A model of nucleation bursts

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[1] A simple linear (with respect to aerosol particle size distribution) model of nucleation bursts in the atmosphere is proposed. The model includes two sources of nonvolatile species, one of which nucleates producing the aerosol particles and the other one condenses onto the particles giving rise to their growth. The most important consequence of the linearity is that the particle size distribution can be presented as a superposition of different regimes. In particular, if the source-enhanced regime is combined with a free one, the latter produces a runaway mode in the particle size distribution appears. The model serves for estimating the CCN productivity by nucleation bursts. *INDEX TERMS:* 0300 Atmospheric Composition and Structure; 0305 Atmospheric Composition and Structure: Aerosols and particles; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; *KEYWORDS:* nucleation burst, atmospheric aerosols, nucleation mode, condensational growth.

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Introduction

[2] Now it becomes more and more evident that the nucleation bursts can contribute substantially to CCN production and can thus affect the climate and the weather conditions on our planet. Commonly accepted opinion connects the nucleation bursts with an additional production of nonvolatile substances in the atmosphere that can then nucleate and/or condense on newly born particles, foreign aerosols, or 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 (submicron fraction, first of all) serving as the condensational sinks for trace gases and the coagulation sinks for the particles of nucleation mode, the interactions with air masses from contaminated or clean regions. Such a plethora of very diverse factors most of which have a stochastic nature prevents direct attacks of this effect. A theoretical modelling of the nucleation bursts is thus of primary importance.

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Why the Model is Linear?

[3] During the last two decades numerous attempts of modelling the nucleation processes in the atmosphere have been made. All of them (with no exception) started from commonly accepted conception that the chemical reactions of trace gases are responsible for the formation of nonvolatile precursors which then give the life to subnano- and nanoparticles in the atmosphere. In their turn, these particles are considered as active participants of the atmospheric chemical cycle leading to the particle formation. Hence, any model of nucleation bursts is included (and includes) *coupled* chemical and aerosol blocks.

[4] 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 rather slippery problem of the mechanisms responsible for embryos formation. Because neither the pathways nor the mechanisms of production of condensable trace gases and the embryos of condense phase are well established so far, our semi–empirical approach is well approved. Moreover, if we risk to start from the first principles, we need to introduce too many empirical (fitting) parameters.

[5] Aerosol particles throughout entire size range beginning with the smallest ones (with the sizes of order 1 nm)

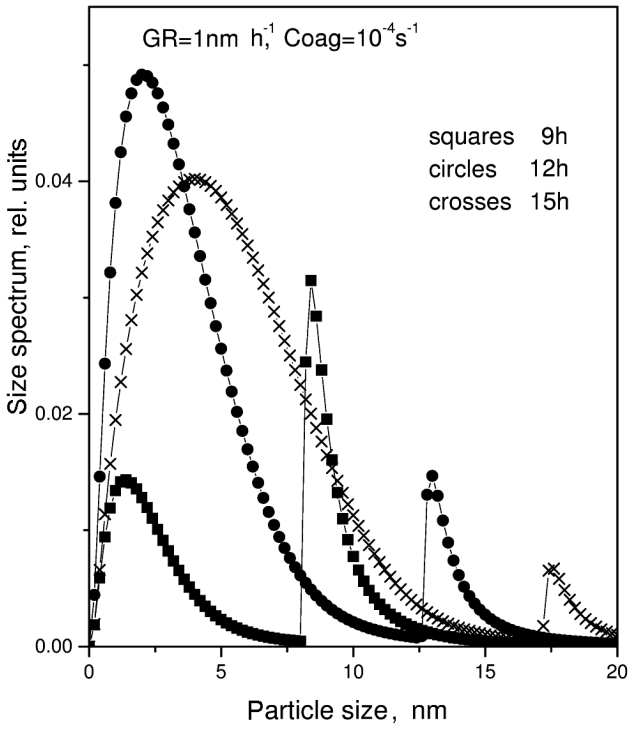

Figure 1. Time evolution of the particle size spectrum. Tiny aerosol particles (protoaerosol) presented in air before the source has begun to produce fresh aerosol are seen to grow by condensation of low volatile vapors. The resemblance with observed pictures of the nucleation burst is clearly seen.

and ending with sufficiently large particles (submicron and micron ones) are shaped by some well established mechanisms. These are: condensation and coagulation. Little is known, (Figures 1, 2) however, on atmospheric nucleation. This is the reason why this very important process together with intra–mode coagulation is introduced here as a source of the particles of the smallest sizes. The final productivity of the source is controlled by two these processes simultaneously and thus always lower than the productivity of the nucleation mechanism alone. Next, coagulation produces the particles distributed over a size interval, rather than the monodisperse ones of a critical size (like in the case of pure nucleation). Respectively, the productivity should be introduced as a function of the particle size and time. In principle, the size dependence of the source can be found theoretically, but it is better to refuse of this idea and to introduce it as the product of a lognormal function and the time dependent total production rate.

