can be expressed in terms of the *molecular diffusivity D*,

$$Kn = \frac{2D}{v_T a}$$
(1.5)

where

$$v_T = \sqrt{\frac{8kT}{\pi m}} \tag{1.6}$$

is the molecular thermal velocity, m is the mass of the foreign molecule, k is the Boltzmann constant, and T is the absolute temperature (K).

1.2.1.4 Peclet Number

The Peclet number Pe defines the regimes of energy transfer from particles to the carrier gas. It is introduced similarly to Kn (Eq. (1.7)):

$$Pe = \frac{2\Lambda}{v_T a}$$
(1.7)

Here Λ is the thermal conductivity of the carrier gas.

1.2.1.5 Mie Number

The Mie number given by the dimensionless group

$$Mie = \frac{2\pi\lambda}{a}$$

defines the optical properties of the particle. Here λ is the wavelength of the incident light.

1.2.1.6 Coulomb Number

The Coulomb number Cu given by

$$Cu = \frac{l_C}{a} = \frac{Ze^2}{akT}$$
(1.8)

is important in the processes of particle charging. Here *e* is the elementary charge, Z is the total particle charge in units of *e*, and

$$l_{\rm C} = \frac{Ze^2}{kT} \tag{1.9}$$

is the Coulomb length. This is the distance at which the influence of the Coulomb forces cannot be ignored.

1.2.2 Particle Size Distributions

Particle size distributions play a central role in the physics and chemistry of aerosols, although direct observation of the distributions are possible only in principle. Practically, what we really measure is just the response of an instrument to a given particle size distribution,

$$P(x) = \int R(x, a) f(a) \, \mathrm{d}a \tag{1.10}$$

Here f(a) is the particle size distribution (normally a is the particle radius), P(x) is the reading of the instrument measuring the property of aerosol x, and R(x, a) is referred to as the linear response function of the instrument. For example, P(x) can be the optical signal from an aerosol particle in the sensitive volume of an optical particle counter, the penetration of the aerosol through the diffusion battery (in this case x is the length of the battery), or something else. The function f(a) cannot depend on the dimensional variable a alone. The particle size is measured in some natural units a_s . In this case the distribution is a function of a/a_s and depends on some other dimensionless parameters or groups. The particle size distribution is normalized as follows:

$$\int_0^\infty f(a/a_s) \,\frac{\mathrm{d}a}{a_s} = 1 \tag{1.11}$$

The length a_s is a parameter of the distribution. Although the aerosol particle size distribution is such an elusive characteristic of the aerosol, it is still convenient to introduce it because it unifies all the properties of aerosols.

In many cases the distribution function can be found theoretically by solving dynamic equations governing the time evolution of the particle size distribution, but the methods for analyzing these equations are not yet reliable, not to mention the information on the coefficients entering them. This is the reason why the phenomenological distributions are so widely spread.

There is a commonly accepted collection of particle size distributions, which includes those outlined in the following subsections.

1.2.2.1 The Log-Normal Distribution

The *log-normal distribution* is given by

$$f_{\rm L}(a) = \frac{1}{\sqrt{2\pi} (a/a_{\rm s}) \ln \sigma} \exp\left[-\frac{1}{2 \ln^2 \sigma} \ln^2\left(\frac{a}{a_{\rm s}}\right)\right] \tag{1.12}$$

Here *a* is the particle radius. This distribution depends on two parameters, a_s and σ , where a_s is the characteristic particle radius and σ ($\sigma > 1$) is the width of the distribution. Equation (1.12) is known as the log-normal distribution. It is important to emphasize that it is not derived from theoretical considerations.

1.2 Aerosol Phenomenology 5





Rather, it was introduced by hand. The function $f_L(a)$ is shown in Figure 1.1 for different σ .

1.2.2.2 Generalized Gamma Distribution

The generalized gamma distribution is given by

$$f_{\rm G}(a) = \left(\frac{a}{a_s}\right)^k \frac{j}{\Gamma((k+1)/j)} \exp\left[-\left(\frac{a}{a_s}\right)^j\right]$$
(1.13)

Here $\Gamma(x)$ is the Euler gamma function. The distribution f_G depends on three parameters, a_s , k, and j. Figure 1.2 displays the generalized gamma distribution for three sets of its parameters.

Once the particle size distributions are known, it is easy to derive the distribution over the values depending only on the particle size:

$$f(\psi_0) = \int \delta(\psi_0 - \psi(a)) f(a) \frac{da}{a_s}$$
(1.14)

Here $\delta(x)$ is the Dirac delta function. For example, if we wish to derive the distribution over the particle masses, then $\psi(a) = (4\pi a^3/3)\rho$, where ρ is the





density of the particle material. Of course, the properties of aerosols do not depend solely on their size distributions. The shape of aerosol particles and their composition are important factors.

The log-normal distribution often applies in approximate calculations of condensation and coagulation. Two useful identities containing the integrals of a product of log-normal distributions can be found in, for example, [1, 2]. A regular theory of the log-normal distribution is expounded in the book [3].

1.3

Drag Force and Diffusivity

If the carrier gas moving with speed v flows past a spherical particle of radius a, the drag force acting on it is

$$F_{\rm drag} = \frac{1}{2} C_{\rm D} \pi a^2 \rho v^2 \tag{1.15}$$

where C_D is the drag coefficient and ρ is the density of the carrier gas. The latter depends on Re as follows:

$$C_{\rm D} = \frac{12}{\rm Re} \qquad {\rm Re} < 0.1$$

$$C_{\rm D} = \frac{12}{\rm Re} \left(1 + \frac{3}{8}{\rm Re} + \frac{9}{40}\ln{\rm Re}\right) \qquad 0.1 < {\rm Re} < 2$$

$$C_{\rm D} = \frac{12}{\rm Re} (1 + 0.15\,{\rm Re}^{0.687}) \qquad 2 < {\rm Re} < 500$$

$$C_{\rm D} = 0.44 \qquad 500 < {\rm Re} < 2 \times 10^5$$

The particle mobility *B* is introduced as

$$\boldsymbol{v} = B\boldsymbol{F} \tag{1.16}$$

When a particle of radius *a* moves in the carrier gas, the latter resists particle motion. The force acting on the particle is proportional to *a* in the limit of small flow velocity $\text{Re} \ll 1$ and Kn (continuum regime),

$$\mathbf{F} = 6\pi\rho v a \mathbf{v} \tag{1.17}$$

where ρ is the gas density and ν is the kinematic viscosity. Equation (1.17) is the Stokes equation.

In the transition regime, Eq. (1.17) should be corrected to

$$F = \frac{6\pi \nu va}{C_{\rm c}} \tag{1.18}$$

with C_c being the Millikan correction factor,

$$C_{\rm c} = 1 + {\rm Kn} \left[1.257 + 0.4 \exp\left(-\frac{1.1}{{\rm Kn}}\right) \right]$$
 (1.19)

The diffusivity D is connected with the mobility B by the *Einstein–Smoluchowski* formula

$$D = kTB \tag{1.20}$$

The diffusivity is then

$$D = \frac{kT}{6\pi a v \rho} C(a) \tag{1.21}$$

where C(a) is the correction factor. We can use $C(a) = C_c$ or C(a) found [4] theoretically,

$$C(a) = \frac{15 + 12c_1 \text{Kn} + 9(c_1^2 + 1)\text{Kn}^2 + 18c_2(c_1^2 + 2)\text{Kn}^3}{15 - 3c_1 \text{Kn} + c_2(8 + \pi\sigma)(c_1^2 + 2)\text{Kn}^2}$$
(1.22)

with

$$c_1 = \frac{2-\sigma}{\sigma}, \qquad c_2 = \frac{1}{2-\sigma}$$

and $\sigma < 1$ being a factor entering the slip boundary conditions. The Knudsen number is Kn = λ/a , with λ being the mean free path of the carrier gas molecules ($\lambda = 65$ nm for air at ambient conditions). The parameter σ changes within the range 0.79–1.0. Equation (1.22) describes the transition correction for *all* Knudsen numbers and gives the correct limiting values (continuum and free-molecule ones). In what follows we put $\sigma = 1$. The correction factors of Eqs. (1.19) and (1.22) are plotted as functions of Kn in Figure 1.3.

All the above formulas are more thoroughly discussed in aerosol textbooks, except Eq. (1.22). This formula was derived from a 13-moment approximate solution of the Boltzmann equation by Phillips in [4]. It is remarkable that the results of Millikan and Phillips almost coincide.

1.4

Diffusion Charging of Aerosol Particles

At first sight the process of particle charging looks similar to particle condensation: an ion moving in the carrier gas approaches the particle and sticks to it. However, the difference between these two processes (condensation and charging) is quite significant. Even in the case when the ion interacts with a neutral particle, one cannot ignore the influence of the image forces. As was explained at the very beginning of this chapter, the motion of the ion is defined by two parameters: $Kn = 2D/v_T a$ (the Knudsen number) and $Cu = Ze^2/akT$ (the Coulomb number). Next, in most practical cases Cu > Kn. For example, at ambient conditions and Z = 1, the Coulomb length $l_C = e^2/kT = 0.06 \ \mu\text{m}$. This value is comparable with the mean free path of molecules in air ($l = 0.065 \ \mu\text{m}$), which means that the free-molecule regime of particle charging demands some special conditions and can be realized, for example, in the ionosphere.

1.4.1 Flux Matching Exactly

The steady-state ion flux J(a) onto the particle of radius *a* can be written as

$$J(a) = \alpha(a)n_{\infty} \tag{1.23}$$

that is, the flux is proportional to the ion density n_{∞} far away from the particle. The proportionality coefficient $\alpha(a)$ is known as the *charging efficiency*. The problem is to find $\alpha(a)$.

Once again, a dimensional consideration shows that $\alpha(a)$ is a function of two dimensionless groups, Kn = l/a and $\text{Cu} = Ze^2/akT$,

$$\alpha(a) = \pi a^2 v_T F(l/a, Ze^2/akT)$$
(1.24)

We can generalize Eq. (1.23) as follows:

$$I(a, R, n_R) = \alpha(a, R)n_R \tag{1.25}$$

where n_R is the ion concentration at a distance R from the particle center. It is important to emphasize that n_R is (still) an *arbitrary* value introduced as a boundary condition at the distance R (also arbitrary) to a kinetic equation that is necessary to solve for defining $\alpha(a, R)$.

