EMPIRICAL MODELS AND OPTICAL PARAMETERS OF AEROSOL POLYDISPERSIONS OF TWO-LAYER SPHERICAL PARTICLES

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We propose a unified approach to the description of models for polydispersions of two-layer aerosol particles to calculate their optical properties. Some concrete models of the polydispersions of two-layer particles are discussed assuming basic physical processes causing their formation in the atmosphere.

1. INTRODUCTION

In real atmosphere there occur conditions favorable for the formation of polydispersions of heterogeneous particles. Among those there are the moistened, aqueous, and ice particles; the soot-coated particles; the sulfuric acid and sulfate particles with a solid cover; the sulfuric acid particles possessing an outer cover formed of small adsorbed particles or a film formed due to the surface chemical and photochemical processes, as well as the hollow microspheres of the volcanic origin. All these systems and their optical properties can be described in terms of polydisperse ensembles of two-layer spheres.

Calculations of the optical characteristics for model sets of homogeneous spherical particles are thought to be a routine procedure. At the same time, there are only few algorithms for two-layer spherical particles developed for some particular problems: e.g., moistening of particles[1] and stratospheric sulfate particles.[2] The Ref. 3 presents a detailed review of such algorithms. The complexity of the above mentioned calculations is on the hand due to restrictions concerning the radius and the imaginary part of the complex refractive index (hereafter CRI) of a single spherical particle cover[4] and due to a too detailed physical models of the two-layer particles formation, on the other hand.

Earlier[5] we have developed an algorithm allowing one to overcome these restrictions in practical calculations of the two-layer sphere optical characteristics. The description of a set of the two-layer particles using the results obtained for a single particle, needs a mathematical model of such an ensemble. First of all, let us note that the mass calculations for ensembles of homogeneous spheres became realistic due to existence of a "standard" set of such models, namely, the size distribution functions for the aerosol particles (see, for example, Ref. 6). Taking this into account, one can conclude that mathematical models for ensembles of two-layer particles, good for unifying calculations of their optical characteristics, must meet the following two principal requirements:

1) the transition from a model ensemble of homogeneous particles to one for ensemble of two-layer particles must involve a minimum number of additional parameters;

2) the algorithm of the integration over the ensemble of homogeneous particles, must apply without any principle modifications to ensembles of two-layer particles.

The first requirement contradicts the physical principles of the formation and evolution of the two-layer particles, however a rigorous and detailed description of such phenomena will lead to a complicated model operating involving a lot of unknown coefficients which can not be measured experimentally. The use of simple empirical or "intuitive-empirical" models with a minimum number of parameters is preferable, since they do not involve much complicated calculations, and allow the statement and solution of the problem on model parameters retrieval by using experimental measurements, and, after that, one can discuss the reliability of a model and its modifications. This approach has already been used for description of the moistening particles (see below). This paper is an attempt to apply it to other cases of the two-layer particles formation.

2. METHOD OF CALCULATIONS

The two-layer spherical particles with a homogeneous core and a cover are described using the following parameters: the outer radius r, the ratio g between the inner radius (radius of the core) and the outer radius of the sphere, CRI of the core, m_1, and the CRI of the cover m_2. In Ref. 5 one can find the algorithms for calculations of the optical characteristics of a single two-layer sphere, i.e., the extinction and scattering factors, scattering phase function or scattering phase matrix, the coefficients of the expansion of the scattering phase function in a power series over the Legendre polynomials. To compute the optical characteristics of a set of two-layer spheres, one must integrate corresponding characteristics for a single sphere over the geometrical parameters of an ensemble, i.e., over r and g weighted with the size distribution function (one needs to take into account the probable dependence of the core and cover CRI on r and g). The integrals can be easily derived from those for ensembles

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of homogeneous particles. Since these expressions are known, let us make the computations for the average extinction cross section, as an example

$$C_\mathrm{e}=\pi\int\limits_0^1 \mathrm{d}g\int\limits_0^\infty \mathrm{d}r\, r^2\, Q_\mathrm{e}\,(r,g,m_1(r,g),m_2(r,g))\,F(r,g), \tag{1}$$

where Q_e is the extinction efficiency factor for a single particle; $F(r, g)$ is size distribution function for an ensemble of two-layer particles.

The practical calculations by Eq. (1) are rather complicated since it contains a double integral and two-dimensional distribution function $F(r, g)$. To facilitate calculations, one may adopt a generally accepted assumption[3] that the physical processes, responsible for the two-layer particles formation, allow one to determine all the parameters of a particle in terms of its outer radius. In this case the double integral, Eq. (1); turns into a one-dimensional one with the size distribution function $F(r)$.

