

Comments on "Concentration and Size Distribution Measurements of Atmospheric Aerosols and a Test of the Theory of Self-Preserving Size Distributions"

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1. Introduction

In their study of the size distribution of natural aerosols, Clark and Whitby (1967) discuss the concept of self-preserving size distributions as a possible explanation for the general shape of observed distributions. The discussion is primarily based on data for the size range between 0.005 and 5 μ radius which they obtained in the vicinity of a large city, i.e., under conditions of moderate air pollution. This very valuable set of data is the first one obtained simultaneously for a large part of the spectrum by a combination of three different methods. The agreement with data from other authors is satisfactory, especially with respect to the characteristic drop in concentration, which for radii larger than $r = 0.1 \mu$, varies as r^{-4} . The authors use these combined data for a test of the theory of self-preserving distributions (SPD) which was introduced by Friedlander and his associates (Friedlander, 1965; Friedlander and Wang, 1966) in aerosol studies. In this note we would like to

point out the difficulties in applying this theory to atmospheric aerosols. We also suggest an alternative explanation in terms of statistics of aerosol sources.

2. Typical features of atmospheric aerosol distributions

The size spectrum of atmospheric aerosols for radii larger than $r \approx 0.1 \mu$ can be approximated by

$$\frac{dN}{dr} = n(r) = c \left(\frac{r_0}{r} \right)^\alpha [\text{cm}^{-4}],$$

or, in logarithmic form

$$\frac{dN}{d \log r} = n^*(r) = \ln(10) c r_0 \left(\frac{r_0}{r} \right)^{\alpha-1} [\text{cm}^{-3}],$$

where $c = n(r_0)$, N is the number of particles cm^{-3} larger than r , and r_0 an arbitrary radius, here 0.1 μ .

We prefer the variable (r_0/r) in order to have simple dimensions for c for all values of α . For the data used by Clark and Whitby (1967) $\alpha \approx 4$. However, it should be emphasized that observations show α to vary between 3 and 5 and that it is not always constant over the size range under consideration, which in most studies is $0.1 \leq r \leq 5 \mu$ [see Clark and Whitby (1967), Bullrich (1964), and Junge *et al.* (1966)]. The power law over the whole size range with $\alpha = 4$ can, therefore, only be considered an approximation for average conditions.

There is another fact which should be taken into account in any attempt to explain atmospheric aerosol distributions. Older estimates and data suggest that the upper size limit of continental aerosols could be expected around 20μ under normal meteorological conditions. Recent measurements at various locations in Central Europe showed, however, that the size distribution could be followed up to $r \geq 100 \mu$, if the samples collected were large enough to determine very low concentrations (Jaenicke and Junge, 1967).

This extension of the size distribution beyond 10μ can also be represented by a power law with $\alpha \approx 4$. The only other set of data available in the literature for comparison is from Japan and goes up to 50μ (Okita, 1955). The agreement with our values is good. Although we would like to see this result confirmed by further studies, we think that this extension of the power law up to about 100μ is a regular feature of continental aerosols. The importance of this finding for our present problem is obvious, i.e., any explanation of the aerosol size distribution must remain applicable up to radii of 100μ .

If the power law holds over the range $0.1 > r > 100 \mu$ with $\alpha \approx 4$, the volume distribution

$$\frac{dV}{d \log r} = v^*(r) = \frac{4}{3} \pi \ln(10) r_0 c r^3 \left(\frac{r_0}{r}\right)^{\alpha-1} \left[\frac{\text{cm}^3 \text{ aerosol}}{\text{cm}^3 \text{ air}} \right]$$

will be more or less constant over the same range, with deviations depending on the extent to which α deviates from 4. In other words, the major portion of the aerosol volume (or mass) can be found between 0.1 and 100μ with a rapid drop of $v^*(r)$ beyond these limits.

3. Behavior of self-preserving distributions

We like to point out some important characteristics of SPD for comparison with the observed facts. According to Friedlander's concept of SPD, aerosols subjected to thermal coagulation will approach asymptotic forms of the size distribution after sufficient time of adjustment. Friedlander and Wang (1966) showed that for Brownian coagulation without slip correction, i.e., for Knudsen numbers $\text{Kn} = \lambda/r \ll 1$, where λ is the mean free path of air molecules, this asymptotic form exists but depends on the form of the coagulation function. The best evidence so far was provided by Hidy (1965)

who calculated the time variation due to coagulation for a variety of initial distributions. His calculations were made for Brownian coagulation including slip correction for the range $0 \leq \text{Kn} \leq 2$. He found that the initial distributions converge toward SPD, the shape of which depends on the initial distribution Knudsen number. The time required for this approach is shortest for monodisperse aerosols and increases for more complex initial distributions.