[6] 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 the reaction graph of all chemical processes 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.

[7] The losses of particles are caused mainly by preexisting submicron and micron particles. There are also other types of losses: deposition of particles on vegetation, soil losses, scavenging by deposits and mists. Here the loss term is introduced as a sink of small particles on preexisting submicron and micron aerosol particles.

[8] Self-coagulation of particles with sizes exceeding 3 nm is entirely ignored in the model. Many authors estimated the characteristic times of the coagulation process and found them to exceed $10^5 s$. 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 should be taken into account.

[9] Now it is easy to answer the question posed in the title of this Section. Our model is linear because the nucleation mode does not affect the surrounding atmosphere whose chemical state is determined 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 the preexisting aerosol particles.

[10] The linearity of the model means that the particle

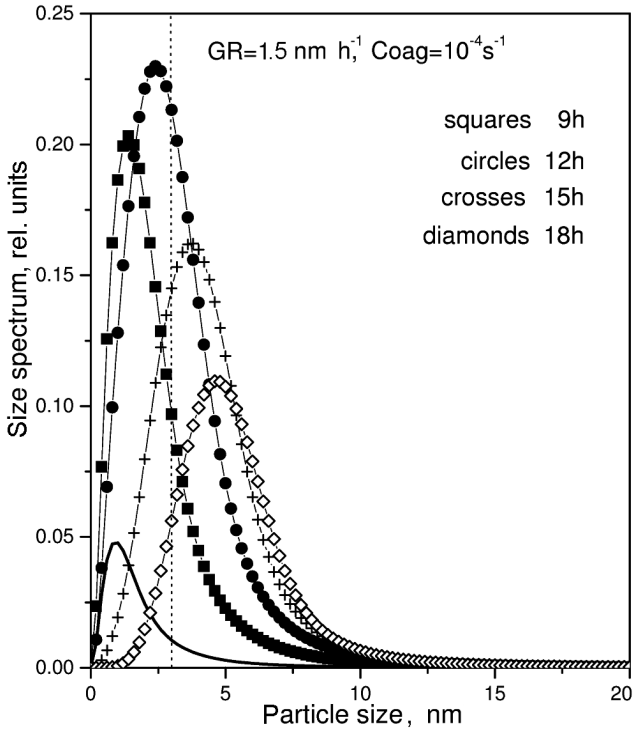

Figure 2. Time evolution of the particle size spectrum. No protoaerosol has presented before the source began to produce fresh particles. Nevertheless, a hump in the spectrum appears in the detectable part of the size spectrum (above 3 nm, vertical dotted line). This is also a nucleation burst, but the picture is qualitatively different from that displayed in Figure 1.

size distribution can be schematically presented (Figures 3, 4) as follows:

$$n(a,t) = \hat{\mathcal{G}}J + \hat{\mathcal{F}}n_0. \quad (1)$$

Here $\hat{\mathcal{G}}$, $\hat{\mathcal{F}}$ are linear evolution operators allowing for restoring the full size distribution functions by the particle source J and the initial conditions n_0. As we will see the first term does not produce a "burst-like" picture, although diurnal increases in the detectable particle concentration are well reproduced. The second term is of special significance. We show that if the source does not work at night time, but a highly disperse (undetectable) aerosol appears from somewhere, then a running-wave type picture typical for the nucleation burst arises. We incline to associate the nucleation events to this very mechanism. The overall situation is displayed in Figure 1. Figure 2 also shows an event picture. Although the daytime increase in the particle number concentration of the nucleation mode occurs, it is not so clearly expressed as in the case displayed in Figure 1. The initially existing fine and undetectable aerosol begins to grow in parallel with the particles from the regular (periodic) source. The linearity of equation (1) is the reason for this running wave picture. Very likely that this initial aerosol (protoaerosol in what follows) is closely related to stable clusters whose existence was theoretically predicted in [*Kulmala et al.,* 2000].

