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SPONTANEOUS DROPLET NUCLEATION
IN CLEAN, SATURATED MOIST AIR
AT ATMOSPHERIC PRESSURE

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Steaming (droplet formation) above the surface of liquid water that is being heated can first be observed at 50 °C under normal atmospheric conditions. The droplets have been presumed by previous observers to form on condensation nuclei that are always present due to impurities in atmospheric air. But simple experiments, reported here, show that droplet nucleation apparently can occur spontaneously with warming, beginning at about 50 °C, even in purified saturated air at atmospheric pressure that is free of nuclei other than water clusters. The observations suggest new ideas about structure in water vapor. A critical cluster size of about 45 molecules can explain observations over a wide range of temperatures and water vapor partial pressures.

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PREFACE

The work described in this report was authorized under Project No. 1L161101A91A, In-House Laboratory Independent Research (ILIR), and was conducted from January 1979 through September 1982. In this report, the work was extended and prepared for publication under a U.S. Secretary of the Army Research Fellowship performed by the author between May 1986 and May 1987 at the University of Manchester Institute of Science and Technology (UMIST), Manchester, England.

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SPONTANEOUS DROPLET NUCLEATION IN CLEAN, SATURATED MOIST AIR AT ATMOSPHERIC PRESSURE

1.   INTRODUCTION

Research results reported here suggest that traditional views of water vapor overlook structure in water vapor and in moist air that is significant at levels affecting vapor phenomena including nucleation and atmospheric electricity. Molecular structuring, taking the form of distributions of large polymers or "clusters" of water molecules (monomers) in the vapor phase, is a phenomenon from which no sample can ever be rendered completely free, regardless, for example, of the cleanliness of an experimental apparatus. The observation of such structure in a clean apparatus is remarkable. The implications of these observations in water vapor impact the interpretation of previous theories and traditional views. Such structure in water vapor is shown here to explain recent experimental observations that otherwise cannot be adequately explained.

2.   EXPERIMENTAL PROCEDURE AND RESULTS

The experimental set-up is shown in Figure 1. A 500 ml clear glass Erlenmeyer flask containing a 7 cm depth (approximately 350 cm^3) of liquid water and a Teflon-coated magnetic stirring rod was placed on a hotplate with continuously adjustable heat and stirrer controls.
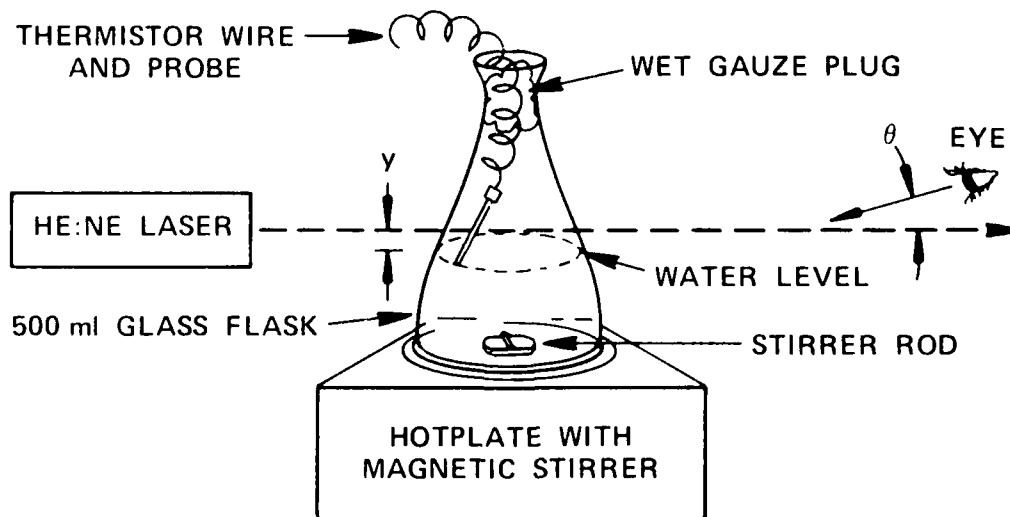

Figure 1.   Experimental Set-Up.