The flux defined by Eq. (1.23) is thus

$$J(a) = J(a, \infty, n_{\infty})$$
 and $\alpha(a) = \alpha(a, \infty)$ (1.26)

The value of $\alpha(a, R)$ does not depend on n_R because of the linearity of the problem.

Let us assume that we know the exact ion concentration profile $n_{\text{exact}}(r)$ corresponding to the flux J(a) from infinity (see Eq. (1.23)). Then, using Eq. (1.25) we can express J(a) in terms of n_{exact} as follows:

$$J(a) = J(a, R, n_{\text{exact}}(R)) = \alpha(a, R)n_{\text{exact}}(R)$$
(1.27)

Now let us choose *R* sufficiently large for the diffusion approximation to reproduce the exact ion concentration profile,

$$n_{\text{exact}}(R) = n^{(J(a))}(R)$$
 (1.28)

with $n^{(J)}(r)$ being the steady-state ion concentration profile corresponding to a given total ion flux *J*. The steady-state density of the ion flux *j*(*r*) is the sum of two terms,

$$j(r) = -D\frac{\mathrm{d}n^{(J)}(r)}{\mathrm{d}r} - B\frac{\mathrm{d}U(r)}{\mathrm{d}r}n^{(J)}(r)$$
(1.29)

where *D* is the ion diffusivity, U(r) is a potential (here the *ion–particle interaction*), and *B* is the ion mobility. According to the *Einstein relation*, kTB = D. On the other hand, the ion flux density is expressed in terms of the total ion flux as follows: $j(r) = -J/4\pi r^2$, with J > 0. Equation (1.29) can be now rewritten as

$$e^{-\beta U(r)} \frac{d}{dr} [n^{(J)}(r) e^{\beta U(r)}] = \frac{J}{4\pi Dr^2}$$

where $\beta = 1/kT$. The solution to this equation is

$$n^{(J)}(r) = e^{-\beta U(r)} \left(n_{\infty} - \frac{J}{4\pi D} \int_{r}^{\infty} e^{\beta U(r')} \frac{dr'}{r'^{2}} \right)$$
(1.30)

On substituting Eqs. (1.28) and (1.30) into Eq. (1.27), one obtains the equation $J(a) = \alpha(a, R)n^{(J)}(R)$ or

$$J(a) = \alpha(a, R) e^{-\beta U(R)} \left(n_{\infty} - \frac{J(a)}{4\pi D} \int_{R}^{\infty} e^{\beta U(r')} \frac{dr'}{r'^2} \right)$$
(1.31)

We can solve this equation with respect to J(a) and find $\alpha(a)$:

$$\alpha(a) = \frac{\alpha(a, R)e^{-\beta U(R)}}{1 + [\alpha(a, R)e^{-\beta U(R)}/4\pi D] \int_{R}^{\infty} e^{\beta U(r')} dr'/r'^{2}}$$
(1.32)

Equation (1.32) is exact if $R \gg l$. We, however, know neither $\alpha(a, R)$ nor R.

1.4.2 Flux Matching Approximately

Current knowledge does not allow us to find $\alpha(a, R)$ exactly. We thus call upon two approximations:

1) We approximate $\alpha(a, R)$ by its free-molecule expression,

$$\alpha(a, R) \approx \alpha_{\rm fm}(a, R) \tag{1.33}$$

2) We define *R* from the condition

$$d_r n_{\rm fm}(r)|_{r=R} = d_r n^{(J(a))}(r)|_{r=R}$$
(1.34)

where $n_{\text{fm}}(r)$ is the ion concentration profile found in the free-molecule regime for a < r < R. The distance *R* separates the zones of the free-molecule and the continuum regimes.

All currently used approximations for α can be derived from Eq. (1.32).

1.4.3 Charging of a Neutral Particle

In this case the ion-particle interaction is described by the potential of image forces,

$$U(r) = -\frac{e^2}{2a} \frac{a^4}{r^2(r^2 - a^2)}$$
(1.35)

This expression for U(r) is valid for metallic particles. The case of dielectric spheres is much more complicated, and we do not analyze it – however, see [5]. As is seen from Eq. (1.35) the image forces are singular at the particle surface. Nevertheless, it



Figure 1.3 When an ion approaches a neutral particle, the image forces strongly enhance the efficiency of ion capture. The correction factors for the free-molecule efficiency $\mbox{ Cu}$ = 1, 3, and 5, respectively. versus dimensionless particle size av_T/D is

shown here. It is seen that at large sizes the correction factor approaches unity. Curves 1-3 correspond to Coulomb numbers:

is possible to find the expression for the charging efficiency following the method of [6]. The final result has the form

$$\alpha(a) = \frac{2\pi a^2 v_T z(a)}{1 + \sqrt{1 + [av_T z(a)/2D\zeta^2]^2}}$$
(1.36)

where

$$z(a) = 1 + \sqrt{\frac{\pi e^2}{2akT}} \tag{1.37}$$

and

$$\zeta^2 = 1 + \sqrt{\frac{2e^2}{\pi akT}} \tag{1.38}$$

Figure 1.3 shows the influence of the Coulomb number (see Eq. (1.8)) on the particle charging efficiency.

1.4.4 Recombination

Let us consider the situation when an ion carrying Z_i elementary charges approaches a particle of radius a carrying Z_p charges of opposite polarity. In this case Eq. (1.32) allows one to find the expression for the recombination efficiency in the continuum limit. We restrict our analysis to the case of non-singular Coulomb forces. Then we can approximate $R \approx a$, ignore unity in the denominator of Eq. (1.32), and come to the well-known Langevin formula,

$$\alpha(a) = \frac{4\pi D l_{\rm C}}{1 - \exp(-l_{\rm C}/a)} \tag{1.39}$$

where $l_{\rm C} = Z_{\rm i}Z_{\rm p}e^2/kT$. In the limit of very small particles, the recombination efficiency is independent of particle size.

There are some difficulties in the case of smaller particles and image potential.

This section is based on the work by Lushnikov and Kulmala [6]. There exists an extensive literature on particle charging. Many authors addressed their efforts to deriving expressions for the charging efficiencies of an aerosol particle by ions. There are no problems in resolving this problem for the continuum limit, where the ion transport is described by the diffusion equation [7–9].

In the free-molecule regime the charging efficiency can be easily found only when the ion-particle interaction is described by the Coulomb potential alone. Attempts to take into account the image forces make the analysis much more difficult. Especially, this concerns the dielectric particles, in which case the ion-particle interaction is described by an infinite and slowly convergent series [10].

The first successful attempt to apply the free-molecule approximation for calculating the charging efficiencies of small aerosol particles was undertaken by Natanson [11, 12]. Since then, this problem has been considered by many authors [13–19]. None of these works could avoid the difficulty related to the very inconvenient expression for the ion-dielectric particle potential. The latter has been replaced by the ion-metal particle potential modified by the multiplier ($\epsilon - 1$)/($\epsilon + 1$), with ϵ being the *dielectric permeability* of the particle material.

Attempts to consider the transition regime using as the zero approximation the solution of the collisionless kinetic equation have been made [18–20] and very recently by us [6, 21]. The analysis of these authors clearly demonstrated the significance of the ion–carrier gas interaction in calculating the *ion–particle recombination efficiency*. The point is that the ion can be captured by the charged particle from bound states with negative energies. This effect has been considered in [20] by taking into account a single ion–molecule collision in the Coulomb field created by the charged particle. A new version of flux matching theory [11, 12, 22] has been applied by us [6] to take this effect into account explicitly. Results of experiments on particle charging can be found in [23–28].

1.5 Fractal Aggregates

It is now well established that fractal aggregates (FAs) appear in numerous natural and anthropogenic processes. Their role in the atmosphere may be immense, for FAs possess anomalous physico-chemical, mechanical, and optical properties, making them extremely effective atmospheric agents.

The main goal of this section is to overview the mechanisms of FA formation and their properties, and to discuss the sources and sinks of atmospheric FAs and their possible contribution to intra-atmospheric processes.

1.5.1 Introduction

The presence of aggregated structures in the atmosphere was detected very long ago: forest fires and volcanic eruptions are well known to produce tremendous amounts of ash and other aggregated particles. Many authors have attempted to estimate the role of the latter in the formation of the Earth's climate. Transport and industrial aerosol exhausts also often contain a considerable amount of aggregated particulate matter, not to mention such intense anthropogenic sources like oil and gas fires. Specialists on the "Nuclear Winter" did not push this problem to one side either.

Irregularly shaped particles have been studied for many years, but until fairly recently there was no unique and effective key idea for their characterization that would reflect the common origin of irregular aggregates or would allow the explanation of their physico-chemical behavior from a unique position.

Therefore, the fractal ideas introduced into physics (and other natural sciences) by Mandelbrot [29] immediately attracted the attention of aerosol scientists, who applied them for the characterization of atmospheric and laboratory-made aggregated aerosol particles.

So the fractal concept quickly found its way into the study of atmospheric aerosols. The success in its application to aerosols gave rise to a splash of fractal activity at the end of the 1980s and the beginning of the 1990s. The main efforts were directed at recording FAs in the atmosphere, attempting to define their fractal dimension, and returning the physics of FAs to the realm of the former and habitual ideas such as aerodynamic diameter, mobility, *coagulation efficiency*, and so on. Although the successes along this route were doubtless – even the optical properties of Titan's hazes were explained by assuming that they consist of FAs – the slight coolness that came later resulted, perhaps, from the impression that there is almost nothing to investigate any further. Of course, this is not so: the newly discovered physical and chemical properties of aggregated particles are pertinent to bear in mind in considering aerosol processes.

This section focuses on the properties of self-similar or, better, *scaling-invariant aggregates* – so-called fractals or fractal aggregates – whose structure is repeated within a considerable range of spatial scales (from tens of nanometers up to fractions of a centimeter or even more). This very kind of order stipulates many unusual properties of FAs.

