On the Minimum Size of Particle for Nucleation in Clouds

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4 November 1976 and 12 July 1977

ABSTRACT

Particles grown from molecular size by ultraviolet irradiation of initially particle-free air were found not to nucleate condensation at slight (~1%) supersaturations until sufficient time had elapsed. By monitoring the size of the growing particles by use of Nuclepore filters a size/critical supersaturation relationship was obtained and compared with the predictions of nucleation theory. Substantial agreement with the theory resulted.

1. Introduction

Nucleation theory, as usually applied in cloud physics, associates with every particle a critical supersaturation—this being the minimum supersaturation which must be applied to the particle to permit it to grow into a cloud droplet. The theoretical value for the critical supersaturation of a soluble particle is a function of particle radius, density and molecular weight as well as of the van't Hoff factor of its aqueous solution. For sodium chloride the theory ascribes a critical supersaturation S_c of 1% to a dry particle of radius 0.012 μm, while $S_c = 0.5\%$ for a radius of 0.019 μm. For other compounds the critical supersaturation varies slightly from the values just given (in proportion to $(M/i)^{\frac{1}{2}}$ if i is the van't Hoff factor and M the molecular weight).

Katz and Kocmond (1973) described experiments in which both the supersaturation spectrum and the size spectrum of a sodium chloride aerosol were measured. They concluded that the theory grossly underestimated the size necessary for nucleation to occur at a given supersaturation. From their experimental data they inferred a radius of about 0.04 μm for 1% critical supersaturation, i.e., over three times the theoretical radius for sodium chloride.

When a sample of atmospheric air previously filtered of particles is exposed to suitable ultraviolet radiation, particles are produced in numbers which vary according to the meterological situation and which often grow during storage. The growth rate also is variable from sample to sample, but growth often occurs for a given sample at a fairly steady rate over periods of tens of minutes; there is evidence of a rather sharp cutoff in the particle size distribution at a maximum size which is quite well-defined—during growth this size is often found to increase steadily with time. The UV-produced aerosol in this respect provides the opportunity for a simple measurement—monitoring the maximum size of the particles while also observing their nucleation behavior in a thermal diffusion chamber. If critical supersaturation is uniquely related to size, a well-defined maximum size implies a well-defined minimum supersaturation, below which no (or negligibly few) droplets would form on the aerosol and above which a sudden onset of cloud formation would occur. The composition of the aerosol produced by UV irradiation is not known—it is certainly not sodium chloride—but the natural cloud nuclei in the atmosphere in the size range ~0.01 μm appear to be similar in some respects to those produced by UV irradiation, especially in that most of the atmospheric particles are relatively volatile and probably originate from the gas phase (Hoppel and Dinger, 1973; Dinger *et al.*, 1970; Twomey, 1971).

2. Experimental procedure

Outside air (at a rural field site) was passed through a large glass-fiber filter which reduced particle concentration (as indicated by a Pollak counter) to instrumental zero, i.e., $\ll 10$ cm^{-3}. It was then passed through a quartz section where it could be irradiated by UV light and then into a large (150 ℓ) Mylar storage bag. Concentration and size of any particles produced were then monitored every few minutes, while air samples were also passed into a conventional thermal diffusion chamber in order to examine the cloud-nucleating properties of the particles.

The experiment, while fundamentally simple, could only be carried out successfully when particles were formed in reasonable concentrations and continued to grow at a reasonable rate for a reasonable time. Since this could not be controlled in advance, many attempts to carry out the experiment were unsuccessful either because the air was too clean, giving few or no particles, or because growth was too fast or too slow. We did not attempt to change artificially the composition of the

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air because the equipment was also used for other purposes, and even exceedingly minute amounts of contamination can be very troublesome and very difficult to eliminate. The outside air was simply accepted as it was and used in that way. If conditions proved unsuitable that experiment was abandoned.

SIZE MONITORING

Nuclepore filters with pores of order 1 μm transmit particles down to sizes of the order of 0.01 μm for flow rates of the order of liters per minute, whereas particles much smaller than 0.01 μm are removed by diffusion. The data of Fig. 1 were obtained using standard procedures for calculating Nuclepore transmissions [Spurny *et al.*, 1969) have confirmed the validity of such calculations by direct measurements]. Fig. 1 shows that by varying the flow rate the cutoff of such filters can be moved between 0.02 and 0.005 μm without having to resort to excessively high or low flow rates; with the lower flow rates of 0.5 and 0.25 ℓ min^{-1} two or four filters were used in parallel to maintain a total flow not less than 1 ℓ min^{-1} (this being about the minimum useful flow rate for a Pollak counter).