It should be mentioned, for $\text{Kn} > 1$ or $r < 0.07 \mu$ under STP conditions, that another correction becomes necessary due to the fact that the mean free path of the smaller aerosol particles can no longer be considered negligible compared with the size of the larger particles with which they collide. Since we will be concerned here primarily with particles $> 0.1 \mu$, the results of Hidy can be applied in the present discussion.

For a proper discussion of the behavior of SPD it is necessary to transform the dimensionless representations into actual distributions of $dN/d(\log r)$. We chose the SPD for $\text{Kn} = 1$ which is closest to our range of interest around $r = 0.1 \mu$ (Hidy, 1965, Fig. 10). In Hidy's notation we obtain

$$\frac{dN}{d \log r} = 6.9 \psi(\eta_i) \eta_i N_\infty,$$

where $\psi(\eta_i) \eta_i$ represents the time independent shape of the distribution and N_∞ the time dependent total number. For comparison with moderately polluted conditions similar to those studied by Clark and Whitby and other authors we chose $dN/d(\log r) = 4.5 \times 10^3 \text{ cm}^{-3}$ for the maximum if this is located at $r = 0.1 \mu$. The radii for distributions of different times vary as $(N_\infty)^{-1/3}$. This means that the whole distributions shift with time to larger particles in such a way that equivalent points of the curves move along slopes of r^{-3} , as indicated in Fig. 1. This simply reflects the condition that the total volume remains constant for coagulation. N_∞ is related to the dimensionless time τ (Hidy, Fig. 4) which in turn can be converted into real time t . In our example we start at $\tau = t = 0$ with a monodisperse aerosol of $r = 0.04 \mu$ and a concentration of $3.55 \times 10^4 \text{ cm}^{-3}$. At $\tau = 3$ or $t = 13.4$ days the SPD is approached and subsequently changes with time as indicated in Fig. 1. During this process Kn changes also and this should be taken into account for an accurate conversion. But this approximation does not affect our present conclusion which we can summarize as follows:

- 1) The shape of the SPD differs from the observed distributions, especially in that the slope beyond the maximum is much steeper than r^{-3} .
- 2) The change with time of the SPD is very slow compared to meteorological time scales for all radii $> 0.1 \mu$. For aerosol concentrations encountered in the troposphere there is no chance for the SPD to become established, so that for this

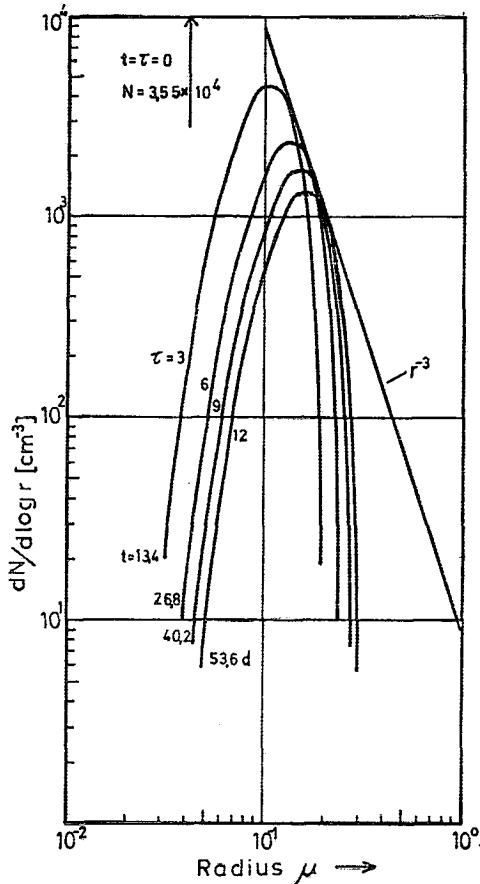


FIG. 1. Initial aerosol distribution for $r=0.04 \mu$, $N=3.55 \times 10^4 \text{ cm}^{-3}$, and subsequent time changes. After $\tau=3$, the SPD has approached the final form (after Hidy, 1965).

reason alone the application of the concept of SPD for atmospheric aerosols is unrealistic at least so far as coagulation is concerned.