The books edited by Avnir [30] and by Pietronero and Tosatti [31] contain sufficiently full information on the directions of the development of fractal physics and chemistry. The interested reader can find a regular account of fractal ideas in the book of Feder [32]. Colbeck *et al.* [33] reviewed the fractal concept and its application to environmental aerosols. The fairly recent textbook by Friedlander [34] also contains a chapter on fractals.

12

1.5.2 Phenomenology of Fractals

A typical FA consists of small spherules with diameters of several tens of nanometers united in an aggregate of size on the order of micrometers. It is important to stress that the sizes of the spherules are much less than the characteristic parameters in the atmosphere, such as the mean free path of molecules or the characteristic wavelength of solar radiation, whereas the total aggregate sizes are either comparable with these parameters or even exceed them. It is also not surprising that the main attention in studying the atmospheric FAs has been on soot aggregates.

In this section the main concepts characterizing FA are introduced.

- 1) **Mass of FA.** Any FA is characterized by its total mass *M*, which can also be measured in units of a spherule mass or, better, by the number *g* of spherules comprising the FA.
- 2) Size of FA. It is natural to introduce the gyration radius of an FA as

$$R^{2} = \frac{1}{g(g-1)} \sum_{i \neq j} (\mathbf{r}_{i} - \mathbf{r}_{j})^{2}$$
(1.40)

where r_i is the position of the *i*th spherule. The maximal size of an FA can also be of use:

$$d_{\max} = \max|\mathbf{r}_i - \mathbf{r}_j| \tag{1.41}$$

1.5.2.1 Fractal Dimension

Not every irregular aggregate is a fractal. The main point of the definition of an FA is the self-similarity at every scale, which eventually leads to rather odd ramified structures of FAs whose local mass distribution cannot be so easily measured.

The most straightforward way to measure *D* is to follow its definition. Let the FA (or other fractal object) be covered with boxes whose size ϵ goes to zero. If the number *N* of boxes filled with the elements of the FA grows as $N \longrightarrow \epsilon^{-D}$, then *D* is identified with the fractal dimension of the FA.

The simplest and yet still non-trivial example of the application of the fractal concept to real objects is the measurement of the length of a diffusion trajectory. The diffusion displacement is given by $\Delta = \sqrt{2Dt_{\Delta}}$. If we represent Δ as the sum of smaller and smaller diffusion displacements $\epsilon = \sqrt{2Dt_{\epsilon}}$, then we find that the number $N(\epsilon)$ of the ϵ displacements necessary to cover the diffusion route is $N(\epsilon) = t_{\Delta}/t_{\epsilon} \propto \epsilon^{-2}$. The fractal dimension of the diffusion trajectory is thus D = 2.

FAs are very loose objects. Their fractal dimension *D* characterizes the part of space occupied by FA matter. This means that the mass of an FA grows with its gyration radius *R* more slowly than R^3 : $M \propto R^D$, where D < 3. Such a dependence assumes that the FA density $\rho(r)$ changes with distance *r* from its center as

$$\rho(r) \propto \rho_0 \left(\frac{r_0}{r}\right)^{3-D} \tag{1.42}$$

at r < R and as $\rho(r) = 0$ otherwise. Here ρ_0 is the density of the spherule and r_0 is its radius. Equation (1.42) provides the R^D dependence of the FA mass to hold:

$$g = k_D \left(\frac{R}{r_0}\right)^D \tag{1.43}$$

where k_D is the fractal prefactor

1.5.2.2 Correlation Function

The density-density *correlation function* also drops as a power of distance *r*:

$$C(\mathbf{r}) = \left\langle \sum_{i} m(\mathbf{r}_{i})m(\mathbf{r}_{i}+\mathbf{r}) \right\rangle \propto r^{-(3-D)}$$
(1.44)

where $m(\mathbf{r})$ is the density at the point \mathbf{r} , the sum goes over all centers of spherules, and the angle brackets stand for averaging over all possible spatial configurations of the spherules.

1.5.2.3 Distribution of Voids

FAs thus mainly consist of "empty space" distributed among voids whose size spectrum is of great importance for the characterization of FAs. This spectrum normalized to unity has the form

$$n(a) = \frac{3 - D}{R^{3 - D}} a^{2 - D} \tag{1.45}$$

One immediately sees that the total volume occupied by the voids is exactly $4\pi R^3/3$ once the shape factor γ defining the dependence of the average volume V(a) of a void on its characteristic size *a* is given as $\gamma = 4\pi (6 - D)/3(3 - D)$ ($V = \gamma a^3$).

1.5.2.4 Phenomenology of Atmospheric FA

Measurements of D of atmospheric FAs have shown the following:

- Atmospheric FAs (mainly soot aggregates) are not well-developed fractal structures whose fractal dimensionality varies within the range 1.3–1.9, indicating that these FAs are of coagulation origin.
- 2) Such low fractal dimensions are explained by non-isotropy of observed FAs, which are mostly aligned in one direction. This anisotropy probably arises due to Coulomb or *dipole-dipole interaction* of FAs.
- 3) The fractal prefactor (Eq. (1.43)) for soot particles is $k_D \approx 27.46$ at D = 1.75.
- 4) The structure of atmospheric (soot) fractals may change by condensation–evaporation cycles: the loose FAs become more dense (*D* grows by 10–15%).

Katrinak *et al.* [35] analyzed urban aggregates within the size range 0.21-2.61 µm and found that *D* varies from 1.35 to 1.38. The maximal value of *D* found in [36] for diesel exhausts was D = 1.2, that is, their particles were strongly aligned. Considerable attention has been given by others [37–41] to the process of the transformation of FAs in a humid atmosphere. The chemical methods were applied by Eltekova *et al.* [42] for determining the *D* of soot FAs. The value of the

fractal prefactor was discussed by Nyeki and Colbeck [43], who showed that $k_{\rm f}$ is close to 1.

1.5.3 Possible Sources of Fractal Particles

The sources of FAs are subdivided into two groups: natural and anthropogenic ones.

1.5.3.1 Natural Sources

Volcanos Volcanic eruptions produce a lot of volcanic ash, consisting of aggregated oxide particles of the size from fractions of a micrometer up to millimeters. In addition, extreme volcanic conditions produce a lot of smaller aggregates.

Forest fires These produce a huge amount of ash flakes whose sizes vary from fractions of a micrometer up to centimeters. Smaller aggregated particles accompany the combustion process (aggregated carbon plus hydrocarbon particles or, better, soot). The chemical content of the ash flakes is known: they consist of the mineral residue of the combustion process, resins, hydrocarbons, and the products of their chemical interaction with atmospheric air.

Thunderstorms High-energy lightning processes are able to release carbon from carbon-containing molecules and thus to produce small (nanometer-sized) charged carbon particles (maybe in the fullerene form), which then aggregate, forming FAs and even aerogels.

Intra-atmospheric chemical processes Intra-atmospheric chemical and photochemical processes are able to produce substances of low volatility that may then solidify into nanoparticles. On colliding, these objects form fractal structures.

1.5.3.2 Anthropogenic Sources

Industrial exhausts These produce a lot of smoke particles, FAs among them. The chemical content of these aggregates corresponds to the average content of the smoke. Unfortunately, what share of these particles is aggregated is not yet established.

Transport exhausts Transport produces aggregated aerosol particles consisting of nanometric soot particles. The sizes of these aggregates rarely exceed a micrometer.

Gas–oil fires Such fires produce aggregated soot particles (black smokes) consisting of nanometric units that reach sizes on the order of fractions of a centimeter.

There are many other less substantial sources of fractal aggregates.

1.5.4 Formation of Fractal Aggregates

One of the most important branches of fractal science is the study of the growth kinetics of fractal objects. There exist two commonly accepted approaches to this problem.

- 1) The first is the direct modeling of the growth process. The elements of fractal construction (spherules or fractal fragments) are assumed to move on a lattice, collide, stick together, and finally form a fractal structure. The whole process is modeled by computer from the very beginning up to the end. This approach allows one to investigate the structure of a single fractal aggregate, and to define its fractal dimension and other individual characteristics. In particular, it was shown that the fractal dimension *D* is totally stipulated by the type of growth process: namely, coagulation leads to the most loose structure, with $D \approx 1.8$; diffusion-controlled condensation gives more dense particles, with $D \approx 2$; and the collision-limited condensation process (low-efficiency collisions do not permit the spherule to join to the aggregate immediately after the first collision) produces the most dense FAs, with $D \approx 2.4$.
- 2) The growth process is considered within a kinetic scheme describing the time evolution of fractal mass spectra irrespective of the details of the motion of the fractal fragments, the latter being included via *kinetic coefficients* whose mass dependence alone defines the characteristic features of the mass spectra. In contrast to direct modeling, this approach accounts for the collective characteristics, first and foremost the mass distribution of growing fractal aggregates.

Below, the second (kinetic) approach – more traditional for aerosol physics – is used for studying the time evolution of the mass distribution of a collection of FAs growing by condensation and coagulation. The collective is assumed to consist of aggregates whose fractal dimension *D* does not change during the growth process. The initial stage of FA formation assumes the formation of monomers (spherules). We do not discuss this process, since it does not contain anything specific to fractal physics.

1.5.4.1 Growth by Condensation

The latter includes the joining of monomeric units (spherules or monomers) of unit mass by one, with the *condensation coefficients* α_g being known functions of the fractal aggregate mass *g*.

It is not very difficult to see that the condensation coefficients α_g should be proportional to the total number of spherules in the FA in the free-molecule limit, and to the FA size in the continuum regime. Indeed, an FA has a loose structure and the incident spherule readily reaches any point inside the FA where it can be captured, unless the collisions with the molecules of the carrier gas make the incident spherule trajectory very long and "knotty." In this latter case the FA becomes a "black absorber," that is, the incident spherule randomly walks inside the FA for long enough to be absorbed even if the absorption efficiency is not very high, and the average density of matter inside the FA is negligibly low. Hence

$$\alpha_g = \alpha_0 g \tag{1.46}$$

in the free-molecule regime, and

$$\alpha_g = A \mathcal{D} n r_0 g^{1/D} \tag{1.47}$$

in the opposite limit (the continuum regime).