When a stored air sample was passed through Nuclepore filters there was found to be a minimum flow rate below which zero counts were obtained. This decreased with duration of storage when the aerosol was growing. To determine maximum size crudely one could use the filter cutoff c at that minimum flow rate, but

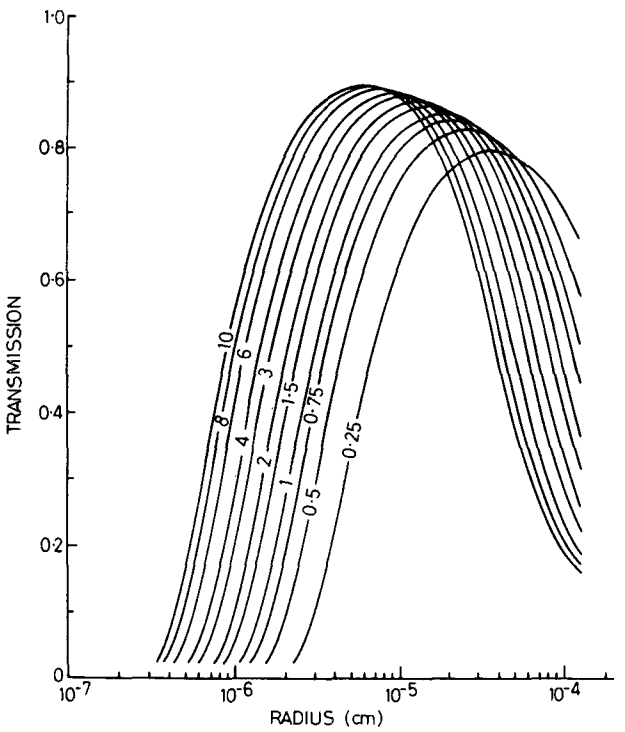

FIG. 1. Filter transmission for Nuclepore filter at several values of flow rate (indicated on the curves in liters per minute).

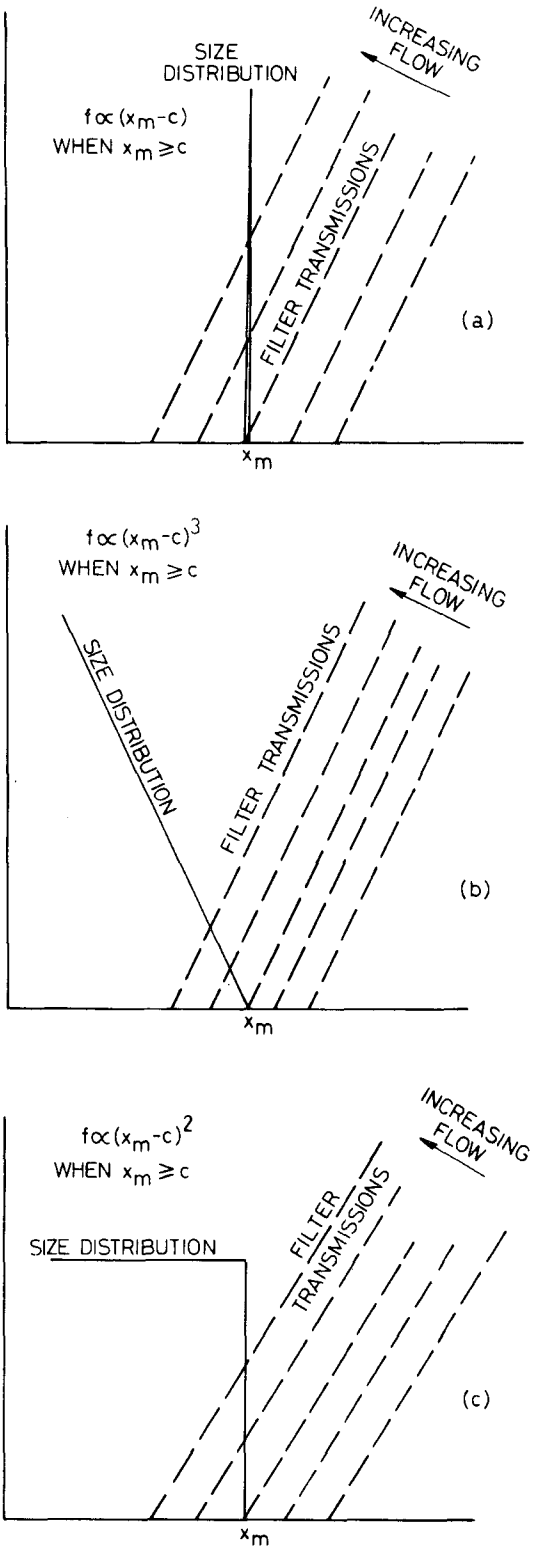

FIG. 2. Schematic diagram illustrating the method of determining maximum size by varying the flow rate of the air samples through the filter. The ordinate represents the number concentration of particles or the filter transmission and the abscissa represents the particle radius.

