

KINETICS OF ATMOSPHERIC WATER-SOLUBLE AEROSOLS

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A kinetic equation of water-soluble aerosols is obtained for the particle size distribution function that considers gas-particle changes including water vapor condensation processes. It is shown that the reciprocal power-law particle size distribution may be formed due to gas-particle changes under stable atmospheric conditions. Analysis of variability of the microphysical parameters of the surface aerosol allows the principal mechanism of growth of the atmospheric damp haze particles to be determined.

The efficiency of investigations into the atmospheric aerosol by optical methods^{1,2} allows one to reveal the influence of the internal atmospheric transformation processes³ on the variability of aerosol microphysical characteristics.¹ However, the interpretation of the observed regularities calls for the development of principles of kinetics (dynamics) of the atmospheric water-soluble aerosol or atmospheric damp haze. The detailed study of the dependences between the relative air humidity and optical and microphysical aerosol characteristics^{4,5} was an important step on the road to the development of water-drop aerosol kinetics.

Spatiotemporal changes in the microstructure of aerosols with preset properties (size of particles, phase state, and chemical composition) are described by the equation for the aerosol number density $C = C(x, y, z, t)$

$$\frac{\partial C}{\partial t} = \left[\frac{\partial C}{\partial t} \right]_{tr} + \left[\frac{\partial C}{\partial t} \right]_{mix} + \left[\frac{\partial C}{\partial t} \right]_{rem} + \left[\frac{\partial C}{\partial t} \right]_{cg} + \left[\frac{\partial C}{\partial t} \right]_{gpc}, \quad (1)$$

where x , y , and z are the Cartesian coordinates, t is the time,³ the terms on the right-hand side of Eq. (1) characterize transport⁶ (*tr*) and mixing⁷ (*mix*) processes and particle removal (*rem*) from the atmosphere as well as internal atmospheric aerosol transformation, namely, coagulation⁸ (*cg*) and gas-particle change (*gpc*) processes. When solving the specific problems of kinetics (or dynamics) of dispersed media including the atmospheric aerosol, one usually restricts oneself by one term or group of two-three terms^{7,9} on the right-hand side of Eq. (1). An example of detailed analysis and solution of three-dimensional nonstationary problem can be found in Aloyan et al.⁹

In the derivation of the kinetic equation for dispersed media with continuous distribution function, unlike the discrete dispersed systems and gases, one should take into consideration that the number density of particles with the preset parameters (a and v , the

radius and volume of the particle) $C = C(a) = \Delta N(a) = g(a)\Delta a = n(v)\Delta v$ is determined by the product of the particle size $g(a)$ or volume $n(v)$ distribution function on the width of the particle sizes Δa (or corresponding volume Δv) distribution, which also can change together with $g(a)$ in the process of aerosol transformation. Therefore, in general one should solve the equation for the function $\psi(a)$, which is proportional to the width of the particle size distribution $\Delta a(a) = m\psi(a)$, where m is the coefficient of proportionality, together with Eq. (1).

If the function $\psi(a)$ does not depend on time, then

$$\frac{d[\psi(a) g(a)]}{dt} = \psi(a) \left[\frac{\partial g(a)}{\partial t} + \nabla \mathbf{u} g(a) \right],$$

where $\mathbf{u} = \mathbf{u}(x, y, z, t)$ is the velocity of air flow. In this case, the aerosol kinetic equation for the distribution function $g(a)$ that considers transport and mixing processes, particle removal on the underlying surface,³ coagulation, and gas-particle change processes, has the form

$$\begin{aligned} \frac{\partial g(a)}{\partial t} + \nabla \mathbf{u} g(a) = \nabla D \nabla g(a) - \nabla \mathbf{w}_{dep} g(a) + \\ + B(a) + \frac{1}{2} \int_0^a K(a', a'') g(a') g(a'') da' - \\ - \int_0^\infty K(a, a') g(a) g(a') da' + \left[\frac{\partial g(a)}{\partial t} \right]_{gpc}, \quad (2) \end{aligned}$$

where $B(a) = B(a, x, y, z, t)$ is the strength of particle sources (in Eq. (2), unlike Eq. (1), generation of new particles in the volume is considered in addition to their transboundary transport, including nucleation processes). The rate of change of $g(a)$ due to the gas-particle change processes is determined by the formula

$$\left[\frac{\partial g(a)}{\partial t} \right]_{\text{gpc}} = - \frac{1}{\psi(a)} \frac{\partial[\psi(a) g(a)]}{\partial a} \frac{da}{dt}.$$

Obviously, $a'' = ((a)^3 - (a')^3)^{1/3}$. In Eq. (2), D is the diffusion coefficient, w_{dep} is the rate of particle sedimentation, and K is so-called coagulation constant.³

The relation

$$\left[\frac{\partial g(a)}{\partial t} \right]_{\text{dep}} = -k(a) g(a)$$

is frequently used for monoreservoir models (for example, for the model of a single-layer atmosphere), where the function $k(a)$ specifies the rate of particle removal from the reservoir.

