Insoluble Condensation Nuclei: The Effect of Contact Angle, Surface Roughness and Adsorption

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ABSTRACT

Condensation of water vapor on various surfaces was studied experimentally. For surfaces with an air-water contact angle θ less than 20°, the experimentally determined values of critical supersaturation S_c agreed with those given by the Volmer theory. At higher θ, the experimental values of S_c were below the Volmer theory values. When the applied supersaturation was less than S_c, condensation was avoided for periods as long as 20 h. Thus, if adsorption of water tends to negate the Volmer theory, the process is a slow one. It was determined both by experiment and theoretical analysis that the effect of surface roughness is to decrease S_c only slightly. These results suggest that most insoluble airborne particles are not likely to serve as cloud condensation nuclei.

1. Introduction

If the Volmer (1939) theory of heterogeneous nucleation is correct, then very few insoluble particles in the atmosphere can be expected to serve as cloud condensation nuclei. McDonald (1964) has shown that according to the Volmer theory only a substance exhibiting a water-air contact angle of less than 7° can have a critical supersaturation (S_c) less than 1%. There are very few water insoluble substances that exhibit this small a contact angle.

In contrast, Jiusto and Kocmond (1968) and more recently Van der Hage (1972) have presented evidence that supposedly hydrophobic surfaces are condensed upon at very low supersaturations. In both papers, the results were interpreted as support for the hypothesis that either surface roughness or adsorption of water vapor negates the Volmer theory so that all insoluble surfaces are condensed upon as if they were fully wettable.

Jiusto and Kocmond prepared a test aerosol by heating wax to 200°C and then cooling the wax vapor to room temperature by mixing it with filtered air. The median particle size, which was measured by electron microscopy, was near 0.05 μm radius. When this aerosol was put into a thermal diffusion chamber operating at 0.55% supersaturation, water drops were produced, presumably due to condensation on the wax particles rather than on a background aerosol. This condition suggests that the wax particles behaved as if they were fully wettable, even though the bulk wax exhibited a contact angle >90° before it was vaporized.

Van der Hage (1972) studied condensation on the surfaces of plastic ribbons, which were placed at the midplane of a small, parallel-plate, thermal diffusion chamber. The ribbons were rinsed with water and then tilted so that the water drops fell off their surfaces and left the surfaces apparently dry. Immediately after this procedure, condensation was observed on the surfaces, even though the applied supersaturation was very low and the ribbons were hydrophobic.

In contradiction to these experiments, there have been three independent investigations which indicate that hydrophobic surfaces do exhibit a finite value of critical supersaturation. Twomey (1959) used a chemical diffusion chamber to develop supersaturations over plastic surfaces. His data agree very well with the Volmer theory. Koutsky *et al.* (1965) and Isaka (1972) developed supersaturations by subcooling a target surface below the temperature of a water vapor source. They found qualitative agreement with the Volmer theory in that the critical supersaturation was found to increase generally with an increasing contact angle. There were deviations from the Volmer theory, however.

The result of Van der Hage need not be interpreted as a contradiction to the Volmer theory; instead it can be explained in terms of water retained in microscopic pits in the surfaces of the ribbons used by Van der Hage. Turnbull (1950) has presented an analysis which indicates that once a surface is wet it can retain nucleating embryos of liquid in microcavities, even in a subsaturated environment. These embryos then act as condensation sites as soon as a slight supersaturation is provided. It therefore seems likely that Van der Hage observed condensation on water that had been retained in the surface cavities of the plastic ribbons.

Other evidence of liquid being retained in microcavities is provided by the experiments of McCormick and Westwater (1965). They identified particular scratches and pits on a condenser surface and found that droplets grew at each site thus identified. As the condensation process continued, each drop coalesced with a neighboring drop and moved across the surface so as to sometimes uncover the scratch or pit. Whenever this happened, the newly exposed pit again nucleated a drop, even at low supersaturations. Moreover, McCormick and Westwater showed that these sites could be deactivated by dry heat and vacuum. This condition indicated that the scratches and pits were active at low supersaturation only when liquid was retained in them.

In view of the above investigations, the question of whether or not insoluble particles can act as cloud condensation nuclei raises at least two other questions:

1) What is the quantitative effect of surface roughness on critical supersaturation when there is originally no water in the cavities of the surface?