The following assumption is also widely accepted. Let us assume the distribution of two-layer particle cores to be independent of the cover parameters, i.e. the physical model of the two-layer particles formation assumes the absence of a cover (or the existence of the core distribution function which is a limit of the $F(r)$ function while the thickness of cover tends to zero). Thus, if $f(r)$ is the core distribution function, one can derive the desirable distribution function $F(r)$ sought from $f(r)$ by making its transformation described by a set of parameters of the cover formation model. This approach allows the use of "standard" distribution functions $f(r)$ for homogeneous particles.

Let us assume the above discussed transformation process to be described by the linear dependence of the two-layer particle outer radius

$$r = q_1(p_1, p_2, \dots , p_n)\, r_\mathrm{c} + q_2(p_1, p_2, \dots , p_n), \tag{2}$$

where q_1 and q_2 are functions of the parameters of the cover formation model $p_1, p_2, \dots , p_n$ (hereafter, this list will be omitted in formulas); r_c is the core radius. One can obtain $F(r) = f(r/q_1 - q_2/q_1)$, by making a formal assumption that $F(r) = 0$ if $r/q_1 - q_2/q_1 \le 0$. Some particular models of q_1 and q_2 functions will be given below.

Let us introduce similar functions for modeling the relative size of the core g and the CRI of the core and the cover:

$$g = q_3(r), \quad m_1 = q_4(r, m_\mathrm{c}, m_\mathrm{s}), \quad m_2 = q_5(r, m_\mathrm{c}, m_\mathrm{s}),$$

where m_c is the CRI of the core substance and m_s is the CRI of the cover substance. Then one can write Eq. (1) in the form

$$C_\mathrm{e}=\pi\int\limits_0^\infty r^2 Q_\mathrm{e}(r, q_3(r), q_4(r, m_\mathrm{c}, m_\mathrm{s}), q_5(r, m_\mathrm{c}, m_\mathrm{s}))\, f(r/q_1 - q_2/q_1)\, \mathrm{d}r.$$

Thus the problem of describing ensembles of two-layer particles reduces to a creation of a set of five functions $q_1 - q_5$ dependent on the model parameters.

Let us check up the validity of the second requirement. The calculation of a two-layer particle parameters in terms of functions q_3, q_4, q_5 as well as the use of Eq. (2) in the distribution function does not change the integration algorithm. At the same time, one can face some problems while computing the moments of the function $F(r)$:

$$M_i(F) = \int\limits_0^\infty r^i\, F(r)\, \mathrm{d}r,$$

used in the algorithm described in Ref. 6. But the integration with the use of Eq. (2) is elementary and results in

$$C(F) = q_1\, C(f),$$

$$M_i(F) = q_2^i + \sum_{j=1}^{i} C_i^j\, q_1^j\, M_j(f)\, q_2^{i-j}, \quad i \ge 1,$$

where $C(F)$ and $C(f)$ are zeroth moments of non-normalized distributions; C_i^j are binomial coefficients; $M_j(f)$ are the moments of the "standard" normalized function $f(r)$ (see Ref. 6).

Let us present the sets of characteristics of the ensembles of two-layer particles as well as examples of model calculations for these ensembles. The values of the CRI for substances forming cores and covers were taken Ref. 1.

3. MOISTENED PARTICLES

The Kasten formula[7] (modified by Hanel[8]) is used to relate the radius r of a moistened particle to that of the core, r_c

$$r/r_\mathrm{c} = (1 - u)^{-P\,\lg(1-u)-Q}, \tag{3}$$

where u is the relative humidity of air; P and Q are empirical constants, the recommended values of which are: $P = 0.0664$, $Q = 0.113$ for continental aerosol and $P = 0.0498$, $Q = 0.173$ for "a mean" aerosol.

Equation (3) is valid for $u < 0.95$. At high values of the humidity there occurs the growth of the water drops. To make the algorithm (3) versatile, let us describe the process of growth by a functional dependence with the properties providing: (i) continuity at $u = 0.95$ and (ii) the average radius of the water drops to be equal to a preset value R:

$$r/r_c = (1 + d - u)^{(\lg R - \lg M_1(f))/\lg d}, \qquad (4)$$

where d is a root of the equation

$$(0.05 + d)^{(\lg R - \lg M_1(f))/\lg d} = (0.05)^{-P\,\lg(0.05)-Q}, \qquad (5)$$

which can easily be resolved by the method of dividing interval $0 < d < 1$ into halves.