The flask was stoppered with a wet gauze plug through which passed a fine wire attached to a thermistor probe that was immersed below the surface of the water in the flask. The wet gauze plug allowed atmospheric pressure to be maintained within the flask but prevented room air impurities that could serve as condensation nuclei from entering the moist air volume of the flask, in keeping with accepted principles of cloud chamber technique.[1]

A 0.95 mW He:Ne laser (Spectra-Physics Model 155) was optically aligned through the diameter of the flask at a height $y = 1$ cm above the liquid water surface, where it traversed an optical path length of 7 cm (see Figure 1). Forward-scattered red laser light was observed by the unaided eye at an angle of approximately $4°$. The stirring rod was used only when agitation of the water in the flask was required before an experiment, for example to wash down the flask walls to aid in the removal of precipitated impurities from the vapor prior to making experimental observations. During the actual observations, the water in the flask was kept perfectly still.

Experimental observations were taken by viewing the red laser beam as the water was allowed to cool slowly after first being heated to near the boiling point, after which the flask was placed on an insulated mat. This procedure insured that saturation of the water vapor in the moist air was maintained during cooling, and very uniform temperatures could be maintained in the flask under these conditions.

Droplets formed in the laser beam at fairly steady rates, although sometimes they appeared as bursts punctuated by periods of a few seconds during which comparatively few were seen. The droplets appeared as randomly-spaced bright dots or streaks of red light, moving in all directions, the numbers of which per cm of beam per second could be crudely estimated especially at lower droplet populations. Since the laser beam cross-section was about 1 mm^2, the droplet nucleation rates in droplets cm^{-3} sec^{-1} could be estimated by multiplying the count per cm of beam per second by 100. Occasionally a droplet would pass along the axis of the laser beam where its velocity could be estimated at 1-2 cm sec^{-1}, corresponding to a droplet size of a few tenths of a micrometer.

Results for water samples kept in the flask for several days were repeatable, giving a further indication that the droplets were not nucleated by impurity nuclei in the moist air volume in the flask. The estimated nucleation rates were not sensitive to laser beam alignment through the flask. That is, beam alignments other than $y = 1$ in Figure 1 gave the same results, indicating that droplet nucleation rates throughout the moist air volume in the flask were uniform, and that significant density or temperature gradients due to convection did not exist inside the flask.

In a typical experiment the flask, after being thoroughly agitated, heated to near the boiling point, and allowed to sit undisturbed for several minutes, began to cool slowly. The first observation was made at time zero, when the temperature of the flask was measured with the thermistor and the droplet nucleation rate was estimated. Some data are shown in the table.

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Table.   Experimental Data

Elapsed Time (min)	Water Temperature (^{o}C)	Estimated Droplet Nucleation Rate (droplets cm^{-3} sec^{-1})	Remarks
0	93	100-200	Flask cooling down (s = 1)
16	84	approx. 100	
56	69	less than 100	
110	57	approx. 50	
115	55	less than 50	
123	53	approx. 20	
139	51	approx. 10	End point (no steaming) varies from about 44 to 50 ^{o}C, average is 47 ^{o}C, conservative value is 50 ^{o}C
170	44	approx. 0	

3.   DISCUSSION

When moist air samples at atmospheric pressure near the boiling point are sampled into a mass spectrometer, water ion spectra like those shown in Figure 2 are obtained readily[2,3]. Other researchers have obtained similar spectra.[4] One interpretation of these spectra is that soft radiation, for example beta radiation used at the spectrometer inlet orifice, enhances the dissociation of size distributions of large, uncharged clusters of water molecules that are already present in the moist air, into ions like the $H^{+}(H_2O)_c$ species shown here, where c is the number of water molecules comprising a water ion cluster. Another interpretation is that ions formed by irradiation of the vapor are "swarmed" by water molecules (monomers) to produce the water ions whose spectra are measured. Large water ions such as these are well-known atmospheric constituents.[5]