- 3) The envelope curve of the individual SPDs has a slope of r^{-3} because of volume conservation. This will, of course, be the case for any set of similar curves, SPD or not, for which the total volume remains constant; it is thus not a proof for SPD.

The extremely slow rate of change of atmospheric aerosol distributions for $r > 0.1 \mu$ was also confirmed by direct calculations, an example which is given in Fig. 2 (Junge and Abel, 1965). Below $r=0.05 \mu$, on the other hand, the rate of coagulation is rather rapid and therefore of importance for atmospheric aerosols.

4. Test for self-preserving distributions

In their Fig. 8 Clark and Whitby compare the results of five different sets of observations after their transformation to dimensionless distributions according to the Friedlander transformation (FT). The five sets show considerable agreement, particularly in the interval from $\eta_r=2.0$ to 30 corresponding to the range $0.04 < r$

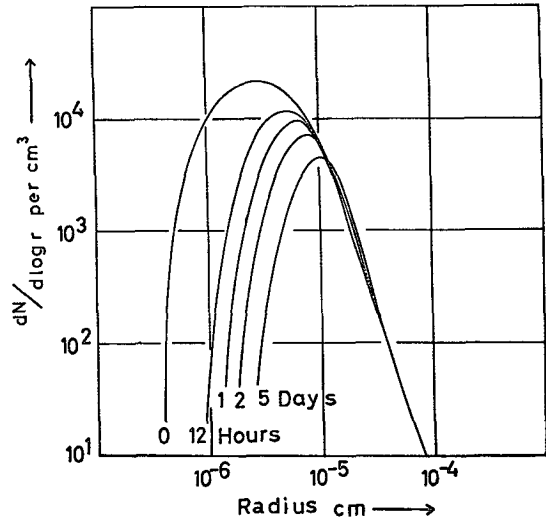


FIG. 2. Numerical calculations of the change of average atmospheric aerosol distributions due to Brownian coagulation (Junge and Abel, 1965).

$< 1.2 \mu$. It can be demonstrated that this agreement is only a necessary but not a sufficient condition for SPD and can thus not be considered as a proof for SPD. For example, let us consider distributions of the form

$$n(r) = \tilde{c} r_0^{-\alpha} \nu\left(\frac{r}{r_0}\right) [\text{cm}^{-4}],$$

where α can assume any value and $\nu(r/r_0)$ is an arbitrary dimensionless function. The characteristic radius r_0 can be considered either as time dependent, $r_0=r_0(t)$, or as being different for different individual sets of observations. From this we obtain

$$N_t = \tilde{c} r_0^{1-\alpha} A [\text{cm}^{-3}],$$

$$\phi = \tilde{c} r_0^{4-\alpha} B [\text{cm}^0],$$

with

$$A = \int_0^\infty \nu\left(\frac{r}{r_0}\right) d\left(\frac{r}{r_0}\right),$$

and

$$B = \frac{4}{3} \pi \int_0^\infty \left(\frac{r}{r_0}\right)^3 \nu\left(\frac{r}{r_0}\right) d\left(\frac{r}{r_0}\right),$$

being independent of r_0 . The FT gives

$$\eta_r = \left(\frac{r}{r_0}\right) \left(\frac{A}{B}\right)^{\frac{1}{3}},$$

$$\psi_r(\eta_r) = \nu\left(\frac{r}{r_0}\right) \left(\frac{B}{A^4}\right)^{\frac{1}{3}},$$

which are independent of r_0 , i.e., are the same for all $n(r)$ distributions. But these distributions do not meet the required condition of ϕ being constant for SPD,

except for $\alpha=4$. Since no assumption was made about $\nu(r/r_0)$ it is clear that the actual SPD as given in Fig. 1 represents only the very special case of $n(r)$, where $\nu(r/r_0)$ has the same shape as in Fig. 1 and where $\alpha=4$.

If we replace the constant \bar{c} by

$$\bar{c} = \phi_r \alpha^{-4} / B,$$

we obtain

$$\bar{n}(r) = \frac{\phi}{r_0^4 B} \nu\left(\frac{r}{r_0}\right).$$

In case $\nu(r/r_0)$ is similar for different $n(r)$ for the same radius range, this means that r_0 is the same. With r_0 a constant for different $n(r)$, it follows that $\bar{n}(r)$ is proportional to the total volume ϕ of the aerosols. The agreement in Fig. 8 of Clark and Whitby within the range of $0.04 < r < 1.2 \mu$ is thus simply equivalent to the fact that all sets of data were similar within this range and that $n(r)$ is therefore proportional to ϕ in correspondence with Eq. 10 in Clark and Whitby's paper. This agreement does not, however, provide any information on SPD.

