ON THE COAGULATION TRANSFORMATIONS OF THE MICROPHYSICAL PROPERTIES OF SMOKE AEROSOLS

R.F. Rakhimov

Institute of Atmospheric Optics, Siberian Branch USSR Academy of Sciences, 634055 Tomsk,
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A numerical simulation procedure for the coagulative transformation of aerosol optical and microphysical properties in a closed volume is reported. The proposed approach relies on a reduced description of the particle size distribution in terms of integrated features of polydispersions. A comparative analysis of data obtained from a laboratory experiment and a numerical simulation on smoke aerosols corroborates the utility of the present procedure.

The aerosol component is one of the main causes of instabilities in the optical properties of the atmosphere. The complicated dependence of the state of the dispersed component on geophysical conditions as well as the need to take into account the combined influence of various processes which have pronounced differences in their spatio-temporal scales probably makes up the larger part of the problem of modeling the light scattering properties of aerosols.

An important factor in the dynamics of the optical properties of atmospheric aerosols is the deformation of the particle size spectrum. Peculiarities in the structure of the dispersed composition of atmospheric hazes arise, on the one hand, from microprocesses occurring on the local scale inside the aerosol field cells, and, on the other hand, as a result of complex exchange processes inside and between the stratification formations under the influence of the meteorological elements.

The concept of fractional modeling of the aerosol component[1–3], being a reasonable modeling compromise, is based on the hypothesis of the relative independence of the formation and development of the dispersed state of atmospheric haze covering not less than 3–4 orders of magnitude of the aerodynamic particle radius. Specifically, it can be written

$$\frac{dN}{dr} = n(r) = A(r)^{-3} \sum_{i=1}^{I} M_i \exp\left\{-b_i\left[\ln\frac{r}{r_i}\right]^2\right\} \qquad (1)$$

where $I \sim 3$–4, dN is the number density of aerosol particles per unit volume within the particle radius interval from r to $r + dr$, $n(r)$ is the particle size density function, and A, M_i, b_i and r_i are the model parameters.

As numerical 'estimates show, the substitution of a real size spectrum $n(r)$ (irregular, as a rule) by a superposition of parabolic (in a double logarithmic scale) approximations is quite acceptable within the limits of 15 to 20% error in the prediction of the aerosol light scattering parameters.

The fractional method of determining the atmospheric haze size spectrum (1) enables us to proceed from the conventional parameters of microstructure A, M_i, r_i, b_i to the integrated characteristics V_i, S_i and N_i representing the total volumes, surfaces, and number densities of the individual fractions using the chain of equations:

$$r_i = (3V_i)^{2/3}/[(4\pi N_i)^{1/6} S_i^{1/2}]; \qquad (2)$$

$$1/b_i = \ln\{(4\pi N_i)^{2/3}(3V_i)^{4/3}/S_i^2\}; \qquad (3)$$

$$F_i = AM_i = S_i/\sqrt{16\pi^3/b_i}\,. \qquad (4)$$

The method proposed for decsribing the haze structure in terms of the integral characteristics (2)–(4) is attractive since the initial values V_i, S_i and N_i are more easily accessible for direct measurements, being also convenient for the parametrization of some subcell microprocesses and the development of reduced approach to mesoscale modeling.

One such microprocesses is, in particular, the coagulation of aerosol particles that always accompanies the evolution of a dispersed system.

The kinetics of the coagulational modification of the atmospheric haze size spectrum is usually described on the basis of the Smoluchovski i integral-differential equation to which terms have been added which represent the presence of particle sinks and sources[4]:

$$\frac{dn(x,t)}{dt} = \frac{1}{2}\int_0^x K(x, x-x')n(x-x', t)\, n(x', t)dx' + \gamma n_j(x) - n(x,t)\int_0^\infty K(x,x')\, n(x',t)dx' - \beta n(x,t), \qquad (5)$$

where $K(x, x')$ is the coagulation coefficient of the particles with sizes x and x'; $n(x, t)$ is the transformed size spectrum; $n_j(x, t)$ is the size spectrum of the

particles generated by the source; β is the effective rate of particle destruction; and γ is the rate of new particle generation. A direct solution of Eq. (15) in the case of complicated size spectra $n(x, 0)$ is possible only by numerical methods[4–5] and requires a considerable computation time (on the order of a few hours) using modern computers.

