THEORETICAL CONSIDERATIONS FOR THE PARTICLE SIZE SPECTRUM OF THE STRATOSPHERIC AEROSOL

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ABSTRACT

An equation is derived for the time rate of change of the size spectrum function of the stratospheric aerosol. Based on the assumption of local equilibrium between the effects of coagulation and sedimentation, a form is deduced for the shape of the upper end of the size spectrum function, that is the range of radii larger than about 0.1 microns. Dimensional considerations indicate that the equilibrium range may include two subranges in which the spectrum function varies with the particle radius as \( r^{-2} \) and \( r^{-4} \). The theoretical predictions are consistent with available experimental data. The theory should permit the estimation of complete particle size spectra from a minimum amount of experimental data.

A similarity transformation is given for the lower end of the size spectrum. Based on the transformation, a law of decay with time, \( t \), is derived for the total particulate concentration, \( N \). The decay law is of the form \( 1/N^2 \sim t \).

1. Introduction

The normal aerosol of the stratosphere is composed of particles brought in by convective currents from the troposphere, matter entering from space, and small amounts of solids or liquids generated by gas-phase nuclear and chemical reactions. Particles having their origin in space may enter in the form of micrometeorites or they may be produced by the condensation of vapor distilled off evaporating meteors or by the break-up of molten meteoritic material. According to Opik (1958), micrometeorites, defined as particles smaller than about 300 microns, constitute the major portion by mass of extra-terrestrial material entering the earth's atmosphere. Because of their small size, most of these particles do not attain speeds sufficient to cause melting or evaporation; hence they retain the form in which they enter from space. Efforts to calculate the rate of influx of cosmic matter have not been very successful and estimates vary widely (La Paz, 1958).

The testing of nuclear weapons has resulted in the introduction of fine radioactive debris into the stratosphere where it has joined the normal aerosol. Air circulation has distributed bomb debris around the earth producing what has been termed a world-wide stratospheric reservoir of radioactive particulates. The aerosol of the troposphere is rapidly washed out by rain and snow; its half life in terms of residence time is estimated to be of the order of months. There is a relatively long time lag in the change of the stratospheric aerosol because of the absence of precipitation and the relatively low rate of vertical exchange. The slow exchange which does take place between stratosphere and troposphere produces a continuing fallout of radioactive matter on the surface of the earth.

As a contribution to our understanding of the nature of the stratospheric aerosol, a theoretical analysis of the factors determining the particle size spectrum is given in this paper. The approach is similar to the one used by the author (Friedlander, 1960, a, b) to explain the striking regularities found experimentally by Junge (1953, 1957, 1958) in the particle size distributions of tropospheric aerosols measured at different places and times. The theory depends on an analysis of the kinetic equation describing the change in the particle size spectrum function with time. Within limits, the theoretical predictions are independent of the origin and size distribution of the original constituents of the aerosol. In principle, the method should also be applicable to the stratospheric aerosol. Indeed, the theoretical prediction for the shape of the spectrum in the lower part of the stratosphere is identical with that for the troposphere so long as the mean free path of the air molecules is less than the particle radius. For example, theory indicates that a coagulation sub-range exists for which the spectrum function varies as particle radius to the \(-5/2\) power. In fig. 1, data reported by Junge, Chagnon and Manson (1960) for

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an altitude of 12.7 km are presented in a recalculated form. At this altitude, the mean free path is about 0.3 micron. Shown also is a line of slope −5/2 which tends to follow the data over a range of radii (0.1 to 0.7 micron) that might reasonably be designated the coagulation subrange. This agreement cannot be cited as conclusive proof of the validity of the theory, especially since the mean free path is rather too large for the theory to be strictly applicable. However, encouraged by the consistency of the theory with tropospheric data, in this paper the author has extended the method to stratospheric regions where the mean free path is much greater than particle radius and continuum theories of coagulation and sedimentation break down.

A review of previous experimental observations of the stratospheric aerosol is given by Junge, Chagnon and Manson in the paper cited above. New data on size spectra at high altitudes are also reported in this paper, based on measurements of samples obtained by impactors carried by balloon up to heights of 30 km. As in the case of the troposphere, remarkable similarities exist in the shapes of size spectra measured at different altitudes and times. This lends further sup-

port to the theory of local equilibrium and local similarity of the aerosol size spectrum.

