Chapter 2
Formation of Aerosols in the Atmosphere

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Abstract Atmosphere aerosol is one of the most important factors affecting the Earth’s climatic and weather conditions. The study of the mechanisms of formation and evolution of atmospheric aerosols is of primary importance for predictions of the climatic changes on our planet. We hope that this short overview of the modern state of art in aerosol science will be of use to all those who are involved to the study of atmospheric processes that form the Earth’s climate. We introduce the readers to the basics of physical chemistry of aerosols. Special attention is given to the latest achievements in the theory of particle formation and their subsequent growth.

Keywords Aerosols · Nucleation · Condensation · Growth

2.1 Introduction

Atmospheric aerosols and trace gases affect considerably the global characteristics of the Earth’s atmosphere [1–7]. The point is that these components play a decisive direct and indirect role in the energy balance of the atmosphere. In particular, the aerosols define the cloudiness of the sky: cloud formation is impossible without cloud condensation nuclei [8]. Submicron atmospheric aerosol particles play the role of such nuclei [4,6,7].

On the other hand, the aerosols are of primary importance in the atmospheric chemical processes. It is enough to recall the ozone holes, not mentioning other atmospheric chemical cycles, where aerosols participate either as catalysts or as an
active reactant. Therefore, it is of interest to know the mechanisms of particle formation in the atmosphere [1,3,6,7].

Attempts to answer questions such as, where are the aerosol particles from? what structure do they have? and what is their chemical composition? appeared already more than one and half century ago (see [9–11]). Up to now no definite answers have been found. Aerosol particles are even less studied objects than the elementary particles and quarks. The reasons for such a situation are clear. The small sizes of aerosol particles do not allow them to be watched through optical microscopes. Normally, the sizes of particles that are especially interesting for investigations do not exceed 100 nm, i.e., these particles are much smaller than the wavelength of visible light. Next, they are transparent (and thus invisible) in UV light and x-rays. The atmospheric aerosol particles immediately evaporate under the electronic beam in electron microscopes. The mass spectrometry is also practically powerless in the study of tiniest atmospheric aerosols, because the samples contain very small quantities of the aerosol substance, and it is impossible to come to some definite conclusions on the chemical composition of the particles [12]. Next, the atmospheric aerosols do appear under well-defined conditions. The point is that the atmosphere is a stochastic medium and it is very difficult (better to say, impossible) to control all the parameters governing intra-atmospheric physicochemical processes.

The submicron atmospheric aerosols were the most popular object for the study since 3 decades ago. The reason for the interest to this item is clear. These very particles are optically active. They play the crucial role in cloud formation. On the other hand, these particles have their predecessors. At present the standard aerosol instruments permit to detect the particles of nanometer sizes [12–15]. It occurs, however, that this limit is not enough for answering all questions concerning the mechanisms of gas-to-particle conversion.

The goal of this short overview is to introduce the outside reader to the circle of problems related to the particle formation and growth in the atmosphere.

2.2 Classification of Aerosols

The aerosols are divided into two classes: primary aerosols and secondary aerosols, according to the mechanisms of their origination. The 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 physicochemical processes like humidification, gas–particle reactions, coagulation, etc. 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 the number of global processes like formation of clouds. They serve as the centers for heterogeneous nucleation of water vapor [8]. No aerosols – no clouds, so one can imagine how our planet would look without the secondary aerosol particles.
Primary and secondary aerosols are characterized with the size, shape, and chemical contents of aerosol particles. As for the shape, one normally assumes that the particles are spheres. Of course, this assumption is an idealization necessary for the simplification of mathematical problems related to the behavior of aerosol particles. There are many aerosols comprising the irregularly shaped particles. The nonsphericity of particles creates a heap of problems. There exist also agglomerates of particles which in some cases reveal the fractal properties.

There are a number of classifications of particles with respect to their sizes. For example, if the particles are much smaller than the molecular mean free path, they are referred to as fine particles. This size ranges from 1 to 10 nm at normal conditions. But from the point of view of aerosol optics these particles are not small if the light wave length 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 one solves a concrete physical problem.

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

\[
P(x) = \int_{0}^{\infty} R(x,a)f(a)da.
\] (2.1)

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 \(x\) of the aerosol, 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 \(f(a)\) is normalized to unity,

\[
\int_{0}^{\infty} f(a)da = 1.
\] (2.2)

Although the particle size distribution is an elusive characteristic of the aerosol, it is convenient to introduce it because it unifies all properties of aerosols.

In many cases the distribution function can be found on solving the general dynamic equation governing the time evolution of the particle size distribution can be found theoretically [1], but the methods for analyzing this equation are not yet reliable, not mentioning the information on the coefficients entering this equation. This is the reason why the phenomenological distributions are so widespread.
There is a commonly accepted collection of particle size distributions. It includes:

The lognormal distribution \[ 1,3,16\],

\[
f_L(a) = \frac{1}{\sqrt{2\pi a_s\ln\sigma}} \exp\left(-\frac{1}{2\ln^2\sigma} \ln^2\frac{a}{a_s}\right).
\] (2.3)

Here \(a\) is the particle radius. This distribution depends on two parameters: \(a_s\) and \(\sigma\) where \(a_s\) is the characteristic particle radius and \(\sigma\) is the width of the distribution. Equation (2.3) is the famous lognormal distribution. It is important to emphasize that it is not derived from a theoretical consideration. Rather, it is introduced “by hands” for different set of the parameters.

Another size distribution (the generalized gamma-distribution) is given by the formula:

\[
f_G(a) = \frac{1}{\Gamma(k/j)} \left(\frac{a}{a_s}\right)^k \exp\left[-\left(\frac{a}{a_s}\right)^j\right].
\] (2.4)

Here \(\Gamma(x)\) is the Euler gamma-function. The distribution \(f_G(a)\) depends on three parameters, \(a_s\), \(k\), and \(j\) \([1,3,17]\).