The parametrization process is considered here for an individual fraction. This will permit us to proceed (for a polydispersed ensemble) to the use of an effective value of the Brownian coagulation coefficient[6]:

$$K = \frac{4kT}{3\mu}\left[1+\exp\left(\frac{1}{2b_i}\right)+\frac{\Lambda C}{r_i}\left\{\exp\left(\frac{1}{4b_i}\right)+\exp\left(\frac{5}{4b_i}\right)\right\}\right], \quad (6)$$

where k is the Boltzmann constant, T is the temperature, μ is the viscosity of air, Λ is the molecular free path; c is the Cunningham correction factor.

Integrating Eq. (5) over the interval 0 to ∞ using the effective value of the coagulation constant given by Eq. (6B), one can easily proceed to the differential equation for the dynamics of the particle integral number density

$$\frac{dN_i}{dt} = -\frac{K}{2}N_i^2 - \beta N_i + \gamma N_j \quad (7)$$

Similar equations for the first (L_i) and second (W_i) moments of the spectrum $n(x)$ can be obtained from Eq. (5) by first multiplying it by x and x^2 respectively, and then integrating it over the indicated interval

$$\frac{dL_i}{dt} = -\beta L_i + \gamma L_j; \quad (8)$$

$$\frac{dW_i}{dt} = \frac{K}{\pi}L_i^2 - \beta W_i + \gamma W_j, \quad (9)$$

where N_i, L_i and W_i are the corresponding moments of the initial size spectrum of the aerosol particles generated by the source.

The solution of system of equations (7)–(9) for the moments allows one to predict the structural changes of the size spectrum, relying upon the relations (2)—(4), as a result of the joint action of the coagulation process and the processes of particle creation and destruction. Specifically, it follows from Eq. (7), that the behavior of $N_i(t)$ can be described by the expression

$$N_i(t) = \frac{B-\xi+D(\xi+B)\exp(2Bt)}{\alpha[1-D\exp(2Bt)]}, \quad (10)$$

where

$$\alpha = -\frac{K}{2};\ \xi = -\frac{\beta}{2};\ B = \sqrt{\xi^2-\alpha\gamma N_j};\ D=\frac{(\alpha N_{i0}+\xi-B)}{(\alpha N_{i0}+\xi+B)}.$$

Analogously, it follows from Eq. (8) and Eq. (9) that

$$L_i(t) = \left\{L_{i0}+\frac{\gamma L_j}{2\xi}\right\}\exp(2\xi t) - \frac{\gamma L_j}{2\xi}; \quad (11)$$

$$W_i(t) = \left\{W_{i0}^t+\frac{\gamma W_j}{2\xi}\right\}\exp(2\xi t) - \frac{\gamma W_j}{2\xi}; \quad (12)$$

where

$$W_{i0}^t = \left\{W_{i0}+\frac{K}{\pi}\left\{\left[L_{i0}+\frac{\gamma L_j}{2\xi}\right]^2\frac{1}{2\xi}[\exp(2\xi t)-1] - \right.\right.$$

$$\left.\left. - \frac{2\gamma L_j}{2\xi}\left[L_{i0}+\frac{\gamma L_j}{2\xi}\right]t-\frac{(\gamma L_j)^2}{(2\xi)^3}[\exp(-2\xi t)-1]\right\}\right\},$$

and N_{i0}, L_{i0}, W_{i0} are the corresponding moments of the initial spectrum at $t = 0$.

Taking the limit in Eqs. (10)–(12) as $\beta \to 0$ and $\gamma \to 0$ gives a solution which describes the coagulational development of the dispersed system:

$$N_i(t)=N_{i0}/\left(1+\frac{K}{2}N_{i0}t\right); \quad (13)$$

$$L_i(t) = L_{i0} \quad (14)$$

$$W_i(t) = W_{i0}+\frac{K}{\pi}L_{i0}^2 t. \quad (15)$$

The following relations, which follow from Eqs. (10)—(12) when $\gamma = 0$, can be useful in analyzing the process of relaxation of the dispersed system in the absence of sources:

$$N_i(t) = \frac{2\beta N_{i0}}{[(KN_{i0}+2\beta)\exp(\beta t)-KN_{i0}]}; \quad (16)$$

$$L_i = L_{i0}\exp(-\beta t); \quad (17)$$

$$W_i(t) = \left\{W_{i0}-\frac{K}{\pi\beta}L_{i0}^2[\exp(-\beta t)-1]\right\}\exp(-\beta t). \quad (18)$$