Whatever the formation mechanism of the water ion clusters of different "size," c, observed by mass spectrometry, their size distributions are found to be sensitive to water vapor partial pressure at constant temperature (as shown in Figure 2) and also to temperature (as shown by measurements at constant water vapor partial pressure),[3] according to the following empirical relationship:

$$c = (sp^0)^{1/2} \exp (1919/T - 4.655) \tag{1}$$

in which c is the most likely cluster size or mean size of the measured cluster distribution at temperature T (^{o}K), where p^0 is the saturation vapor pressure of water (mm Hg, or Torr) and s is the saturation ratio (%RH/100) in the moist air sample, i.e., the fractional relative humidity.
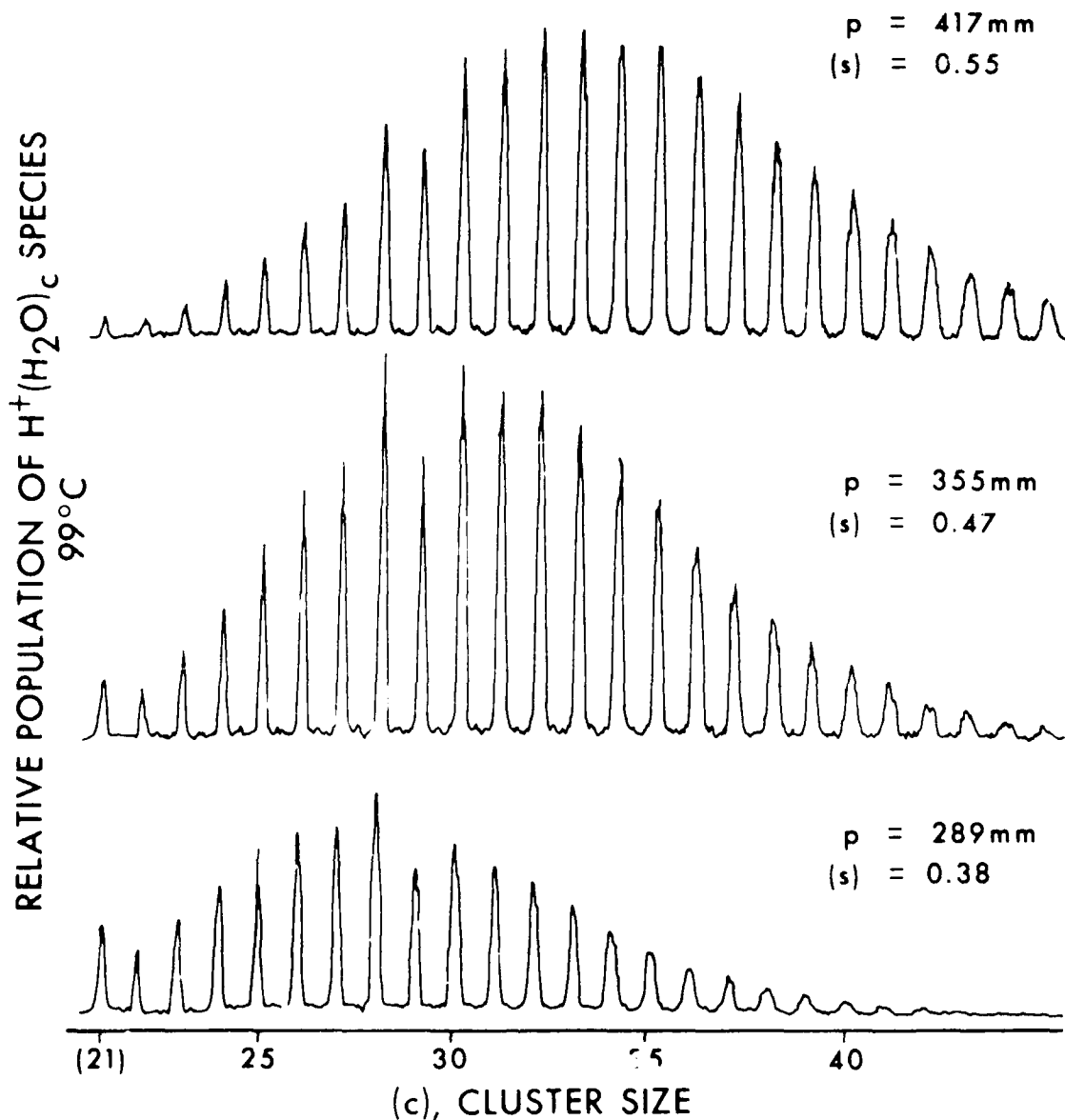
Figure 2. Mass Spectra for Constant Temperature and Varying Water Vapor Partial Pressure in Air at 1 Atmosphere, 99 °C