2. The kinetics of coagulation and sedimentation in the stratosphere

The most important parameter of the theory, the particle size spectrum function \( n(r) \) is defined by the expression

\[
dN = ndr
\]

where \( dN \) = number of particles per unit volume with radii between \( r \) and \( r + dr \). The time rate of change of \( n \) is obtained as follows.

The rate at which particles of classes \( r' \) and \( r'' \) combine by coagulation is given by the equation of Smoluchowski (see, for example, Chandrasekhar, 1943):

\[
G(r', r'') = 4\pi[D(r') + D(r'')] \times (r' + r'')n(r')n(r'')dr'dr''
\]

where \( D \) is the particle diffusion coefficient. The upper end of the size distribution of the tropospheric aerosol is composed of particles larger than the mean free path (about 0.1 micron) of the air molecules. In this range, the diffusion coefficient can properly be taken to be the Stokes-Einstein diffusivity. In the case of the stratosphere, the mean free path may be larger than most of the particles of interest. For example, at an altitude of 100,000 ft the mean free path is about 5 microns. In this case, it is reasonable to use the Chapman-Enskog expression, based on kinetic theory, for the diffusion coefficient of spherical particles. If the particle diameter is large compared with the diameter of the molecules of gas through which diffusion is taking place, this can be written:

\[
D(r) = \frac{3}{8n_o} \left( \frac{kT}{2\pi m} \right)^{1/2} = \frac{K_1}{8\pi r^2}
\]

where \( n_o \) = molecular density of the air molecules, (volume)\(^{-1} \)

\( k \) = Boltzmann’s constant

\( T \) = absolute temperature

\( m \) = mass of an air molecule

\( K_1 \) = coagulation constant (defined by this expression).

The rate of loss of particles from the range \( dr \) by coagulation with particles of every size is given by integrating \( G(r, r') \) over all values of \( r' \):

\[
\int_0^\infty G(r, r')dr' = \frac{K_1}{2}n(r) \int_0^\infty \phi(r, r')n(r')dr'
\]

where

\[
\phi(r, r') = \left( \frac{1}{r^2} + \frac{1}{r'^2} \right)(r + r').
\]
The rate at which matter enters the range \(dr\) by coagulation of smaller particles is given by

\[
\frac{K_1}{4} \int_0^r \phi(r', r'') (r', r'')^2 n(r') n(r'') dr'.
\] (5)

It is assumed that collision results in coalescence, that is \(r'^3 + r''^3 = r^3\). The ratio \((r/r')^2\) is the Jacobian for the transformation to the coordinate system \((r, r')\).

The net rate at which particles are lost from the element by sedimentation is given by

\[
- \frac{\partial n}{\partial y} v_s dr
\] (6)

where \(v_s\) = sedimentation velocity and \(y\) = distance measured in the direction of the gravitational field. In the troposphere where the mean free path is relatively small, the Stokes settling velocity may be used for \(v_s\), at least for the particles at the upper end of the size spectrum. For the stratosphere, the sedimentation velocity can be calculated by using the equation of Epstein (see, for example, Kennard, 1938) for the resistance to the motion of a particle when the free path is much greater than the particle diameter. This expression is based on kinetic theory and is consistent with the use of kinetic theory diffusivities. By equating the resistive force to the weight of the particle, the sedimentation velocity of a spherical particle is found to be:

\[
v_s = \frac{2 \pi \rho_p g r}{3 \alpha n_p} \left( \frac{\pi}{2 m k T} \right) = S_1 r
\] (7)

where \(g\) = gravitational constant
\(\rho_p\) = particle density
\(\alpha\) = dimensionless constant of order one which depends on the manner of molecular reflection from the surface of the particle
\(S_1\) = sedimentation constant (defined by this expression).

In the absence of diffusion, the rate of change of the size spectrum function with time is given, finally, by

\[
\frac{dn}{dt} = \frac{K_1}{4} \int_0^r \phi(r', r'') (r', r'')^2 n(r') n(r'') dr' - \frac{K_1}{2} n(r) \int_0^r \phi(r, r') n(r') dr' - S_1 \frac{\partial n}{\partial y}
\] (8)

where \(r'^3 + r''^3 = r^3\) in the first term on the right.