### 2.3 Nucleation Scenarios

Nucleation is responsible for production of the tiniest particles due to gas-to-particle conversion \([18–21]\). Condensable vapors cannot exist in the vapor phase under certain conditions; normally when the vapor pressure exceeds the saturation value that, in turn, depends on the temperature. Statistical mechanics predicts the phase transition in these cases, but it does not answer the question, how does the transition go on. For example, the vapor can condense either on the walls of the vessel containing the gas–vapor mixture, or on foreign aerosol particles suspended in the carrier gas, or form the particles itself without any help from other external factors. The latter case is referred to as spontaneous nucleation. There are some principal difficulties in the theoretical description of the nucleation process. We will try to elucidate the nature of these difficulties and outline the ways for avoiding them.

Although everybody saw how a kettle boils producing visible vapor from its nose, the quantitative measurements on the nucleation are very far from being simple. The point is that respective nucleation theories are applicable for steady-state and very clean (no foreign condensation nuclei) conditions. To provide such conditions is not an easy task.

Already for many decades there exists an irreconcilable conflict between the theoretical predictions and the experimental data on the spontaneous nucleation of vapors. The reason for this is quite clear: the problem itself is far from being simple.
either theoretically or experimentally. This opinion is commonly recognized and shared by most of the researchers investigating the nucleation of vapors (and not only vapors). After the brain storm of 60th and 70th (everybody remember the hot battles around the Lothe–Pound correction) the development of our knowledge on the nature of this remarkable phenomenon returned to a quiet stream. Although the necessity in a correct and reliable Nucleation Theory had been emphasized many times by very diverse leaders of Physics of Aerosols and Physics of Clouds, nobody yet died because of the absence of such a theory. Decades elapsed, but as it was many years ago the new generations of scientists continue to investigate the properties and the content of critical embrii, investigate the details of the particle formation under different specific conditions, and seek for the interpretable nucleation events in the atmosphere. Of course, the situation with the experiment and especially with theory principally changed. First of all, it became possible to model the nucleation processes on computers that allowed for performing very complicated and quite informative numerical experiments. And still the nature of the discrepancies remains unclear.

The diversity of the results of nucleation measurements makes us to think that there could exist a number of principally different scenarios of the nucleation processes. This section introduces the readers to some of them.

### 2.3.1 Thermodynamically Controlled Nucleation

Statistical physics predicts that after a long time under nucleation conditions a one droplet $+\text{nucleating gas}$ will occur in the thermodynamic equilibrium [22–24]. The mass of the droplet is $\propto V$ (here $V$ is the total volume of the system), i.e., it is infinitely large. The starting point for the thermodynamic consideration is the Gibbs distribution

$$W \propto \exp \left( \frac{H(p, q)}{kT} \right),$$

(2.5)

where $p, q$ are generalized moments and coordinates respectively, $k$ is the Boltzmann constant, and $T$ is the temperature in K. The Hamiltonian $H$ possesses the property of the translation invariance, which means that all correlation functions depend on the differences of respective spatial variables. The density is thus independent of the coordinates. This fact is somewhat strange in view of existence of the macroscopic droplet. The latter should possess a boundary (interface) that should locate somewhere. On the other hand, the distribution (2.5) predicts the spatially uniform density, i.e., it does not see the interface. Next, the pair correlation function should distinguish the molecules in the gas and liquid phases. No conflict, however, arises, for the distribution function does not specify the location of the interface. The droplet is simply spread over the coordinate space. If we fix the
location of the interface, then the translation invariance is broken (this step is
equivalent to adding an external force field depending on coordinates). Pay attention,
that in doing so we introduce (by hands) a new information in the system thus
changing its entropy.

The first attempts to describe the nucleation process based on the thermodynamic
theory of fluctuations (see [24] and references therein). The idea was (and is)
quite clear and transparent: the molecules of a condensing vapor should occur in a
volume, where the intermolecular interaction is sufficiently strong to keep them
together. In order to find the probability to form such a cluster (critical or supercritical
embryo), it is necessary to find the free energy of the cluster and exponentiate it.
The problem is just how to find this free energy. It is quite natural to assume that
this free energy is identical to the free energy of a liquid (solid) droplet of the
condensing substance. This assumption is not so bad for large droplets, but if the
embryo is small, the doubts in the validity of such approach can arise. Of course, it
is possible to try to find the free energy starting with the microprinciples, that is,
to calculate the free energy of the cluster by solving the respective classical or
quantum mechanical problem.

It is commonly accepted to express the nucleation rate in terms of the probability
for the critical embryo to exist and a kinetic factor describing the flux of nucleating
vapor toward the growing embryo,

\[ J = Z_c \exp \left( -\frac{G}{kT} \right). \]  

(2.6)

Here \( Z_c \) is the flux of vapor.

The values of central interest are the formation energy \( G \) and the size of the
critical embryo. There exist numerous models of critical embryo beginning with the
macroscopic (droplet) model describing the energetics of the critical embryo in
terms of macroscopic characteristics (surface tension, bulk density) and ending with
entirely microscopic models that use the pair intermolecular potential for evaluating
the partition functions of the embryo.

This scenario will be referred to as “thermodynamically controlled nucleation”,
for it assumes setting a thermodynamic equilibrium inside the embryo. Many
nucleation processes (but not all) are thermodynamically controlled. The flux of
nucleating vapor to the growing embryo is reported in refs [25–30].

### 2.3.2 Kinetically Controlled Nucleation

It is very difficult to imagine that a very slow thermodynamically controlled
nucleation scenario can realize in the atmosphere. More likely is another scenario
that assumes the formation of the critical embryo after one successful collision of
two vapor molecules. In this case a dimer forms. This dimer can grow and cast to a
trimer etc., once the latter is stable. The formation of the dimer requires the presence of a third body that takes away the excess of energy appearing after the formation of the bound state of two molecules. The nucleation rate in this case is proportional to the second power of the vapor concentration. This scenario has been recently investigated in detail in ref. [25]. It has been shown that only the bound states of the dimer contribute to the growth process, which means that a thermodynamic equilibrium is never attained in this case. The states in the continuous spectrum have a short lifetime and thus should be ignored in the kinetic consideration of the process.