At the same time, the asymptotic behavior of the solution of Eqs. (16)—(18) for $t \gg 1/\beta$ can be well approximated by exponential functions with effective initial values of the moments

$$N_i(t)=N_{i0}\exp(-\beta t)/\left(1+\frac{K}{2\beta}N_{i0}\right); \quad (19)$$

$$L_i(t) = L_{i0}\exp(-\beta t) \quad (20)$$

$$W_i(t) = \left(W_{i0}+\frac{K}{\pi}L_{i0}^2 t\right)\exp(-\beta t) \quad (21)$$

And finally, the coagulation process in the absence of particle sources, leads to a reduction of the particle number density down to a level at which the effective rate of destruction of particles β dominates over the

values of $\frac{KL_{i0}^2}{\pi W_{i0}}$ and $\frac{K}{2}N_{i0}$. The behavior of the system in this case is described by the expressions

$$N_i(t) = N_{it_k} \exp(-\beta t) \tag{22}$$

$$L_i(t) = L_{it_k} \exp(-\beta t) \tag{23}$$

$$W_i(t) = W_{it_k} \exp(-\beta t) \tag{24}$$

which is equivalent to the process of degradation of the fraction without any essential changes in its spectrum.

In this case it is quite easy to see from Eqs. (2)–(3) that the size spectrum does not (undergo qualitative changes since $r_i(t > t_k) \simeq r_{it_k} = \text{const}$ and $b_i(t > t_k) \simeq b_{it_k} = \text{const}$.

The question of a real mechanism of the coagulational cohesion of separate aerosol particles into one particle is an open one, and, in this connection, an ambiguity can occur in the interpretation of the solutions given by Eqs. (10)–(24). In particular, if x is taken to mean particle radius in a formal writing of Eq. (5), then the integral linear dimension will be an invariant of the coagulational transformation of the spectrum, as is easily seen from Eq. (14).

Equation (12) in turn describes the in dynamics of variation of the total particle surface. One can use the interconnection between the model moments give by Eq. (1) to evaluate the behavior of $V_i(t)$, namely

$$V_i(t) = \pi N_i(t)\, S_i^3(t) / [6L_i^3(t)] \tag{25}$$

This version of the solution seems to be unlikely at first sight since in this case the process is characterized by growth of S_i and V_i. But if one takes into account the fact that the water-vapor mass content in the atmosphere exceeds the content of the dispersed component by a few orders of magnitude, then the hypothesis[7] becomes quite realistic, according to which the formation of microcapillaries due to cohesion of the coagulation particles can stimulate the process of heterogeneous micropore moisture condensation, thereby ensuring an increase of the aerosol component. An alternative hypothesis to the above-considered mechanism of coagulational cohesion is the hypothesis of complete cohesion of the colliding particles into one spherical particle with volume equal to the sum of the initial volumes before the interaction. It is evident that the process invariant in this case will be the total volume of the aerosol particles, provided that no particle creation or destruction processes take place, which is equivalent to the formal substitution of $v = 4\pi r^3/3$ for the variable x in Eq. (15).

Equation (11) describes the behavior of $V_i(t)$ for this mechanism, after substitution of the corresponding boundary conditions. In analogy with the first version one can use the interconnection of the moments of the spectrum, given by Eq. (1), to determine the time dependence of $S_i(t)$:

$$S_i(t) = \left\{ \frac{4\pi}{9W_i(t)} [3V_i(t())]^8 [4\pi N_i(t)]^2 \right\}^{1/9} \tag{26}$$

where $W_i(t)$ in this case describes the variation with time of the sixth moment of the spectrum $n_i(r)$ or of the second moment of the distribution density $n_i(v)$.

An intermediate mechanism of the incomplete (partial) cohesion of coagulation particles (into one spherical particle) can be considered if the variable κ in Eq. (5) is understood as the surface area of a spherical particle $S = 4\pi r^2$. Equation (11) in this case then describes the behavior of $S_i(t)$ and for $V_i(t)$ we have the following relation:

$$V_i(t) = \frac{1}{3} \left\{ W_i^3(t)\, S_i^6(t) / [16\pi^2 N_i(t)] \right\}^{1/8}, \tag{27}$$

where $W_i(t)$ describes the time behavior of the fourth moment of the spectrum $n(r)$ or the second moment of $n_i(s)$ to within a proportionality factor.