Since the measured cluster size distributions are near-Gaussian, the mean size of the distribution is the most stable cluster size for those particular conditions under which a given mass spectrum was taken.

In measurements of the spectra in Figure 2 and related spectra, it was found that when s was greater than 0.55 at 99-100 °C the distributions remained smooth to the left of the mean but began to deteriorate very badly to the right of the mean for cluster sizes greater than about c = 45. One interpretation of these results was that clusters reaching a size of about c = 45 were able to nucleate "spontaneously" into droplets in moist air that was approaching saturation (s = 1).

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That is, they could nucleate or condense droplets upon themselves without the need for large, conventional condensation nuclei to be present. Common atmospheric observations of nucleation, such as the steaming of water that begins at about 50 °C as the liquid is heated, have been presumed by previous observers to be explicable as droplet condensation on impurity nuclei that are always present in atmospheric air. Thus considerable caution was taken in arriving at the interpretations presented in this report.

Given that some population of large, uncharged or charged water cluster species like $H^+(H_2O)_c$ (Figure 2) is present in any moist air sample, it is straightforward to show schematically how they would respond to changes in temperature or water vapor partial pressure. If the deviation in water vapor density from the Ideal Gas Law were due solely to these large clusters, then the cluster fraction in the vapor could be calculated and a figure like, for example, Figure 3 could be constructed using standard tables for the saturation vapor pressure of water versus temperature.

In Figure 3, the saturation ratio, s, is the abscissa and the relative cluster fraction or population in the vapor is the ordinate. Curves for several expected cluster sizes, c, are plotted from Equation 1 (negative slopes). Also shown in Figure 3 are near-horizontal dashed curves showing the loci of constant partial pressure from standard tables for two different water vapor samples, and a near-vertical dashed line connecting points on the T = 100 °C and s = 1 curves.

This latter dashed line intersects s = 1 at about 50 °C (actually, 47 °C), and its upper point represents the mean size of the cluster distribution shown at the top of Figure 2. This distribution also is shown in Figure 3 atop the 100 °C curve for which it was obtained. The region to the right of s = 1 in Figure 3 corresponds to the region of "supersaturation." The heavy curve which extends through the point 100 °C, s = 1 and into the "supersaturation" region can be approximated closely by the equation:

$$(s)^* = \frac{p^*}{p^o} = \frac{(c)^2}{p^o} \exp (9.31 - 3838/T) \tag{2}$$

(which follows directly from Equation 1) where $(s)^*$ is the critical saturation ratio for droplet nucleation, p^* is the critical water vapor partial pressure for this to occur at temperature T, and data are available from many experimenters to validate the equation, for example,[1] $(s)^* = 4.85$ for condensation on large uncharged nuclei at a final temperature after a cloud chamber expansion of T = 264 °K.