In some particular cases the rates of change of particle volume and radius, caused by the gas-particle change processes,^{3,10} can be represented in the following form (neglecting the Kelvin effect^{3,11}):

$$\frac{dv}{dt} = A_{\beta} a^{\beta} \quad \text{and} \quad \frac{da}{dt} = A_{\beta}^* a^{\alpha}, \quad (3)$$

where $\alpha = \beta - 2$, the parameter β does not depend on the particle size in a wide range of its variations, and the quantities A_{β} and A_{β}^* depend on the molecular parameters.³

It should be noted that when $\beta = 1$ or $\beta = 2$, the relative width of the particle size distribution decreases with the increase of particle sizes.

The laws of growth (Eq. (3)) are applicable for the dry atmosphere (the relative air humidity $r = 0$), i.e., for $a_{\text{dry}}(t)$ and $v_{\text{dry}}(t)$. For small Knudsen numbers (the ratio of the mean free path length of molecules to the particle radius) $\beta = 1$, and therefore the rate of growth of the particle size decreases with its increase, whereas for large Knudsen numbers ($\beta = 2$) it does not depend on the particle size. For heterogeneous condensation it is expedient to use more general expression for the law of particle growth,¹¹ applicable not only for small but also for large Knudsen numbers.

For humid atmosphere the rate of growth of volume of the particle comprising water-soluble substances increases due to accumulation of the substance of dry residue, because the volume of the drop is much large than the volume of the dry particle. Therewith, it should be considered that under conditions of thermodynamic equilibrium simultaneously with the substance of dry residue the corresponding quantity of water vapor is settled on the particle.

Therefore, the law of particle (drop) radius growth for the humid atmosphere will be the following:

$$da_{\text{wet}}/(dt) = \zeta_v(r) A_{\beta}^* a_{\text{wet}}^{\alpha}, \quad (4)$$

where $\zeta_v(r)$ specifies the dependence of the particle volume on the relative air humidity. Gorchakov et al.¹² pointed out that the dependences of the components of the light scattering phase matrix on the relative air humidity¹³ in a wide range of variations of r , approximately from 0.3 to 0.95, can be described by the

reciprocal power-law empirical supersaturation functions¹⁴ of $1 - r$:

$$\zeta_v(r) = (1 - r)^{-\lambda_v} = \zeta_a^3 = (1 - r)^{-3\lambda_a}. \quad (5)$$

We note that $\beta = 3$ ($\alpha = 1$) corresponds to the particle growth caused by the chemical reactions inside the drop (aerosol particle).

Let us consider the stationary problem of particle growth for the submicron range of particle sizes, when we can consider that $k(a) = \text{const} = k$. Neglecting coagulation, transport, and mixing processes for the monoreservoir model, we obtain the equation

$$\frac{1}{\psi(a)} \frac{\partial[\psi(a) g(a)]}{\partial a} \frac{da}{dt} = -kg(a).$$

Obviously, for $\beta = 2$ the particle radius $a(t)$ is the linear function of time and therefore the width Δa remains constant. This leads to significant simplification of the kinetic equation.

We can say that in case of voluminous growth of particles ($\beta = 3$), when the dry particles with radius a_0^* entering the atmosphere immediately change into the drop with radii $a_0(r_0) = \zeta_a(r_0) a_0^*$ (the model with a continuous source), the stationary distribution function turns out to be the reciprocal power-law function (the model of the kinetic equilibrium haze):

$$g(a) = g_0(a/a_0)^{-(1 + k/\zeta_0 A_{\beta}^*)}. \quad (6)$$

The reciprocal power-law distributions of the atmospheric aerosol were observed long ago¹⁵ and previously were interpreted as a consequence of coagulation transformation of the aerosol. Distribution (6) shows that the particle growth caused by chemical reactions running inside the water-soluble submicron aerosols are important for the formation of the atmospheric damp haze. It should be emphasized that the shape of the stationary distribution is determined by the relation between the parameters that characterize the rate of particle removal from the atmosphere and the rate of growth of particle sizes. Additional information is necessary for determination of absolute rates of particle growth and removal from the atmosphere.

A single-parametric microphysical model of the surface aerosol¹ based on the general statistical regularities of the light scattering phase matrix variability¹ and determination of the microstructural parameters and optical constants of the aerosol as functions of the input model parameter (scattering coefficient or meteorological visibility range L) allows one to refine the peculiarities of the formation of the typical atmospheric damp haze. The corresponding values of the volume fill factor V (the volume of the aerosol per unit volume of the air), the volume fill factor for dry aerosol residue V_{dry} , and conventional average relative air humidity r , as well as the parameters of the microstructure a^* , N , and v of the approximating lognormal distribution

$$g(a, L) = \frac{N(L)}{\sqrt{2\pi} v(L)a} \exp \left\{ -\frac{\ln^2 \frac{a}{a^*(L)}}{2v^2(L)} \right\}. \quad (7)$$

are given in Table I for three values of L .

