NUMERICAL SIMULATION OF THE KINETICS OF SIZE SPECTRUM FORMATION OF A SUBMICRON AEROSOL AT COAGULATION IN THE FREE MOLECULAR COLLISION MODE

K.P. Koutsenogii and A.I. Levykin

Institute of Chemical Kinetics and Combustion, Novosibirsk
Institute of Computational Mathematics and Mathematical Geophysics, Novosibirsk
Received February 4, 1998

The peculiarities of size spectrum formation dynamics for submicron aerosols at coagulation in the mode of free molecular collisions are studied using numerical simulation by Smolukhovsky system of equations.

Aerosol generation is a wide spread phenomenon often observed both under natural conditions and in various processes related to human activity.[1–4] In many cases, when aerosols are formed in photochemical and chemical reactions, quick condensation in various gas dynamic flows,[5–7] and burning,[8–9] particles of submicron size are generated. In this connection, processes of aerosol formation have been being studied intensely both experimentally[9–14,19–26] and theoretically[9–18] in recent 10–15 years.

As experimental data are accumulated and methods for measuring the aerosol size spectra and concentration are developed, both theoretical models of aerosol generation processes and the methods for solving equations describing the generation kinetics and growth of aerosol particles are permanently being improved.[27–30] As a rule, the measured parameters in experiments are the concentration and size spectrum of aerosol particles with the size not exceeding 1 μm. The minimum diameter is determined by the type of a condensation device used to coarsen the particles. Most advanced systems are capable of detecting clusters starting from 1–3 nm and even particles of molecular size for some nuclei.[31–32] In the case of aerosol particles formation from complex organic molecules, the size spectrum of an ensemble to be studied may involve particles containing from 10 to 10^{10} monomer units.

Now there exist two different approaches describing nucleation and growth of aerosols. The first one is based on the classical description of the generation kinetics of a new phase. The principal attention here is paid to determination of the expression that describe the free energy needed to form a cluster of critical nucleus. The expression for the rate of generation of new particles is written using the commonly accepted methods. Further formation of the size spectrum is determined by the rate of condensation growth of particles generated, as well as by the rate of creating new critical nuclei. Another one approach relies on solving a system of kinetic equations (Smolukhovsky equations), the number of which equals the number of monomers in a particle of maximum size. Within the frames of a strict approach we would face, at the final stage, the problem of solving a system of about 10^{10} equations to find the size spectrum of particles smaller than 1 μm.

In our previous papers,[33,34] we described in detail the method for numerical solution of the system of Smolukhovsky equations. Next the results were used for a comparison with the experimental data on the kinetics of photochemical aerosol generation obtained under laboratory conditions. Apart from the laboratory experiments, the experimental data are available on evolution of the size spectrum and number density of aerosol particles generated at photolysis of the atmospheric air.[35,36] The aforementioned theoretical and experimental investigations have stimulated further development of numerical simulations with the results presented in Ref. 37.

This paper describes the results of numerical simulations aimed at revealing the peculiarities in the size spectrum formation for a submicron aerosol at coagulation in the free molecular collision mode.

To simulate the dynamics of aerosol formation, we used the system of coagulation equations of the following form:

$$\frac{dN_1}{dt} = - N_1 \sum_{i=1}^{\infty} \beta_{1i}\, \alpha_{1j}\, N_i + F(t), \qquad (1)$$

$$\frac{dN_l}{dt} = \frac{1}{2} \sum_{i+j=l} \beta_{ij}\, \alpha_{ij}\, N_i\, N_j - N_l \sum_{i=1}^{\infty} \beta_{li}\, \alpha_{li}\, N_i, \qquad (2)$$

where β_{ij} are the gas-kinetic constants of collision for particles consisting of i- and j-monomer units; α_{ij} is the efficiency of particle coagulation at a collision; $N_l(t)$ is the number density of particles consisting of l monomers; and $F(t)$ is the intensity of the source of monomers.