The following circumstance should be taken into account in this model. At big volumes of the cover and the density of non-soluble core being less than that of the water, destruction of a core may occur and fragments may come to surface of the drop cover (this assumption is confirmed by the electronic microscope images of soot particles in a water drop). For this reason, let us introduce the value G as a critical value of the parameter g. The cores collapse at $g = G$ ($G < 0$ for non-destructive cores).

Thus, one has the following model for particles with a non-soluble moistened core: $q_1 = r/r_c$ is derived from Eqs. (3)–(5); $q_2 = 0$. If $1/q_1 > G$, than $q_3 = 1/q_1$, $q_4 = m_c$, $q_5 = m_s$. If $1/q_1 \le G$, than $q_3 = (1 - 1/q_1^3)^{1/3}$, $q_4 = m_s$, $q_5 = m_c$.

For particles with a soluble moistened core, one again needs to use Eqs. (3)–(5) for correlating the outer and core radii of a particle. By introducing a dissolution coefficient, one can obtain a radius of the core remained after the dissolution process in terms of the masses of core and cover. Unfortunately, such a detailed approach requires a lot of additional parameters to be introduced: i.e., the core and cover densities; dependence of the solution density on the amount of the dissolved substance, etc. It does not meet our first requirement. Taking into account the lack of information on chemical composition of the atmospheric aerosol as well as the approximate assumptions used in the aerosol models, let us simplify the description of the "volume" parameters of the dissolution model. Let us introduce a parameter D, the ratio of the core substance volume converted into the saturated solution to the total solution volume (i.e., $0 \le D \le 1$). Since similar parameter will be used not only for the dissolution process description, let us refer to it as to a "coefficient of penetration" of the core substance into that of the cover. Within the frameworks of this "idealized" model, one can assume the solution volume to be equal to the sum of volumes of substances forming it. The CRI of the solutions and mixtures will be calculated as an average volume weighted value.

The above mentioned assumptions result in a model that allows for a possibility of total dissolving of the core: for q_1 see the above expressions, $q_2 = 0$. One calculates that $\Delta = (1 - 1/q_1^3 D)/(1 - D)$. Than, $\Delta > 0$ (only a core remains), $q_3 = \Delta^{1/3}/q_1$, $q_4 = m_c$, $q_5 = Dm_c + (1 - D)m_s$ If $\Delta \le 0$ (total dissolving), $q_3 = 0$, $q_4 = q_5 = m_c/q_1^3 + (1 - 1/q_1^3)\, m_s$. Note that there are two important particular cases of the model. One has the above considered case of a non-soluble and non-destructive core (at $D = 0$); at $D = 1$, one has always the case of total dissolving, i.e. a homogeneous particle with the average weighted CRI, this is the model in the approximation of a homogeneous mixture.

The computations for moistened particles are illustrated with data in Fig. 1. The solid curve *1* shows the dependence of the average absorption cross section at the wavelength 0.5 μm for a model of moistened soot particles on the air humidity.

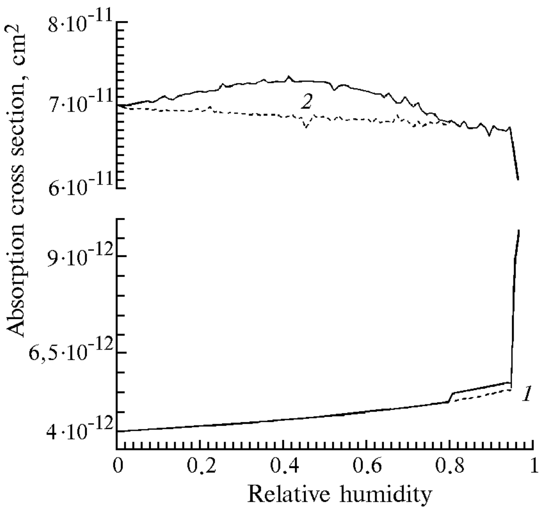

FIG. 1. Dependence of the mean absorption cross section of moistened particles on the relative humidity: 1) soot particles: solid line corresponds to the destructive core, dotted line corresponds to non-destructive core; 2) organic particles: solid line – two-layer structure, dotted line – homogeneous mixture approximation.