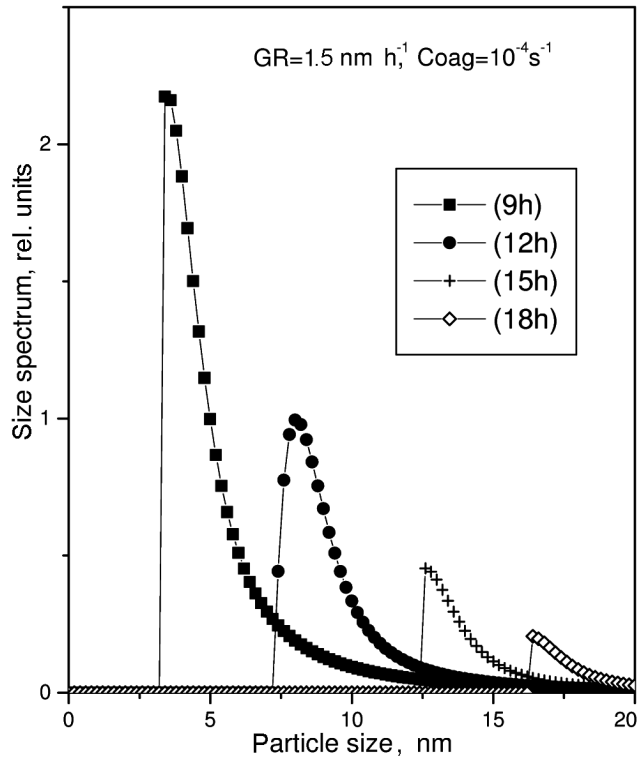

Figure 3. Time evolution of the particle size spectrum. No protoaerosol has presented before the source began to produce fresh particles. But in contrast to Figure 2 the source stops to work at 7 a.m. The aerosols formed by the source before this time begins to grow. The picture reminds that shown in Figure 1.

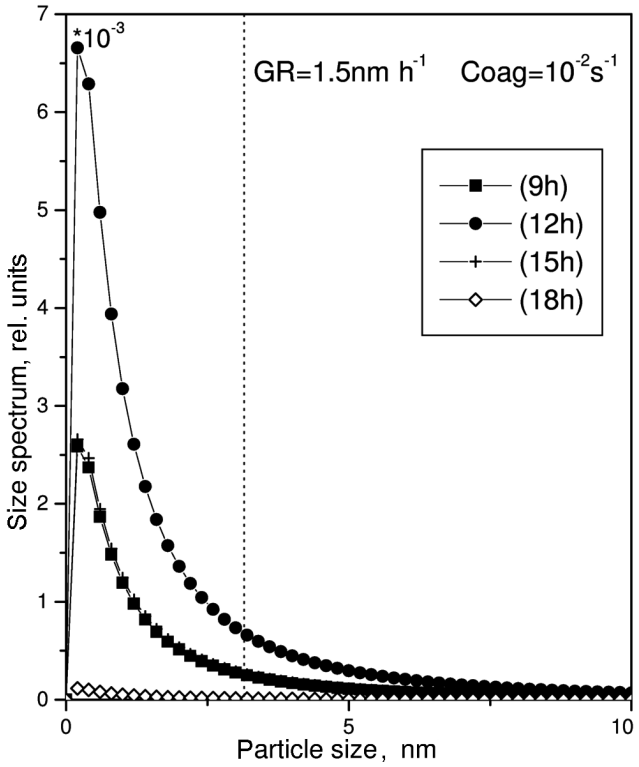

Figure 4. Time evolution of the particle size spectrum. The sinks are so strong that they do not permit the hump to cross the detectable size $a = 3$ nm (vertical dotted line). No nucleation burst is observed, although the source forms fresh particles. Almost all of them die on colliding with the particles of accumulation mode.

[11] Another type of nucleation burst is shown in Figure 3. If the source abruptly (at $t = t_c$) ceases to produce fresh particles then the particles produced before t_c begin to grow in the regime of free condensation and their spectrum moves to the right along the size axis as a running wave. There are some reasons to believe that such type of nucleation burst can realize in the atmosphere. The activity of the nucleation process can be suppressed by a slight increase in the concentration of preexisting particles [*Lushnikov and Kulmala,* 2000].

[12] So the model considered below is linear, i.e., the evolution equation governing the particle size distribution is linear. This is the main and very principle difference of our model from other ones.