If the source intensity is constant $F(t) = F = const$, then having changed the variables

$$N_i = n_i \left(\frac{F}{\beta_{11}} \right)^{1/2}, \qquad (3)$$

$$t = \tau \left(\frac{1}{F\, \beta_{11}} \right)^{1/2} \qquad (4)$$

Eqs. (1) and (2) are reduced to the dimensionless form

0235-6880/99/01 85-04 $02.00

$$\frac{dn_1}{d\tau} = 1 - n_1 \sum_{i=1}^{\infty} K_{1i}\, \alpha_{1j}\, n_i, \qquad (5)$$

$$\frac{dn_1}{d\tau} = \frac{1}{2} \sum_{i+j=1} K_{ij}\, \alpha_{ij}\, n_i\, n_j - n_l \sum_{i=1}^{\infty} K_{li}\, \alpha_{li}\, n_i, \qquad (6)$$

where

$$K_{ij} = \beta_{ij}/\beta_{11}. \qquad (7)$$

In the case of free molecular collisions,

$$K_{ij} = \frac{1}{4\sqrt{2}} (i^{1/3} + j^{1/3})^2 (1/i + 1/j)^{1/2} \qquad (8)$$

and $\beta_{11} = 7.8 \cdot 10^{-10}$ cm^{-3} s^{-1} at $\rho = 1$ g/cm^3.

The method for solution of the system of equations (5) and (6) is described in detail in Ref. 33. The accuracy of the solutions obtained is also estimated there. The numerical solution was aimed at revealing qualitative peculiarities in the dynamics of size spectrum formation both at a continuously acting source of monomers and at a source of a pulsed type.

The principal peculiarities of the size spectrum shape are shown in Figs. 1–3 for the continuously acting source. Figure 1 presents the total number density of aerosol particles as a kinetic function of the minimum cluster size (in monomer units) measurable in measurements of the aerosol particle number density. The upper curve shows the case, when the minimum detectable particle (cluster) contains 20 monomer units. The lower curve describes the situation with $j_{\min} = 10^4$. The characteristic feature of these curves is that the total number density of aerosol particles sharply increases, reaches maximum, and then slowly decreases. The smaller the minimum detectable size of particles, the earlier the maximum is reached and the higher and sharper is it.

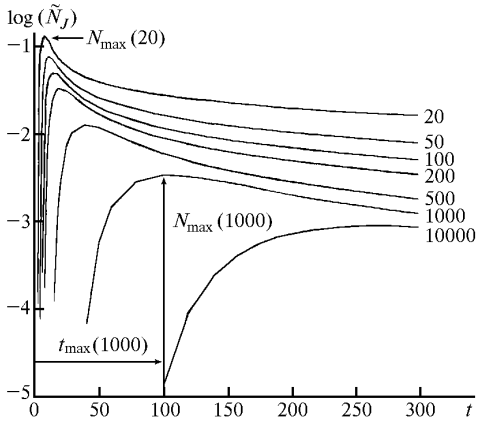

FIG. 1. Time dependence of the total number density of particles with the size greater than $j_{\min}$.

Figure 2 shows the kinetic curves at the initial stage for clusters starting from a dimer. It is seen that at the beginning the slope of the kinetic curves noticeably varies as the minimum detectable cluster size changes. It increases with increasing j. However, starting from $j = 10$ the slope of the kinetic curve is practically constant. Thus, the kinetic curves are very similar to each other varying only in the position along the time axis.

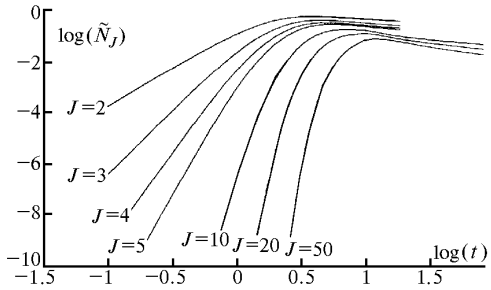

FIG. 2. Kinetic curves $N_J(t) = \Sigma N_i$ for the values of J from 2 to 50.