TABLE I.

L , km	a^* , μm	N , cm^{-3}	v	$V \cdot 10^{12}$	$V_{\text{dry}} \cdot 10^{12}$
5	0.079	8800	0.7	165	48
10	0.061	9100	0.7	80	33
20	0.048	10200	0.7	44	23

We note that when L changes from 2 to 50 km, the parameter of the aerosol condensation activity $\chi_v \cong 0.58$ in accordance with the data of Table I. When L changes from 20 to 5 km, the shape of the distribution remains unchanged, and the total number density of particles decreases approximately by 10%.

Because in the surface layer of the atmosphere the time periods with the increased relative air humidity ($r \geq 0.6$), as a rule, are short, we can assume that beyond these periods in the surface and boundary layers of the atmosphere for $r \leq 0.4-0.5$ the finely dispersed haze is formed, whose microstructure is satisfactorily approximated by the lognormal distribution with the parameter $v \cong 0.7$ and the median radius $a^* \leq 0.03-0.04 \mu\text{m}$. With the further increase of r , the haze particles grow so that the ratio $a(r)/a_0(r_0)$ is independent of the initial particle sizes. As r increases, the accumulation of the dry particle residue mass occurs in addition to the increase of a^* and V , which is manifested through the increase of the fill factor V_{dry} ($r \geq 0.4$).

To evaluate the dependence $V_{\text{dry}}(r)$ in the range of variations of r from 0.45 to 0.95, the empirical relation¹

$$V_{\text{dry}}(r) = V_0 \exp(3.25 r) \quad (8)$$

can be used. The values of V_{dry} are given in Table I.

Thus, the microphysical model¹ also demonstrates that for the damp haze and the increased relative air humidity the mechanism of voluminous growth of particles caused by chemical reactions running inside the drop is of primary importance. Obviously, the processes of water vapor condensation and accumulation of water-soluble substance of the dry residue of particles intensify one another. Under these conditions we cannot speak about the equilibrium size of particles at the fixed value $r = r_0$ and equilibrium-soluble haze.¹⁴ The real atmospheric haze is nonequilibrium, i.e., nonstationary.

If at the relative air humidity r_0 the particle has the volume $v_0(r)$, with the fast increase of r from r_0 to r_1 its volume will increase to $v_1(r_1)$ due to the increase of the parameter ζ_v from $\zeta_v(r_0)$ to $\zeta_v(r_1)$ (the model with a pulsed source). Further for the fixed value $r = r_1$ and $A_3 = \text{const}$ the particle volume increases by the law

$$\frac{v(t)}{v_1} = \exp [A_3 \zeta_v(r_1)t]. \quad (9)$$

The time of the particle volume doubling

$$\tau_2 = \ln 2 / A_3 \zeta_v(r_1) \quad (10)$$

is determined by the constant of the rate of growth A_3 . The conventional average values of $a^*(r)$, $V(r)$, and $V_{\text{dry}}(r)$ or in accordance with Ref. 1, $a^*(L)$, $V(L)$, and $V_{\text{dry}}(L)$ are determined by the average lifetime of the damp haze \bar{T} .

The average lifetime of the damp haze in the surface layer of the atmosphere can be estimated under assumption that \bar{T} does not depend on r and L and that the decrease of the average particle number density N (see Table I) with the increase of r is determined by particle coagulation. This change of particle number density can be estimated from the relation

$$\frac{\Delta N}{N} = -\bar{K} N \bar{T}, \quad (11)$$

where \bar{K} is the effective constant of coagulation.³ Taking the value $\bar{K} = 10^{-9} \text{cm}^3/\text{s}$ (Ref. 16), we obtain $\bar{T} = 10^4 \text{s}$. From here it follows that by orders of magnitude, $A_3 = 1 \text{h}^{-1}$ and $\tau_2 = 10^4 \text{s}$.

The atmospheric aerosol cannot be considered every time as homogeneous and single-component. Thus, for example, for industrial regions the model of the three-component aerosol including water-soluble, field, and soot fractions is frequently used. Obviously, in case of multicomponent aerosol one must consider the system of kinetic equations instead of kinetic equation (2).

Some fractions of mixed aerosol are formed due to intercomponent coagulation. This means that the above-given equations are interrelated and cannot be considered separately. All mixed fractions are to a certain degree water-soluble; therefore, the problem of the water-soluble aerosol kinetics is the key problem for the Earth's atmosphere. Of course, the regularities in the growth of the particles for each mixed fraction will differ significantly.

MAIN RESULTS

1. The equation of the water-soluble aerosol kinetics has been derived for the preset particle size distribution function.

2. It is shown that due to the gas-particle change processes, the reciprocal power-law particle size distributions may be formed in the atmosphere under stationary conditions.

3. Analysis of the transformation of the microphysical parameters of the surface aerosol shows that the process of voluminous growth of particles is of primary importance for the gas-particle change in kinetics of the damp haze.

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