Details of the Model

[13] The particle growth is described by the continuity equation

$$\frac{\partial n}{\partial t} + \frac{\partial \dot{a} n}{\partial a} + \lambda n = J\ . \quad (2)$$

Here $n = n(a,t)$ is the distribution of the aerosol particles over their size a so that $n(a,t)da$ is the number concentration of the particles in the size interval $[a, a+da]$. $\dot{a}$ is the particle growth rate (the change of the particle size at a time)

$$\dot{a} = \alpha C(t) = \frac{V_0 v_T C(t)}{4} \ , \tag{3}$$

where v_T is the thermal velocity of a condensing molecule, V_0 is the volume of one condensing molecule, and $C = C(t)$ is the number concentration of the condensing molecules in the gas phase. This expression is valid in the free-molecule regime. If, however, we wish to consider larger particles another formula should be used. It is commonly accepted to use the Fuchs–Sutugin formula. Here we prefer another expression derived in [*Lushnikov and Kulmana,* 2004],

$$\alpha(a) = \frac{2\pi a^2 v_T}{1 + \sqrt{1 + \left(\frac{a v_T}{2D}\right)^2}} \ . \tag{4}$$

Here D is the molecular diffusivity of the condensing species. This formula reproduces the results obtained with the aid of the Fuchs–Sutugin formula. In contrast to the latter equation (4) does not operate with such not well defined values like the molecular mean free path. The diffusivity enters instead.

[14] The coagulation sink λ is either a fitting parameter or can be calculated if we believe that the main cause for the particle sink is the intermode coagulation with the particles of preexisting aerosol.

$$\lambda(a) = \int K(a,b) N(b,t) db \ , \tag{5}$$

where $N(b,t)$ is the size distribution of the preexisting particles and $K(a,b)$ is the coagulation efficiency

$$K(a,b) = \frac{2\pi (a+b)^2 v_T(a,b)}{1 + \sqrt{1 + \left(\frac{(a+b) v_T(a,b)}{2D(a,b)}\right)^2}} \ . \tag{6}$$

Here a, b are the radii of the colliding particles, $v_T(a,b) = \sqrt{\frac{8kT}{\pi \mu_{a,b}}}$ is the thermal velocity, $\mu_{a,b} = \frac{m_a m_b}{(m_a + m_b)}$ is the reduced mass, with m_a, m_b being the masses of colliding particles, $D_{a,b} = D_a + D_b$ is the diffusivity of the colliding pair, D_a, D_b are the diffusivity of each particle (should be found for the transition regime). The diffusivity $D(a)$ is given by the formula, $D = \frac{kTC(a)}{6\pi a \nu \rho_{air}}$ where ν is the kinematic viscosity of air, ρ_{air} is the air density and C is the correction factor [*Phillips,* 1975],

$$C(a) \ = \tag{7}$$

$$\frac{15 + 12c_1 Kn + 9(c_1^2+1)Kn^2 + 18c_2(c_1^2+2)Kn^3}{15 - 3c_1 Kn + c_2(8+\pi\sigma)(c_1^2+2)Kn^2} \ ,$$

where $c_1 = \frac{2-\sigma}{\sigma}$, $c_2 = \frac{1}{2} - \sigma$, with σ being a factor < 1 entering a slip boundary conditions (equation (9)). The Knudsen number $Kn = \frac{\lambda}{a}$ with λ being the mean free path of the carrier gas molecules. The parameter σ changes within 0.79–1. Equation (7) describes the transition correction for all Knudsen numbers and gives the correct limiting values (continuous and free-molecule ones).

[15] $J(a,t) = J(t) f(a)$ is the source productivity of the stable embryos. The function $f(a)$ describes the size dependence of the embryos produced by cooperative action of nucleation and intra-mode coagulation.

Discussion and Conclusion

[16] Equation (2) can be solved exactly. The final result is expressed in terms of some integrals that can be easily calculated numerically by any primitive program as well as all moments of the particle size distribution. Figures 1–4 give the examples of our calculations. The simplicity of our results is again, a consequence of the linearity of the model. Another useful consequence of the linearity is the fact that the shape of size spectra is independent of the total particle number concentration. The latter is proportional to the productivity of the particle source and can also be introduced as a fitting parameters. There are many other fitting parameters in this model like the periodical functions describing the particle source and the diurnal variations of the concentration of condensable gases. So many parameters in hands do not depreciate the model. Their introduction is an eventual step.

[17] As has been mentioned above, the full model of aerosol evolution in the atmosphere includes two interacting blocks: i. the chemical block describing formation of condensable gases and ii. the aerosol block. We separated these blocks by paying for this a good price: we introduced the concentrations of condensable gases and the fresh particle source as external parameters. But in return we acquired the linearity of the model. The point is that the aerosol-trace gases interaction make the full model nonlinear. Meanwhile, as we explained in Section 2 the aerosol process governing the time evolution of the nucleation mode is linear.

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