Chapter I

1 Introduction

The general problem considered in this research is liquid containment at zero gravity. The specific problem is the effect of container geometry on the static and dynamic behavior of liquid free surfaces that are controlled primarily by surface-tension forces. Research on this problem at Caltech has been carried out from 1979 to 1990, with some interruptions. Because no other coherent and accessible record exists, a short account of the entire effort is given here, using material extracted from proposals and contract reports submitted by Caltech to NASA.

The foundations of the research were laid about 1974 by two mathematicians, Paul Concus (U.C. Berkeley/Lawrence Berkeley Laboratory) and Robert Finn (Stanford University). Their mathematical investigations (Concus and Finn 1974, Finn 1983) have led to several novel and important ideas about the configuration of static interfaces at zero gravity. In 1979, when NASA offered a prospect of space experiments, Concus and Finn enlisted Donald Coles (California Institute of Technology) as co-investigator to assist in design of a practical experiment. In 1981, when it became apparent that sophisticated optical instrumentation would play a central role in such an experiment, Lambertus Hesselink (Stanford University) became the fourth co-investigator. The research was supported through NASA Lewis Research Center as part of a program called Physics and Chemistry Experiments in space (PACE). This program was administered by the Office of Aeronautics and Space Technology (OAST) until 1984, when it was transferred to the Microgravity Science Applications Division in the Office of Space Science and Applications (OSSA).

The planning of a space experiment has several aspects that can interact strongly. First, a suitable geometry is required that embodies the critical mathematical conditions for existence or non-existence of a bounded solution surface. Second, the working liquid or liquids must be acceptable in terms of toxicity and flammability and also in terms of reproducibility of physical properties, especially contact angle. Third, some means is required for observing and measuring the position of the meniscus in three space dimensions and time. A rough division of responsibility was agreed on for the proposed space experiment. Geometry was primarily the responsibility of Concus and Finn. Materials were primarily the responsibility of Coles, aided by Frederick Fowkes (Lehigh University) as a consultant on questions of physical and surface chemistry. Instrumentation was primarily the responsibility of Hesselink.

2 Geometry

Some of the more recent work by Concus and Finn is outlined in chapter 4. This work considers a limited part of the general problem of liquid containment at zero gravity. The container is taken to be a cylinder of infinite length, and the liquid and its interface are taken to be at rest. The non-linear equation describing the interface position, and its boundary condition, are then well understood. A variational method is used to determine whether a static interface exists, in the sense that it occupies a finite length along the cylinder, or does not exist, in the sense that it extends to infinity. The cylinder cross-sectional shapes chosen for study all have one plane of symmetry and are all defined by two geometric parameters. Examples, in chronological order, are the trapezoid, the bathtub (a trapezoid with rounded ends) and the keyhole. They all show a discontinuous dependence of the shape of the interface on the boundary data, but not necessarily in a simple way. The trapezoid, in particular, has two acute corners and two obtuse corners, and it is possible for the interface to extend to infinity in the corners if the condition $\alpha + \gamma \leq \pi/2$ is satisfied (Concus and Finn 1974), where α is the half angle of the corner and γ is the contact angle. This mechanism acts for arbitrary values of gravity and is discussed pragmatically in the next section. However, at zero gravity the interface can also extend to infinity, when the local condition just stated is not satisfied, by responding to a quite different and more general global minimum-energy mechanism.

In general, the existence of a bounded interface depends critically on the contact angle and in a non-evident way on subtle variations in the shape of the container cross section. The liquid tends to occupy regions of higher wall curvature, with a sharp corner as a separate case. In fact, the recent development at UCB/Stanford of simple rules for existence or non-existence of a bounded capillary surface in a general cylindrical geometry was motivated in part by the observation at Caltech that contact angles greater than 45° are very difficult to achieve. For almost all of the liquid pairs studied so far, the internal contact angle is in the range from 7° to 20° . This finding essentially disqualifies the trapezoid geometry, because the corners will fill with liquid and interfere with observation of the global criterion for unboundedness. A difficulty with the bathtub geometry, given the contact angles just mentioned, is that only a small fraction of the cross sectional area, at most 5 to 10 percent, will be associated with the region of unbounded displacement. Hence only a small part of the finite test volume is associated with equilibrium configurations for the heavier fluid, and difficulties can be expected at the ends of the container when the critical state is passed. The question of geometry is to some extent still open.

For engineering and design purposes, some quantitative values for the critical condition to be satisfied for the three shapes already mentioned have been worked out in detail, as described in chapter 4. One issue that has evaded resolution is the need to vary the container geometry in flight, or to provide an array of containers covering a range of parameters on both sides of the critical configuration. A fourth shape, the eccentric cylinders, is therefore also studied because it allows at least one of the two geometric parameters to be varied continuously.

As one application of these design curves, a drop-tower test was carried out in 1986 in the 2-second tower at NASA Lewis Research Center. The geometry studied was a bathtub shape whose geometry was chosen to exceed the critical condition for small contact angles (23 degrees for 50% ethanol in water under air) and not to exceed it for large contact angles (56 degrees for 10% ethanol in water). The test was complicated by the poor quality of instrumentation supplied with the drop carriage, but led to some useful results that are described in chapter 3.