The physical meaning of the constants entering Eqs. (1.46) and (1.47) is apparent: α_0 (Eq. (1.46)) is the rate of capture of an incident spherule by a vacancy incorporated into the FA. The right-hand side of Eq. (1.47) repeats the expression for the rate of condensational growth of a sphere in the continuum regime, except that the constant *A* is replaced by the usual coefficient 4π specific for spherical geometry. Equation (1.47) thus describes the diffusion growth of an FA whose radius is proportional to $g^{1/D}$. The values of α_0 and *A* cannot be found from theoretical considerations and should be thus considered as fitting parameters.

1.5.4.2 Growth by Coagulation

Coagulation seems to be the most effective mechanism of FA growth. Sufficiently large fractal aggregates grown by coagulation have rather low fractal dimensionality $D \approx 1.8$. The rate of the coagulation process depends on the form of the coagulation kernel – the efficiency for two colliding particles to produce a new one whose mass is equal to the sum of the masses of the particles. The coagulation kernel is the collision cross-section multiplied by the relative velocity of the colliding fragments. The easiest way to estimate the coagulation kernels is just to extend well-known expressions for the coagulation kernels for the free-molecule, continuum or transition regimes by substituting $R \propto g^{1/D}$ instead of $R \propto g^{1/3}$. So, one may expect that the following collection of coagulation kernels governs the time evolution of mass spectra of coagulating FAs:

• free-molecule regime

$$K(x, y) \propto (x^{1/D} + y^{1/D})^2 \sqrt{x^{-1} + y^{-1}}$$
(1.48)

• continuum regime

 $K(x, y) \propto (x^{1/D} + y^{1/D})(x^{-1/D} + y^{-1/D})$ (1.49)

• turbulent regime

$$K(x, y) \propto (x^{1/D} + y^{1/D})^3$$
(1.50)

• coagulation of magnetic or electric dipoles

$$K(x,y) \propto x^{1/D} y^{1/D} \tag{1.51}$$

· coagulating FA form linear chains

$$K(x, y) \propto xy$$
 (1.52)

Here *x* and *y* stand for the masses of the colliding particles. All the above kernels are homogeneous functions of the variables *x* and *y*: $K(ax, ay) = a^{\lambda}K(x, y)$. The homogeneity exponent $\lambda < 1$ for the first two kernels, and may exceed unity otherwise. The latter fact means that the *aerosol–aerogel transition* is possible in the last three cases.

1.5.4.3 Aerosol-Aerogel Transition

This remarkable phenomenon consists of the formation of a macroscopic object (or objects) from initially microscopic aerosol particles. Everyone has seen the web-like structures or lengthy filaments suspended in the air or attached to the walls of cleaning devices. Sometimes such objects spontaneously arise in the carrier gas as a consequence of the coagulation process in cases when the coagulation kernel grows sufficiently fast with the colliding particle masses ($\lambda > 1$). Aerosols consisting of fractal aggregates are the most probable candidates to form aerogels by coagulation.

Atmospheric aerogel objects may play a crucial role in the formation of ball lightning. According to the model developed by Smirnov [44], ball lightning is a plasma ball spanned on an aerogel framework. This aerogel framework may form after a linear lightning strike, which is able to produce fractal aggregates by ablation or directly from carbon-containing molecules in the air. Although the dynamics of this process is not yet fully understood, the aerogel model was shown to be a useful perspective for explanation of many properties of ball lightning.

A huge literature is devoted to computer modeling of FA formation. It is summarized in the review article by Meakin [45]. The mass spectrum of a growing FA meets the set of kinetic equations describing FA condensational growth. These equations were analyzed and solved by Lushnikov and Kulmala [46].

Coagulation of fractals in the free-molecule regime was theoretically investigated by Wu and Friedlander [47, 48], who found considerable broadening of the particle mass spectra on decreasing the fractal dimensionality. Similar results were reported by Vemury and Prastinis [49]. Wu *et al.* [50] proposed a method for definition of *D* from the kinetics of coagulation. The interested reader will find a rather simple introduction to fractal physics in the review by Smirnov [51], where considerable attention is given to the kinetics of FA formation.

The coagulation in the system with the kernel K = xy was analyzed by Lushnikov [52–58], who showed that a gel should form from coagulating sol after a finite interval of time. Experimentally, this process was observed by Lushnikov *et al.* [59, 60], who supposed that the dipole–dipole interaction of FAs is responsible for this phenomenon.

1.5.5

Optics of Fractals

Atmospheric fractals reveal very specific optical properties interacting intensely with sunlight. This fact is linked closely with their structure: the geometrical size of the atmospheric FAs lies in the micrometer range, that is, the particle

1.5 Fractal Aggregates 19

sizes are comparable with the wavelength of visible light and infrared radiation. On the other hand, FAs are composed of tiny nanometer-sized units whose electrodynamic properties often differ from those of macroscopic objects. This felicitous combination of micro- and macro-properties together with a kind of spatial order (scaling invariance) stipulate specific optical properties of fractal aggregates.

Strong spatial correlations of the nanospherules (Eq. (1.44)) lead to the singularity in the differential elastic cross-section at small angles:

$$\frac{\mathrm{d}\sigma_e}{\mathrm{d}\Omega} \propto \int \mathrm{d}^3 r \ C(r) \,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \propto \frac{1}{q^D} \tag{1.53}$$

where $q = 2\pi\lambda^{-1}\sin(\theta/2)$ and θ is the scattering angle. This singular behavior serves in some cases for the experimental determination of the fractal dimension *D*.

Voids in FAs (Eq. (1.45)) may create the conditions for the capture of light quanta inside them. Sometimes (under special resonance conditions) FAs consisting of weakly absorbed spherules are able to absorb light.

In their comparison of a fractal smoke optical model with light extinction measurements, Dobbins *et al.* [61] used the following expressions for the absorption and elastic scattering cross-sections:

$$\sigma_{\rm abs} = \frac{6\pi E(m)}{\lambda \rho_p} \tag{1.54}$$

and

$$\sigma_{\rm sca} = \frac{4\pi \,\overline{n}^{(2)} F(m)}{\lambda \rho_p \overline{n}^{(1)}} \left(1 + \frac{4}{3D} k^2 R_{\rm g}^2\right)^{-D/2} \tag{1.55}$$

with $\overline{n}^{(1,2)}$ being the first and second moments of the FA size distribution function, $k = 2\pi/\lambda$, $x_p = 2\pi r_0/\lambda$, λ being the wavelength of the incident light,

$$E(m) = \operatorname{Im}\left(\frac{m^2 - 1}{m^2 + 2}\right)$$
 and $F(m) = \left|\frac{m^2 - 1}{m^2 + 2}\right|$ (1.56)

These rather simple expressions were applied for the analysis of the results on the light extinction of aggregated soot aerosols with D = 1.75, and a reasonable agreement of predicted and measured values was found.

The paper by Berry and Persival [62] gave the starting push to the studies of the optics of FAs. The computational analysis of the *Rayleigh–Debye–Gans theory* performed by Farias *et al.* [63] (see also references therein) showed its applicability for soot FAs. The authors concluded that this theory should replace other approximations for the description of soot optical properties, such as Rayleigh scattering and Mie scattering for an equivalent sphere. Lushnikov and Maximenko [64] investigated the localization effects in FAs and found that FAs with D < 3/2 consisting of weakly absorbing materials may nevertheless be "black" due to the capture of the incident light quanta by voids inside the FAs. Other optical properties (hyper-combinational scattering, scattering at small angles, and photoabsorption) of FAs were also investigated [65]. Cabane and colleagues [66, 67] explained the contradictions between the results of polarization and photometric measurements of the upper layer of Titan's atmosphere by assuming that FA clouds are responsible for the light scattering effects.

1.5.6 Are Atmospheric Fractals Long-Lived?

The answer to this question depends on the mobility of FAs, which is expected to be much lower than that of compact particles of the same mass. The experimental and numerical studies of the mobilities of aggregated particles allow for some useful semiempirical relations to be established.

In the continuum regime, it was found [68] that the mobility diameter of an FA is

$$d_{\rm mc} = 2\beta R_{\rm g} = \beta d_1 \sqrt{\frac{D}{D+1}} g^{1/D}$$
(1.57)

with $\beta = 0.7-1.0$ and d_1 being the spherule diameter. In the free-molecule kinetic regime, $d_{mk} \approx d_A$, where d_A is the radius of the equivalent projected sphere. The rather ancient "adjusted sphere" interpolation expression for the equivalent diameter by Dahneke (cited in [68]) has the form

$$\frac{d_{\rm m}}{C_{\rm c}({\rm Kn}_{\rm m})} = \frac{d_{\rm mc}}{C_{\rm c}({\rm Kn}_{\rm ck})}$$
(1.58)

where $d_{\rm m}$ is the transition mobility diameter, $d_{\rm mc}$ and $d_{\rm mk}$ are the kinetic and continuum regime mobility diameters defined above, ${\rm Kn}_{\rm m} = 2\lambda/d_{\rm m}$, and ${\rm Kn}_{\rm ck} = 2\lambda d_{\rm mc}/d_{\rm mk}^2$. The slip correction factor is introduced as

$$C_{\rm c}({\rm Kn}) = 1 + {\rm Kn}\left[A + B\exp\left(\frac{-C}{{\rm Kn}}\right)\right]$$
(1.59)

with A = 1.257, B = 0.4, and C = 1.1; λ is the mean free path. The sinks of FAs in the atmosphere are:

- diffusion deposition, which is smaller by $g^{2/D-2/3}$ in the free-molecule regime, and by $g^{1/D-1/3}$ in the continuum regime;
- sedimentation losses, which are smaller by $g^{1/D-1/3}$.

Other mechanisms are as follows:

- collapse by humidification, in which water condensation on atmospheric fractals may effectively enlarge their fractal dimensionality by 10–15%, making them more and more compact;
- water capture by (even hydrophobic) FAs;
- · scavenging by rain- and snowfall.

The latter two mechanisms are likely the most effective.

