MODELING OF OPTICAL CHARACTERISTICS OF NEAR-GROUND ATMOSPHERIC AEROSOL IN THE 0.3–15 1m WAVELENGTH RANGE.
II. MODEL OF AEROSOL COMPOSITION AND STRUCTURE

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Choice of microstructure characteristics is discussed for use in calculations of optical characteristics of atmospheric aerosol. Corresponding data are presented which are used to describe the particle size distribution functions of the basic fractions of near–ground atmospheric aerosol. Values of the complex index of refraction are provided for the 0.3–15 μm *wavelength range, and procedure for allowing the aerosol transformation due to varying air humidity is described.*

Theoretical calculations of optical characteristics of a disperse medium are impossible without knowing such its characteristics as particle concentration, size distribution function, and spectral values of the optical constants of aerosol matter. In the atmosphere, whose aerosol composition permanently changes due to varying air humidity and various sources and sinks of aerosol particles, the description for the above–indicated mechanisms is needed. Let us briefly consider the ways of description used in this case.

1. PARTICLE SIZE DISTRIBUTION AND CONCENTRATION

Now is widely recognized that atmospheric aerosol particles of different origins have different properties and interact with each other only weakly. It is therefore assumed that the size distribution functions of real aerosols are represented as a sum of distributions of individual aerosol fractions. Not detailing how these individual fractions are generated and transformed, we only note that, as studies of the aerosol optical constants in the atmosphere indicate,[1] three basic aerosol fractions persist, with distinct composition and physical–chemical properties, whose mean particle radii are $r_{01} \cong 0.03$, $r_{02} \cong 0.3$, and $r_{03} \cong 1$ μm. Under certain conditions in the ground atmospheric layer, there may exist many other fractions, but only in addition to those three. It is important to note that the data of Ref. 1, concerning the complex index of refraction of aerosol particles and the mean radii of the fractions identified, are not contradictory to that available in the literature.

For description of particle size spectrum, various analytical expressions are in practical use now, whose specific form is chosen by subjective reasons such as to be convenient, physically sound (or, more correct, to be indicative of the notion of their authors of mechanisms of particle formation), and to conform to the views of the subject. Thus, the Junge distribution had long been used (a particular case of power law), despite it was formulated for stratospheric aerosols[2] in the range $0.1 \le r \le 1$ μm and was found to be valid in about 40% of observations. More recently, of common utility have been different modifications of lognormal distribution,[3] valid for polydispersions formed by fragmentation of material, but its applicability to the description of the aerosol formed by condensation and being most widespread in the real atmosphere, is questionable.

Any size distribution functions are obtained by fitting the experimental data available. For this reason, discussion of applicability of one or other way of analytic description of the distribution function must be based primarily on an analysis of initial experimental data.

Atmospheric aerosols widely vary in size. Taking atmospheric haze alone and just addressing its optical properties, particle size spans from 4 to 5 orders of magnitude extending from 10^{-3} to 10^{1}–10^{2} μm. None of techniques is capable of simultaneous and standard measuring the particle concentration in such a size range. Things go worse due to the fact that large ($0.2 \le r \le 1$ μm) and gigantic ($r \ge 1$ μm) particles rapidly decrease in number density with increasing radius. The practical consequence is to determine the particle size distribution either within a limited size range or by a set of diverse techniques.

Most current techniques allow relatively accurate (up to 10–15%) measurements over size ranges of about one order of magnitude. However, up to now the problem of meteorological support of aerosol measurements has not yet been adequately solved. Moreover, treating atmospheric aerosols as a set of independent fractions, the choice of a specific size distribution for an individual aerosol fraction is almost an arbitrary practical exercise. The said is illustrated in Fig. 1, by fitting experimentally determined particle size distribution by a number of analytically diverse curves.

As seen for the unimodal distribution of Fig. 1*a*, the fits agree to within the measurement error in the vicinity of mode, while diverge considerably for particle size from 3 to 5 r_0 off–mode. In practice, any size spectrum sampled from a size range extended by about an order of magnitude can be fitted equally accurately, to within the sampling error, by several analytical curves (by adjusting their parameters), whose number may substantially increase when used in combinations (Fig. 1*b*).