The model with non-soluble, non-destructive core is characterized by the following parameters: the lognormal distribution of the core radii

$$f(r) = 1/(r\sigma\sqrt{2\pi})\,\exp([\ln^2(r/r_0)]/(2\sigma^2)) \qquad (6)$$

where $r_0 = 0.01$ μm and $\sigma = 0.7$; $m_c = 1.82 - i0.74$, $m_s = 1.33 - i10^{-9}$, $P = 0.0498$, $Q = 0.173$, $G = 0.8$, $R = 20$ μm. The results calculated for the same model, but without the account of the destruction of the core ($G = -1$), are shown, for a comparison by the dotted curve *1*. As seen from the figure the account for the possibility of the core destruction does not considerably influence the value of the aerosol absorption, so one can recommend to use a traditional model with a non-destructive core.

Another one example of the results of computations of the dependence of the air humidity on the average aerosol absorption cross section at the wavelength 0.5 μm for moistened organic particles (soil aerosols) are shown in Fig. 1 (curves *2*). The model with a soluble core was used. Its parameters are as follows: the lognormal distribution of cores (Eq. 6) with $r_0 = 0.1$ μm and $\sigma = 0.9$; $m_c = 1.45 - i0.001$, $m_s = 1.33 - i10^{-9}$, $P = 0.0498$, $Q = 0.173$, $D = 0.5$, $R = 20$ μm. Results for the model just mentioned are depicted by solid curve whereas the results for the same model in the approximation of a homogeneous mixture ($D = 1$) are depicted by dotted curve (we use them for a comparison). The analysis of this figure shows that the model of a homogeneous mixture results in quite a different picture even for a readily soluble core, and, therefore, the account for the two-layer structure is really needed for a more reliable modeling of the atmospheric aerosol optical properties.

4. STRATOSPHERIC SULFURIC ACID PARTICLES

The processes of formation and growth of these aerosol particles are yet poorly studied and they are a subject of discussions.[9] The heterogeneous heteromolecular nucleation, i.e. the formation of 75% sulfuric acid cover around the cores, soluble or non-soluble in the sulfuric acid, is considered to be a mechanism of these particles formation. There exists an evident and experimentally tested correlation between the radii of the sulfuric acid particles and the atmospheric concentration of the sulfurous gas. Since the mechanism of the H_2SO_4 cover growth is similar to that due to moistening of particles, one can use the model of the particles transformation (2) with the following parameters: $q_2 = 0$, the function q_1 must increase at the SO_2 concentration increase in case of a stationary dynamic balance of the SO_2 concentration (constant flux) or for the same moment in time after the beginning of the SO_2 emission due to a volcanic eruption.

Analysis of the approximation of experimental measurements and the model computations[9,10] allow one to assume a simple dependence describing q_1: $q_1 = 1 + CQ$, where Q is the SO_2 concentration (in cm^{-3}), C is the empirical constant characterizing the rate of the SO_2 oxidation process into the SO_3. One can estimate that $C \approx 10^{-7}$ cm^3. The functions $q_3 - q_5$ may be set to be the same, as those used in the moistening case: the model for a soluble core with the account for the limiting case of $D = 0$ for non-soluble cores.

The dependence of the average value of the aerosol scattering cross section at the wavelength 0.5 μm on the SO_2 concentration (for silicate cores with the sulfuric acid cover) is shown in Fig. 2. We used the inverse gamma distribution for the core size distribution function $f(r) = Ar^{-1-a}\exp(-r_0/r)$, where A is the normalizing factor (see Ref. 6), and the parameters $a = 5$, $r_0 = 0.01$ μm were taken from Ref. 2. The CRI values $m_c = 1.48 - i2.5 \cdot 10^{-4}$, $m_s = 1.43 - i10^{-8}$; the core is non-soluble, i.e. $D = 0$. The dotted line depicts the computation results obtained using the same model, but for homogeneous sulfuric acid particles. Figure 2 demonstrates the importance of the account for the internal structure of particles, especially for small particles (background models of the stratospheric aerosol).