This point is shown in Figure 3 at the intersection of the curves for c = 45 from Equation 1 and -9 °C (264 °K) from Equation 2; the dashed curve (constructed from standard tables of water vapor partial pressure) also passing through the point indicates that this condition could be reached by expanding a cloud chamber adiabatically from the starting condition s = 1 at about 13 °C (286 °K).
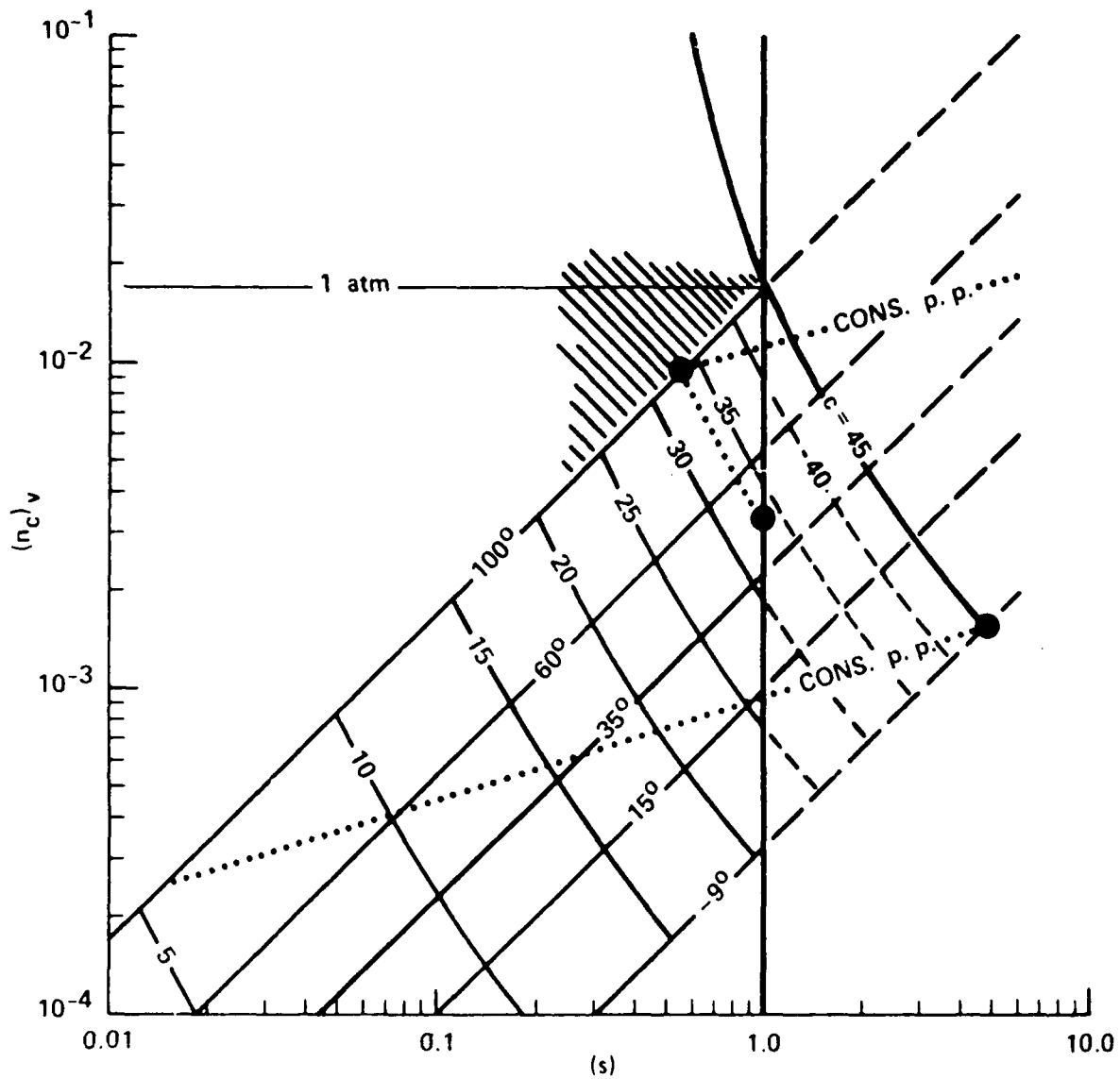
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Figure 3.   Relative Cluster Fraction or Population in the Vapor, $(n_c)_N$, and Cluster Size, c, From Equation (1).