It is necessary to add a restriction on the size of the volume element to which eq (8) can be applied. The element under consideration must be large enough to contain many particles since coagulation is a statistical phenomenon. At altitudes between 10 and 30 km, Junge, Chagnon and Manson (1960) found concentrations of particles larger than 0.1 micron of the order of 1/cm³ of air. Hence a cube containing 10⁶ particles would be about 10 cm on a side at these altitudes. To apply the theory, a volume element of this size must retain its integrity over a period long by comparison with the times characteristic of the decay of particle concentration. Otherwise (8) is no longer applicable since the derivation (see, for example, Chandrasekhar, 1943) makes no allowance for local flows.

In principle, it would be possible to solve (8) given suitable initial and boundary conditions. Actually, this information is not available for the atmosphere, and a complete solution is quite unattainable. By making certain assumptions based on physical arguments concerning the dynamics of the coagulation-sedimentation process, the author (1960, a, b) derived a form for the upper end \((r > 0.1\) micron) of the tropospheric size distribution. This form was consistent with the kinetic equation and showed general agreement with the available experimental data. The assumptions made it possible to transform the kinetic equation from a partial integro-differential equation in three independent variables \((r, t, y)\) to an ordinary integro-differential equation. In the discussion which follows, a similar approach is used for the upper end of the stratospheric size distribution; a different similarity transformation is proposed for the lower end of the spectrum.

3. The upper end of the stratospheric aerosol size spectrum

The regularities observed in the size spectrum of tropospheric aerosols have led a number of investigators to suggest that a dynamic equilibrium exists between cluster formation by coagulation and loss by sedimentation. This idea was put on a quantitative basis by the author (1960, a, b) who developed a theory of local equilibrium and local similarity for the tropospheric aerosol. In this paper it is proposed that an equilibrium of the same type exists in the stratosphere. This state is defined by two assumptions. First, it is assumed that the upper end of the spectrum has attained a state of dynamic equilibrium such that the rate (volume of particulates per unit volume of air per unit time) at which matter enters from just below the equilibrium range by coagulation is equal to the net loss from the equilibrium range by sedimentation. The value of the radius separating the "upper" end from the "lower" end in the troposphere can be estimated from experimental measurements to be about 0.1 micron. Based on the experimental data available, the radius separating the lower from equilibrium range in the stratosphere is about the same. It is not difficult to see how local equilibrium can be attained when an element of air starts out with a high concentration of particles about 0.1 micron in diameter.
ter and perhaps, some "gaps" in the upper end of the spectrum. At the beginning, more matter will enter the upper region of the spectrum by coagulation than will be lost by sedimentation. However, as the concentration around the 0.1-micron peak decreases and that of the rest of the spectrum increases, the two rates will tend to equalize. Simultaneously, the linearity of the loss terms [the second and third on the right of eq (8)] and the non-linearity of the gain term (the first) suggest that there will be a tendency for the gaps in the spectrum to fill.

The equilibrium state ultimately reached by the upper end of the spectrum is local in the sense that it exists in each elemental air volume. When local equilibrium exists, the rates in and out of the upper end of the spectrum are equal but there is a net loss of matter from the lower end. It is possible that this depletion can be made up by diffusion of fine particles from the surrounding air. If the loss is not made up, it is assumed that the upper end of the spectrum is in a quasi-stationary state characterized by a slow change in concentration with time. The maintenance of local equilibrium may also be looked upon as a self-cleaning process in which the larger particles "wash out" smaller ones as they sediment.