Colbeck and Wu [69] used the relation $d_{\rm m} \propto d_V^{3(D-1)/2D}$ linking the mobility diameter $d_{\rm m}$ with the volume equivalent diameter d_V for determination of *D* of smoke FAs. They found *D* to lie within the interval 1.40–1.96. A useful relation linking the particle mobility with the optical diameter of soot aggregates ($d_{\rm opt} \propto d_{\rm m}^{1/3}$) has been reported [70]. Expressions for thermal and sedimentation velocities in terms of a geometric particle diameter have also been given [71]. Huang *et al.* [38] performed experiments with diesel engines that emit chain–agglomerate particles

1.6 Coagulation 21

and found changes in *D* from 1.56 to 1.76 and from 1.40 to 1.54 depending on the sulfur content. The "rigidity" of the chains was demonstrated to grow on increasing the sulfur content.

1.5.7 **Concluding Remarks**

The fractal concept is undoubtedly fruitful for characterization of the present-day aerosol situation in the Earth's atmosphere. At the same time, it should be noted that the concept itself needs development when applied to atmospheric aerosols. The still not numerous observations of atmospheric fractal aggregates show that their sizes (better, the numbers of spherules comprising the aggregates) are not large enough to expose a well-developed fractal picture. Perhaps, distributions over *D* will be of use for their proper characterization.

The fractal aggregates manifest anomalous physico-chemical properties: their lifetimes are much longer than those of compact particles of the same mass (by 10-100 times in the case of atmospheric fractals); their light scattering and absorption cross-sections are higher by orders of magnitude than those of the equivalent collective non-aggregated spherules; and their chemical and catalytic activities are also enhanced by the specifics of the fractal aggregate morphology. This is why even a small admixture of fractal aggregates may seriously change the existing estimates of aerosol impact on the global radiation and chemical cycles in the atmosphere.

The condensation of atmospheric moisture on fractal aggregates was shown to restructure them, making the aggregates more compact. This process reduces their lifetimes. The recognition of this fact helps to answer the question of where to seek them. The upper layers of the atmosphere and near-space are the most probable places for the accumulation of fractal aggregates.

The fractals of the lower troposphere are mainly of anthropogenic origin and hardly to be thought as very desirable guests. Being good absorbers, they are able to accumulate harmful substances and radioactivity, and to transport them inside living organisms. Hence, the environmental aspects of the atmospheric fractal aggregates are of great importance.

1.6

Coagulation

Coagulation is a collective aerosol process. This means that the equation describing the kinetics of this process is nonlinear with respect to the particle size distribution (see Eq. (1.60) below). This section introduces the reader to some fairly new concepts that appeared not very long ago [54-58, 72, 73]. We begin with a short description of the coagulation process. More details can be found in the chapter written by Maisels in this book [74].

At first sight the coagulation process looks rather offenceless. A system of *M* monomeric objects begins to evolve by pair coalescence of *g*- and *l*-mers according to the scheme

$$(g) + (l) \longrightarrow (g+l) \tag{1.60}$$

It is easy to write down the kinetic equation governing this process as

$$\frac{\mathrm{d}c_g(t)}{\mathrm{d}t} = \frac{1}{2} \sum_{l=1}^{g-1} K(g-l,l) c_{g-l}(t) c_l(t) \, \mathrm{d}l - c_g(t) \sum_{l=1}^{\infty} K(g,l) c_l(t) \, \mathrm{d}l \tag{1.61}$$

This equation is known as the *Smoluchowski equation*. Here the coagulation kernel K(g, l) is the transition rate for the process given by Eq. (1.60). The first term on the right-hand side of Eq. (1.61) describes the gain in the *g*-mer concentration $c_g(t)$ due to coalescence of (g - l)- and *l*-mers, while the second one is responsible for the losses of *g*-mers due to their sticking to all other particles. Equation (1.61) can be rewritten in the integral form (sums on the right-hand side of Eq. (1.61) are replaced with integrals)

$$\frac{\partial c(g,t)}{\partial t} = \frac{1}{2} \int_0^g K(g-l,l)c(g-l,t)c(l,t) \, \mathrm{d}l - c(g,t) \int_0^\infty K(g,l)c(l,t) \, \mathrm{d}l \quad (1.62)$$

Eqs. (1.61) and (1.62) should be supplemented with the initial conditions,

$$c_g(0) = c_g^0$$
 or $c(g, 0) = c^0(g)$ (1.63)

where c^0 are known function of *g*.

There are a number of coagulation kernels that are commonly used in aerosol physics, and they look as follows:

1) Coagulation in the free-molecule regime:

$$K(g,l) = \pi a_0^2 \sqrt{\frac{8kT}{\pi m_0}} (g^{1/3} + l^{1/3})^2 \sqrt{g^{-1} + l^{-1}}$$
(1.64)

The physical meaning of this expression is apparent: it is just the geometrical cross-section of g- and l-mers times their mutual thermal velocity times their reduced mass. Here m_0 stands for the mass of the monomer. The analogy with the formula for the *condensation efficiency* of small particles is clearly seen.

2) Coagulation in the continuum regime:

$$K(g,l) = \frac{2kT}{3\rho\nu} (g^{1/3} + l^{1/3}) (g^{-1/3} + l^{-1/3})$$
(1.65)

3) Coagulation in laminar shear flow:

$$K(g,l) = \frac{4}{3}\Gamma m_0 (g^{1/3} + l^{1/3})^3$$
(1.66)

where Γ is the velocity gradient directed perpendicular to the flow of the carrier gas.

1.6 Coagulation 23

4) Coagulation in turbulent flow:

$$K(g, l) = \sqrt{\frac{\pi\epsilon}{120\nu}} 8a_0^3 (g^{1/3} + l^{1/3})^3$$
(1.67)

where ϵ is the rate of dissipation of kinetic energy of the turbulent flow per unit mass.

It is important to emphasize that the above kernels are homogeneous functions of g and l, that is,

$$K(ag, al) = a^{\lambda} K(g, l) \tag{1.68}$$

where λ is the homogeneity exponent.

Equations (1.61) and (1.62) can be modified by adding a source of fresh particles (the term *If*(*g*) on the right-hand side of these equations), a sink of particles (the term $\lambda_g c_g$), and the particle condensational growth (the term $\partial (\alpha_g c(g, t)/\partial g)$ on the left-hand side of Eq. (1.62)). Then the full equation (the general dynamic equation in the terminology of Friedlander [34]) has the form

$$\frac{\partial c(g,t)}{\partial t} + \frac{\partial \alpha(g)c(g,t)}{\partial g} = I(g) + (\operatorname{Kcc})_g - \lambda(g)c(g,t)$$
(1.69)

where $(Kcc)_g$ stands for the right-hand side of Eq. (1.62):

$$(\text{Kcc})_g = \frac{1}{2} \int_0^g K(g-l,l) c(g-l,t) c(l,t) \, \mathrm{d}l - c(g,t) \int_0^\infty K(g,l) c(l,t) \, \mathrm{d}l \qquad (1.70)$$

1.6.1

Asymptotic Distributions in Coagulating Systems

In what follows, we will use the dimensionless version of this equation, that is, all the concentrations are measured in units of the initial monomer concentration $c_1(0)$ and time in units of $1/c_1(0)K(1, 1)$. More details can be found in the review articles [75, 76].

Let us introduce a family of homogeneous kernels [72, 73, 77]

$$K(g,l) = \frac{1}{2} (g^{\alpha} l^{\beta} + l^{\alpha} g^{\beta})$$
(1.71)

Then

l

$$\lambda = \alpha + \beta \tag{1.72}$$

We also introduce the exponent μ , as

$$\iota = |\alpha - \beta| \tag{1.73}$$

In addition, we assume that the condensation efficiency may be approximated by an algebraic function,

$$\alpha_g \propto g^{\gamma}$$
 (1.74)

The late stages of the time evolution of disperse systems, when either coagulation alone governs the temporal changes of particle mass spectra or simultaneous

condensation complicates the evolution process, are studied under the assumption that the condensation efficiencies and coagulation kernels are homogeneous functions of the particle masses, with γ and λ , respectively, being their homogeneity exponents. Three types of coagulating systems are considered: (i) free coagulating systems, where coagulation alone is responsible for disperse particle growth; (ii) source-enhanced coagulating systems, where an external spatially uniform source permanently adds fresh small particles, with the particle productivity being an algebraic function of time, $I(t) \propto t^s$; and (iii) coagulating systems, in which a condensation process accompanies the coagulation growth of disperse particles. The particle mass distributions of the form

 $c_A(g,t) = A(t)\psi(gB(t))$ (1.75)

are shown to describe the asymptotic regimes of particle growth in all the three types of coagulating systems (g is the particle mass).

Friedlander [78] was the first to introduce the self-preserving form of the mass spectra in free coagulating systems. According to the hypothesis of self-preservation $A(t) = N^2(t)$, B(t) = N(t), with N(t) being the total number concentration of the coagulating particles. However, the family of self-preserving spectra is much wider (see [72, 73] and references therein).

The functions A(t) and B(t) are normally algebraic functions of time whose power exponents are found for all possible regimes of coagulation and condensation as functions of λ and γ . The equations for the universality function $\psi(x)$ are formulated. It is shown that in many cases $\psi(x) \propto x^{-\sigma}$ ($\sigma > 1$) at small x, that is, the particle mass distributions are *singular*. The power exponent σ is expressed in terms of λ and γ .

We have given the classification of the singular self-preserving regimes in coagulating systems and have defined the conditions for their realization. They are listed below.

1) In the free coagulating systems $\psi(x) \propto 1/x^{1+\lambda}$ at $x \ll 1$, which corresponds to the mass distribution of the form:

$$c_A(g,t) \propto \frac{1}{g^{1+\lambda}t} \tag{1.76}$$

The condition for the realization of this asymptotics is $\alpha, \beta > 0$. At $\beta = 0$ the singularity is weaker, $\psi(x) \propto 1/x^{1+\gamma}$, where $0 < \gamma < \lambda$.

It is not so difficult to understand the physical meaning of this condition: the rate of interaction of small particles ($g \propto 1$) with large ones ($g \gg 1$) is on the order of $K(1,g) \propto g^{\alpha}$ and $K(g,g) \propto g^{\lambda}$, respectively, that is, the smaller particles interact with the larger ones much more slowly than the large ones between themselves ($\alpha \leq \lambda$). Strongly polydisperse mass spectra thus form, in which the role of larger particles is less than that of smaller ones.