Thus the surprising result is obtained that the curve for c = 45 in Figure 3 satisfies not only classical cloud chamber measurements at lower temperatures, but the condition for spontaneous droplet nucleation at

atmospheric pressure (without "supersaturation") for the largest cluster size (c = 45) of the distribution shown in Figures 3 and 2 (top) which is centered on a mean cluster size of about c_u = 33 for s = 0.55 at about 100 °C. That is, c = 45 would correspond to the cluster size of an incipient liquid water droplet, beginning to have the physical properties (surface tension, etc.) of the liquid phase. Note that the critical saturation curve falls to values of s less than unity as temperatures greater than 100 °C (and pressures greater than atmospheric) are attained.

All of these observations indicate that a cluster of size c = 45, or some size close to 45, is the critical cluster size to explain nucleation in water vapor over a wide range of temperatures and partial pressures, i.e., (c^*) is approximately 45. This suggests that a cluster size, c, of approximately 45 corresponds to a clathrate-like structure that is liquid water for purposes of nucleation.

Thus the experimental observations reported here can be explained by the presence of large clusters like $H^+(H_2O)_c$ in water vapor or moist air, but they cannot be explained by conventional heterogeneous or homogeneous nucleation theories.[6] For purposes of convenient calculation near ambient temperatures in the atmosphere, Equation 2 can be given by an approximate form for $(s)^*$:

$$(s)^* = \frac{1}{p^0} \exp (16.82 - 3801/T). \tag{3}$$

Equation 3, when plotted, gives a curve resembling that of an equation derived from classical nucleation theory[1]:

$$\ln (s)^* = k(S/T)^{3/2} M/d \tag{4}$$

where S is the surface tension of water, M is its molecular weight and d is its liquid density, and the "constant" K is troublesome because in fact it changes with the other parameters. Presumably the conversion of terms and equations of the large-cluster theory presented here into equivalent free energy expressions and conventional homogeneous nucleation equations could show a compatibility between this new theory and observation. Electrical conductivity measurements of moist air[7] show that large water ions in direct proportion to temperature and humidity are present in water vapor.

The distributions (mass spectra) in Figure 2 show that as the water vapor saturation ratio (s) is increased, the clusters grow proportionately larger and the cluster distributions can be thought of as moving to the right. The physical interpretation of these observations is that when additional water vapor becomes available some quantity of it immediately associates with the clusters, thus causing them to "grow" to larger

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sizes that still maintain a similar near-Gaussian distribution shape. The saturation ratio can be increased either by adding water vapor and thus increasing partial pressure at a constant temperature, or by maintaining constant partial pressure and dropping the temperature, as in a cloud chamber adiabatic expansion event, for example.

In Figure 3, increasing water vapor partial pressure at constant temperature can be thought of as "sliding" the equilibrium cluster size distribution along a constant temperature line, e.g., sliding the distribution shown atop the 100 °C line there (centered on s = 0.55 corresponding to a mean cluster size, c_u, of about 33 as shown at the top of Figure 2) upward and to the right.

Adiabatic expansion can be thought of as sliding the distribution, which still follows the slope of the constant temperature curves, along the upper dashed, near-horizontal curve in Figure 3 labeled "CONS. p.p." (constant partial pressure). Both operations cause cluster sizes successively smaller than c = 45 to cross the solid curve for critical supersaturation (s^*, Equations 2 and 3), and thus they spontaneously nucleate.

Excess water vapor condensing on these new "droplets" grows them rapidly to sizes large enough for optical detection (if enough excess water vapor is present), or until the condition of "supersaturation" is removed and s is approximately unity. The rates of droplet nucleation are determined by the rate of increase in s, the amount of excess water vapor made available, and the shape of the cluster distribution to the right of the mean (since successively smaller clusters must be grown successively larger to reach the lower limit of optical detection).

