Reports

Millikan "Oil Drop" Stabilized by Growth

Abstract. *A diffusion cloud chamber has been used to qualitatively study some dynamic properties of liquid drops by suspending them in an electric field at the plane of saturation* ($p/p_s = 1$, *where* p *is the actual partial pressure of the vapor at a given elevation and* p_s *is the equilibrium pressure at that temperature characteristic of that elevation). By varying the strength of the electric field, it is possible to change the size of the suspended droplets and even, if desired, to isolate a single drop.*

We have succeeded in suspending liquid droplets in a diffusion cloud chamber by means of an electric field. The phenomenon was first observed accidentally in this laboratory by H. Reiss, R. H. Heist, and J. B. Fenn, Jr.; however, attempts to reproduce this configuration were unsuccessful for several years. At last we have been able to reproduce it at will, and this report describes our method as well as some numerical studies of the drop trajectories.

An understanding of the equilibrium and kinetic behavior of liquid drops is of critical importance to many technological processes including atmospheric phenomena (*1*). Aspects of this behavior that have yet to be fully explained include (i) the rates and mechanisms of growth and evaporation (*2*), (ii) diffusion, (iii) the coagulation of droplets (*3*), and (iv) thermodynamic phenomena affecting droplet stability. Procedures for studying individual drops have usually called for the suspension of macroscopic (millimeter range) drops from capillaries (*4*) or of submicron-sized drops in a Millikan oil drop apparatus (*5*).

Our technique for the stable suspension of drops in a diffusion cloud chamber can best be described as the Millikan "oil drop" apparatus stabilized by growth. We first observed the phenomenon accidentally while carrying out vapor-phase nucleation experiments with a diffusion cloud chamber (*6*). As shown in Fig. 1, the chamber consists of two parallel metal plates maintained at temperatures T_1 and T_2, respectively, with $T_2 < T_1$. A pool of "working fluid" (for example, water) rests on the lower plate. The space above the pool is filled with a light, inert gas such as He or H_2. The water evaporates from the pool on the lower plate, diffuses upward, condenses on the slightly beveled upper plate, and flows back down the walls of the chamber to the lower plate, leading to a steady state of supersaturation, p/p_s (where p is the actual partial pressure of water at a given elevation, and p_s is the equilibrium pressure at that temperature characteristic of that elevation). One can compute the dependence of supersaturation on elevation by solving the appropriate heat and mass flux equations (*6*).

In the above description the vapor is just saturated at the temperatures T_1 and T_2 which prevail at the lower and upper plates, respectively; that is, $p/p_s = 1$ on both plates. However, in an experiment with aqueous H_2SO_4 as the working fluid, the vapor is saturated at the upper plate but undersaturated at the lower plate as a result of the presence of the nonvolatile H_2SO_4 in the pool. This leads to a supersaturation curve similar to that shown in Fig. 2.

In their accidental discovery Reiss, Heist, and Fenn observed the formation of a stationary, plane layer of drops in the chamber at the saturation level. The drops were produced by effervescence at the lower plate (caused by the H_2SO_4 attacking imperfections in the protective gold surface of the plate) and hurled into the upper regions of the chamber where, because the vapor is supersaturated, droplets grow. The net force on the charged droplet consisted of upward components due to drag, buoyancy, and the electric field (which was used to sweep out ions that ordinarily serve as condensation nuclei) and a downward component due to gravity. Eventually, a droplet of the proper mass and charge settled at the plane of saturation. In principle, by varying the electric field it is possible to vary the size of the suspended droplet and study its static and dynamic properties. If the drop enters a region that is supersaturated, it will grow in size and consequently fall back to the plane of saturation. If the drop falls to a region that is undersaturated, it will evaporate and rise back up to the plane of saturation. This is the stabilizing principle of the experiment.