The kinetic approach allows one to assume that the supercritical embryo can form via the formation of mixed clusters comprising the molecules of the condensing vapor and the molecules of the carrier gas. When such a cluster grows and reaches a thermodynamically controllable size, the molecules of the carrier gas are lost (they evaporate back from the droplet). The mixed states of the growing embryo are apparently non-equilibrium and thus cannot be predicted within the scopes of the thermodynamically controlled scenario. As far as we know, nobody yet tried to consider such a type of nucleation. Meanwhile, the existing experiments sometimes display the dependence of the nucleation rate on the pressure of the carrier gas.

The kinetics of the particle formation–growth process is described by the Szillard–Farcas scheme which assumes that the vapor molecules can join to (or escape from) by one until the growing particle reaches the critical mass. This kinetic scenario produces a well-known chain of equations for the concentrations of growing particles. This set of equations can be solved in the steady-state limit and gives the expression for the nucleation rate in terms of the evaporation and condensation efficiencies. If one assumes the Principle of Detailed Balance to be applicable under nucleation conditions, then the evaporation efficiencies could be expressed in terms of the equilibrium concentrations and condensation efficiencies. Then the Szillard–Farcas scheme leads to the well-known expression for the nucleation rate. The kinetic approach denies this step. Now it has become evident that the secondary atmospheric aerosols in most cases form according to the kinetic scenario.

### 2.3.3 Fluctuation-Controlled Nucleation

Even very strongly supersaturated vapors consist of independent (noninteracting) molecules (the interaction time is much shorter than the free flight time). The nucleation rate, however, in such vapors is extremely high. Moderately supersaturated vapor, in principle, always contains very highly supersaturated areas that are formed due to the density fluctuations. The nucleation process within these areas goes very quickly, so the rate of nucleation is limited by the rate of formation of the fluctuation areas. Therefore the details of the nucleation process inside these highly supersaturated areas are not important, it goes instantly. Here we return to the
ancient idea on the role of fluctuations in the nucleation process. But in contrast to the classical thermodynamic approach we consider the fluctuation areas wherein the molecules do not (yet) interact. The vapor density is sufficient for creating high supersaturation, but it consists of noninteracting molecules. It is clear that such a scenario can be described by the scheme

$$1 + 1 + 1 + \cdots + 1 \rightarrow g^*$$

and the rate of the process is proportional to the vapor concentration to the power $g^*$. This very type of nucleation has been introduced and investigated in ref. [26]. It is important to emphasize that the formation of particles by nucleation alone cannot be observed directly. The point is that the nucleation process is accompanied by coagulation, and the latter process is also very swift. So just formed (by nucleation) particles coagulate, and we observe only the final result of this process. This means that the observed nucleation rate is much slower than that predicted by the nucleation theory alone.

### 2.3.4 Ion-Induced Nucleation

Although the role of ions in the formation of aerosols has been understood long ago, the ion-induced nucleation in the atmosphere has become popular only now after the papers [27–29]. Cosmic rays are known to produce ions that serve as active centers on which the aerosol particles can form. These charged clusters then evolve forming neutral and charged aerosol particles. The rate of formation of such particles has been shown to be enough for accounting for the rate of aerosol particle formation observed in rural regions. In this presentation we discuss the role of an additional mechanism of the particle charging, the aerosol photo effect. It is commonly believed that the thresholds of photo effect are too high for the photoelectrons from the aerosol particles to play any role in the evolution of the atmospheric aerosols. Indeed, normally the photo effect thresholds correspond to the wave lengths of the order of 250 nm. The ozone layer cuts off these photons in the lower atmosphere. But there exists another mechanism of photoionization: (the two-quantum photoeffect) that which assumes simultaneous absorption of two photons. The wavelengths of these photons correspond to green light, where the Sun’s radiation spectrum is a maximum. Of course, the efficiency of the two-quantum photo effect is by $\propto 100$ times smaller than the single-quantum photo effect, but still it is enough to produce the photoelectrons in noticeable quantity. In order to investigate the role of the photo effect we apply a simple kinetic model that describes the formation of aerosols and includes all charging mechanisms. The photoeffect is shown to produce the overcharging of the smallest particles, that is, the total charge of the smallest fraction is always negative.
2.4 Kinetics of Nucleation

Everyone knows what is going on when a vapor is supersaturated. Very many tiny particles are formed. These particles then grow and are lost somewhere, let us say, because of sedimentation or some other reasons. It is clear that this picture does not bear on any thermodynamics and requires a kinetic description. The whole process can be described by the scheme

Independent vapor molecules $\rightarrow$ collective of tiny droplets

The droplets are, however, not quite independent. They grow by consuming the vapor molecules and thus interact via vapor (condensation).

The Szillard–Farcas scheme assumes that nucleation goes along the route [1,3],

$$ (g) + 1 \leftrightarrow (g + 1). \quad (2.7) $$

The rates of the forward and backward processes are assumed to be known.

In the case of kinetically controlled nucleation the chain of reactions remains unchanged. The reaction rates, however, are controlled by the kinetic processes in the carrier gas. For example, the dimerization requires triple collisions, where one of the participants is a carrier gas molecule. Of course, a dimer decay never occurs without a collision with a third body.

In principle, the mixed embrii can arise. For instance, the dimer can form as follows:

$$ 1 + 1' \rightarrow (1 + 1') \rightarrow (2 + 1') \quad (2.8) $$

The idea is clear. Very tiny embrii may consist of a mixture of the vapor and the carrier gas molecules. At later stages of the nucleation process the carrier gas molecules escape the growing embrii.

2.4.1 The Szillard–Farcas Scheme

The Szillard–Farcas scheme assumes the rates of the elementary processes $g + 1 \leftrightarrow (g \pm 1)$ to be known. Although this scheme is widely known [1–3,30], we refresh some central moments of the derivation of the expression for the nucleation rate. Respective kinetics obeys the following set of equations

$$ J_{g-1}(C) = J_g(C) \quad (2.9) $$

with $J_g$ being the total rates of jumps from the state $g - 1$ to $g$

$$ J_g = J = \alpha_{g-1}C_{g-1} - \beta_gC_g. \quad (2.10) $$
The notation is standard and is explained in detail elsewhere. The nucleation rate $J$ is independent of $g$ if the steady state is assumed.