2) If supersaturation is applied for periods longer than a few minutes, will water adsorption eventually lead to condensation under even slightly supersaturated conditions?

We undertook to answer these two questions and to determine whether Twomey's agreement with the Volmer theory could be repeated in a system in which the condensing liquid was pure water. We decided to use a thermal diffusion chamber to provide the supersaturation environment, because such a chamber, for a given accuracy of temperature control, gives about 20 times more accuracy in supersaturation control than does the type of chamber used by either Koutsky *et al.* or Isaka.

2. Experimental apparatus

The apparatus (Fig. 1) is a thermal diffusion chamber of the horizontal, parallel-plate type, consisting of a warm wet upper plate, a cold wet lower plate, and a sidewall to complete the enclosure, which measures 10 cm high and 76 cm diameter. When the air-water vapor mixture inside the enclosure is at steady-state conditions, the local temperature T and vapor pressure p increase linearly with distance from the cold plate. Thus, p is linearly proportional to T, and at each plate saturation exists. This situation produces a supersaturation profile, because the equilibrium vapor pressure P is nonlinearly dependent upon temperature. The shape of the supersaturation profile is approximately parabolic, with the maximum supersaturation occurring near the midplane of the chamber.

A test surface, whose critical supersaturation is to be measured, is in the form of a disk, which is about 1 mm thick and 6 mm diameter. This disk is called the target and is suspended vertically in the center of the chamber from a Teflon-coated wire, 0.25 mm diameter, that is stretched midway between the plates. The wire to one side of the target is copper, to the other side constantan, and at the target a copper-constantan thermocouple junction is formed. Calculations (Mahata, 1974) show that heat conduction along this target suspension wire can cause only a 5.8×10^{-4}°C average temperature difference between the target and the surrounding air.

The target is made of either glass or plastic, and for each material the thermal conductivity is high enough so that the Biot number is less than 0.1, indicating that the target can be assumed to be isothermal (Mahata, 1974). However, because the vapor pressure is higher near the top of the target than near the bottom, a slightly higher supersaturation is produced near the top. In order that this nonuniformity of supersaturation across the target be kept small compared with the average value, it is necessary that the target's diameter be small compared to the height of the chamber. It should be mentioned here that the supersaturations used in correlating the data (Table 1) are those at the top edge of the target (Mahata, 1974).

The proper operation of the chamber depends upon the avoidance of convection currents. Because of the large vertical dimension of the chamber, this avoidance is not easily achieved. It was found that, despite the fact that the plates were level to within 1° and isothermal to within 0.1°C, convection currents would appear if the sidewall temperature did not agree to within 0.2°C of the linear temperature profile within the chamber. To achieve this sidewall temperature control, it is necessary to have the sidewall in good thermal contact with the top plate and bottom plate of the chamber and well insulated from outside air. Because it is desirable that the top plate be removable, the temperature control of the sidewall is achieved by permanently attaching a separate water passage to the top of the sidewall.

The top and bottom plates of the chamber are made of aluminum, 2.5 cm thick and 107 cm diameter. The plate temperatures are controlled by passing water through 1 cm diameter copper tubing which is pressed into grooves machined into the outer surfaces of the plates. The sidewall is a clear plastic cylinder, 2 mm thick by 76 cm diameter, which is lined on the inside by 10 layers of 0.025 mm thick aluminum foil and insulated on the outside by a 15 cm thick layer of fiberglass insulation. The sidewall is permanently attached to the bottom plate by a large fillet of silastic rubber. The demountable seal with the top plate is achieved by pressure between the top plate and a soft