As the duration of coagulation increases, the bimodal size spectrum is formed (see Fig. 3). The size spectra in both regions of fine and coarse-disperse particles are approximately described by the same functions. In the region of fine particles, it is a power-law function with the minus valued exponent. The size spectrum of coarse-disperse particles can be presented, in the first approximation, by a lognormal distribution. The spectral width is practically the same, and the modal size of the coarse fraction increases with the increasing duration of coagulation ($d^3 \sim \tau$).

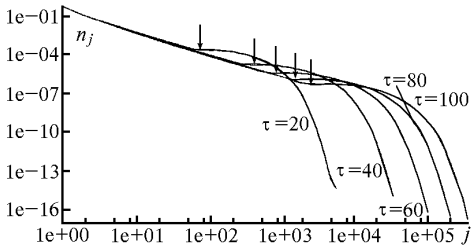

FIG. 3. Number density $N_J(\tau)$ as a function volume of j-sized particles at different duration of source operation τ.

Figure 4 shows the transformation of the size spectrum after termination of the monomer generation. It is seen that the coarse fraction is practically "frozen," while the fine fraction becomes significantly variable. As the observation time increases, fine particles disappear due to high mobility, and the size spectrum of fine particle becomes narrower. As the calculations show, if the coagulation efficiency is 100% at the beginning, the most noticeable changes in the kinetic curves are observed for clusters less than 10 monomers. So, the next stage of our study was to reveal peculiarities of the kinetic curves at different probability of collisions between clusters of different size.

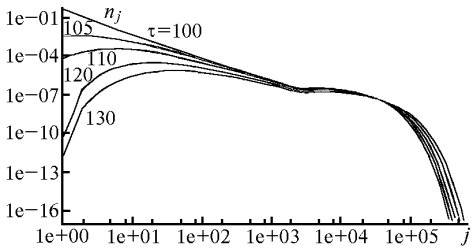

FIG. 4. Transformation of the particle size spectrum after termination of monomer generation at $\tau = 100$.

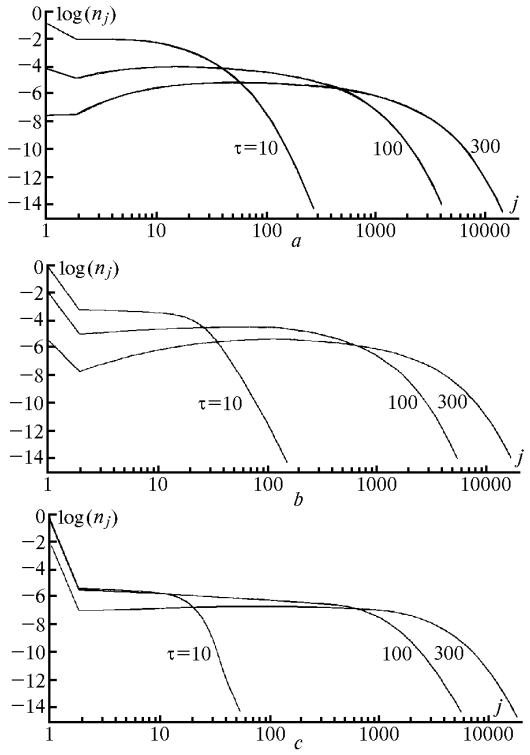

FIG. 5. Particle size spectra for different values of the coagulation efficiency: $\alpha_{11} = 10^{-1}$ *(a);* 10^{-3} *(b);* 10^{-5} *(c);* τ *is the dimensionless time.*