The probability of a binary collision is proportional to the product of the noninteracting particle number densites. The atmospheric haze particle size spectrum on average follows the Pareto distribution law, yielding the power dependence $r^{-\nu}$, where $\nu = 3$ or 4. Therefore, the efficiency of the disperse structure coagulational transformation depends essentially upon the amount of fine aerosol fraction which, is present. The products of thermal evaporation of different substances, of the so-called smoke aerosols, play an important role in the formation of the atmospheric aerosol component, particularly its fine dispersed fraction. According to estimates[8], about 10^{22} to 10^{23} fine particles come into being in the atmosphere after a middle-sized steppe fire over the area of 1 hectare. Weak exchange between the near-ground layer and the free atmosphere, which sometimes occurs under certain meteorological conditions can facilitate their anomalous accumulation.

The approach developed in this paper has been to analyze the coagulational transformation of the optical-microphysical properties of smoke aerosols, nephelometric methods of recording the angular function[9] of light scattering, being extremely sensitive to the faintest changes of the aerosol phase microstructure, show themselves to be sufficiently informative for analysis of these mieroprocesses.

Figures 1–5 depict the results of our numerical simulations compared with the averaged data of the laboratory experiments[9]. The angular light scattering functions (scattering matrix) were calculated for the polydispersed ensemble according to Mie theory using the algorithm presented in Refs. 1 and 2.

The following parameters were used to compare the results of our model estimations, using the conclusions drawn from Eqs. (10)–(24), with the laboratory data[9]: the asymmetry coefficient K_A of the normalized scattering phase function $g(\theta)$, which is equal to the ratio of the light fluxes scattered into the forward and backward

hemispheres; the degree of polarization of the radiation scattered at the angles $\theta = 110$ and $\theta = 165°$, denoted as P_1 and P_2, respectively; and the ratio $A_s = g(15°)/g(110°)$, which characterizes the degree of stretching of the normalized scattering phase function in the forward direction.

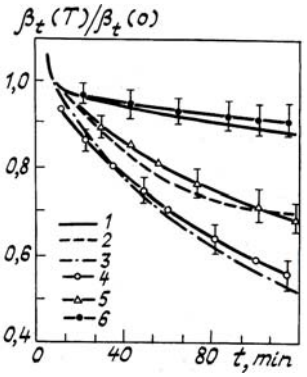

FIG. 1. The dynamics of the coagulational degradation of the normalized extinction coefficient β_t/β_{t0} in a closed volume at the wavelenght $\lambda = 0.63$ μm. Curves 1, 2, and 3 represent the calculated data for $\beta_{t0} = 0.007$ m^{-1}, 0.03 m^{-1}, 0.22 m^{-1}, respectively; curves 4, 5, and 6 represent the results of laboratory experiments[9].

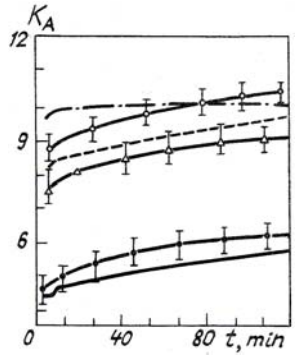

FIG. 2. The dynamics of the asymmetry coefficient K_A of the normalized scattering phase function (designations are the same as in Fig. 1).

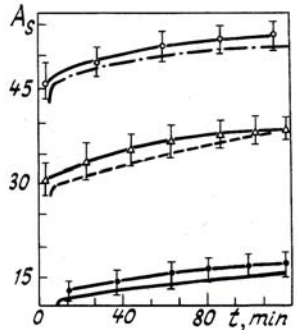

FIG. 3. The time behavior of the forward stretching factor of the normalized scattering phase function A_s (designations are the same as in Fig. 1).

The results of the model experiment show that the dynamics of the optical properties of the smoke aerosol under laboratory conditions is the result of the coagulational transformation of the size spectrum and of the diffusional dissipation and sedimentation of the particles on the chamber walls. Moreover, as the model estimated show, the characteristic features of coagulational aging of smoke aerosols revealed in the laboratory investigations[9] are dependent to a great extent on the conditions under which the formation of the initial spectrum takes place at the first stage, which lasts from 5 to 8 minutes. On the basis of a series of pilot numerical experiments providing the possibility of varying the smoke generator power we managed to reproduce the most acceptable versions of the model process with the aid of calculations based on the third mechanism of two-particle coagulational cohesion.