The diffusion cloud chamber used in these preliminary experiments with water and H_2SO_4 is very similar to those used in homogeneous nucleation studies (*6*). The chamber plates were coated with an acid-resistant gold plating to resist corrosion by the working fluid. After preliminary work with water and H_2SO_4, an aqueous H_3PO_4 solution was used as the working fluid since it has a significantly lower vapor pressure than pure water (*7*) and is less corrosive than H_2SO_4 solution. We used H_2 as the carrier gas so that the total density of the vapor–carrier gas mixture decreases from the bottom of the chamber to the top; in this way, it is possible to reduce convection. In order to maintain a constant electric field across the plates of the chamber, a lip was attached to the wall of the chamber. Water vapor condensed on the upper plate, ran down the walls to the lip, and fell to the lower pool. This prevented a steady stream of condensate from returning from the upper plate to the pool and thus shorting the field.

To produce the effervescence necessary to spew charged droplets up into the chamber, an iron wire was placed in the working fluid. This not only produced effervescence for a controlled amount of time but also made it possible to do experiments without destroying the lower plate, as had occurred in earlier experiments with H_2SO_4. In practice, it was more feasible to place the iron wire in the chamber first and then add the acid solution.

A 0.2-g ring of iron wire was found to react with a 50 to 60 percent H_3PO_4 solution for 10 minutes. The cloud of droplets produced by the effervescence quickly stabilized at 100 percent relative humidity ($p/p_s = 1$). Eventually the cloud formed a small cluster of drops in the center of the chamber. Drops were observed slightly above and below the saturation plane because of the mutual repulsion of the charged droplets and distortion in the vapor pressure distribution due to the presence of the drops.

By varying the strength and reversing the polarity of the field, we found it possible to sweep out some of the drops. It was also possible to continue this procedure until only a single drop remained.

A constant electric field is necessary in order for the plane of drops to remain stable; however, it is interesting to observe the behavior of the drops under the influence of small fluctuations in the field (an increase in the electric field strength of 700 V). This can occur either by conduction down the walls of the chamber or by a deliberate perturbation of the field. Under these conditions the plane of

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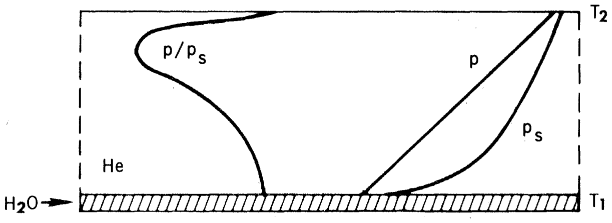

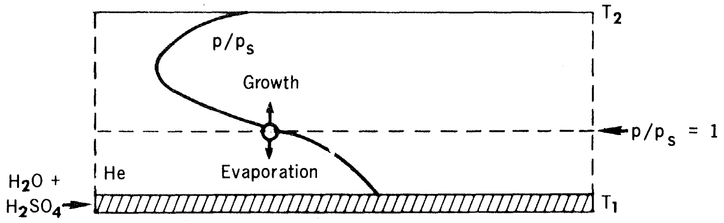

Fig. 1 (left). Dependence of partial pressures on elevation in the cloud chamber. For the various curves (p, p_s, and p/p_s), pressure is assumed to increase horizontally to the left; p is the actual partial pressure, p_s is the equilibrium vapor pressure, and p/p_s is the supersaturation. The relative humidity is given by $(p/p_s) \times 100$. Fig. 2 (right). A plot similar to Fig. 1, except that the working fluid is now aqueous H_2SO_4. Only the curve p/p_s is shown. Now the vapor is undersaturated at T_1, at the pool surface. The plane of saturation is shown as a horizontal dashed line. Droplets grow above this line and evaporate below it.

drops oscillates in a manner analogous to the vibrations of a membrane (the "membrane" vibrated only a few millimeters). For large perturbations, some of the drops will be lost either through collisions with the upper or lower plate or else will not be able to grow or evaporate rapidly enough to remain stable in the field.