The situation changes drastically at $\beta < 0$. In this case $K(1,g) \gg K(g,g)$, that is, the larger particles "eat" the smaller ones much faster than each other. A hump in the distribution at large masses develops, while the concentrations of

small particles drops with time. A singular and a non-singular distribution are shown in Figure 1 of [73].

The inequality $\lambda, \mu \leq 1$ defines the conditions for the singular distributions to 2) exist in source-enhanced coagulating systems. It is simply the conditions for the convergence of the integral on the right-hand side of Eq. Eq. (1.62). The singularity of the mass spectra in the source-enhanced coagulating systems is $\psi(x) \propto x^{-(3+\lambda)/2}$ or, in terms of the particle masses,

$$c_A(g,t) \propto g^{-(3+\lambda)/2} t^{-(1-s)(1+\lambda)/2(1-\lambda)}$$
(1.77)

At s = 1 (a source that is constant in time) the time-dependent multiplier turns to unity. The mass spectrum has a steady-state left wing, that is, the spectrum of the highly disperse fraction is independent of time, although the source permanently supplies the system with fresh portions of small particles. These particles deposit mainly on the larger ones, providing the right wing of the spectrum to move to the right along the mass axis. The steady-state regimes of coagulation in source-enhanced systems have been investigated [79, 80] (see also [73] and references therein).

- We have considered systems of coagulating particles in which a source that is 3) constant in time produces a vapor of low volatility condensing onto the particle surfaces. The particle growth in such systems is similar in many respects to that in source-enhanced and (sometimes) free systems. Several regimes have been detected.
 - a. The disperse phase consumes all the mass of the vapor. In this case $\psi(x) \propto 1/x^{2-\gamma+\lambda}$, or

$$c_A(g,t) \propto 1/t^{2\gamma - 1 - \lambda} g^{2 - \gamma + \lambda} \tag{1.78}$$

The conditions for realizing these distributions are: $\gamma < 1$ and $2\gamma > 1 + \lambda$. At $\lambda < \gamma < (\lambda + 1)/2$ the coagulating-condensing system behaves like a source-enhanced coagulating system with linearly growing mass concentration.

b. When the mass of the disperse phase grows more slowly than t, the asymptotic mass distribution in coagulating-condensing systems is the same as in source-enhanced systems. The singular asymptotics, however, is never realized. At $\gamma \leq 2\lambda - 1$ condensation is so slow that the coagulating disperse system consumes only a finite part of the vapor and the coagulation process goes like in free coagulating systems.

Singular asymptotic distributions have been known since 1975 [81]. But what is especially wonderful is the fact that such distributions had appeared in the exactly solvable model K(g, l) = g + l [82], but people (including me) did not want to notice them. A thorough numerical analysis by Lee [83] showed that the characteristic time for reaching the singular asymptotics is much longer than in the case of non-singular distributions. I did not cite here very many of my own papers on asymptotic distributions (a false modesty), but one can find almost a full list of these works in Lushnikov and Kulmala [72, 73].

1.6.2 **Gelation in Coagulating Systems**

A half a century ago it had become clear that there is something wrong with Eq. (1.61). An attempt by Melzak [84] to find an exact solution to this equation for the kernel proportional to the masses of coalescing particles

$$K(g,l) \propto gl \tag{1.79}$$

had led to a strange conclusion that the total mass concentration ceases to conserve after a finite time $t = t_c$ (in what follows t_c is referred to as the critical time) and the second moment of the particle mass distribution $\phi_2 = \sum g^2 c_g$ has a singularity,

$$\phi_2(t) \propto \frac{1}{t_{\rm c} - t} \tag{1.80}$$

Even more strange is the fact that at $t = t_c$ nothing wrong happens either to the particle mass spectrum or the particle number concentration. The whole situation is displayed in Figure 1.4.

Immediately, the problems of the existence of the solution to Eq. (1.61) and of its uniqueness were posed and resolved [85-88]. But this did not help to answer the question of what does happen after $t = t_c$.

On the other hand, it is clear that, if we consider a finite coagulating system, then at any time we see a number of bigger and bigger particles whose total mass M cannot disappear somewhere. It is worthwhile to characterize such a system



concentrations of sol particles as functions of time (dimensionless units). After the critical time $t = t_c$ the mass concentration ceases to conserve, because a massive gel particle forms and begins to consume the mass of the sol. On the other hand, the

Figure 1.4 The total number and total mass number concentration does not feel the loss of one (although very big) gel particle. Still the post-critical behavior of the number concentration found from Eq. (1.61) differs from that predicted by the Smoluchowski equation (n(t) = 1 - t, dashed line).

by the set $\{n_g\}$ of occupation numbers of g-mers. Then it becomes possible to introduce the probability $W(\{n_g\}, t)$ for the realization of a given set at time *t*. Now the evolution of the coagulating system is fully described in terms of *W*. But a truncated description in terms of the average occupation numbers is also admissible:

$$\overline{n}_g(t) = \sum_{\{n_g\}} W(\{n_g\}, t) n_g \tag{1.81}$$

The particle concentrations are introduced as

$$c_{\rm g}(t) = \frac{\overline{n}_{\rm g}(t)}{V} \tag{1.82}$$

Here *V* is the total volume of the coagulating system.

Now we are ready to return to the question of what is going on in our system. The point is that the concentrations appearing in the Smoluchowski equation are defined as the thermodynamic limits of the ratios \overline{n}_g/V (where $V \rightarrow \infty$, $n_g \rightarrow \infty$, and their ratio is finite), that is, if \overline{n}_g are not large enough (for example, some of them $\propto V^{\alpha}$, $\alpha < 1$), then these particles are not "seen" in the thermodynamic limit, even if they exist. Still, these particles can have large masses, comparable to the mass of the entire system, and thus contribute to the mass balance. In coagulating systems, such particles can form *spontaneously* during a *finite* time (see Figure 1.5). This is gelation.

Two approaches have been applied for considering the *sol-gel transition*. The first approach does not conflict with the Smoluchowski description of gelling systems, that is, it starts with the Smoluchowski equation (see, for example, [89]). The mass deficiency appearing after the critical time is attributed to an *infinite* cluster (a gel), which is introduced "by hand" (its existence does not follow from the Smoluchowski equations) and serves only to restore mass conservation. The gel can be assumed to be either passive or active with respect to the sol fraction (defined as the collection of particles whose population numbers are macroscopically large). In the former case the gel grows due to a finite mass flux toward infinite particle sizes. The active gel grows, in addition, by consuming the sol particles. These two



Figure 1.5 The particle mass spectrum at $t - t_c = 0$, 0.05, and 0.1. It is seen how the gel appears from nothing.

mechanisms are thoroughly discussed in [90], where the reader will find references to earlier works.

More accurately (but, again, within the Smoluchowski scheme) this process had been considered in [91], where an instantaneous sink of particles with masses exceeding a large one, *G*, was introduced. Then the kinetics of coagulation can be described by a truncated Smoluchowski equation, and no paradox with the total mass concentration comes up, for the mass excess is attributed to the deposit: the particles with masses g > G consumed by the sink. Nevertheless, the difference between gelling and non-gelling systems manifests itself in the fact that during the whole pregelation period the mass is almost conserved, and only immediately after the critical time does a noticeable mass loss appear. The description of this model can be found in [58, 92].

The second, alternative, approach applying the Marcus [93] scheme to the gelation problem appeared earlier in [54–57, 94, 95]. The idea of this approach relies upon the consideration of finite coagulating systems. As mentioned above, this approach operates with the occupation numbers and the probability for the realization of a given set of occupation numbers. Within this scheme, the gel manifests itself as a narrow hump in the distribution of the average particle numbers over their masses. This hump appears after the critical time at macroscopically large mass $g \propto M$ and behaves like the active gel, that is, it influences the particle mass spectrum of the sol.

The master equation governing the time evolution of the probability is extremely complicated, but on replacing it by another one, for the generating functional of the probability *W*, it acquires a similarity with the Schrödinger equation for interacting quantum Bose fields. Although many features of the solution to the evolution equation for the generating functional were clear almost three decades ago, only very recently was I able to find the exact solution to this equation in a closed form and to analyze the behavior of the particle mass spectrum in the thermodynamic limit [54–58].

The description of the coagulation process in terms of occupation numbers (numbers of g-mers considered as random variables) was first introduced by [93]. This approach was then reformulated by me [52–58, 94, 95] in a form strongly reminiscent of the second quantization. Below I outline this approach.

The idea of this approach is very simple. Let us consider a process in which a pair of identical particles *A*, on colliding, produce one *A* particle (the process $A + A \longrightarrow A$). Let there be *M* such particles moving chaotically in the volume *V*. They collide and coalesce. Two particles produce one. This is exactly like in a coagulation process. The *collision rate* (the probability per unit time for a pair of particles to collide) is introduced as κ/V , where κ is the rate constant of the binary reaction $A + A \longrightarrow A$. The rate equation for the particle number concentration c(t) describes the kinetics of the process:

$$\frac{\mathrm{d}c}{\mathrm{d}t} = -\kappa c^2 \tag{1.83}$$

1.6 Coagulation 29

However, we can choose an alternative route and introduce the probability W(N, t) to find exactly N particles at time t in our system. It is also easy to guess that

$$\frac{\mathrm{d}W(N,t)}{\mathrm{d}t} = \frac{\kappa}{2V}[(N+1)NW(N+1,t) - N(N-1)W(N,t)]$$
(1.84)

The first term on the right-hand side of this equation gives the positive contribution to the rate $d_t W$ because of the coalescence of two particles ((N + 1)N/2) is the number of ways to choose a pair of coalescing particles from N + 1 particles). The second term describes the negative contribution to $d_t W$, because the particles continue to coalesce and transfer the system from the state with N particles to the state with N - 1 particles.

Hence, a simple nonlinear equation (1.83) is replaced by a set of linear equations (1.84). However, we do not stop at this point and will make a step forward. We introduce the generating function for our probability,

$$\Psi(z,t) = \sum_{N} W(N,t) z^{N}$$
(1.85)

From Eq. (1.84) we can derive the equation for Ψ as

$$V\frac{\partial\Psi}{\partial t} = \frac{\kappa}{2}(z-z^2)\frac{\partial^2\Psi}{\partial z^2}$$
(1.86)

This equation should be supplemented with the initial condition

$$\Psi(z,0) = \psi_0(z) \tag{1.87}$$

where $\psi_0(z)$ is a reasonable function (it should be analytical at z = 0). For example, if we fix the number of particles N_0 at the beginning of the process, then $\psi_0(z) = z^{N_0}$. Alternatively, the function $\psi_0(z) = e^{N_0(z-1)}$ corresponds to an initial Poisson distribution.