The design of the experiments reported here required that saturated water vapor be maintained in a clean chamber at atmospheric pressure as the temperature was reduced from near the boiling point to near ambient temperature. These conditions correspond in Figure 3 to moving a point vertically down the s = 1.0 line beginning near 100 °C and ending below the point corresponding to 47 °C on this line.

One can consider the cluster distribution shown in Figure 3 as being slid to the right along the 100 °C curve to a point where its mean, c_u = 45, rests at s = 1 (it is questionable whether such conditions could ever be obtained in practice because of the resulting extent of nucleation; perhaps a value of s near 0.55 represents some sort of practical limit on s at the atmospheric boiling point).

Now consider that this distribution, still with its mean at s = 1, slowly descends the s = 1 line. This results in successively fewer large cluster sizes in the distribution attaining the critical saturation condition (s* curve) at a value of c near 45 as the temperature decreases. When the temperature has fallen to about 47 °C (shown by the point on the vertical s = 1 line), the cluster distribution has a mean size c_u of about 33, which is the same c_u as that for the distribution shown in Figure 3 centered at the point s = 0.55 on the 100 °C curve. These points are connected by a short dashed line to indicate that the cluster size is the same. Thus at 47 °C, spontaneous droplet nucleation just occurs since the largest clusters in the distribution just correspond to the critical size for nucleation, i.e., a value of c^* near 45.

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As the temperature of the saturated vapor continues to fall below 47 °C on the s = 1 line in Figure 3, even the largest-sized clusters in the distribution fail to attain the critical size of approximately $c^* = 45$. Thus, spontaneous nucleation (steaming) ceases abruptly at about this point. This was exactly the observation in the experiments discussed here.

The cluster size distributions can grow to accomodate the excess water vapor within the vapor volume, thus tending to keep the saturation ratio near s = 1.0. These equilibrium distributions can be retained until something happens to change the equilibrium, and this can include the addition of more water vapor sufficient to cause nucleation.

It is easy to show that physical limits exist on the number of droplets that can be grown to sizes for optical detection using a given sample of water vapor in a cloud chamber.[8] Interestingly, these limits prevent more than 10^8-10^9 droplets cm^{-3} from being detected. Thus only a very small fraction of large clusters- on the order of 10^{-8} -need exist in water vapor to spontaneously nucleate all of the vapor present to droplets reaching the physical limits of optical detection given that sufficient excess water vapor is available to attain the critical cluster size of approximately $c^* = 45$.

This excess vapor can be made available by subjecting saturated water vapor to a lower temperature, as in an adiabatic expansion cloud chamber. What is indicated here, then, at least for the unique case of water, is an appealing adjunct to existing nucleation theory[6] which holds that the critical cluster size, c^*, varies widely depending on the thermodynamic state of the vapor.

Instead, the new theory indicates that a single, critical cluster size of about $c^* = 45$ corresponds to the actual physical state of water-substance at its phase transition from the clustered vapor to liquid droplets over the full range of temperatures and partial pressures for which these phases exist together. Thus $c^* = 45$, or a critical size near 45, must correspond to a specific clathrate-like structure that is incipient liquid water, just as, for example, incipient ice commonly attains a hexagonal lattice structure. Identifiable bulk liquid properties such as surface tension would first appear in the "$c^* = 45$" clathrate, suggesting that it would have a near-spherical configuration.

4.   CONCLUSIONS

The experimental results reported here indicate that:

●   Spontaneous droplet nucleation occurs in clean moist air at atmospheric pressure, saturated with water vapor as the temperature is raised above about 50 °C; common examples include the steaming of a domestic kettle, although impurity nuclei also play a role in the earth's unclean atmosphere.

●   A critical cluster size of $c^* = 45$, approximately, can explain nucleation in water vapor over a wide range of temperatures and partial pressures; a specific clathrate-like structure must be associated with this critical size.

●   Water vapor contains at least small fractions or populations
of large water clusters which exist in peaked statistical size distributions.

●   Figure 3 provides a useful tool for visualizing the dynamics
of large cluster distributions in water vapor or in moist air.

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