Equation (2.10) is a set of linear algebraic equations with respect to population concentrations $c_g$. The boundary condition (particles disappear on reaching a large size) allows one to resolve the set and to find

$$J(C) = J_2 \frac{1}{1 + x_2 + x_2x_3 + \cdots}. \quad (2.11)$$

Here $J_2(C)$ is the rate of dimerization.

$$J_2(C) = \frac{1}{2} \alpha_1 C^2. \quad (2.12)$$

The notation $C$ stands for the monomer concentration. This value is specially introduced instead of the supersaturation

$$x_g = \frac{\beta_g}{\alpha_{g-1} C}. \quad (2.13)$$

The nucleation rate $J(C)$ is thus expressed in terms of $C$, $\alpha_g$, and $\beta_g$. The concentration $C$ can be measured (in principle). The situation with $\alpha_g$ and $\beta_g$ is much less clear.

### 2.4.2 Condensation and Evaporation

From the first sight the evaporation is a very simple process and is as follows:

$$\alpha_g = v_T \sigma_c \quad (2.14)$$

with $v_T$ being the thermal velocity (depends on $g$ via the particle mass) and $\sigma_c$ is the capture cross-section. The condensation is always an inelastic process. The dynamics of the collision process is far from simple. For example, the dimerization requires the presence of the third body (usually a molecule of the carrier gas). For larger particles the energy excess can be transferred to the internal degree of freedom.

The force fields like van der Waals forces or particle charge can affect the value of the capture cross section. In the simplest case cross-section equals $\sigma_c = \pi a^2$. The situation with $\beta$ is more complex [31]. A molecule of vapor should escape from the particle. The picture looks as if the molecule diffuses inside a self-consistent field created by other interacting molecules. Its energy fluctuates and it can escape reaching the interface (if it has an energy excess enough for over-jumping the
potential barrier). In principle, it is possible to find the evaporation rate by considering this or that model of interacting molecules.

However, very few researchers risked to apply this straightforward approach. Most of them prefer to apply the principle of detailed balance. The idea is an attempt to express the evaporation rate in terms of the condensation rate. It is assumed that the conditions exist when a droplet of mass $g$ is in thermodynamic equilibrium with the surrounding vapor–gas mixture. If yes, then

$$a_{g-1}Cc_0^g = \beta g c_0^g.$$  \hspace{1cm} (2.15)

This condition means that we can fit the temperature and the vapor concentration in such a way that this condition fulfills. Actually this condition is just the application of the method of variable constants. Indeed, such choice of $c_0^g$ makes $J = 0$. This step is typical for the method of variable constants. The solution to Eq. (2.10) is sought as a sum of the solution to the homogeneous equation ($J = 0$) + particular solution of inhomogeneous equation ($J > 0$). On the other hand, Eq. (2.15) reminds the condition of the equilibrium which permits one statistical mechanics for calculating the concentration $c_0^g$. But the equilibrium under the nucleation conditions is impossible. Here we wish to emphasize that the introduction of $c_0^g$ is just the formal trick for solving the set of equations (2.10).

### 2.4.3 Nucleation via Dimers

It is possible to imagine a different (and even opposite) scheme: very few vapor molecules are grouped into a stable cluster whose life time is not related to the contact with the carrier gas. In order to understand what we want to say, let us consider a “dimer-controlled nucleation”. The dimers (serving as critical embryos) form by three molecular reactions. Once occurred in the bound state the dimer cannot leave it without colliding with a carrier gas molecule. The difference between such microscopic critical embryo and the commonly accepted critical embryos is seen from the first sight: nothing happens inside the embryo giving rise to its decay. Of course, the dimer is distributed over its energy states, but this distribution is controlled by the kinetics of the three body collisions between vapor molecules and a molecule of the carrier gas [25]. Not all dimers can serve as the critical embryos.

The rate of kinetically controlled nucleation is expressed as follows:

$$J = Ae^{-g^*}.$$  

Here again $g^*$ is the mass of the critical embryo. Very close to this scheme is “quasi-chemical nucleation” where a couple of substances can form a stable molecule. This type of nucleation is known and quite widespread. For example, the sulfuric oxides
can form stable compounds with water molecules. These compounds have a tendency to agglomerate and form rather stable clusters of several molecules. These clusters can serve as critical embryos for a nucleation process. In this case the binding energy of such embryos exceeds the thermal energy. The excess of energy should be somehow taken away. The radiation processes or further multiple collisions can serve to this end. The kinetics of such a nucleation process can be very complicated and related to numerous specific factors.

### 2.5 Growth by Condensation

The role of particle condensational growth and evaporation is extremely important for the particle size spectra formation. These very mechanisms are responsible for appearance of climatically active aerosols (of sizes 100–1,000 nm) in the atmosphere. It is commonly accepted to consider three regimes of the particle growth: the free-molecule regime, the continuous regime, and the transition regime. Each regime is characterized by the Knudsen number (Kn) – by the ratio of the molecular mean free path to the particle size. Large Knudsen’s number corresponds to the free-molecule regime, that is, the molecules of the carrier gas do not prevent the condensable molecules to approach the target particle. In this case the efficiency $\alpha$ of the molecule trapping is limited by the total particle surface area. The exact result looks as follows [1,3]:

$$\alpha = \pi a^2 v_T,$$

(2.16)

where $a$ is the particle radius and $v_T$ is its thermal velocity. The condensational efficiency is introduced as follows

$$j = \alpha (n_\infty - n_e),$$

(2.17)

where $n_\infty$ and $n_e$ are the concentrations of the condensable vapor far away from the particle and over its surface, respectively. The notation $j$ stands for the vapor flux toward the particle. Most frequently $n_e$ is the equilibrium vapor concentration over the particle surface. If, however, the processes of evaporation or condensation are very fast then this concentration is different from its equilibrium value and should be found after solving the diffusion-reaction equation inside the particle. This situation is typical for the fast evaporation.

The expression for the condensational efficiency in the continuous regime is also very simple [1,3,9]

$$\alpha = 4 \pi Da.$$

(2.18)

Here $D$ is the diffusivity of the condensing molecules. In this case the condensational efficiency is proportional to the particle size.
In order to find the condensational efficiency in the transition regime a more sophisticated approach should apply. In this case the full solution of the Boltzmann kinetic equation should be found. It is impossible to do analytically. Therefore, already long ago there appeared the semiempirical versions of the expressions for $\alpha$ [1,2,13] that reproduced the respective limiting expressions and described the experimental data on the transition regime.

