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GEOPHYSICS

Periodic Regimes in the Source-Enhanced Condensing Aerodisperse System

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At present, the role of atmospheric aerosols in the formation of climatic and weather conditions is commonly accepted [1]. Therefore, the investigation of the processes of aerosol formation in atmospheric conditions is a pressing issue. It is known that the formation of secondary atmospheric particles is caused by intraatmospheric chemical and photochemical cycles, which produce low-volatile vapors of sulfuric acid and high-molecular organics with their subsequent nucleation, condensation growth, and coagulation. Many details of the stage of atmospheric particle growth up to the size of the cloud condensation nucleus are currently unknown. For example, it has been considered up to the present time that the processes of particle growth cannot lead to oscillating regimes in evolving aerodisperse systems [1–4]. In our paper, we demonstrate that sinks of particles of sufficiently large size in the presence of the source of new particles can lead to decaying oscillation regimes.

Investigations of nucleation and condensation processes in aerodisperse systems are important for practical purposes and for the solution of fundamental problems of aerosol kinetics. The implication of such studies is, first of all, related to the forecast of the results of aerosol formation in the atmosphere and in the generation of nanoparticles in aerosol reactors. Work with such systems requires knowledge of whether or not a new phase will form and whether the newly formed particles will continue to grow or evaporate.

In order to answer this question, it is necessary to solve equations describing the corresponding processes and interpret them correctly. A large number of original articles and monographs have been dedicated to the solution of this problem [1–4]. In the traditional works, the authors usually consider stationary or quasi-stationary condensation and nucleation regimes. In the present work, we investigated the time-dependent evolution to the stationary regime in the growing aerodisperse system with a permanently active source of condensing vapor. We show that the concentration of particles in such a system can change periodically before the evolution to the stationary regime.

It is traditionally assumed in the description of the processes of formation and growth of particles that the volume of the aerodisperse system is infinitely large ($V \to \infty$), the number of particles is also very large ($N \to \infty$), and the concentration of particles $\left(\frac{N}{V}\right)$ is a finite value (thermodynamic limit). The infinite number of particles implies that particles of arbitrary size can exist in the system. The limiting size of the particles (the number of monomers G related to the largest particle) is not limited ($G \to \infty$). An infinite system of differential equations is usually solved for the description of such behavior of the system:

$$\begin{aligned} \dot{c}_1 &= (I - \alpha_1 c_1^2) - c_1 \sum_{i=1}^{\infty} \alpha_i c_i, \\ \dot{c}_i &= \alpha_{i-1} c_{i-1} c_1 - \alpha_i c_i c_1, \end{aligned} \qquad (1)$$

where c_i is the concentration of particles consisting of i monomers; α_i is the frequency of collision between a particle consisting of i monomers with a monomer particle (vapor molecule); and I is the power of the source of monomers supplying vapor molecules into the system (superscript dot denotes time derivative). These equations describe the variation in concentration of vapor molecules (first equation) as a result of the

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appearance of new molecules supplied by the source (I) and the merger of these molecules with other particles (the second and third additives in the right part). All other equations take into account only two additives: input to fraction i by the merger of vapor molecules with the particles from the previous fraction ($i - 1$) and output from the given fraction also due to the merger of vapor molecules with the particles from the given fraction.

We assume for mathematical simplicity that $c_1 \gg c_i$; i.e., the concentration of the monomer is assumed to be much greater than the concentration of any other particles in the system. Thus, we neglect coagulation in the system. Furthermore, we shall not take into account evaporation, because this process only intensifies the effect discussed below. The i value can be arbitrarily large. Consequently, all molecules appearing in the system remain there and the mass of the system of particles increases linearly with time.

The stationary regime is inaccessible for system (1), in which the size of the largest particles is unlimited: an infinitely large time interval is needed for this.

Indeed, the particle size is unlimited in any real system, because large particles are removed from the system due to different processes (diffusion and sedimentation of particles both in the atmosphere and in artificial reactors). Therefore, it is necessary to introduce in system (1) a limiting parameter G, which is the maximal size of particles (G is the number of monomers included in the largest particle). Then, system (1) takes the following form:

$$\begin{aligned} \dot{c}_1 &= I - \alpha_1 c_1^2 - c_1 \sum_{i-1}^{G} \alpha_i c_i, \\ \dot{c}_1 &= \alpha_{i-1} c_{i-1} c_1 - \alpha_i c_i c_1, \quad i \le G, \\ c_i &= 0, \quad i > G. \end{aligned} \tag{2}$$

In order to obtain solutions, systems (1) or (2) should be supplemented by initial conditions. The simplest method for solving systems of differential Eqs. (1) and (2) without qualitative limitations of the generality of the approach is to assume that

$$c_i(0) = 0$$

for all i, i.e., to assume that the system is free from particles at the initial moment.