Two questions immediately come up: (i) Why should we introduce such a complex scheme for describing the kinetics of the reaction – why not use Eq. (1.83)? (ii) If the second scheme describes the same process as Eq. (1.83), then how do we derive Eq. (1.83) from Eq. (1.86)?

First, I answer the second question. Let us expand the right-hand side of Eq. (1.86) near z = 1, that is, we replace $z - z^2 \approx -2\xi$, where $\xi = z - 1 \ll 1$. We find from Eq. (1.86) that

$$V\frac{\partial\Psi}{\partial t} = -\kappa\xi \frac{\partial^2\Psi}{\partial\xi^2} \tag{1.88}$$

Now it is easy to solve this equation to obtain

$$\Psi(z,t) = e^{c(t)V(z-1)}$$
(1.89)

On substituting this into Eq. (1.88) we come to the conclusion that the concentration c(t) satisfies Eq. (1.83). Thus the probability has Poisson form. This approximation works well at very large N.

Now let us return to the first question. If we want to describe a *finite* system, then eventually we should use Eq. (1.84) or, better, Eq. (1.86). Because the description of

a gel demands a step beyond the scope of the thermodynamic limit, I will use this very approach, although it requires much more serious efforts for operating and understanding the final results.

Here the "pathological" coagulating systems have been considered, that is, systems whose development in time leads to the formation of an object that is not provided for by the initial theoretical assumptions. In our case it is the gel whose appearance breaks the hypothesis that the kinetics of coagulation can be described in terms of the particle number concentrations defined as the thermodynamic limit of the ratio (occupation numbers)/volume.

The coagulating system with kernel proportional to the product of the masses of two colliding particles is the central object of the present study. Although the main decisive step in understanding the nature of the sol–gel transition in finite systems with $K \propto gl$ had been done long ago, only recently was I able to find the exact solution of this salient problem [54–58, 92, 96]. The central goal of this section was to introduce the reader to the main ideas of the approach that I so adore. Here I have demonstrated that this approach is eminently applicable to the solution of other problems, like the time evolution of random graphs or gelation in coagulating mixtures.

At first sight, the coagulation process cannot lead to something wrong. Indeed, let us consider a *finite* system of *M* monomers in the volume *V*. If the monomers move, collide, and coalesce on colliding, the coagulation process, after all, forms one giant particle of mass *M*. The concentration of this *M*-mer is small, $c_M \propto 1/M$. It is better to say that it is zero in the thermodynamic limit $V, M \longrightarrow \infty$, $M/V = m < \infty$. In other words, no particles exist in coagulating systems after a sufficiently long time. But still something unexpected goes on in gelling systems after a finite interval of time. The gel forms.

Two scenarios of gelation in coagulating systems have been considered in [54–58, 92]. The first one considers the coagulation process in a system of a finite number M of monomers enclosed in a finite volume V. In this case any losses of mass are excluded "by definition." The gel appears as a *single* giant particle of mass g comparable to the total mass M of the whole system.

What happens then in the system with $K(g, l) \propto gl$ in the thermodynamic limit? The answer is simple, although in no way apparent. In contrast to "normal" systems, where the time of formation of a large object grows with M, a giant object with a mass on the order of M forms during a *finite* (independent of V and M) time t_c . After $t = t_c$ this giant particle (gel) actively begins to absorb the smaller particles. Although the probability for any two particles to meet is generally small ($\propto K(g, l)/V$), in the case of $g \propto M$ this smallness is compensated by the large value of the coagulation kernel proportional to the particle mass M, which is, in turn, proportional to V. Hence, the gel whose concentration is zero in the thermodynamic limit can play a considerable role in the evolution of the whole system. The structure of the kernel is also the reason why only one gel particle can form. The point is that the time for the process $(l) + (m) \longrightarrow (l + m)$ is short for $l, m \propto M$: $\tau \propto V/K(l, m) \propto V/M^2 \propto 1/V \longrightarrow 0$ in the thermodynamic limit.

Of course, the Smoluchowski equation is not able to detect particles with zero concentration.

As mentioned above, the total mass concentration of the spectrum $\overline{n}_g^{(s)}(t)$ is not conserved at $t > t_c$. It is easy to show [54–57] that the deficit of the mass concentration after the critical time t_c is

$$2t = \frac{1}{\mu_{\rm c}(t)} \ln\left(\frac{1}{1 - \mu_{\rm c}(t)}\right) \qquad \text{or} \qquad \mu_{\rm c} = 1 - e^{-2\mu_{\rm c}t} \tag{1.90}$$

This equation has only one root $\mu_c(t) = 0$ at $t < t_c$ and two roots at $t > t_c$. It is clear why we should choose the positive non-zero root after the critical time.

The mass distribution in the variables g, ϵ has the form (see also [54])

$$\overline{n}_g(t) = C(g,\epsilon) \exp\left(-\frac{g^3}{8M^2} + \epsilon \frac{g^2}{M} - 2g\epsilon^2\right)$$
(1.91)

Unfortunately, our asymptotic analysis does not allow for restoring the normalization factor $C(g, \epsilon)$. Still, some conclusions on its form can be retrieved from the mass conservation,

$$C(g,\epsilon) = \frac{M}{\sqrt{2\pi g^5}} + \frac{\sqrt{\epsilon}\,\theta(\epsilon)}{\sqrt{2\pi M}}$$
(1.92)

with $\theta(\epsilon)$ being the Heaviside step function. Indeed, below the transition point the total mass is conserved and the asymptotic mass spectrum is known. Equations (1.91) and (1.92) reproduce the latter at $g \ll M$. Above the transition point the second term normalizes the peak appearing at $g = \mu_- M$ to unity.

Now it becomes possible to describe what is going on. Below the transition point (at $\epsilon < 0$) the mass spectrum drops exponentially with increasing *g*. The terms containing *M* in the denominators (see Eq. (1.91)) play a role only at $g \propto M$. At these masses, the particle concentrations are exponentially small. In short, in the thermodynamic limit and at $\epsilon < 0$ the first two terms in the exponent on the right-hand side of Eq. (1.91) can be ignored. The spectrum is thus given by the equation

$$\overline{n}_g(t) = \frac{M}{\sqrt{2\pi g^5}} e^{-2g\epsilon^2}$$
(1.93)

At the critical point ($t = t_c$ or $\epsilon = 0$) the spectrum acquires the form

$$\overline{n}_g(t) = \frac{M}{\sqrt{2\pi g^5}} e^{-g^3/8M^2}$$
(1.94)

Although the expression in the exponent contains *M* in the denominator, we have no right to ignore it, for this exponential factor provides the convergence of the integral for the second moment $\phi_2 = M^{-1} \sum g^2 \overline{n_g}$ in the limit $M \longrightarrow \infty$. We thus have

$$\phi_2(t_c) = \frac{1}{\sqrt{2\pi}} \int_0^M \frac{e^{-g^3/8M^2} \, dg}{\sqrt{g}} \approx \frac{1}{3\sqrt{\pi}} \Gamma\left(\frac{1}{6}\right) M^{1/3}$$
(1.95)

Here $\Gamma(x)$ is the Euler gamma function.

The second (and the most widespread) scenario assumes that after the critical time the coagulation process instantly transfers large particles to a gel state, the latter being defined as an infinite cluster. This gel can be either passive (it does not interact with the coagulating particles) or active (coagulating particles can stick to the gel). In the latter case, the gel should be taken into account in the mass balance and no paradox with the loss of total mass comes up (see [52, 53, 94, 95]). Still, neither this definition nor the post-gel solutions to the Smoluchowski equation give a clear answer to the question of what the gel is.

The situation becomes more clear on considering a class of so-called truncated models (Section 1.5). In these models a cutoff particle mass G is introduced. The truncation is treated as an instant sink removing very heavy particles with masses g > G from the system. So we sacrifice mass conservation from the very beginning. The particles whose mass exceeds G form a deposit (gel) and do not contribute to the mass balance. Of course, the total mass of the active particles plus deposit is conserved. The time evolution of the spectrum of active particles (with masses g < G) is described by the Smoluchowski equation as before, with the limit ∞ in the loss term being replaced with the cutoff mass G. The set of kinetic equations then becomes finite and no catastrophe is expected to come up. We have shown that, indeed, nothing wrong happens even for the coagulation kernel $K \propto gl$. The total mass concentration of active particles drops with time, as it should, because the largest particles settle out to deposit. But as $G \longrightarrow \infty$ the total mass concentration of active particles is almost conserved at $t < t_c$ and only after the critical time ($t_c - t \propto G^{-1/2}$) does the deposit begin to form and the mass to drop down with time.

The question immediately comes up: What kernels are pathological? In 1973 I tried to answer this question. A primitive analysis of [97] (see also [73]) shows that for homogeneous kernels $K(ag, al) = a^{\lambda} K(g, l)$ the self-preserving asymptotic solution to the Smoluchowski equation should have the form:

$$c_g(t) \approx t^{-2/(1-\lambda)} \psi(gt^{-1/(1-\lambda)})$$
 (1.96)

This asymptotic formula shows that something wrong should happen at $\lambda > 1$. So the kernels with $\lambda > 1$ occurred under suspicion. This opinion has survived until now. People continue to attack this problem, but the problem remains too hard. What is known up to now? For the kernels $K_{\alpha}(g, l) = g^{\alpha} l^{\alpha}$ it has been proved that the sol-gel transition exists [76]. At $\alpha > 1$ a gel appears already from the very beginning of the coagulation process ($t_c = 0$). So we know very little.

The model $K \propto gl$ considered in detail here admits an exact solution. As has been shown, this solution is not so simple, especially if one tries to consider a finite system. More general models are less pleasant in this respect. Still, the approaches described above can help to answer quantitatively what is going on in more general systems. For example, the truncated models can be analyzed numerically. We can find the time behavior of particle mass concentration, to detect the gelation point (there is a chance that the mass ceases to be conserved very near the critical

point), and to try to look for a solution that decreases as t^{-1} (post-critical behavior). Moreover, such attempts have been reported (see [76]).