The assumption of local equilibrium or the quasi-stationary state means that the term $dn/dt$ in eq (8) can be neglected for the upper end of the spectrum. This assumption in itself is not sufficient to permit integration of the equation since the boundary conditions on $n$ in space are unknown. It is necessary to introduce an additional assumption as follows: in the quasi-stationary state, the form of the upper end of the spectrum is completely determined given the constants $K_1$ and $S_1$ and $\epsilon(y, t)$ the volumetric rate at which matter is transferred from the lower end of the spectrum and then lost by sedimentation. This second assumption means that only one particle size distribution is possible given $K_1$, $S_1$, and $\epsilon$ and this can be written formally as $n(K_1, S_1, \epsilon, r)$. For additional discussion concerning these assumptions the reader is referred to the author's papers on the tropospheric aerosol and to references on the Kolmogoroff theory of local equilibrium in a turbulent fluid (Von Karman and Lin, 1951, and Batchelor, 1953).

On dimensional grounds alone, it is possible to establish the form of the distribution function. The variables have the following dimensions

$$
\begin{align*}
n & \quad L^{-\eta_1-1} \\
K_1 & \quad l L T^{-1} \\
S_1 & \quad L T^{-1} \\
\epsilon & \quad b L^{-3} T^{-1}
\end{align*}
$$

where $l = \text{a length unit of particle radius}$
$L = \text{a length unit referred to the gas phase}$
$T = \text{a unit of time}$.

By dimensional analysis,

$$
n = \frac{\epsilon l S_1}{K_1} \psi_1(\eta_1)
$$

where

$$
\eta_1 = \frac{r}{l}, \quad l_1 = K_1 l^{1/4} \eta_1^{1/8} S_1^{-1/8}.
$$

The parameter $l_1$ is a characteristic spectral length.

It is easy to show that this form of the distribution function is consistent with eq (8). The local loss rate, $\epsilon(y, t)$, is obtained by multiplying the sedimentation term by $\frac{2}{3}\pi r^2$ and integrating from $r = r_0$, the lower end of the equilibrium range, to $r = \infty$ as follows

$$
\epsilon = \frac{2}{3}\pi S_1 \frac{\partial n}{\partial y} \approx \frac{2}{3}\pi S_1 \frac{\partial n}{\partial y}.
$$

As a good approximation, the lower limit of the integral is extended to $r = 0$ since the $r^4$ weighting term makes contributions from the lower end of the spectrum negligible.

Substituting eq (10) into eq (11) gives

$$
\frac{\partial \epsilon}{\partial y} = \frac{6 \epsilon}{7\pi I_1 L_1}
$$

where

$$
I_1 = \int_0^\infty \psi_1 \eta_1 d\eta_1
$$

$L_1 = K_1 l^{1/8} S_1^{-1/8}$.

The parameter $L_1$ is a characteristic atmospheric scale factor. Substituting (10) and (12) into (8) with $dn/dt = 0$ and rearranging gives, finally

$$
0 = \int_0^\infty \phi(\eta_1', \eta_1'') (\eta_1'' / \eta_1') \psi_1(\eta_1') \psi_1(\eta_1'') d\eta_1'
$$

$$
- 2 \psi_1(\eta_1) \int_0^\infty \phi(\eta_1, \eta_1') \psi_1(\eta_1') d\eta_1'
$$

$$
- \frac{6 \eta_1}{7\pi I_1} \left( \psi_1 - \eta_1 \frac{d \psi_1}{d \eta_1} \right)
$$

where $\eta_1'' + \eta_1' = \eta_1$ in the first term on the right. Eq (13) is an ordinary integro-differential equation with the dependent variable $\psi_1$ expressed as a function of only the dimensionless radius $\eta_1$. Hence the assumption that $n$ can be written as a function only of $K_1$, $S_1$, $\epsilon$ and $r$ is consistent with the kinetic equation for the stationary state. The analysis shows that eq (10) represents a particular form for the solution of eq (8).

It would be possible to obtain the complete shape for the upper end of the spectrum by solving eq (13) with boundary conditions such as $\psi_1 = \psi_{10}$ at $\eta = \eta_0$ (the lower end of the equilibrium range) and $\psi_1 = 0$. 
at \( \eta = \infty \). Such a calculation seems possible but is not within the scope of this paper. Instead, the shape of the upper end of the spectrum will be examined by a further application of dimensional concepts.