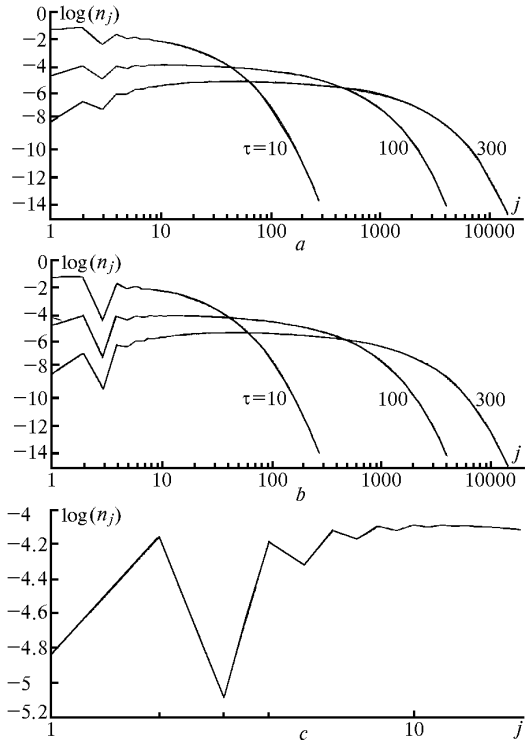

FIG. 6. Particle size spectra for different values of the coagulation efficiency: $\alpha_{12} = \alpha_{21} = 10^{-1}$ *(a);* 10^{-3} *(b);* 10^{-5} *(c); the initial part of the spectrum.*

Figure 5 shows the peculiarities in the size spectrum of particles coagulating at different efficiency of dimers ($\alpha_{11} = 0.1$, 10^{-3}, and 10^{-5}) coagulation. Similar dependence for a tetramer is shown in Fig. 6. These curves for a dimer are characterized by the formation of a single-mode distribution. At α_{11} of not very small value, the size spectrum is the same as at $\alpha_{11} = 1$ at a longer duration of coagulation. In the case, when the aerosol particle size is limited by a tetramer, polymodal size spectra appear.

REFERENCES

1. S.K. Friedlander, *Smoke, Dust, and Haze* (J. Willey & Sons, 1977), 317 pp.
2. D.T. Shaw, ed., *Recent Development in Aerosol Science* (J. Willey & Sons, 1978), 325 pp.
3. J.H. Scienfeld, *Atmospheric Chemistry and Physics of Air Pollution* (J. Willey & Sons, 1986), 738 pp.
4. P.E. Wagner and G. Vali, eds., *Atmospheric Aerosols and Nucleation. Lecture Notes in Physics* (Springer-Verlag, Berlin, 1988), Vol. 309, 729 pp.
5. A.G. Amelin, *Theoretical Principles of Fog Formation at Condensation* (Khimiya, Moscow, 1972), 304 pp.
6. V.N. Gorbunov, U.G. Pirumov, and Y.A. Ryzhov, *Non–Equilibrium Condensation in High–Speed Gas Flows* (Mashinostroenie, Moscow, 1984), 200 pp.
7. I.V. Petryanov and A.G. Sutugin, Kolloid. Zh. **51**, No. 3, 480–489 (1989).
8. R.C. Flagan and S.K. Friedlander, in: *Recent Development in Aerosol Science* (1978), pp. 25–59.
9. "*Proceedings of the 1989 European Aerosol Conference.*" *Vienna, Austria, 18–23 September 1989*, Aerosol Sci. **20**, No. 8, 1624 (1989).
10. P.H. McMurry and S.K. Friedlander, Atmos. Environ. **13**, 1635–1651 (1979).
11. G.A. Kirichevskii, "*Nucleation in supersaturated water vapor in a Wilson chamber,*B Author's Abstract of Cand. Phys.-Math. Sci. Dissert., Odessa (1988), 16 pp.
12. B.A. Ulyavichus, "*Investigation of fine aerosol by the electric spectrometry method,*B Author's Abstract of Cand. Phys.-Math. Sci. Dissert., Moscow (1989), 12 pp.
13. K. Okuyama, Y. Kousaka, D.R. Warren, R.C. Flagan, and J.H. Sceinfeld, Aeros. Sci. Technol. **6**, 15–27 (1987).
14. K. Okuyama, Y. Kousaka, S.M. Kreidenweis, R.C. Flagan, and J.H. Sceinfeld, J. Chem. Phys. **89**, No. 10, 6442–6453 (1988).
15. J.E. Stern, R.C. Flagan, and J.H. Scienfeld, Aeros. Sci. Technol. **10**, 515–534 (1989).
16. S.M. Kreidenweis, R.C. Flagan, J.H. Scienfeld, and K. Okuyama, J. Aeros. Sci. **20**, No. 5, 585–607 (1989).
17. A.A. Vostrikov and D.Yu. Dubov, "*Real Properties of Clusters and the Condensation Model,*" Preprint No. 112, Institute of Heat Physics of the Siberian Branch of the Academy of Sciences of the USSR (Novosibirsk, 1984), 53 pp.