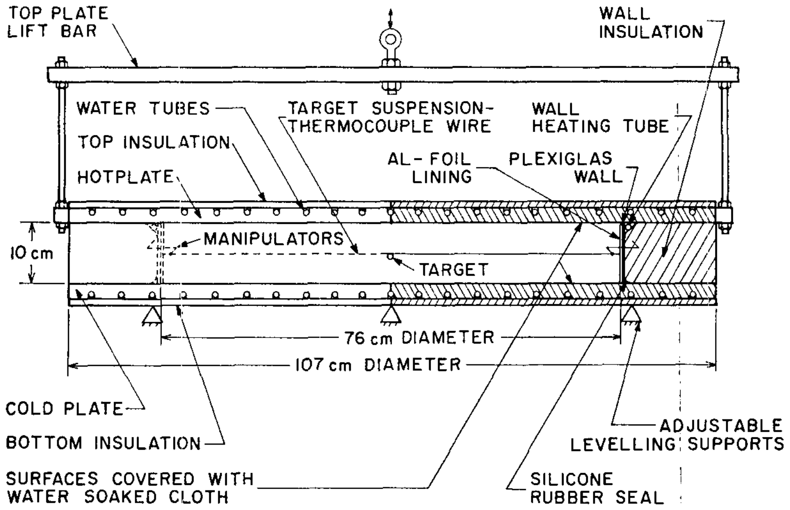

FIG. 1. The thermal diffusion chamber.

plastic tubing attached to the top of the sidewall by means of silastic rubber. Water flows through this plastic tubing as explained above.

For illumination of the target, a 3 mW He–Ne laser beam expanded to 2.5 cm diameter is directed horizontally through the chamber. It was found that this light source causes a target temperature rise of only 0.025°C, as measured by the target thermocouple. To observe the target, a 10-power telescope located outside the chamber is used. Windows for the telescope and laser were formed by removing sections of the fiberglass insulation and the aluminum foil.

To keep the top and bottom surfaces of the chamber wet, a cloth is attached to each surface with epoxy cement and is soaked with distilled water prior to each data run. In addition, the top surface is continually supplied with water while the chamber is in operation. This is achieved by a network of 0.5 mm diameter plastic tubes which are sandwiched between the top aluminum plate and the wet cloth. Water is forced through the 0.5 mm tubes and escapes through holes made by puncturing the tubing with a pin at about 5 cm intervals. Also sandwiched between the aluminum and the cloth are four thermocouples on the top plate and four thermocouples on the bottom plate.

There was some concern that a significant temperature difference might occur across the thickness of the wet cloths. Therefore, the temperature profile within the chamber was measured with the target thermocouple. This was moved up and down by means of manipulators that were located at each end of the suspension wire. The results of thus measuring the air temperature profile are shown in Fig. 2. The measurement of sidewall temperature is also shown. It can be seen that the temperature profile within the chamber and in the wall are linear and identical within the accuracy of the thermocouples.

The method used to check the chamber for convection currents was as follows. Room air was put into the chamber, and a supersaturation was formed so that water droplets could be seen in the chamber. The freely growing water drops fell quickly to the bottom of the chamber, but for a period of hours small haze droplets remained in the chamber and fell very slowly, at about 0.1 cm s^{-1}. These haze droplets were watched through the 10-power telescope. When they were observed to fall straight down, it was considered as proof that no convection currents were present in that part of the chamber. By using the above diagnostic test at numerous locations within the chamber, it was determined that when the sidewall temperature was properly controlled, no convection currents occurred.

3. Experimental procedure

The targets were first cleaned with a commercial glass cleaner, rinsed with distilled water, and finally dried by a 10-min exposure to a jet of dry clean air from a bottle. The glass targets were additionally

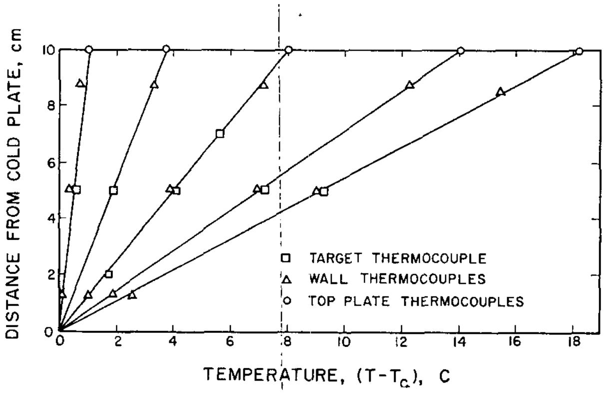

FIG. 2. Measured temperature distributions in the chamber.

decontaminated by being heated to 475°C in an oven and then cooled to room temperature. By controlling the duration of subsequent exposure of the glass targets to room air, any desired contact angle between 5° and 20° was obtained (Table 1).