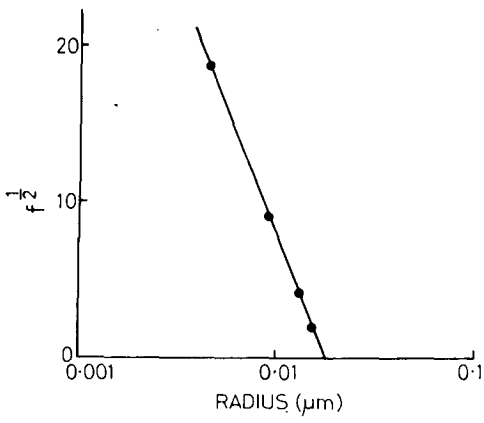

FIG. 3. Plot of $f^{\frac{1}{2}}$ against the filter cutoff for an aerosol sample after 40 min storage.

this would obviously underestimate somewhat the maximum size, since particles which are only a little larger than the transmission cutoff, being transmitted with very low efficiency, could have produced instrumental zero or near-zero counts.

The exact size distribution of the particles is not of course known *a priori*. One can take three very simple models: (a) a uniform aerosol, giving a delta function at $x=x_m$ for the size distribution; (b) a sloping line meeting the axis at x_m; and (c) a flat-topped distribution up to size x_m, dropping to zero at that point. When log-radius is used to measure size the filter transmission is well-approximated by a line sloping upward with slope β from a cutoff c; the interaction of the filter with the aerosol—which in the most general situation is described by writing for the number transmitted

$$f=\int_0^\infty F(x)n(x)dx,$$

$F(x)$ being the filter transmission and $n(x)$ the size distribution—can be reduced to very simple algebraic formulas (see Fig. 2). In model (a) one obtains the uniform particles $[n(x)=\delta(x-x_m)]$, so

$$f\propto(x_m-c);$$

for model (b), the sloping line, the relationship is

$$f\propto(x_m-c)^3;$$

and for (c), the flat-topped distribution, the dependence is

$$f\propto(x_m-c)^2$$

(f of course is always zero when $x_m<c$; the above relations apply only when $x_m>c$).

When the number of particles transmitted through the filters at flow rates which gave small, but nonzero, readings was plotted against c, the result was not a straight line—implying that (a) is a poor model. The same occurred when $f^{\frac{1}{3}}$ was plotted against c, but $f^{\frac{1}{2}}$ plotted against c followed a linear trend closely. An example is shown in Fig. 3. The intercept of a line through plots of $f^{\frac{1}{2}}$ against c was therefore used as an estimate of the maximum radius x_m.

When the air sample for which Fig. 3 was obtained (maximum radius 0.017 μm) was introduced into a thermal diffusion chamber no droplets formed until the supersaturation reached 0.7%; at that value a few droplets ($\sim$30 cm^{-3}) appeared; this increased to 50 cm^{-3} at 0.85% and 180 cm^{-3} at 1%. The critical supersaturation is therefore established fairly closely, and so also is the maximum size. The size/critical supersaturation relationship given by nucleation theory can be written (see Fletcher, 1962) as

$$r_d=1.45\times10^{-6}S_c^{-\frac{2}{3}},$$

when S_c is in percent units and data appropriate to ammonium sulphate ($M=132$, $i=3$) are used. [For other materials r_d varies from the above in proportion to $(M/i)^{\frac{1}{3}}$, M being the molecular weight and i the van't Hoff factor.] Insertion of $S_c=0.7\%$ in the above relationship gives $r_d=1.8\times10^{-6}$ cm, which is close to the value 1.7×10^{-6} cm given by the filter data. To obtain 30 cm^{-3} or so droplets, the maximum radius must exceed the critical radius r_d, not just equal it; use of