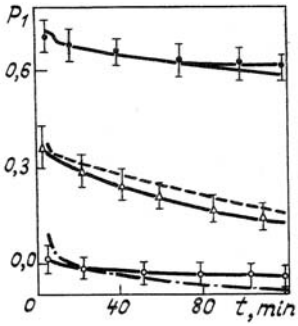

FIG. 4. The time behavior of the degree of the polarization of the radiation scattered at the angle $\theta = 100°$ (Curves are marked as in Fig. 1)

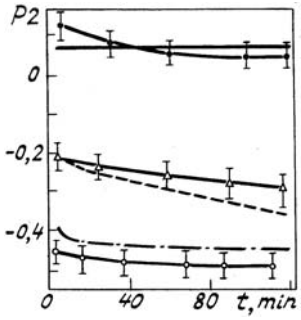

FIG. 5. Comparison of the computed values of the degree of polarization of radiation scattered at the angle $\theta = 160°$ with the experimental data[9] *(designations are the same as in Fig. 1).*

Table 1 gives the values of the output parameters of the smoke aerosol generator for which the angular light scattering function is closest to the results of physical experiment. The calculated results marked in the Figures as curves 1 were obtained using the hypothesis that the smoke aerosol source with the parameters listed in the first row of Table 1, in parallel with the processes of particle coagulational growth and sedimentation on the chamber walls facilitates the formation of the initial spectrum in such a way that the initial values of the optical characteristics K_A, P_1, P_2, A_s and, specifically, the extinction coefficient $\beta_t = 0.007$ m^{-1}, also given in the first column of Table 1, are achieved. The values listed in the second and third rows of Table 1, respectively, have a similar meaning.

TABLE 1.

β_t	N_{source}	S_{source}	V_{source}	r_{source}	b_{source}
[m^{-1}]	[$cm^{-3}s^{-1}$]	[$cm^{-3}s^{-1}\mu m^2$]	[$\mu m^3 cm^{-3} s$]	[μ m]	—
0.007	6.04×10^3	4.46×10^1	1.15×10^0	0.0525	0.646
0.030	3.90×10^5	1.13×10^3	2.77×10^1	0.0435	0.476
0.220	2.34×10^5	2.53×10^3	1.77×10^2	0.1089	0.381

The error of evaluation of K_A by nephelometric methods is contingent meinly upon problems of recording of $g(\theta)$ within the aureole region and at the angle $\theta = 180°$. It is possible that the marked discrepancies between the theoretical and experimental data, plotted in Fig. 2, can be explained by this circumstance and, specifically, by the angles $\theta = 0°$ and $\theta = 180°$.

It should be noted that the irregularities in the variation of the calculated optical characteristics at the primary stage of the process were not revealed in the experimental data because of time averaging. The time required for measuring characteristics at one point of the experimental curve was not less than 3 to 4 minutes.

The results of the numerical experiment show that the laboratory data cannot be explained successfully only by the coagulational aging of smoke aerosols without taking into account the sedimentation of the particles on the chamber walls. This is also true for the case of one sink. It is not difficult to understand this if one examines the data presented in Tables 2a and 2b, which illustrate the current changes of the microphysical parameters of the smoke aerosol values were $\beta_t = 0.33 m^{-1}$ and $0.22 m^{-1}$, respectively. It follows from these Tables, in particular, that the smoke aerosol number density decreases rather rapidly because of the intensive coagulation of the aerosols. The decrease can amount to two orders of N_t magnitude during two hours.

TABLE 2a.

t	R_t	b_t	$N_t \times 10^{-6}$	$S_t \times 10^{-6}$	$V_t \times 10^{-3}$
[min]	[μm]	—	[cm^{-3}]	$\mu m^2 cm^{-3}$	$\mu m^3 cm^{-3}$
5	0.044	0.476	107.0	32.3	8.03
20	0.070	0.579	15.80	17.6	6.35
50	0.093	0.664	4.490	10.9	4.92
80	0.113	0.742	1.880	7.89	4.18
120	0.142	0.852	0.757	5.91	3.74

TABLE 2b.

t	R_t	b_t	$N_t \times 10^{-6}$	$S_t \times 10^{-6}$	$V_t \times 10^{-3}$
5	0.111	0.405	56.60	79.9	50.4
20	0.202	0.504	5.820	40.9	45.2
50	0.250	0.552	2.300	29.6	38.9
80	0.279	0.579	1.370	23.7	34.0
120	0.305	0.604	0.846	18.9	29.1

The sedimentation of the particles onto the walls cannot be less efficient since the total volume V_t decreases by almost a factor of two. The combined effect of both processes can be judged from the changes of the model radius R_t (it increases by more than a factor of three).

Simultaneously, there takes place a pronounced narrowing of the spectrum, which can be easily seen from the dynamics of the parameter b_t whose inverse value is proportional to the spectrum width (1).

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