For convenience of calculation and obtaining universal solutions of Eq. (2), we shall measure time in units $t_0 = \dfrac{1}{\sqrt{\alpha_1 I}}$ and concentration in units $c_0 = \sqrt{\dfrac{I}{\alpha_1}}$.

At zero initial conditions, the solutions of system (2) are oscillatory functions, which evolve to stationary regimes. Generally speaking, system of differential Eqs. (2) describes the time evolution of a finite system with condensation. This system represents generalized Lotka–Volterra equations [5, 6], which also have oscillating solutions.

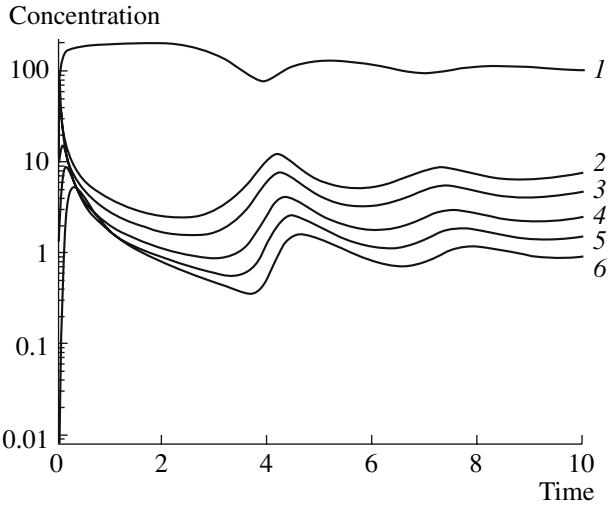

Fig. 1. (*1*) Time variation of the total concentration of particles. Concentration of particles of other fractions: (*2*) monomers, (*3*) dimers, (*4*) pentamers, (*5*) decamers, (*6*) icosamers. Evaporation is not taken into account. Time is dimensionless. The concentration axis is in logarithmic scale. The maximal particle size is 200 molecules.

Figure 1 shows the time evolution of several concentrations: (*1*) total concentration of all fractions; (*2*) concentration of monomers; (*3*) concentration of dimers; (*4*) concentration of particles of five molecules; (*5*) concentration of particles of ten molecules; and (*6*) concentration of particles of twenty molecules. In this version, 200 equations were solved; i.e., the size of the greatest particle in the system corresponded to $G = 200$ molecules. As seen from the system of differential Eqs. (2), evaporation of particles is not taken into account in this system. The first maximum of all curves corresponds to the input of new particles to the corresponding fraction. The first minimum of the total concentration of particles corresponds to the time when the maximum of the last particle fraction c_G is reached and the particles are removed from the system. Unlike system of Eqs. (1), it is possible to gain the stationary regime in system (2): the system reaches size G during a limited time period. It can be estimated from the following considerations:

$$\frac{dg}{dt} = \dot{g} \quad \text{or} \quad \int_0^G \frac{dg}{\dot{g}} = \tau, \tag{3}$$

where g is the size of the particle (number of molecules in one particle); $\dot{g}$ is the rate of displacement along the size axis; and τ is the mean time, after which the concentration of particles with size G becomes nonzero.

In order to obtain stationary concentrations corresponding to system (2), it is necessary to set the left parts of Eqs. (2) equal to zero, which corresponds to $\dot{c}_i = 0$; i.e., all concentrations do not depend on time.

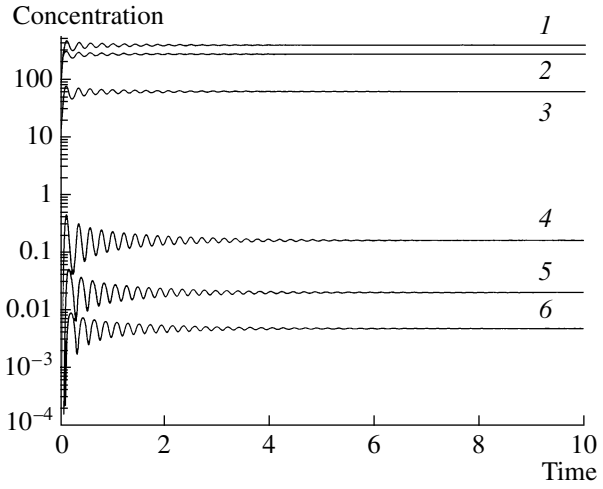

Fig. 2. Time variation of the concentration of particles in a system with condensation and evaporation of particles. The solutions correspond to system of differential Eqs. (3). The system considered is similar to the version for which solutions are shown in Fig. 1 with the difference that evaporation is taken into account in this system. Notations are as in Fig. 1.