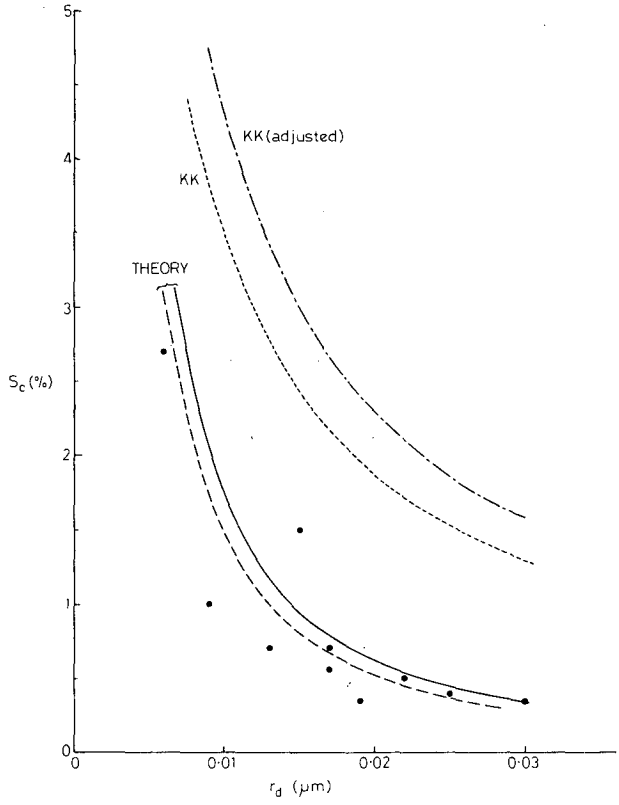

FIG. 4. Experimental results contrasted with theoretical relationships (solid and broken curves) and with the results of Katz and Kocmond (1973) [(K-K) dotted and dash-dotted curves].

the *maximum* radius (e.g., 0.017 μm in the case of the data in Fig. 3) slightly overestimates r_d. In view of the steep slope of the curves of number against filter cut-off radius c, the extent of the overestimation is not serious, well under a tenth of a decade in radius. Corrections can easily be devised for this effect but are hardly warranted in view of the (greater) uncertainty attached to the ratio M/i.

3. Results

The experiment described above was successfully carried out on six separate occasions with similar results. On about 10 other occasions growth was either too slow or too fast to allow useful data to be obtained. In practice only one or two pairs of values of maximum radius and critical supersaturation could be obtained from one stored air sample. The data are plotted as points in Fig. 4 on a linear scale of radius and supersaturation. For comparison with the data the following curves were included in Fig. 4: 1) the theoretical relationship, using M and i for ammonium sulfate (solid curve), 2) a similar curve using data for sulfuric acid (broken), 3) the experimental data given by Katz and Kocmond (1973) for sodium chloride (dotted), and 4) the latter curve, adjusted for ammonium sulfate using the theoretical prediction $S_c \propto (M/i)^{\frac{1}{2}}$ (dash-dotted).

A regression line through the logarithms of the data points gave the relationship

$$r_d = 1.25 \times 10^{-6} S_c^{-0.63}.$$

That relationship is close to the theoretical both with respect to coefficient and to the power of S_c (it virtually coincides with the theoretical relationship for $M=85$, $i=3$ or $M=56$, $i=2$).

4. Conclusions

Since the particles used were certainly *not* sodium chloride, the present results do not necessarily conflict with those of Katz and Kocmond (1973). They do, however, conflict with the conclusion sometimes drawn from the latter work that atmospheric particles must be about three times larger than the minimum size given by nucleation theory in order to be effective as cloud nuclei at supersaturations of 1% and below. They also suggest that there is no fundamental conflict in ascribing a radius of 0.01–0.025 μm to natural atmospheric cloud nuclei, as was quite clearly indicated by multiple filter measurements (Twomey, 1972). This point is quite important since in the laboratory at least it is relatively easy to grow particles to 0.01 μm or slightly larger direct from the gas phase but it seems to be very difficult to produce particles by gas-to-particle conversion which are considerably larger.

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3. FREQUENCY OF ISSUE: MONTHLY	A. NO. OF ISSUES PUBLISHED ANNUALLY: 12 — B. ANNUAL SUBSCRIPTION PRICE: $60. & $20. members

4. LOCATION OF KNOWN OFFICE OF PUBLICATION *(Street, City, County, State and ZIP Code) (Not printers)*: 45 Beacon St., Boston, Suffolk, Mass. 02108

5. LOCATION OF THE HEADQUARTERS OR GENERAL BUSINESS OFFICES OF THE PUBLISHERS *(Not printers)*: 45 Beacon St., Boston, Mass. 02108

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PUBLISHER *(Name and Address)*: American Meteorological Society, 45 Beacon St., Boston, Ma. 02108

EDITOR *(Name and Address)*: Dr. Richard A. Craig, Florida State University, Tallahassee, Fl. 32306

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