A very important problem in calculation of aerosol optical characteristics is the choice of the minimum and maximum size and of the integration step.[4] It has two aspects. On the one hand, contribution of all particles described by the chosen size distribution function must be considered in calculations. However, considering the laborious calculational technique, it is always desirable to shorten the particle size range under consideration to the maximum extent. From this view point, concerning first of all the problems of implementation of calculational technique, the problem of choosing minimum and

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maximum size may be considered as already solved. A set of definite generally accepted criteria for such a choice has already been developed. On the other hand, as has already been noted above, all the analytical functions are based on experimental data, and their use in the particle size range uncovered with experimental investigations may result in significant errors (see Fig. 1*a*).

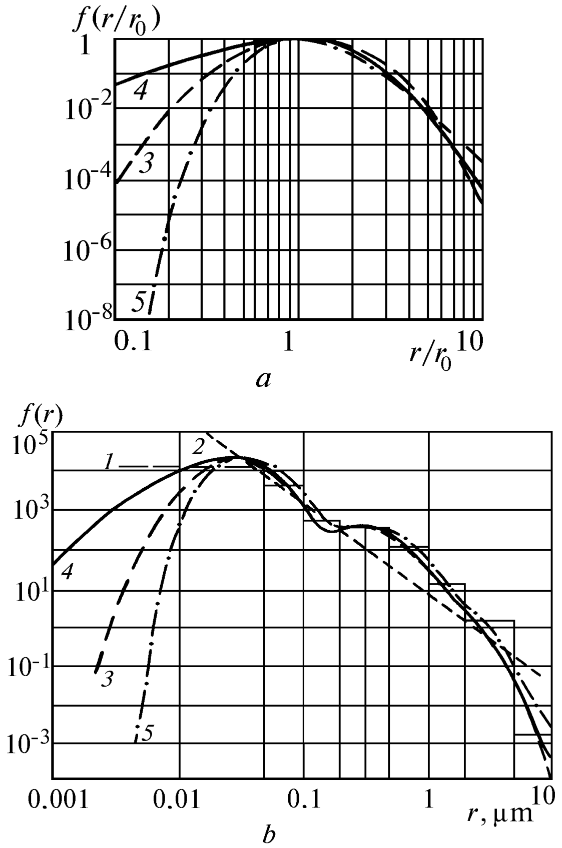

FIG. 1. Analytical fits of the aerosol particle size distribution: unimodal distribution (a) and polymodal distribution (b). 1) experimental data (histogram), 2) Junge distribution, 3) lognormal function ($\sigma = 1.86$)*, 4) gamma–distribution* ($\nu = 3.8$, $\gamma = 1.9$)*, 5) gamma–distribution with negative degrees of freedom* ($\nu = -6$, $\gamma = 1.27$)*.*

At the same time, various optical characteristics of aerosols are different functions of particle size. This allows one to restrain considerably the arbitrariness in estimation of the form of size distribution functions and probable values of the parameters of these distributions with a complete set of experimentally determined optical characteristics. However, even in the visible spectral range, where all elements of the scattering phase matrix are measurable in principle, realization of such a measurement complex is a challenging problem. In calculation of the optical characteristics of aerosol polydispersions, the problem of optimization of the step size upon integrating polydispersed distribution is no less important than the choice of maximum and minimum size of particles. These problems were discussed in detail in Refs. 4 and 5.

In what follows, we will describe particle size distribution of individual aerosol fractions by gamma–distribution with negative degrees of freedom

$$\frac{\mathrm{d}N}{\mathrm{d}r} = a\,r^{-\mathrm{m}}\exp\left(-\,b\,\frac{I}{r^{\mathrm{c}}}\right) \qquad (1)$$

taking $\nu = 6$ and $\gamma = 1$.

2. COMPLEX INDEX OF REFRACTION OF AEROSOL MATTER

The need in spectrally resolved aerosol complex index of refraction to calculate the spectral aerosol absorption has been recently widely recognized; however, the data now available are few and contradictory. In practice, such data are obtained either experimentally, by measuring the absorption coefficient of samples of atmospheric aerosols, or by calculation for a definite model of particle composition assigning the values of the refractive index of the material of the particles.

Experimental studies of optical constants of atmospheric aerosol substance have been intensively conducted during recent one to one and a half decades, but the results obtained are contradictory. On the one hand, the spectral structure of aerosol absorption (locations of basic absorption bands, estimates of their relative intensities, and so on), according to studies performed by various authors, appears to be very stable.[4,9] On the other hand, quantitative estimates of both real and imaginary parts of the refractive index differ sometimes substantially.[6] Moreover, differently interpreted is the nature of the absorption lines themselves. Thus, practically always recorded infrared absorption band near $\lambda \approx 9.5$ μm is attributed to the presence of sulfates (specifically, $(NH_4)_2SO_4$) by one group of researchers, and to silicates or even organic substances by another group.