The first simplest theories applied the continuous models of condensation (the particle radius $a$ much exceeds the condensing molecule mean free path $l$). Such models were not able to describe very small particles with sizes less than the $l$ [9]. It was quite natural therefore to try to attack the problem starting with the free-molecule limit, that is, to consider a collisionless motion of condensing molecules. Respective expressions for the condensational efficiencies had been derived and can be found in refs. [1–3]. The important step directed to the reconciliation of these two limiting cases was done by Fuchs [9] who invented the flux-matching theory.

The flux-matching theories are well adapted for studying the behavior of aerosol particles in the transition regime. Although these theories mostly did not have a firm theoretical basis, they successfully served for systematizing numerous experiments on the growth of aerosol particles and until now these theories remain rather effective and are very practical tools for studying the kinetics of aerosol particles in the transition regime (see [9,32]). On the other hand, these theories are always semi-empirical, that is, they contain a parameter that should be taken from somewhere else, not from the theory itself.

We introduce the reader to the ideology of the flux-matching theories by considering the condensation of a nonvolatile vapor onto the surface of an aerosol particle. The central idea of the flux-matching procedure is a hybridization of the diffusion and the free-molecule approaches. The concentration profile of a condensing vapor far away from the particle is described by the diffusion equation. This profile coincides with the real one down to the distances of the order of the vapor molecule mean free path. A limiting sphere is then introduced inside with which the free-molecule kinetics governs the vapor transport. The concentration profile in the free-molecule zone is considered to be flat. The equality of the fluxes in both the zones and the continuity of the concentration profile at the surface of the limiting sphere define the flux and the reactant concentration at the particle surface. The third parameter, the radius of the limiting sphere, cannot be found from such a consideration.

Hence, we apply a more sophisticated scheme [33]. We also introduce a limiting sphere outside of which the density profile of condensing vapor can be described by the diffusion equation. But inside the limiting sphere we solve the collisionless Boltzmann equation subject to a given boundary condition at the particle surface and put an additional condition: the vapor concentration at the surface of the limiting sphere coincides with that found from the solution of the diffusion equation. Even in the absence of any potential created by the particle the vapor profile in the free-molecule zone depends on the radial coordinate, because the particle surface adsorbs all incoming molecules. We thus gain the possibility to call for the continuity of the first derivatives of the profile on both sides of the limiting
sphere. This additional condition defines the radius of the limiting sphere \([13]\). The respective expression for the condensational efficiency has a serious advantage over the formulas used before. The point is that the final result is expressed in terms of the diffusivity and the thermal velocity of the condensable molecules, rather than in terms of the mean free path. The final result is,

\[
\alpha = \frac{2\pi a^2 v_T}{1 + \sqrt{1 + \left(\frac{a v_T}{D}\right)^2}}. \tag{2.19}
\]

The extension of this formula to the case of an arbitrary external potential is,

\[
\alpha(a) = \frac{\alpha(a,R) e^{-U(R)/kT}}{1 + \alpha(a,R) e^{-U(R)/kT} \int_{R}^{\infty} e^{U(r)/kT} \frac{dr}{4\pi r^2}}. \tag{2.20}
\]

This formula widely applies for calculation of the charging efficiency.

Charged particles play a notable role in the processes of tiny particles formation. The nucleation process in the presence of ions goes much easier. The particle growth also becomes faster because bipolar charges on particles accelerate the coagulation. The study of atmospheric charged particles began a century ago \([35–48]\). First simplest theories were grounded on the use of the diffusion equation and applied to the particles of large sizes, much exceeding the ion mean free path in air. Such models were not able to describe the charging of smaller particles, with the sizes of order or less than the ion mean free path. Latest attempts to attack the particle charging problem applied the free-molecule approximation, that is, the collisionless motion of ion was considered as the charge transport mechanism. Respective expressions for the charging efficiencies were reported in refs. \([33,34]\). However, as was shown in ref. \([34]\) the free-molecule regime does not realize even at normal conditions and arbitrary small particles. The point is that in the case of charged particles another characteristic length comes up. It is the Coulomb length \(l_c = q Q e^2/kT\). Even at the particle charges equal to unity this length is equal to 60 nm, i.e., it is comparable with the mean free path of ions. This fact means that the ion–molecular collisions are of importance at the distances where the Coulomb energy of the charge particle is comparable with the thermal energy \(kT\). Hence, the criterion of validity of the free-molecule regime \(l >> l_c\) fulfils only at very low air pressure, i.e., in upper layers of the atmosphere. Next, the bound states of ions in the Coulomb or the image potentials are also of importance for bipolar charging processes. The point is that an ion can occupy a bound state only on colliding with the carrier gas molecule. The diffusion model assumes that all bound states are occupied. In the free-molecule model all these states are empty. On the other hand, it is clear that both the models have nothing common with the reality. The ions
cannot lose a very large energy and occur very deep in the potential well. This fact creates huge difficulties because it is necessary to solve the collision task in an external field.

### 2.6 Uptake of Trace Gases by the Aerosol Particles

Trace gases are commonly recognized to react actively with the aerosol component of the Earth’s atmosphere [3,49–59]. Substantial changes to the atmospheric chemical cycles due to the presence of aerosol particles in the atmosphere make us look more attentively at the nature of the processes stipulated by the activity of atmospheric aerosols (see, e.g., [3]). The process of the gas–particle interaction is usually a first-order chemical reaction going along the route:

\[
X + AP \rightarrow (APX),
\]

where \(X\), \(AP\), and \(APX\) stand respectively for a reactant molecule, an aerosol particle and the final product resulting from the reaction Eq. (2.21).

As an example we refer to ozone, which is a key substance for our atmospheric system since it protects the living systems on our planet against the Sun’s UV radiation. However, since the discovery of the ozone hole in the mid-1970s (details, last achievements, and references see in [3]), it has been well established that ozone is subject to periodical large depletion events at the poles and to continuous decay in the global stratosphere. These trends are initiated by the presence of halogenated radicals that are produced by a cycle of photochemical processes. The amplitudes of ozone level variations are also driven by heterochemical reactions occurring on the surfaces of polar stratosphere clouds which transform stable reservoir molecules into radical precursors.