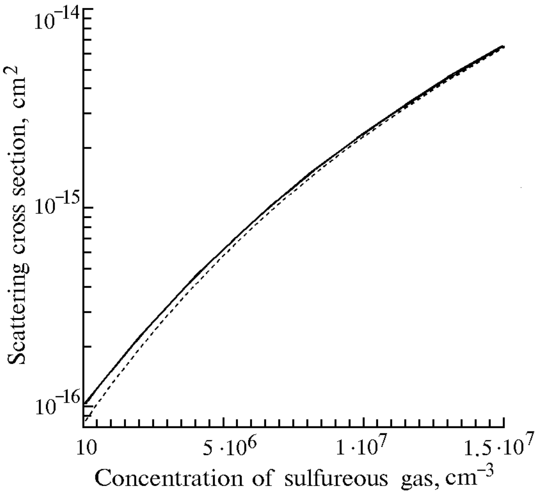

FIG. 2. Dependence of the average scattering cross section for an ensemble of sulfuric acid stratospheric aerosols on the SO_2 *concentration: the solid curve is for the -two layer particles; the dotted curve is for homogeneous particles.*

5. PARTICLES WITH THE ADSORBED COVER

There are a number of processes which can be described using the two-layer particles model, for example, the coating of the stratospheric sulfuric acid aerosol by a mineral substance, the interaction of soot particles with the cloud drops, the coating of the aerosol particles by salts over the seas and oceans. There may occur variants depending on a concrete substance of the core and cover (e.g., solid or liquid, soluble or non-soluble, etc.). However, a unified mathematical description good for all cases can be developed, if one uses models of two-layer spheres with a homogeneous core and cover.

Let us assume that cores and particles adsorbed exist independently. Than, assuming the regular coating of the core with a cover substance, one obtains the following parameters of the particle radius growth: $q_1 = 1$, $q_2 = 1/3\, C R^3/[M_2(f)]$, where C is relative concentration of the adsorbed particles (i.e., the ratio of the number of the particles adsorbed to that of cores contained in a unit volume); R is the average radius of the adsorbed particles. Note that such a model causes a relative ("conditional") physical meaning of C and R. As in the case with the moistened particles, let us describe possible interaction (dissolution) of the core and cover in terms of the "volume" approximation. Let us introduce two formal parameters: D_1 − the coefficient of penetration of the core substance into that of the cover, and D_2 − the coefficient of penetration of the cover substance into that of the core. In this case, by calculating the values $v = (1 - q_2/r)^3$, $\Delta = v/(1 - D_2) - (1 - v)D_1/(1 - D_1)$, one obtains the following expressions: if $0 < \Delta < 1$, than $q_3 = \Delta^{1/3}$, $q_4 = (1 - D_2)\, m_c + D_2\, m_s$, $q_5 = D_1\, m_c + (1 - D_1)\, m_s$; if $\Delta \le 0$ or $\Delta \ge 1$ (total dissolution), than $q_3 = 0$, $q_4 = q_5 = v m_c + (1 - v) m_s$.

Let us consider the applications of the formal model proposed to concrete cases. For particles with a solid core and a liquid cover, one has: $D_2 = 0$, $D_1 > 0$ for soluble core and $D_1 = 0$ for non-soluble one. As to the particles possessing both a liquid core and a liquid cover, one uses an "approximation of mixing", i.e. the coefficient of penetration of the core substance into the cover is assumed to be equal to the coefficient of penetration of the cover substance into the core ($D_1 = D_2 = D$). The case of $D = 0$ corresponds to a non-interacting core and cover. In case of particles with a solid core and a solid cover, the cover is formed as separate elements on the core periphery. Let us assume the regular distribution of the cover substance on the core surface to be uniform, and use the approximation of mixing of a part of the core substance and the whole cover to account for the presence of separate elements. Than one has: $D_2 = 0$ and D_1 is the parameter determining the mixing degree (the higher the value of D_1, the thicker is the cover, but its CRI is more close to the CRI of the core). Finally, it is necessary to take into account a possibility of the cover dissolution in the core. This is the general case requiring both D_1 and D_2 to be set *a priori*.

To illustrate this model, let us consider the interaction of soot particles with the cloud drops. The latter is described by Khrigian-Mazin distribution $f(r) = Ar^2\exp(-br)$, where A is the normalizing factor (see Ref. 6), $b = 0.03\ \mu\text{m}^{-1}$. The m_c and m_s values for water and soot are listed above, R =0.05 μm, $D_2 = 0$.