The method of measuring the contact angle was as follows. A drop of distilled water from a microsyringe was placed upon the horizontal target surface. The volume of this sessile drop was about a microliter. The drop was viewed through a cathetometer telescope fitted with a protractor eyepiece, and the contact angle was measured by moving one of the radial lines on the eyepiece into tangency with the profile of the cap-shaped water drop. The contact angle thus measured is the advancing contact angle. To measure the receding contact angle, a small amount of water was removed from the same droplet by using the microsyringe. The measuring procedure with the telescope was then repeated. The measured values of both the advancing and receding contact angles are recorded in Table 1. In plotting the data (Fig. 3), the average contact angle was used, because nucleation is a statistical process in which an embryo experiences alternating shrinkage and growth.

The experimental procedure for operating the chamber was as follows. With the chamber open and both plates at a temperature of 23°C, distilled water was sprayed on the top and bottom cloths. The prepared target was then attached by means of a wire hoop to the horizontal suspension wire in the chamber. The top plate of the chamber was then lowered into place, and the chamber was flushed with bottled air for 15 min to remove all condensation nuclei. The temperature of the top plate was then raised at a rate of about 0.15°C min^{-1} for about 10 min. This rise period was then followed by a 5-min period in which the top plate temperature was held constant. The cycle was then repeated. It has been shown (Mahata, 1974) that the finite rise rate gives rise to only small errors in target supersaturation.

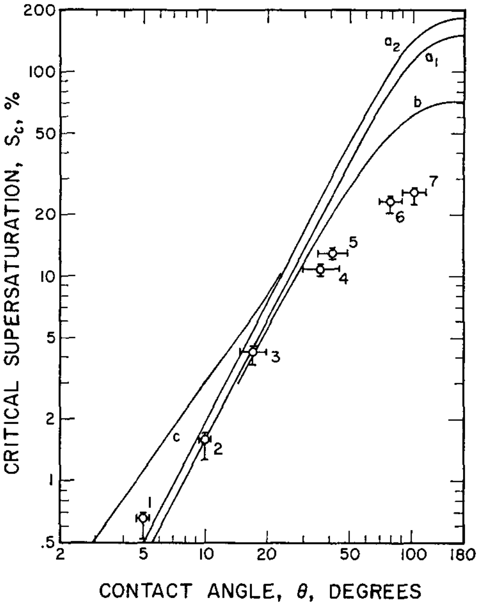

Fig. 3. Comparison of data with Volmer theory: a_1, a_2, effect of nucleation rate; b, effect of variable surface tension; c, effect of line tension.

Table 1. Experimental data for critical supersaturation.*

Target	θ (deg) Advancing	θ (deg) Receding	T_h-T_c (°C)	S_c (percent)
1. Decontaminated glass (shortly after heating to 475°C)	5	5	2.40	0.66
2. Glass after 9 h of exposure to room air	10	10	4.53	1.55
3. Glass after long exposure to room air	20	15	8.42	4.2
4. Plexiglas with thin oil film	45	30	15.0	10.5
5. Glass with thin oil film	50	35	16.5	12.5
6. Plexiglas (methyl methacrylate)	90	70	23.8	23.0
7. Wax coated on Plexiglas	115	90	24.8	25.0

* T_c=23C.

While the supersaturation was being raised on this cycle, the target was constantly observed through the telescope. When fogging of the target was observed, the critical supersaturation was reached, and the test was ended.

The above procedure was used in all tests in which critical supersaturation was determined. The procedures used for other tests are described separately.

4. Results for standard procedures

Table 1 gives the measured advancing and receding contact angles for each target. The two right-hand columns contain for each target the recorded temperature difference at which condensation occurred and the corresponding critical supersaturation. Targets 4 and 5 were each coated with a very thin layer of oil. The oil, supplied by Welch Scientific Company, is generally used in mechanical vacuum pumps. Target 7 was prepared by dipping a Plexiglas disk in molten wax and draining off the excess wax before it solidified.