For such conditions, it is easy to obtain stationary concentrations:

$$c_1 = \sqrt{\frac{I}{\alpha_1(G+1)}},$$
$$c_i = \frac{1}{\alpha_i}\sqrt{\frac{\alpha_1 I}{G+1}} \quad \text{for} \quad i < G+1. \tag{4}$$

As was mentioned above, the condition that Eqs. (2) are valid in real situations is $c_i \ll c_1$, which means that according to (3)

$$\frac{c_i}{c_1} = \frac{\alpha_1}{\alpha_i} \ll 1. \tag{5}$$

In order to take evaporation into account, it is necessary to supplement the system of differential equations with summands proportional to the concentrations of the corresponding particles. If we assume that evaporation of one molecule from a particle with mass g per time unit is equal to β_g, system (2) can be transformed to

$$\dot{c}_1 = I - \alpha_1 c_1^2 - c_1 \sum_{i=1}^{G} \alpha_i c_i + \sum_{i=2}^{G} \beta_i c_i,$$
$$\dot{c}_i = \alpha_{i-1} c_{i-1} c_1 - \alpha_i c_i c_1 - \beta_i c_i + \beta_{i+1} c_{i+1}, \quad i \le G, \tag{6}$$
$$c_i = 0, \quad i > G.$$

The solutions of system of differential Eqs. (6) presented in Fig. 2 show that the inclusion of the evaporation mechanism led to the following: (1) increase in the period of oscillations and (2) intensification of attenuation of oscillations. The phase trajectories of the solutions are spiral lines that converge at the point of the stationary solution. Without account for evaporation, the corresponding curves make a smaller number of rotations. If evaporation is taken into account, they make more rotations before reaching the attractor point. The number of rotations before the curves converge at the point also depends on the limiting size G. The greater this size, the greater the number of rotations the phase curves can make. Coefficients α and β proportional to $i^{2/3}$ were used in the solution of Eqs. (1) and (2), which corresponds to the free molecular regime of collision between particles and vapor molecules; i.e., the frequency of collisions between vapor molecules and particles was proportional to the surface of the particles. However, it should be taken into account that the form of the dependence of α and β on i is insignificant. Similar solutions were obtained for α proportional to $i^{1/6}$. This dependence influences the period of oscillations and the attenuation rate of the amplitude of the oscillations.

Measurements made in background regions sometimes yielded situations corresponding to scenarios described by Eqs. (2). In this case, periodical variations in the concentrations of atmospheric ozone were observed. These variations were interpreted as spatial inhomogeneities of atmospheric ozone. Actually, they can be related to the effect of finiteness of the aerosol system manifested in the periodical variations of its concentration.

Numerical experiments show that attenuation of the amplitude of oscillations decreases if limiting size G increases. At the same time, the period of oscillations shows a positive correlation with limiting size G for different collision frequency dependences and evaporation regimes. The particle size distribution as a function of collision frequency can be monotonous or maximum at large times. The faster the collision frequency increases proportionally with the size of particles, the sooner a maximum appears in the distribution by size.

Numerical experiments indicate that the variation in the initial conditions does not lead to any variation in the stationary state; i.e., the attractor does not change its position. At the same time, if the initial conditions are nonzero, periodical variation in the concentrations before reaching the stationary regime becomes less prominent or it is reached after a certain time period.

Application of Eqs. (2) and (5) for forecasting the evolution of the spectrum of particle sizes in the system with condensation and nucleation is related to the satisfaction of condition (4). This condition for aerodisperse systems is practically satisfied in both atmospheric and laboratory conditions, because dimers are formed as a result of collision between monomers, whose efficiency is significantly smaller than unity [7]. This means that the concentration of monomers at any time is much greater than the concentration of any other particles. This is actually the condition for applying Eqs. (2) and (5). The possibility of using the suggested formalism in realistic systems is determined by characteristic time τ, i.e., the time needed for the system to reach the limiting size G. If we limit ourselves with the free molecular

regime and sizes of the particles of the nucleation mode, then according to (2), time τ can change from seconds to tens and hundreds of minutes depending on the concentration of monomers (vapor, which promotes condensation). This procedure allows us to associate dimensionless time with a physical sense.

It is planned to use the suggested approach, first, for forecasting the variations in the distribution of atmospheric aerosol by size when conditions for nucleation appear. In particular, this relates to the appearance of new particles in the background regions and other regions with a small contribution of anthropogenic sources. In particular, the appearance of periodical variations in the aerosol concentration can indicate that new particles are generated in the atmosphere by source-enhanced particles.

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