Agreement in Fig. 8 would not have occurred if the different sets had not been similar. With variations of α between 3 and 5 this in general should not happen. Since the similarity between atmospheric aerosol distributions becomes rather poor in the Aitken range, i.e., for $r < 0.1 \mu$, and since the contribution of this range to the value of ϕ is small, the scatter should become larger, as indicated in Fig. 8. We agree with the authors that the larger scatter for $\eta_r \gtrsim 10$ may partly be due to insufficient statistics for some of the data.

5. Quasi-stationary distributions (QSD)

Friedlander (1960) introduced an explanation for atmospheric aerosol size distributions which is quite different from that of SPD discussed in later aerosol work. Whereas SPD applies to a single process such as coagulation, the concept introduced by Friedlander refers to quasi-stationary distributions for which the effects of two or more processes are balanced. In particular, he considers the possibility that the observed similarities of atmospheric aerosol distributions are determined by steady state conditions in which the increase of concentration of particles $\gtrsim 0.1 \mu$ due to coagulation and attachment of smaller ones is balanced by sedimentation. He discussed this concept on the basis of considerations of dimensions and similarity transformations similar to those used in analyzing the spectrum of turbulence. More recently (1965) he pointed out that the upper end of maritime aerosols shows similarities which may represent QSD without specifying the processes. For the troposphere as a whole Junge and Abel (1965) studied quantitatively the possibility of QSD by model calculations including a variety of processes which are associated with the formation and dissipation of clouds.

Since the concept of SPD can be ruled out as an explanation for the size distributions of atmospheric aerosols for $r > 0.1 \mu$, the question arises to what extent and for what size ranges QSD can be expected for continental surface air for which most of the aerosol data so far have been obtained. Basically the approach to QSDs in the atmosphere can only be expected at least for restricted size ranges if 1) gain and loss processes exist which can balance each other, and 2) the net rate of these processes is higher than the rate of change of meteorological conditions, so that the approach can proceed to some extent.

We can discuss this question here only briefly because it would be beyond the scope of this note to go into detailed quantitative considerations for the numerous processes which we know can affect atmospheric aerosols. We will further restrict our discussion to the planetary boundary layer since this is where most of the aerosol data are available. For this case we can thus exclude all those processes which are associated with the presence of water clouds; the remaining processes are as follows:

- 1) Production by natural and artificial sources.
- 2) Growth of particles by heterogeneous gas reactions on the surface of particles.
- 3) Growth of particles by homogeneous gas reactions and subsequent attachment of the reaction products to the aerosols.
- 4) Net change of particle concentrations due to thermal coagulation.
- 5) Net change of particle concentrations by scavenging of smaller particles by larger ones during their fall.
- 6) Net change of particle concentrations by scavenging of particles due to turbulent velocity gradients.
- 7) Loss of particles by gravitational sedimentation.
- 8) Loss of particles by impaction on obstacles at the earth surface.
- 9) Loss by washout under clouds.

Processes 5) and 6) are negligible, except for 5) at the upper end of the spectrum. Processes 1)–3) cause an increase in aerosol volume, 4)–6) do not change the total volume, while 7)–9) result in a decrease of the total volume. In a complete evaluation, which can only be made for given models, one has to come up with the net rate of concentration changes for the individual processes as a function of radius. It is very difficult to give representative estimates for processes 1)–3) because they vary considerably with local conditions, particularly in polluted areas. The same is true for 9).

It is very hard to estimate the order of magnitude of the rate of change of meteorological factors which influence aerosol concentrations, such as dilution by vertical mixing with higher layers, transport to areas with other source conditions, etc., but 1 day^{-1} seems to be a reasonable figure. On the basis of this figure, only

those processes of aerosol modification whose rates of change exceed or are of the same order of this figure can be considered of importance. On the basis of numerical studies which will be published elsewhere, the following table lists those processes which can be considered of sufficient importance for average conditions in the planetary boundary layer. From this list QSD can

Aerosol radius	Processes increasing aerosol concentration	Processes decreasing aerosol concentration
$r \leq 0.1 \mu$	1), 2), 3)	4)
$0.1 < r < 1 \mu$	1), 2), 3)	9)
$r > 1 \mu$	1), 2), 3)	7), 8), 9)

be expected at the lower and upper end of the size spectrum but for the center part of the size range this is only possible under very special circumstances, e.g., for very long duration, high aerosol concentrations (as in extreme cases of air pollution) which result in higher rates of coagulation. In the absence of such conditions there are no reduction processes efficient enough to counterbalance any production. Only rainout and washout, together with the other processes associated with clouds, can remove these particles on a global basis from the troposphere.