Yet some important aspects of aerosol heterochemistry are not so well studied (see, however, [60–64]). Among them is the interconnection between uptake and mass accommodation efficiencies [61]. Still there exist discrepancies between the results because of different understanding of the meaning of uptake coefficient. The whole issue of *Journal of Aerosol Science* 32(7) (2001) is entirely devoted to the problems of gas–aerosol interaction in the atmosphere.

In the following paragraphs we wish to outline our point of view. Let a particle of the radius \(a\) initially containing \(N_B\) molecules of a substance B be embedded to the atmosphere containing a reactant A. The reactant A is assumed to be able to dissolve in the host particle material and to react with B. The particle will begin to absorb A and will do this until the pressure of A over the particle surface will be enough for blocking the diffusion process. Our task is to find the consumption rate of the reactant A as a function of time. Next, we focus on sufficiently small particles whose size is comparable to or less than the mean free path of the reactant...
molecules in the carrier gas. The mass transfer of such particles is known to depend strongly on the dynamics of the interaction between incident molecules and the particle surface. In particular, the value of the probability $\beta$ for a molecule to stick to the particle surface is suspected to strongly affect the uptake kinetics. The question “how?” has not yet found a full resolution.

Below we are trying to answer this question starting with a simple analysis of the boundary condition to the kinetic equation for the molecules of a reactant $A$.

Let an aerosol particle be put in the atmosphere containing a reacting gas admixture $A$. The molecules of $A$ are assumed to react with a guest reactant $B$ dissolved in a host material of the particle (in principle, $B$ itself can be the host material). The reactant $A$ is assumed to react with the reactant $A$ along the route:

$$A + B \rightarrow C$$  \hspace{1cm} (2.22)

The particle initially containing no molecules of $A$ begins to consume those crossing the particle–carrier gas interface. Our goal is to investigate the kinetics of this process.

Our basic integral principle asserts:

$$\text{Flux of } A \text{ from outside } = \text{ total consumption of } A \text{ inside}$$  \hspace{1cm} (2.23)

We consider four stages of the uptake process:

1. The diffusion of $A$ toward the particle
2. Crossing the particle–air interface
3. Diffusion-reaction process inside the particle
4. Accumulation of nonreacted $A$-molecules in the particle

Balancing the fluxes gives the equation for the uptake rate.

In principle, the consideration of the uptake requires a solution of the time-dependent transport problem. Here we give some order-of-magnitude estimations allowing for a correct statement of the problem in realistic conditions of the Earth’s atmosphere. Our idea is to get rid of the non-stationarity wherever it is possible. Below we use the notation $D_X$ ($X = A, B$), $D_{gA}$ for the diffusivity of the reactant molecules inside the particle and in the gas phase respectively.

The characteristic time of the non-stationarity in the gas phase is estimated as $\tau \propto a^2 / D$. This time is extremely short. For $D = 0.1$ cm$^2$/s and $a = 1,000$ nm $\tau \propto 10^{-7}$s. So the transport in the gas phase can be considered in the steady-state limit. The diffusion process in the liquid phase is much slower. Its characteristic time is $\tau \propto 10^{-3}$s for micron particles and $DX \approx 10^{-5}$ cm$^2$/s.

The time for the chemical reaction of $A$ molecules in the liquid phase is estimated as $\tau_A \propto \kappa n_B$ where $\kappa$ is the binary reaction rate constant for the reaction given by Eq. (2.22). The maximal value of $\kappa \propto DXa_m \propto 10^{-13}$ cm$^3$/s for the molecule radius $a_m \propto 10^{-5}$ cm. The book [3] cites the values within the interval $\kappa = 10^{-11} - 10^{-18}$ cm$^3$/s.
The estimate of the characteristic of time $\tau_A$ depends on the value of $n_B$. If the gaseous reactant reacts with the host material, the characteristic reaction times are very short $\tau \propto 10^{-9}$ s for diffusion controlled reactions and much longer for other types of chemical processes (up to seconds or even minutes).

The characteristic transport times should be compared to the characteristic times of substantial chemical changes inside the particle that are stipulated by the flux of $A$ from outside. These times are of the order of $\tau_{\text{changes}} \propto 1/j_A$, where $j_A$ is the total flux of $A$-molecules trapped by the particle. This is the characteristic time for one molecule of $A$ to attach to the particle surface. Actually this time depends on the sticking probability $\beta$ and can reach 10 s.

These estimates show (see also [3]) that all the characteristic times for the transient processes inside and outside the particle are much shorter than the characteristic time for the particle to change its chemical composition due to uptake. This means that a quasi-steady-state approximation can be used for the description of very slow changing parameters such as the total number of molecules inside the particle or its size. Fast transport processes establish instantly the steady-state concentration profiles.

Let us first consider condensation of $A$-molecules onto a spherical particle of $B$-liquid. In the gas phase the distribution function $f_A$ of $A$-molecules over coordinates and velocities satisfies the Maxwell boundary condition [11],

$$f_A^{-} = (1 - \beta)f_A^{+} + \frac{\beta}{2\pi} n_{Ae}, \quad (2.24)$$

where $\beta$ is the sticking probability, $f_A^{-}$ is the velocity distribution function of molecules flying outward the particle, $f_A^{+}$ is the same for molecules flying towards the particle surface, and $n_{Ae}$ is the equilibrium concentration of $A$-molecules over the particle surface. The first term on the right of this equation describes the mirror rebound of $A$-molecules from the particle surface. The second term gives the density of the accommodated and then emitted from the surface molecules of $A$. The coefficient $1/2\pi$ reflects the fact that the molecules fly only in the outward direction. At $f^{+} = f^{-} = n_e/2\pi$ (full thermodynamic equilibrium) Eq. (2.24) satisfies automatically. The total flux of $A$ is expressed as

$$j_A = \alpha(a)(n_{A\infty} - n_{Ae}). \quad (2.25)$$

Here $n_{A\infty}$ is the concentration of $A$ far away from the particle.