The nature of individual absorption bands can be determined by simple aerosol fractionation by composition in a manner described in Refs. 1, 4, 7, and 8. At the same time, contradiction among quantitative measurement results is of fundamental nature as it is connected not only with problems of obtaining representative aerosol samples for reliable measurements, which is a complicated problem by itself, but also with the fact that many problems of optics of polydispersions have not yet been solved. Many of the problems outlined above were considered semiempirically in Refs. 8 and 9 and received at least qualitative solutions there. As we think, most challenge could be resolved by applying fractal theory of systems and their optical properties.[10]

Most data available for complex index of refraction of aerosol particles, $\tilde{m}(\lambda) = n(\lambda) - i\kappa(\lambda)$, was calculated based on definite assumptions on particle composition and data on $m(\lambda)$ values of individual substances. It is a doubtful approach however, for two reasons: 1) questionable is the possibility of representing aerosol particles as a uniform mixture of diverse substances, and 2) it is hardly the case that the abundance of natural aerosols is described by a limited set of compounds. Apparently, an optimal solution was proposed in one of the first works on the subject,[9,11] which considered aerosol particles as compound types with quite stable and distinct optical properties rather than as a mixture of specific minerals. The model of optical constants of aerosol matter of individual fractions, relying heavily on the results of experimental studies,[1,6–9,11,12] exploited the ideas proposed in Refs. 7 and 9. The assumption of a homogeneous mixture of substances making up individual aerosol fractions, artificial as it may seem, appears to be quite efficient for our purpose. That is supported by estimates of possible variations of effective $\tilde{m}(\lambda)$ values, made for aerosol particles modeled as two–layer spheres.[1]

Model values of complex index of refraction, employed in our calculations, are presented in Table I. The $\tilde{m}$ values for water were borrowed from Ref. 13.

TABLE I. Complex refractive index of basic aerosol fractions $\tilde{m}(\lambda) = n(\lambda) - i\kappa(\lambda)$.

λ, μm	Fractions							
	I		II		III		Organic substances	
	n	κ	*n*	κ	*n*	κ	*n*	κ
1	2	3	4	5	6	7	8	9
0.30	1.572	0.0091	1.653	0.0055	1.590	0.0015	1.460	0.055
0.325	1.572	0.0091	1.653	0.0054	1.588	0.0014	1.490	0.048
0.35	1.571	0.0091	1.653	0.0053	1.587	0.0012	1.492	0.044
0.375	1.571	0.0091	1.653	0.0052	1.586	0.0010	1.496	0.041
0.40	1.570	0.0091	1.653	0.0051	1.585	0.0008	1.497	0.041
0.425	1.570	0.0091	1.653	0.0051	1.583	0.0006	1.502	0.046
0.45	1.570	0.0091	1.653	0.0050	1.581	0.0004	1.509	0.042
0.475	1.570	0.0091	1.653	0.0050	1.580	0.0003	1.517	0.060
0.50	1.569	0.0091	1.652	0.0050	1.579	0.0002	1.543	0.042
0.525	1.569	0.0091	1.652	0.0050	1.578	0.0002	1.537	0.027
0.55	1.569	0.0091	1.652	0.0050	1.577	0.0002	1.530	0.016
0.575	1.569	0.0091	1.652	0.0050	1.576	0.0001	1.528	0.025
0.60	1.569	0.0091	1.652	0.0050	1.575	0.0001	1.527	0.027
0.625	1.569	0.0091	1.652	0.0050	1.574	0.0001	1.525	0.021
0.65	1.569	0.0091	1.652	0.0050	1.573	0.0001	1.524	0.021
0.675	1.569	0.0091	1.651	0.0050	1.572	0.0001	1.529	0.022
0.70	1.569	0.0091	1.651	0.0050	1.570	0.0000	1.531	0.020
0.75	1.569	0.0091	1.650	0.0050	1.567	0.0000	1.530	0.017
0.80	1.568	0.0091	1.650	0.0050	1.565	0.0000	1.526	0.011
0.85	1.568	0.0091	1.649	0.0050	1.562	0.0000	1.526	0.008
0.90	1.567	0.0091	1.649	0.0050	1.559	0.0000	1.525	0.006
0.95	1.565	0.0091	1.648	0.0051	1.556	0.0000	1.523	0.005
1.00	1.563	0.0091	1.648	0.0051	1.554	0.0000	1.521	0.004
1.1	1.560	0.0091	1.647	0.0052	1.552	0.0000	1.518	0.0001
1.2	1.557	0.0092	1.647	0.0052	1.549	0.0000	1.514	0.0012
1.3	1.555	0.0093	1.646	0.0060	1.547	0.0000	1.512	0.0001
1.4	1.553	0.0095	1.646	0.0068	1.545	0.0000	1.509	0.0003
1.5	1.552	0.0105	1.645	0.0072	1.540	0.0000	1.507	0.0004
1.6	1.551	0.0113	1.644	0.0076	1.537	0.0000	1.504	0.0002
1.7	1.550	0.0115	1.644	0.0082	1.535	0.0000	1.503	0.0003
1.8	1.549	0.0115	1.643	0.0088	1.533	0.0000	1.499	0.0000
1.9	1.548	0.0119	1.643	0.0094	1.530	0.0000	1.496	0.0000
2.0	1.546	0.0125	1.642	0.0100	1.528	0.0001	1.492	0.0000
2.2	1.538	0.0134	1.641	0.0120	1.522	0.0000	1.481	0.0031
2.4	1.538	0.0172	1.640	0.0141	1.517	0.0000	1.472	0.0148
2.6	1.527	0.0211	1.630	0.0181	1.509	0.0001	1.465	0.0118
2.8	1.492	0.0575	1.608	0.0456	1.499	0.0079	1.447	0.0120
2.9	1.507	0.0760	1.603	0.0732	1.492	0.0112	1.426	0.0123
3.0	1.561	0.0945	1.646	0.0760	1.508	0.0139	1.370	0.0133
3.2	1.596	0.0674	1.665	0.0512	1.510	0.0038	1.237	0.0087
3.4	1.602	0.0380	1.678	0.0215	1.502	0.0090	1.665	0.323
3.6	1.590	0.0286	1.653	0.0199	1.492	0.0009	1.734	0.120
3.8	1.580	0.0194	1.644	0.0180	1.481	0.0002	1.602	0.371
4.0	1.570	0.0193	1.635	0.0179	1.471	0.0002	1.578	0.0123
4.2	1.560	0.0194	1.628	0.0180	1.460	0.0003	1.547	0.0123
4.4	1.552	0.0194	1.618	0.0179	1.446	0.0005	1.536	0.0146
4.6	1.550	0.0204	1.611	0.0180	1.429	0.0007	1.517	0.0031
4.8	1.540	0.0208	1.598	0.0180	1.412	0.0008	1.491	0.0000