Figure 3 illustrates the dependence of the single scattering albedo of a cloud (i.e., the ratio of the average scattering cross section to the extinction one) at the wavelength 0.5 μm on the relative concentration C of soot. Four values of D_1 (*1* − 0; *2* − 0.1; *3* − 0.3; *4* − 0.5) were used. The analysis of Fig. 3 shows that the decrease of the albedo value down to 0.999–0.990 (i.e. when one can observe light absorption in clouds) requires an enormous quantity of soot (tens thousand than soot particles per a water drop, i.e. no less than 10 mg/m^3). This confirms the impossibility of explanation of the anomalously high absorption in the stratus clouds[11] within the frameworks of the model computations of their optical properties.[12]

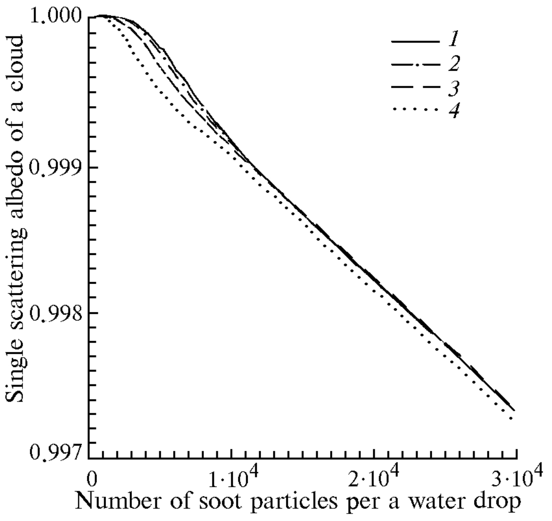

FIG. 3.

6. PARTICLES WITH A CONSTANT THICKNESS COVER

Some physical processes have to lead to the formation of two-layer particles with a constant thickness cover. For example: thin films formed due to chemical (photochemical) reactions on the particle surface, or hollow particles ("bubbles") formed due to the evaporation and sprinkling of the volcanic lava. The above mentioned particles are described by the model parameters: $q_1 = 1$, $q_2 = B$, $q_3 = 1 - B/r$, $q_4 = m_c$, $q_5 = m_s$, where B is the cover thickness.

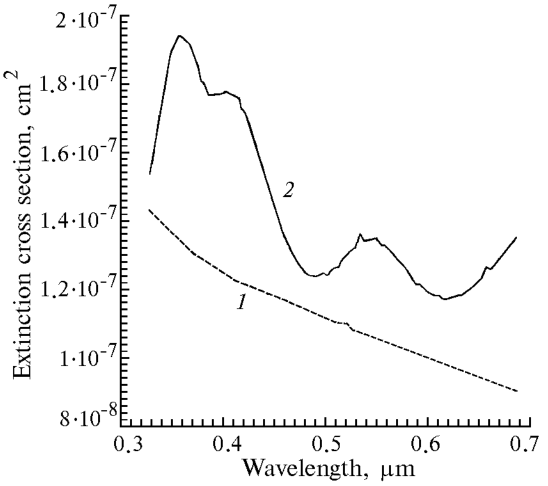

FIG. 4. Spectral dependence of the average extinction cross section for an ensemble of hollow particles: for the cover thickness 0.1 μm *(curve 1); for the cover thickness* 0.5 μm *(curve 2).*

An example of two computations of the spectral dependence of the aerosol extinction cross section in the visible for hollow particles at $B = 0.1$ and 0.5 μm is shown in Fig. 4. The lognormal distribution, Eq. (6), with $r_0 = 0.5$ μm, $\sigma = 0.9$ was used for the core size distribution function. The parameters $m_c = 1$ (gas), and m_s correspond to the spectral curve for silicates taken from Ref. 1. According to Fig. 4, there are no anomalies in the spectral dependence of the extinction cross section, caused by the interference in the cover,[5] for particles with a thin cover. On the other hand, explicit anomalies are seen for particles possessing the cover thickness comparable with the wavelength. However, taking into account that the fraction of hollow volcanic particles is negligible compared to the whole atmospheric aerosol, it is doubtful that one can detect such anomalies from the spectral transparency measurements.

7. HOMOGENEOUS PARTICLES.

It is obvious that homogeneous particles can be considered as a particular case of the developed approach to the integration over ensembles of two-layer particles with the parameters: $q_1 = 1$, $q_2 = 0$, $q_3 = 0$, $q_4 = q_5 = m_c$. This means a good possibility of applying the codes developed for the integration over ensembles of two-layer particles to computations of the parameters of the ensembles of homogeneous spheres.

8. CONCLUSION

The approach proposed for computation of optical parameters of the ensembles of two-layer spherical particles allows one to pass from the routine calculations for ensembles of homogeneous spheres to the routine programs for two-layer spheres. This will allow one to develop more reliable optical models of the atmospheric aerosol since there are a number of important phenomena which can not be described using spheres models of homogeneous sphere.

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