The solution of the kinetic equation defines the concrete form of the dependence of the condensational efficiency $\alpha(a)$ on the particle radius and $\beta$. The form of the second multiplier is universal and in neither way is related to any approximation.

Now we are returning to uptake. In this case the inward flux inside the particles makes concentration $n_A^{+}$ of outflying particles lower than $n_{Ae}$. The boundary condition Eq. (2.24) is replaced by

$$f_A^{-} = (1 - \beta)f_A^{+} + \frac{\beta}{2\pi} n_{Ae}^+, \quad (2.26)$$
with the value of the reactant concentration $n_A^+$ being determined from balancing the fluxes. This is the principal point of our further consideration. This equation differs from Eq. (2.24) by replacement $n_{A,e} \rightarrow n_A^+$. Hence, the flux of $n_{A,e}$ toward the particle looks as follows:

$$j_A = \alpha(a) \left( n_{A,e} - \frac{n_A^+}{\beta} \right).$$  

(2.27)

Instead of solving the kinetic equation, we apply any semi-empirical formula for $\alpha(a)$. For example, the Fuchs–Sutugin formula

$$\alpha(a) = \frac{\alpha_{fm}(a)}{1 + \beta S(Kn)},$$  

(2.28)

where

$$\alpha_{fm}(a) \beta = \pi v_T a^2$$  

(2.29)

is the condensational efficiency in the free-molecule regime and

$$S(x) = \frac{3}{4x} - \frac{0.466}{x + 1},$$  

(2.30)

$$n_A^* = H n_{A_e}^+,$$  

(2.31)

where $H$ is the dimensionless Henri constant defined as

$$H = \frac{H_s RT}{0.981 \times 10^9}$$  

(2.32)

Here $H_s$ is the Henri constant (in units mol/a, see the definition in [3]). At $T = 300$ K

$$H = 26.4 H_s.$$  

(2.33)

We demonstrate the application of the above scheme for the case of complete mixing the reactants inside the particle, that is, we assume that the reactant concentration profiles are independent of coordinates. Then the following set of equations describes the evolution of the particle chemical composition,

$$\frac{dN_A}{dt} = \alpha(a) (n_{A,\infty} - \frac{N_A}{HV}) - \frac{\kappa}{V} N_A N_B,$$  

(2.34)

$$\frac{dN_B}{dt} = - \frac{\kappa}{V} N_A N_B,$$  

(2.35)

$$V(t) = v_a N_A + v_b N_B + v_c N_C,$$  

(2.36)

where $v_x$ is the molecular volume of each component ($x = a, b, c$).
2.7 Nucleation Bursts in the Atmosphere

Regular production of nonvolatile species of anthropogenic or natural origin in the atmosphere eventually leads to their nucleation, formation of tiny aerosol particles, and their subsequent growth. Thus formed aerosol is able to inhibit the nucleation process because of condensation of nonvolatile substances onto the surfaces of newly born particle surfaces. This process is referred to as the nucleation burst [1].

The dynamics of atmospheric nucleation bursts possesses its own specifics, in particular, the particle production and growth is suppressed mainly by preexisting aerosols rather than freshly formed particles of nucleation mode [12]. In many cases the nucleation bursts have heterogeneous nature. The smallest (undetectable) particles accumulated during nighttime begin to grow at daytime because of sunlight-driven photochemical cycles producing low volatile (but not nucleating) substances that are able to activate the aerosol particles [65]. Stable sulfate clusters [66–72] can serve as heterogeneous embryos provoking the nucleation bursts.

The nucleation bursts were regularly observed in the atmospheric conditions and were shown to serve as an essential source of cloud condensation nuclei [12,73–77]. Now it becomes more and more evident that the nucleation bursts in the atmosphere can contribute substantially to the cloud condensation nuclei production and can thus affect the climate and weather conditions on our planet (see e.g., [3,6,7] and references therein). Existing at present time opinion connects the nucleation bursts with additional production of nonvolatile substances that can then nucleate producing new aerosol particles, and/or condense onto the surfaces of newly born particles, foreign aerosols, or on atmospheric ions. The production of nonvolatile substances, in turn, demands some special conditions to be fulfilled imposed on the emission rates of volatile organics from vegetation, current chemical content of the atmosphere, rates of stirring, and exchange processes between lower and upper atmospheric layers, presence of foreign aerosols (accumulation mode, first of all) serving as condensational sinks for trace gases and the coagulation sinks for the particles of the nucleation mode, the interactions with air masses from contaminated or clean regions [12,68,77]. Such a plethora of very diverse factors most of which have a stochastic nature prevents direct attacks on this effect. A huge amount of field measurements of nucleation bursts dynamics appeared during the last decade (see [12,68,77] and extensive citation therein).

The attempts of modeling this important and still enigmatic process also appeared rather long ago. All models (with no exception) start from a commonly accepted point of view that the chemical reactions of trace gases are responsible for the formation of nonvolatile precursors which then give life to subnano- and nanoparticles in the atmosphere. In turn, these particles are considered as active participants of the atmospheric chemical cycles leading to the particle formation. Hence, any model of nucleation bursts included (and includes) coupled chemical and aerosol blocks. This coupling leads to strong nonlinearities which means that all intra-atmospheric chemical processes (not all of which are, in addition, firmly established)
are described by a set of nonlinear equations. In addition, there is no assurance that we know all the participants of the chemical cycles leading to the production of low volatile gas constituents that then convert to the tiniest aerosol particles.

Our main idea is to decouple the aerosol and chemical parts of the particle formation process and to consider here only the aerosol part of the problem. We thus introduce the concentrations of nonvolatile substances responsible for the particle growth and the rate of embryo production as external parameters whose values can be found either from measurements or calculated independently, once the input concentrations of reactants and the pathways leading to the formation of these nonvolatile substances are known. Next, introducing the embryo production rate allows us to avoid a rather slippery problem of the mechanisms responsible for embryos formation. Since neither the pathways nor the mechanisms of production of condensable trace gases and the embryos of condense phase are well established so far, our semiempirical approach is well approved. Moreover, if we risk to begin from the basic principles, we need to introduce too many empirical (fitting) parameters.