When the field is increased (to a few thousand volts), the plane of drops breaks up and the center of the chamber becomes filled with a mist of rain droplets. This is similar to the effect observed by Dellicolli *et al.* (*8*), who reported that highly charged droplets suspended in a strong electric field would begin to deform, rotate, and explode when a minimal size was reached.

One problem affecting the stability of the chamber was the nature of the H_2 given off by the effervescence. When the H_2 concentration becomes large enough, a density inversion could occur in the vapor phase, leading to convection. In this case the cluster of drops is observed to rotate about a central axis.

We have observed (qualitatively) that by varying the strength of the electric field it is possible to cause a droplet to vary in size. For example, if the field is increased, the drop will rise; however, the region it enters is more saturated and thus the drop will grow in size. This in turn will cause the drop to fall and eventually after a few oscillations to settle back to the plane of saturation. Similarly, we can cause a drop to shrink by decreasing the strength of the field.

We have carried out an analysis involving the numerical simulation of the droplet dynamics. As in the Millikan experiment, the following relation applies

$$qE_0 = 4/3\pi r^3 g(\rho - \rho_0) \qquad (1)$$

where q is the charge on the drop, E_0 is the strength of the electric field, r is the drop radius, g is the acceleration of gravity, and ρ and ρ_0 are the densities of the drop medium and the vapor phase, respectively. In the cloud chamber experiments we must also take into account the small force due to the steady transport of vapor from the lower plate to the upper plate. Thus

$$qE_0 + 6\pi\eta_1 r v_0 = 4/3\pi r^3 \rho g \qquad (2)$$

where η_1 is the viscosity of water vapor and v_0 is the velocity of the vapor moving from the lower to the upper plate.

By varying the electric field, we can study the dynamics of growth of the drop. The force-balance equation along the z axis of the chamber (Eq. 2) now becomes

$$4/3\pi r^3 \rho \frac{d^2z}{dt^2} = qE(t) - 4/3\pi r^3 \rho g + 6\pi\eta_1 r v_0 + 6\pi\eta_2 r \frac{dz}{dt} \qquad (3)$$

where η_2 is the viscosity of the vapor phase (composed of He and H_2O).

Solution of this problem also requires the assumption of a law of growth for the drop. We can assume a kinetic growth scheme in which we find

$$\frac{dr}{dt} = \frac{(p - p_s)v}{\sqrt{2\pi mkT}} \qquad (4)$$

where v is the volume per molecule, m is the mass per molecule, T is the temperature at a given height (z), and k is Boltzmann's constant. We can also assume diffusion-controlled growth, in which case the growth law is

$$\frac{dr}{dt} = c\,\frac{D_{12}}{r}\,\frac{(p - p_s)}{T} \qquad (5)$$

where D_{12} is the binary diffusion coefficient (for H_2O and He) and c is a constant. With these assumptions we are able to see not only how the changing electric field affects droplet stability but also the effect of the growth law.

Solutions of these simultaneous equations (Eq. 3 with either Eq. 4 or Eq. 5) demonstrate that the droplet can be driven by the electric field but that the oscillations are unstable. For a sinusoidal field the drop will oscillate in resonance with the field; however, the amplitude of the oscillations will increase slowly until the drop either crashes into one of the plates or else enters a region in which the supersaturation is high enough and there is such rapid growth that the drop no longer responds rapidly enough to the field and is lost.

Since the experimental observations indicate that the drops are stable in the presence of an electric field, then either our assumed growth law (Eq. 5) is invalid or the numerical technique is not appropriate. We are investigating other techniques to explain the inappropriateness of the numerical technique. It may also be necessary to change the growth law, which would yield valuable information on the nature of the growth process of small drops.

The technique of suspending a stable plane of liquid droplets in a diffusion cloud chamber and, by varying the electric field which supports the drops, changing their size should prove very useful in the study of the dynamic properties of liquid drops.

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11 August 1978; revised 1 December 1978