The data from Table 1 are represented in Fig. 3 by flagged circles. The right and left extremes of the flags represent the advancing and receding contact angles, respectively, and the circles represent the average value of these angles. The vertical flags show

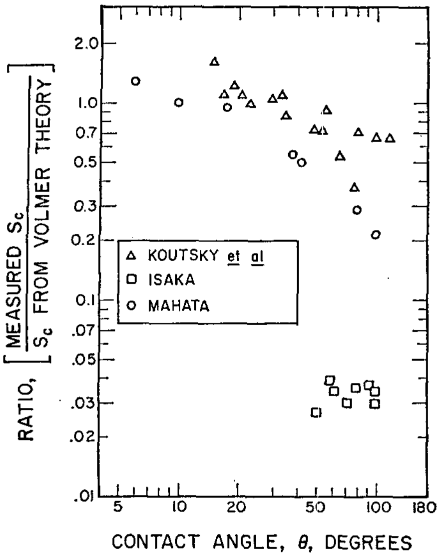

FIG. 4. Comparison of data with other experimental results.

the error limits on the supersaturation as calculated by Mahata (1974).

The Volmer theory predicts a relationship (Fletcher, 1966) between applied supersaturation and the resulting nucleation rate J. It is difficult to estimate precisely what nucleation rate corresponds to visible fogging of the target, but the rate surely lies between 1 and 10^8 cm^{-2} s^{-1}. In Fig. 3, curves a_1 and a_2 indicate the Volmer theory predictions for these respective nucleation rates and for the temperatures of our experiments. It should be pointed out here that whereas all of Twomey's data agreed with the Volmer theory, it can be seen from Fig. 3 that our data fall below the Volmer theory at high values of contact angle.

The data of Koutsky *et al.* and those of Isaka are not plotted in Fig. 3, because for our experiment the temperature rose as the contact angle increased, whereas in the case of Koutsky *et al.* it decreased. In the case of Isaka, the temperature remained constant. The plot shown in Fig. 4 overcomes this difficulty. The ordinate is the ratio of the measured S_c divided by the value of S_c given by the Volmer theory at $J=1$ cm^{-2} s^{-1} and for the measured contact angle shown on the abscissa. It can be seen that our data are somewhat below those of Koutsky *et al.* and far above those of Isaka. With regard to the measurements of Koutsky *et al.*, it is felt that vapor depletion, which resulted from early condensation on surfaces adjacent to their target, may have influenced their results. The very low values of S_c reported by Isaka may be due to the fact that he was studying ice nucleation rather than condensation.

In the curves a_1 and a_2 of Fig. 3, the surface tension is assumed not to depend upon the curvature of the cap-shaped embryo. Tolman (1949) provided a relation between surface tension and drop curvature. Curve b in Fig. 3 shows the effect of Tolman's relation upon the Volmer theory. Here the Kelvin equation (Fletcher, 1966) was used to relate radius of curvature of the embryo to the critical supersaturation.

Gretz (1966a, b) and Evans and Lane (1973) incorporated the effect of line tension into nucleation theory. This line tension acts along the periphery of the cap-shaped embryo. A value of 10^{-11} N, which Evans and Lane suggest is a conservative estimate, when used for this line tension, gives curve c in Fig. 3.

In summary, there are deviations between our data and the Volmer theory, even when various corrections are applied to the Volmer theory. The deficiencies of the Volmer theory that might account for these deviations have been frequently discussed [see, for example, Adamson (1967, p. 387) or Andres (1969)]. They stem chiefly from the fact that a partially macroscopic model is applied to nucleation clusters of relatively few molecules.

5. Experiments on water adsorption

To determine whether a slow process of water adsorption would eventually nullify the Volmer theory, target 3 (Table 1) was subjected for 10 h and target 6 for 20 h to a supersaturation of 0.75 S_c, of which S_c is the determined critical supersaturation. No condensation occurred on the surfaces of either target.

Because the time required for some chemical adsorption processes might exceed 24 h (Adamson, 1967, p. 569), we do not rule out the possibility that the Volmer theory might eventually be nullified by such a process. However, when atmospheric applications are considered, it is realistic to study the adsorption effect only in the lifetime of the natural nuclei in the atmosphere. Twomey and Wojciechowski (1969) have estimated the lifetime to be approximately 1–3 days. Because the exposure time in our investigation is of the order of the estimated lifetime, we conclude that naturally occurring insoluble nuclei are not likely to become wettable by adsorption of water vapor.