For the ocean the upper end of the sea spray aerosol spectrum can under normal conditions be considered a well established QSD between production and subsequent penetration of the particles upward by turbulent diffusion and sedimentation (Toba, 1965). This QSD depends only on wind speed.

6. Statistical explanation for the size distribution

The preceding discussion indicates that neither SPD nor QSD can provide an explanation for the observed regularities of the aerosol distributions for $r > 0.1 \mu$. This difficulty is particularly severe with respect to the fact that the distributions with $\alpha \approx 4$ extend all the way to $r \approx 100 \mu$. It does not seem possible to make one mechanism responsible for a uniform distribution over such a wide range as $0.1 < r < 100 \mu$. On the other hand it would be rather coincidental if such uniform distributions were the result of different mechanisms acting over different parts of the range.

We suggest, therefore, an explanation which is based on the observation that for average conditions in continental surface air the resulting log-volume distribution is approximately constant (Junge and Abel, 1965). It seems to us that this tendency for constant log-volume distributions is the important feature to be considered. Because of the observed deviations of α from 4, the actual volume distributions, in most cases, are not constant; this is indicated in Fig. 3 for a few typical examples. The best approximation for $\alpha = 4$ is apparently observed in the continental planetary boundary layer and it is perhaps important to note that here

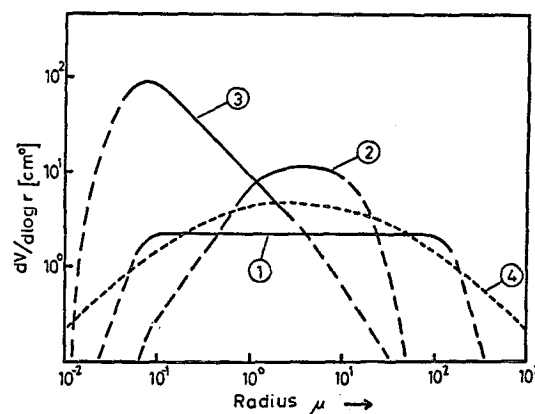


FIG. 3. Log-volume distributions for atmospheric aerosols under typical conditions. The ordinate scale is arbitrary, dashed parts of the curves uncertain. Curve 1: continental surface air, $\alpha = 4$; curve 2: maritime surface air, $\alpha \approx 3$ but not constant; curve 3: upper tropospheric air, $\alpha = 5$; curve 4: log-normal distribution, $\alpha \approx 4$ but not quite constant.

the aerosols originate from a large number of independent sources, natural and artificial. This suggests that the observed tendency for atmospheric aerosols to form quasi-constant log-volume distributions may simply be the result of statistics. Under ideal conditions this may lead to a broad log-normal volume distribution as indicated in Fig. 3 centered around $r = 30 \mu$.

It is well known that artificial processes such as grinding form log-normal volume distributions and it is therefore possible that contributions from the various aerosol sources occur in such a way that about equal portions of mass are distributed over the range $0.1 < r < 100 \mu$. The upper and lower end of this distribution would be subject to rapid reduction due to sedimentation and coagulation.

The problem would thus be reduced to the question of why and under what circumstances a large number of independent aerosol sources gives rise to such a distribution. If this question can be answered all the observed features can easily be explained. Deviations from $\alpha = 4$ may indicate that sources at the lower or upper end of the spectrum are more dominant, resulting in a skewed distribution. Deviations from a constant α over the whole range may be expected if the number of sources are not large enough so that the statistics are insufficient to form smooth spectra. The maritime aerosols are a good example. For $r > 0.3 \mu$ there is only one source, sea spray, which forms a broad peak in the volume distribution between $r = 1$ and 10μ , shifting to somewhat larger particle sizes as the wind speed increases. For aerosols in very clean tropospheric air masses, i.e., "tropospheric background aerosols," there seems to be a tendency for $\alpha \approx 5$. Most likely this represents a global QSD by which the original statistical distribution is modified. Similar deviations from $\alpha = 4$ can be expected whenever one or only a few sources or processes become dominant.

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