TABLE I (continued).

1	2	3	4	5	6	7	8	9
5.0	1.522	0.0207	1.591	0.0180	1.386	0.0006	1.464	0.0000
5.2	1.521	0.0195	1.579	0.0179	1.363	0.0005	1.461	0.0344
5.4	1.506	0.0196	1.566	0.0180	1.324	0.0009	1.439	0.047
5.6	1.491	0.0227	1.550	0.0200	1.280	0.0018	1.386	0.040
5.8	1.480	0.0301	1.544	0.0291	1.199	0.0051	1.360	0.030
6.0	1.461	0.0503	1.514	0.0453	1.101	0.0436	1.156	0.034
6.2	1.451	0.0476	1.453	0.0427	1.075	0.0445	1.563	0.418
6.5	1.441	0.0422	1.403	0.0415	1.024	0.0457	1.371	0.584
6.8	1.280	0.371	1.280	0.361	1.158	1.321	1.794	0.554
7.0	1.503	0.503	1.527	0.432	1.820	1.461	1.965	0.518
7.5	1.588	0.0692	1.559	0.0708	1.930	0.217	1.834	0.083
7.8	1.412	0.0218	1.414	0.0748	1.578	0.115	1.711	0.0192
8.0	1.314	0.0256	1.269	0.0178	1.369	0.120	1.650	0.0113
8.5	1.064	0.333	1.186	0.597	1.278	0.637	1.605	0.141
8.7	1.152	0.682	1.219	0.741	1.325	0.663	1.559	0.039
9.0	1.711	1.012	1.648	1.234	1.353	0.883	1.501	0.195
9.2	2.086	0.652	2.165	1.084	1.474	1.140	1.647	0.224
9.5	2.047	0.464	2.336	0.598	2.597	0.996	1.554	0.396
9.7	2.012	0.353	2.297	0.361	2.313	0.397	1.805	0.315
9.8	1.991	0.252	2.256	0.254	2.213	0.330	1.824	0.222
10.0	1.904	0.124	2.135	0.126	2.100	0.234	1.776	0.120
10.2	1.847	0.099	2.027	0.091	1.977	0.189	1.719	0.0841
10.4	1.788	0.095	1.994	0.080	1.892	0.140	1.680	0.0753
10.6	1.746	0.099	1.866	0.078	1.804	0.110	1.642	0.0668
10.8	1.698	0.107	1.805	0.088	1.673	0.140	1.594	0.0647
11.0	1.668	0.131	1.747	0.118	1.534	0.194	1.568	0.149
11.3	1.714	0.148	1.678	0.234	1.536	0.248	1.589	0.137
11.5	1.766	0.173	1.780	0.330	1.996	0.818	1.575	0.320
12.0	1.691	0.124	1.753	0.229	1.718	0.191	1.841	0.118
12.5	1.662	0.163	1.710	0.270	1.474	0.509	1.663	0.0081
13.0	1.681	0.194	1.786	0.297	1.888	0.376	1.600	0.0482
13.5	1.658	0.172	1.876	0.243	1.689	0.257	1.542	0.0728
13.9	1.618	0.207	1.751	0.435	1.542	0.323	1.495	0.118
14.5	1.704	0.212	1.795	0.296	1.696	0.390	1.469	0.765
15.0	1.648	0.234	1.768	0.316	1.652	0.423	1.910	0.672