6. Experiments on surface roughness

For this study, the surfaces of two targets were roughened by the methods described below, and critical supersaturations on them were then obtained by using the procedure described in Section 3. Target 3 was sand-blasted with spherical beads of size 0.043 mm diameter at a pressure of 2.76 kg cm^{-2} for about 30 s. The sand blasting operation chipped off tiny pieces of glass at random from the glass surfaces and produced small pits. The number of such pits was found to be about 10 mm^{-2}. The target was then cleaned, as described earlier, and exposed for 48 h to room air. In determining the critical supersaturation, it was found that condensation occurred at 4% supersaturation on the rough surface as compared to 4.2% on the smooth surface (Table 1).

Target 6 was roughened by a silicone carbide abrasive paper, which was supplied by the Carborundum Company. The standard grid size of the abrasive is 200 (per inch basis), which amounts to a grain size of about 0.10–0.12 mm. The target's surfaces were rubbed by the abrasive paper in perpendicular directions. After cleaning in the usual manner, the target was inserted into the chamber. The critical supersaturation was found to be 21% as compared to 23% for the smooth surface (Table 1). In both the above tests, there was a reduction in S_c as a result of surface roughness, but the value of the reduction was small.

7. Theoretical investigation of surface roughness

Any scratch or pit on a surface constitutes surface roughness. Such a scratch or pit has a rounded concave bottom and a minimum radius of curvature. Mahata (1974) performed an analysis for nucleation on such concave surfaces. The analysis is similar to that of Fletcher's (1958) for convex surfaces. Because the details of the analysis are given in the thesis by Mahata (1974), only the results are given here.

The ordinate of Fig. 5 shows the critical supersaturation of a concave surface having the radius of curvature R shown on the abscissa. The various curves are for the indicated value of θ, the contact angle the substrate would exhibit if it were flat As expected, the effect of negative curvature is opposite to that of positive curvature as studied by Fletcher. Thus, as the value of R decreases, the effect is to decrease S_c.

Fig. 5 is based upon a model that treats the solid substrate as a continuum. Because surface roughness is also a continuum, macroscopic concept, both Fig. 5 and the concept of surface roughness are expected to become invalid at some minimum value of R. For example, it seems meaningless to speak of a scratch having a 10 Å radius of curvature in a solid such as iron, which has a bond length of about 2.5 Å. It is difficult to say at what minimum value of R the concept of surface roughness becomes invalid. We rather arbitrarily take it to be 100 Å.

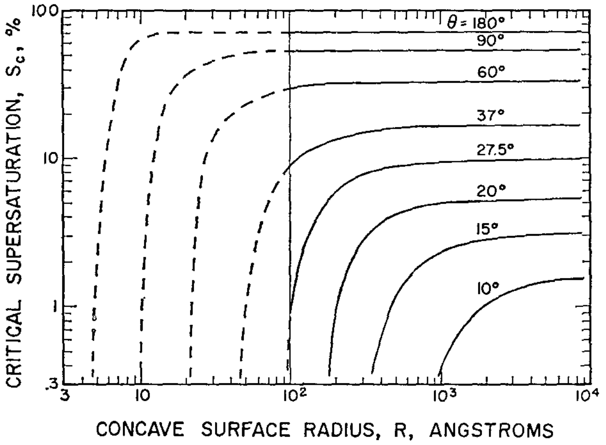

FIG. 5. Effect of surface roughness on critical supersaturation.

Based on the 100 Å cutoff, the question of whether insoluble particles can act as cloud condensation nuclei is again considered. McDonald (1964) set the maximum contact angle for this to be 7°, whereas Fig. 5 indicates that with the effect of surface roughness a particle could have a contact angle as large as 27.5° and still have $S_c < 1\%$. If one considers how many materials have a contact angle $<27.5°$, the list is still small. Thus, we have shown that neither surface roughness nor adsorption of water is likely to allow many insoluble particles to act as cloud condensation nuclei.

8. Conclusions

The behavior of the surfaces tested is in qualitative agreement with the Volmer theory; however, for surfaces with air-water contact angles larger than 20°, the experimentally determined values of critical supersaturation S_c are below those given by Volmer theory. The deviation between theory and experiment increases with increasing contact angle.

It was found that when the applied supersaturation is less than S_c, condensation is avoided for periods as long as 20 h. Thus, if adsorption of water vapor tends to negate the Volmer theory, the process is a slow one.

It was determined both by experiment and by theoretical analysis that the effect of surface roughness is to decrease S_c only slightly.

These results suggest that very few insoluble airborne particles are likely to serve as cloud condensation nuclei.

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