18. G.G. Kodenev, M.N. Baldin and V.S. Vaganov, in: *Physics of Clusters* (Novosibirsk, 1987), pp. 110–115.
19. E.N. Rybin, M.E. Pankratova, and Ya.I. Kogan, Zh. Fiz. Khimii **50**, No. 3, 769–771 (1976).
20. E.N. Rybin, M.E. Pankratova, and Ya.I. Kogan, Zh. Fiz. Khimii **51**, No. 5, 1036–1040 (1977).
21. M.P. Anisimov, S.N. Vershinin, A.A. Aksenov, A.M. Sgonov, and G.L. Semin, Kolloid. Zh. **49**, No. 5, 842–846 (1987).
22. S.N. Dubtsov, G.I. Skubinevskaya, and K.P. Koutsenogii, Khim. Fiz. **6**, No. 8, 1061–1068 (1987).
23. G.I. Skubinevskaya, S.E. Pashchenko, S.N. Dubtsov, et al., Khim. Fiz. **3**, No. 11, 1622–1624 (1984).
24. S.E. Pashchenko, K.P. Koutsenogii, A.E. Pashchenko, A.I. Ankilov, and A.M. Baklanov, Pis'ma Zh. Tekh. Fiz. **6**, No. 22, 1380–1383 (1980).
25. N.B. Frish, and G. Wilemski, in: *Atmospheric Aerosols and Nucleation*, P.E. Wagner and G. Vali, eds. (Springer-Verlag, Berlin, 1988), pp. 527–530.
26. K. Okuyama, and Y. Kuosaka, in: *Atmospheric Aerosols and Nucleation*, P.E. Wagner and G. Vali, eds. (Springer-Verlag, Berlin, 1988), pp. 79–92.
27. K.P. Smidovich, V.A. Zagaynov, A.A. Lushnikov, and A.G. Sutugin, in: *Atmospheric Aerosols and Nucleation*, P.E. Wagner and G. Vali, eds. (Springer-Verlag, Berlin, 1988), pp. 96–99.
28. P.H. McMurry, and S.K. Friedlander, J. Coll. Inter. Sci. **64**, No. 2, 248–257 (1978).
29. S.K. Friedlander, W. Koch and H.H. Main, J. Aeros. Sci. **20**, No. 8, 887–890 (1989).
30. K. Smidovich, A. Majerovich, and P.E. Wagner, Aeros. Sci. Technol. **11**, 1–10 (1989).
31. J. Porstendorfer, H.G. Schneibel, F.G. Pohl, et al., Aeros. Sci. Technol. **4**, 65–79 (1985).
32. Ya.I. Kogan, Dokl. Akad. Nauk SSSR **161**, 388–391 (1965).
33. K.P. Koutsenogii, A.I. Levykin, and K.K. Sabelfeld, J. Aeros. Sci. **27**, No. 5, 665–679 (1996).
34. S.N. Dubtsov, K.P. Koutsenogii, A.I. Levykin, and G.I. Skubinevskaya, J. Aeros. Sci. **26**, No. 5, 705–716 (1995).
35. K.P. Koutsenogii, "*Measurements of Remote Continental Aerosol in Siberia*," Doktorarbeit, Jochannes Gutenberg Universitet Mainz (1993), 105 pp.
36. K.P. Koutsenogii and R. Jaenicke, J. Aeros. Sci. **25**, 377–383 (1994).
37. K.P. Koutsenogii, A.I. Levykin, and K.K. Sabelfeld, J. Aeros. Sci. (in press).