1.7

Laser-Induced Aerosols

The idea to use powerful lasers for aerosol particle production appeared rather long ago (see [59] and references therein). Although the laser technologies are typically expensive and not very productive, their advantages are apparent: in irradiating the targets (solid, liquid or even gaseous), it is easy to reach the necessary regimes for particle formation by changing the parameters of the incident laser beam and the carrier gas inside the vessel containing the target.

The laser beam interacting with a solid target creates a heated spot erupting plasma consisting of ionized vapor molecules and molecules of the carrier gas. This plasma cloud screens partially (or even totally in the case of breakdown) the incident light, heating itself by photoabsorption. Simultaneously it begins to expand. On cooling enough, the vapor of the target material begins to form aerosol particles, that then grow by condensing vapor molecules and coagulation. The balance of the characteristic times of all these processes defines the characteristics of the produced aerosol particles: number concentration, the shape of the particle size distribution, degree of agglomeration, and so on.

The chain of events leading to aerosol formation looks as follows:

The latter stage goes only in specially chosen conditions. Below, all the stages of the *laser-induced aerosols* are considered step by step.

1.7.1 Formation of Plasma Cloud

Focused laser irradiation heats the spot on the target surface up to temperatures above the boiling point. At the characteristic pulse energies of our experiment, the time for heat propagation inside the target body is much longer than the evaporation time, that is, all *absorbed* energy is spent on evaporating the atoms of the target material. The pressure of the vapor in the plasma cloud formed in this way is typically a little below the saturation pressure. The erupted vapor forms a one-dimensional plasma beam, the front of which propagates with the sound speed, has a temperature of $T_f \approx 0.7T_0$ (T_0 is the spot temperature), and has a density of $\rho_f = 0.25\rho_s$. The flux of evaporated atoms is $J \propto v_T N_0$. The vapor plasma is strongly non-equilibrium and the density of ions exceeds its equilibrium value by several decimal orders and reaches the value $N_i \propto 10^{18}-10^{20}$ cm⁻³.

1.7.1.1 Nucleation plus Condensational Growth

The front temperature of the plasma cloud is sufficiently low for aerosol particles to form. The characteristic times for particle formation are typically on the order of 10^{-9} s, that is, much shorter than the cloud formation times (10^{-7} s). This fact means that all erupted vapor is spent for particle formation and allows one to evaluate the total particle number per pulse. Most likely, the number concentration of the aerosol particles is on the order of the ion number concentration, that is, heterogeneous nucleation on ions plays the central role. In this case the nucleation–condensation process should produce the particles are typically several times bigger, which likely means that not all ions are effective condensation nuclei. There is another explanation of this fact: not all particles are formed simultaneously. The earlier particles may then deplete the vapor and not permit the other smaller embryos to grow up to the particle size.

1.7.1.2 Coagulation

The concentration of forming particles is extremely high, so the characteristic coagulation times should be of the order of 10^{-5} s (this is the upper estimate). The coagulation process is thus longer than the lifetime of the plasma cloud, which means that already cooled (solid) particles enter the coagulation process, thereby forming rather loose fractal aggregates with fractal dimensionality close to the D = 1.8 characteristic for the coagulation process. It is not easy to treat respective experimental data, for measurements of the aggregate mass spectra are still impossible. Nor are the mechanisms of aggregate–aggregate interaction well recognized.

The resulting particle mass spectra depend strongly on the form of the coagulation kernels. Wu and Friedlander [47, 48] assumed that the extension of free-molecule coagulation is enough in order to describe the coagulation of fractal aggregates. They replaced the colliding particle radii by $r \propto M^{1/D}$ in the expression for the coagulation kernel and investigated the dependence of the asymptotic mass spectra on *D*. The latter was shown to become broader with decreasing *D*. Another assumption was made by Lushnikov *et al.* [59]; the coagulation kernel is proportional to $(r_1 + r_2)^{\alpha}$ with $\alpha = 2$ or 3. In this case the homogeneity exponent of the coagulation kernel exceeds 1, and a gelation process should occur [59].

1.7.2

Laser-Induced Gelation

A strong laser beam hitting a solid target produces an eruption of vapor. Subsequent condensation of the cooling vapor gives nanometric particles that are able to form very crumbly fractal aggregates of micrometer size. In turn, aerosols consisting of such aggregates continue to coagulate. The most enigmatic is the final stage of the ageing process: the fractal aggregates form a web-like structure of macroscopic size. The experimental observation of this effect was reported by Lushnikov, Negin and Pakhomov [59] (hereafter LNP). Later, similar experiments were performed by

1.7 Laser-Induced Aerosols 35

Friedlander's group, which investigated in addition some properties of the *fractal filaments* [98]. A theoretical explanation of this effect appeared much earlier [52, 53, 94, 95], who gave an exact analysis of the *Flory–Stockmeyer model* of polymerization (coagulation kernel $K \propto gl$ with g and l being the masses of colliding particles) and showed that *one* giant object (superparticle) should appear after a *finite* interval of time. This effect was then studied theoretically by a number of authors (for citations see the book *Fractals in Physics* [31]) who gave some evidence in favor of the fact that such a phenomenon is not a rarity and is of great significance for understanding the processes of fractal structure growth.

Let us consider the coagulation of particles placed in a uniform electric field of strength *E*. This field induces the dipole moment $d = \alpha E$, with α being the particle polarizability. The interaction energy of two particles is proportional to d_1d_2 and maximal for two aligned dipoles. The latter fact means that the coagulating particle should form a needle-like structure as observed in LNP. Below, we assume that the mutual particle motion is due to their dipole–dipole interaction. The kinetics of needle-like particle formation is thus described by the Smoluchowski equation, with the coagulation kernel proportional to the scalar product of the field-induced dipole moments: $K(g, l) \propto d_1d_2$. The polarizability of each needle is proportional to its maximal size, which, in turn, is proportional to the total mass of the needle *g*. This means that the coagulation kernel has the form

$$\mathbf{K} = k_0 E^2 g l \tag{1.97}$$

with k_0 being a proportionality coefficient.

The equation for the second moment of the particle mass spectrum, $\phi_2(t) = \sum g^2 c_g(t)$, describes the kinetics of the pre-gelation period $t < t_c$:

$$\phi_2(t) = [Kc_0(t_c - t)]^{-1}$$
(1.98)

where the critical time

$$t_{\rm c} = [k_0 E^2 \phi_2(0)]^{-1} \tag{1.99}$$

depends on the strength of the external electric field. Equations (1.98) and (1.99) were checked experimentally. To this end Fe, Ti, Ag, and Al targets placed in a specially designed vessel filled with inert carrier gas at different pressures were irradiated by pulsed ruby and CO_2 lasers. The time dependence of the scattered light signal was recorded and the dependence of t_c on *E* was found.

The comparison of the theoretical and experimental results clearly favors the coagulation mechanism of gelation. The coagulation kernel is proportional to the product of the dipole moments of the coagulating particles. Such a mechanism evidently produces needle-like structures. The specifics of the coagulation interaction eventually lead to the phase transition: during a finite period of time, a macroscopic object forms (in this particular case, it is a set of fractal filaments).

Fractal filaments that result from the aerosol-aerogel transition are of interest for those who develop the technology of nanomaterials. Although the laser method has many disadvantages (it is expensive and complicated), it does allow the

production of aerogels made out of any thermostable material. There are many other processes giving fractal filaments: plasma discharge (for example, electric sparks), and thermal or chemical decomposition (for example, it is no problem to produce aerogels by thermal decomposition of Fe(CO)₅). The application of fractal filaments is a matter for the future.

1.8

Conclusion

Aerosol science does not belong to the group of sciences that are based on one equation or principle, like, for example, classical mechanics (Newton's equation), quantum mechanics (Schrödinger's equation), classical electrodynamics (Maxwell's equations), and so on. Rather, aerosol science applies the results and methods adopted from all other sciences. In particular, Newton's equation applies in aerosol mechanics, Maxwell's equations are used in the theory of light scattering by aerosols, quantum-mechanical approaches are needed for studying the structure of small clusters, and even quantum field ideas have been used in aerosol science – the theory of gelation, the derivation of Mie theory from quantum principles [99], and the study of inelastic electromagnetic processes on aerosol particles [100]. This rather speckled structure of aerosol science makes it difficult to write a review enveloping all branches of aerosol science. Here I have restricted myself to the problems of kinetics of aerosols.

Coagulation Aerosol particles are not simply suspended in a carrier gas. They always move due to their collisions with the carrier gas molecules. On colliding, the moving particles coalesce, forming a new daughter particle with mass equal to the total mass of the parent particles. This process continues until very few particles remain in the system.

There are two problems in the theory of coagulation: (i) how to find the efficiency of particle collisions; and (ii) how to describe the time evolution of coagulating aerosols, once the collision rates are known functions of the particle sizes. Both problems have been considered. Sometimes coagulation leads to gelation. I have explained in short the conditions under which the gel can form (without entering into the heavy mathematical details).

Charging of particles Charging of aerosol particles is of undoubted importance. An aerosol particle can carry from one to thousands of elementary charges. I have discussed the kinetics of particle charging. My starting point was the flux matching theory of charge transport in the carrier gas. The Coulomb and image forces make the problem extremely complicated, especially because the image forces are singular at the particle surface. Without derivation, I exposed the final results for the charging efficiency of aerosol particles.

References 37

Drag on aerosol particle In this section I discussed the drag force on an aerosol particle of a given radius. The central result is the formula proposed by Millikan and derived by Phillips from the numerical analysis of the Boltzmann equation. Mobility, electromobility, and diffusivity are discussed in the light of this formula.

Condensation, evaporation, nucleation These problems are discussed in a separate chapter in this book [101]. The situation with nucleation remains unsatisfactory. As for condensation, I showed that semiempirical formulas by Fuchs and Sutugin and by Dahneke give results very close to the expression derived theoretically by Lushnikov and Kulmala. The advantage of the latter approach is the possibility to extend it to more complicated situation when a single particle–molecule interaction is switched on.

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