The dependence of \( n \) on \( r \) is given functionally by eq (10). To obtain specific forms for the dependence, the method used by the author (1960 a, b) is employed again. At the lower end of the equilibrium range, concentration is high and sedimentation is negligible. The particles in this subrange tend to cluster two by two thereby cascading into the upper part of the equilibrium range from which they may be removed by sedimentation. The distribution function for this subrange, designated the coagulation subrange, depends only on \( K_1 \), \( \epsilon \) and \( r \) and not on \( S_1 \). By dimensional analysis, the only form which can be assumed by \( n \) is

\[
n = A_1 (\epsilon/K_1)^{3r-2},
\]

where \( A_1 \) is an absolute constant.

At the upper end of the equilibrium range, it is assumed that a sub-range exists independent of coagulation effects. Particles growing into this range from the coagulation sub-range settle out without change in size by agglomeration. For this sub-range, the sedimentation sub-range, \( n \) is a function only of \( S_1 \), \( \epsilon \), and \( r \) and by dimensional analysis

\[
n = A_2 (\epsilon/S_1)^{r-4}
\]

where \( A_2 \) is an absolute constant. An approximate value for the radius separating the coagulation and sedimentation subranges can be obtained by equating (14) and (15). The result is

\[
(A_2/A_1) K_1^{14/4} S_1^{-2/5} \approx l_1.
\]

That is, the radius separating the two regions is of the order of the characteristic spectral length \( l_1 \).

Eq (10) for the spectrum function can also be written

\[
n/l_1^2 = (S_1/K_1)^{4} \psi_1(\eta_1).
\]

Size distribution data taken at different altitudes and times should fall on a generalized correlation when \( n/l_1^2 \) is plotted vs \( \eta_1 \). (If differences in altitude are not very great, the variation of \( S_1/K_1 \) with temperature may be neglected.) To test these conclusions, some of the data of Junge, Chagnon and Manson (1960) have been recalculated and replotted in fig. 2. The measurements were made at altitudes of 24.5, 27.5 and 30.2 km corresponding to mean free paths of 2.0, 3.0 and 4.7 microns. The values chosen for \( l_1 \) obtained by trial and error, are those which best collapse the data to a single plot. Shown also is the expression

\[
n/l_1^2 = 0.2/(\eta_1^2 + 2\eta_1^4).
\]

This empirical form satisfies the requirements imposed by (14) and (15): For \( \eta_1 \ll 1 \), \( n \sim r^{-2} \) and for \( \eta_1 \gg 1 \), \( n \sim r^{-4} \). The expression fits the data quite well except for the last point at the largest radius. This discrepancy is not significant since there is doubt concerning the reliability of the experimental point (Junge, 1960). While this discussion does not constitute verification of the theory, it is clear that the predictions of the form of the spectrum are consistent with the experimental results.

![Figure 2: Generalized plot of data in the equilibrium range of the size spectrum for stratospheric aerosols. (Data of Junge, Chagnon and Manson, 1960.]

4. The lower end of the spectrum

The range of radii with which this section is concerned is defined as that part of the spectrum for which the sedimentation term in eq (8) can be neglected. This includes the coagulation sub-range and all smaller particles. Based on the experimental data, it is the region below a few tenths of a micron. Experimental data are difficult to obtain for this range since the efficiencies of sampling devices are uncertain, and the particle size is below the limit of resolution of the light microscope. The general form of the spectrum is unknown and it is not even clear what particulates should be included in the aerosol inventory. For example, the Becker-Döring theory of condensation predicts the existence of large numbers of molecular clusters of water molecules even in unsaturated systems. These volatile clusters probably do not contribute to the coagulation process and it will be assumed that the spectrum function, \( n(r) \), vanishes for \( r \to 0 \), passes to a peak value and then vanishes.
rapidly in the equilibrium range, the region which has been observed experimentally.  
In principle, it should be possible to solve eq (8) with the sedimentation term neglected given an initial value for the spectrum function and the loss rate, $c$, from the coagulation sub-range.  However, consistent with the method developed in this paper, another similarity transformation will be sought to reduce the computational effort and simplify the physical picture.