3. IMPACT OF ATMOSPHERIC HUMIDITY ON AEROSOL MICROPHYSICS AND EFFECTIVE COMPLEX INDEX OF REFRACTION OF THE MATERIAL OF AEROSOL PARTICLES

An important atmospheric variable, governing most aerosol properties, is the air humidity. From the view point of aerosol optical properties, the effect of atmospheric humidity is manifested in two ways. First, the change in the air humidity transforms the size spectrum of aerosol particles, but the specific mechanisms of this transformation have yet to be elucidated. Most investigators suggest that the particles grow in size due to condensation of water vapor on their surface.

Additional mechanism of humidity impact on aerosol structure was considered in Ref. 14, where it was suggested to take into account the effect of moistening of particle surfaces on the rate of particle growth by coagulation and at the same time, on the ease of vapor condensation in gaps among coagulants caused by capillarity resulting in sharp increase of water content of particles (condensation–coagulation mechanism).

Irrespective of the specific mechanism of aerosol–humidity interaction, change of amount of water on the particle surface (or inside), in addition to transformation of the particle size spectrum, results in the change of the effective value of complex index of refraction. Undoubtedly, the change in the atmospheric humidity affects specific sources and sinks of aerosols in the atmosphere. While the former complex of processes has been sufficiently studied both in the field and laboratory experiments (for a review of main results, see Refs. 14 and 15), the effects of humidity on sources and sinks of aerosols may be discussed only tentatively and largely speculatively. One would expect to obtain additional information about the effects of this type from comparison of calculations of optical characteristics of aerosols with allowance for their transformation with the data of integrated microphysical and optical measurements.

In the present calculation, the dependence of particle size on atmospheric humidity was accounted for semiempirically through Kasten's formula[16]

$$r(f) = r(f_0)\left(\frac{I - f_0}{1 - f}\right)^{-\varepsilon}, \qquad (2)$$

where f is the relative humidity of air (in fractions of unity), and ε is an empirical constant whose values were determined experimentally for a wide class of substances included as compounds in atmospheric aerosols. In accordance with the assumed particle composition of different aerosol fractions, in this study we chose $\varepsilon = 0.32$, 0.18, and 0.08 for fractions 1, 2 and 3, respectively.

Since with varying humidity, particle radius changes due to the occurrence of water shell after formula (2), the amount of liquid water in the mixture is readily determined as a function of air humidity. Changes in the refractive index and absorption coefficient are then calculated for resulting mixture (aerosol substance plus water) following Ref. 17. Next, optical properties of three aerosol fractions adopted here are easily evaluated for the aerosol–water mixture. Likewise, consideration of a water–droplet fraction, deeply involved in the formation of the optical properties of atmospheric coastal haze, is not a particular problem. At present, something definite cannot be said about the transformation of the physical–chemical properties of the finely–dispersed aerosol fraction of the atmosphere made of organic substance under conditions of variable humidity.[18]

Also problematic is to consider the humidity dependence of the properties of industrial aerosols that in many practical cases completely determine the local optical properties of the atmosphere. Whereas for organic aerosol main difficulty lies in that this process is poorly known and experimental data are almost entirely lacking, difficulty with industrial aerosol is primarily because of a variety of its forms, thus requiring additional studies and modeling of each concrete case.

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