Aerosol particles throughout the entire size range beginning with the smallest ones (with the sizes of order 1 nm in diameter) and ending with sufficiently large particles (submicron and micron ones) are shaped by some well-established mechanisms. They are condensation and coagulation. Little is known, however, on atmospheric nucleation. This is the reason why this very important process together with self-coagulation is introduced here as an external source of the particles of the smallest sizes. The final productivity of the source is introduced as a fitting parameter whose value is controlled by these two processes simultaneously and is thus always lower than the productivity of the nucleation mechanism alone. Next, coagulation produces the particles distributed over a size interval, rather than monodisperse ones of a critical size (like in the case of nucleation alone). The productivity should be introduced as a function of the particle size and time, respectively. In principle, the size dependence of the source can be found theoretically, but it is better to refuse this idea and to introduce it as the product of a lognormal function and a time-dependent total production rate.

The condensational growth depends on the concentrations of condensable vapors, with the condensational efficiencies being known functions of the particle size. The concentrations of condensable trace gases are introduced as known functions. They can also be calculated, once all reactions responsible for conversion of volatile trace gases to low volatile ones and respective reaction rates are known (+ stoichiometry of the reactions + initial concentrations of all participants and many other unpleasant things). Of course, nothing like this is known and there is no chance to get this information in the near future.

The losses of particles are caused mainly by preexisting submicron and micron particles. There are also other types of losses: deposition of particles onto leaves of trees, soil losses, scavenging by deposits, and mists. Here the term ‘loss’ is introduced as a sink of small particles on preexisting submicron and micron aerosol particles.
Self-coagulation of particles with sizes exceeding 3 nm in diameter is entirely ignored in the model. Many authors estimated the characteristic times of the self-coagulation process and found them to exceed $10^4$ s. In what follows we ignore this process. On the contrary, the intermode coagulation (the deposition of newly born particles onto preexisting aerosols) is of great importance and must be taken into account.

Now it is easy to answer the question why the linear model is able to describe the nucleation bursts in the atmosphere. The nucleation mode does not affect the surrounding atmosphere whose chemical state is defined by other numerous external factors. For example, the lifetimes of trace gases and the particles of nucleation mode depend on the concentration and the size distribution of preexisting aerosol particles.

The mechanisms of particle growth (condensation and coagulation) are well established for the whole size interval of interest. This is the reason why the model for the description of atmospheric particles is based on the continuity equation

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial a} + \lambda n = J.$$  \hspace{1cm} (2.37)

Here $n = n(a,t)$ is the particle size distribution, $\dot{a}$ is the rate of particle growth

$$\dot{a} = zC(t) = \frac{v_T V_0 C(t)}{4},$$ \hspace{1cm} (2.38)

where $v_T$ is the thermal velocity of condensing molecules, $V_0$ is the volume of the single molecule, and $C = C(t)$ is the number concentration of condensing molecules in air. The value $\lambda$ is the coagulation sink (a fitting parameter), $J = J(a,t) = j(t)f(a)$ is the productivity of the stable embrii source. The function $f(a)$ describes the size distribution of the newly born particles.

At this stage it is especially important to emphasize that the coagulation sink is created mainly by foreign aerosols with the sizes of order 1,000 nm. Then the continuity equation (2.20) becomes linear. We removed all the sources of nonlinearity which arises from the nucleation term and the coagulation sink (the concentration of condensing gases are considered to be known functions of time). Next, we ignore the intra-mode coagulation. Equation (2.20) is the first-order partial differential equation, whose solution can be presented in the form:

$$n(a,t) = n_0(a,t) + n_J(a,t),$$ \hspace{1cm} (2.39)

where $n_0(a,t)$ is the general solution of the homogeneous equation and $n_J(a,t)$ is a particular solution of the inhomogeneous equation. The full spectrum in the form of Eq. (2.39) allows one to classify the scenarios of nucleation bursts.

**Scenario 1.** At the initial moment of time (night time) the nucleation mode is entirely absent. At sunrise the trace gases appear that are able to nucleate. They...
form the particles growing further by condensing low volatile trace gases that cannot form the aerosol particles themselves. An example of such situation is shown in Fig. 2.1. It is seen that if the coagulation sinks are sufficiently large the particles larger 3 nm do not appear at all (see Fig. 2.2). It is important to stress that there is no well-distinguishable peak in the particle size distribution.

**Scenario 2.** Nucleation does not occur at all, but the smallest particles formed during nighttime are still present in the atmosphere. Then these particles begin to grow as soon as condensable gases appear after the sunrise. These particles can pass the threshold 3 nm in diameter and become detectable. In this case the peak in the particle distribution is well expressed. The picture of the nucleation burst is shown in Fig. 2.3.

**Scenario 3.** The running mode can appear after a new, more clean air mass comes to the observation point.

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**Fig. 2.1** The evolution of size distributions typical for summer periods is shown. Source produces the particles of the nucleation mode. The sinks are seen not to prevent the particle growth up to sizes 10 nm. This situation is typical for boreal regions of Finland and Siberia in summer period.
Fig. 2.2 In winter time the rate of particle formation is low. The sinks suppress the particle growth and they do not reach up to detectable sizes.

Fig. 2.3 If the particle formation precedes the condensational growth (e.g., small particles were born at nighttime due to dark reactions), then a well distinguishable peak appears at daytime.
2.8 Concluding Remarks

We have presented a short overview of existing data on the processes of aerosol formation in the atmosphere. Our conclusions are as follows:

1. Although there is not full clarity in theory of gas-to-particle conversion, the productivity of the nucleation process can be introduced as a fitting parameter to the equation describing the atmospheric aerosol particle formation and growth.

2. The mechanism of the condensational growth is clear and can be described theoretically. Very often we do not know the participants of this process therefore their concentrations should be introduced as parameters or calculated from the respective chemical block.

3. Extremely important achievement is the theoretical description of the condensation growth of mixed particles. Now we know how to include the accommodation coefficient to the expression for the condensational efficiency of mixed particles.

4. At sufficiently short times (of order of 24 h) the intra-mode coagulation processes do not play an essential role. The inter-mode coagulation can be included into the coagulation sinks and be considered as a fitting parameter of the formation-growth models.

References