A reasonable form for a "self-preserving" spectrum function is given by:

$$n = g(t)\psi_2(\eta_2)$$

(19)

where $\eta_2 = r/l_2$ and $g$ and $l_2$ are functions of $t$.  Substituting this expression into eq (8) and neglecting sedimentation gives

$$\left(\frac{dg}{dt}\right)\psi_2 - \left(\frac{l_2}{g}\right)\frac{d\psi_2}{d\eta_2}$$

$$= \frac{K_1}{4} \int_{\eta_2}^{\infty} \left(\psi_2(\eta_2') \psi_2(\eta_2'')\right) d\eta_2'$$

$$- 2\psi_2(\eta_2) \int_{\eta_2}^{\infty} \phi(\eta, \eta') d\eta'$$

(20)

where $\eta^2 + \eta'^2 = \eta$ in the first term on the right.  Similarity is preserved provided

$$\frac{dg}{dt} = A_2 K_1 g^2$$

(21)

and

$$\frac{dl_2}{g dt} = A_4 K_1 g,$$

(21a)

where the constants $A_2$ and $A_4$ are non-dimensional.  The solution of the first equation is

$$g = (A_2 K_1 t + A_4)^{-1}.$$  

(22)

The total concentration of particles is given by

$$N = \int_{0}^{\infty} n dr.$$  

(23)

If it can be assumed that $n$ vanishes rapidly for large values of $r$, eq (19) can be substituted in eq (23) to give

$$l_2 = N/gI_2$$

(24)

where

$$I_2 = \int_{0}^{\infty} \psi_2(\eta_2) d\eta_2.$$  

This substitution is permissible since the number of particles associated with the upper end of the spectrum is negligible and even a large error in the estimate for this region contributes little to the integral (23).

The spectrum function takes the form

$$n = g\psi_2(r/l_2/N).$$

(25)

This expression must apply also in the coagulation sub-range.  For this range of radii, one may write

$$n = A_2 (r/K_1)^{b-2} = N^3 I_2^2 g^{-1} t^{-3}.$$  

(26)

Substituting eq (22) in eq (26) gives

$$1/N^2 = A_4 K_1 t^{-1}(t - t_0),$$

(27)

where $A_4$ is an absolute constant and $t_0$ is the (virtual) initial time when the concentration is infinite. Hence a plot of $1/N^2$ should vary in a linear fashion with the time.  Such a plot would furnish an experimental check on the theory.  It should be noted that the theory developed in this section should apply also to the tropospheric aerosol since the kinetics of coagulation of the lower end of the size spectrum will be given by eq (8) with the sedimentation term neglected.  In a proper experiment, a large volume of air should be trapped and the decay of particle concentration with time observed.  The decay law given by eq (27) differs from the classical aerosol decay law derived from the Smoluchowski equation of coagulation.  The classical theory, derived for homogeneous aerosols, predicts that $1/N$ should vary in a linear fashion with time.  This has been confirmed experimentally for fairly homogeneous aerosols, (Whytlaw-Gray and Patterson, 1937).

5. Summary

An equation has been derived for the rate of change with time of the stratospheric aerosol size-distribution function. While this equation cannot be solved as it stands, possible forms for the solution based on similarity considerations have been investigated.  The method employed is similar to one used by the author in analyzing the distribution of the tropospheric aerosol and draws heavily on similarity theory for the spectrum of turbulence.  It is assumed that an equilibrium range exists at the upper end of the size spectrum.  In this spectral region, a quasi-stationary state exists such that the rate at which matter enters by coagulation is equal to the rate at which matter is lost by sedimentation.  This process may be considered a type of self-cleaning by the larger particles.  The structure of the equilibrium range is assumed to be completely determined given the constants $K_1$, $S_1$, and $c$, the volumetric rate of transfer through the equilibrium range.  These assumptions allow a similarity transformation consistent with the kinetic equation.  On dimensional grounds, it is suggested that the equilibrium range may consist of two sub-ranges for which the dependence of the distribution function on radius can be predicted explicitly.  In the lower sub-range,
$n \sim r^{-2}$ and in the upper, $n \sim r^{-4}$. The theory is consistent with the available experimental data.

A different similarity transformation is proposed for the lower end of the spectrum where sedimentation can be neglected. This spectrum region includes the coagulation sub-range and the transformation assumes the proper form for this region. The transformation is consistent with the kinetic equation provided that $1/N^2$ (where $N$ is the total concentration of particles) is linear in time.

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