3 Materials

The shape of a capillary surface depends on container geometry, liquid density, apparent gravity, surface tension, and contact angle. The contact angle, which enters through the boundary condition for the governing equation, is usually assumed to be a property only of the materials involved. The contact angle is known to be sensitive to many factors, including temperature, surface roughness, composition of the third phase, contamination of the solid surface or the liquid volume, and direction of approach; i.e., whether the contact line is advancing, stationary, or receding. Hence it is not surprising that there is a substantial lack of agreement among various measured values for particular combinations of materials.

Even a brief study of the literature on contact angles (e.g., Fowkes 1964, Bikerman 1970, Dussan 1979) is discouraging. An initial effort at Caltech in 1980 therefore undertook development of a technique that is capable in principle of measuring contact angle accurately. This technique is not new, except that the instrumentation uses the refractive rather than the reflective properties of a free liquid surface and is nearly equivalent to the shadowgraph method commonly used in gas dynamics. The apparatus constructed for this purpose consisted of a glass-bottomed tank having a volume of about one liter, a means of partially submerging a glass plate at a known angle, and a source of parallel monochromatic light directed vertically downward on the contact region. The contact line was stationary, and a moving light detector under the tank recorded the pattern of refracted light in a direction normal to the contact line. The contact angle is measured as the rotation angle of the glass plate (from the horizontal) for which the refracted light has uniform intensity, indicating a flat liquid surface. The apparatus can be used with almost any combination of liquid and solid materials as long as both are transparent.

Figure 1 is the only available record of work with this original apparatus. The light source was a short-arc mercury lamp without reflector. An optical interference filter was used to isolate the green line at 0.5461 μm, and a lens and front-surface mirror were used to produce a parallel beam of light normal to the fluid surface. The liquid used in obtaining the figure was acetone, and the solid surface was a glass plate rotated about an axis near the contact line. No special precautions were taken to avoid contamination. The light detector was a laser power meter whose sensing element was masked to a pinhole aperture of diameter 0.02 cm and was traversed along a line below the glass bottom of the tank, about 10 cm below the contact line. The traverse was motorized and was equipped with a potentiometer to provide position information for the abscissa of figure 1. The total travel of the detector in the figure is 1.0 cm. The lowest trace in the figure is for the glass plate at 16.6 degrees from the horizontal. The other traces (slightly displaced for clarity) are for decrements of 1 degree from 16.6 to 1.6 degrees. Minor irregularities are caused by an unintended variation of traverse speed along the various traces. The contact angle is estimated to be about 7 degrees. The potential sensitivity of the method is probably a small fraction of a degree, although this sensitivity has by no means been achieved.

The report to NASA of this work says

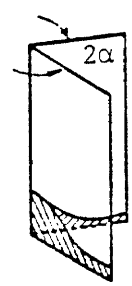
> "The results so far amount mostly to proof of principle. On the experimental side, several elements of the apparatus need improvement. A better approximation to a monochromatic high-density point light source is required. The spatial resolution at the detector could be improved by an order of magnitude by using a stationary photo-conducting array (such as a Reticon array), with the further advantage that an essentially instantaneous trace could be recorded over an interval in x of about 2 cm, thus allowing dynamic measurements of contact angle as a function of rate and direction of displacement for the contact line. For this purpose rotation of the glass plate needs to be automated and instrumented. Finally, it is desirable to minimize mechanical vibration, which causes annoying waves in the liquid surface. For best results, the apparatus should be mounted on a vibration-isolated table."

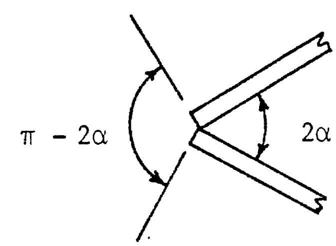
Implementation of these proposed improvements has taken ten years. The improved apparatus and some results are described in chapter 5.

Since the contact angle is a critical parameter in the present research, Concus and Finn in 1981 asked Coles to look at the feasibility of using their corner criterion (Concus and Finn 1974) to measure the contact angle. The corner criterion, valid with or without gravity, states that the height of an interface in a corner will be bounded or unbounded accordingly as

$$\alpha + \gamma > \frac{\pi}{2} \quad \text{or} \quad \alpha + \gamma \leq \frac{\pi}{2} \tag{1}$$

where α is half of the interior angle, as indicated in the first sketch, and γ is the contact angle measured in the liquid.





A Caltech undergraduate student, Minami Yoda, worked on this task during the summer of 1983 under the Caltech Summer Undergraduate Research Fellowship (SURF) program. Much of what follows is taken from her SURF report. The technique was to hold two microscope slides in contact at their corners, to insert one end of the slides in a petri dish containing the liquids, and to vary the angle between the slides while observing the meniscus. A mechanism for holding and rotating the slides about their line of contact was designed and constructed by Coles and functioned well. Two photographs of this mechanism are shown in figure 2. The angle between the two slides can be smoothly changed from 180° to about 20° ; i.e., contact angles from 0° to about 80° can be measured. The slides were placed with their lower ends in a petri dish (60 mm diameter, 15 mm deep) containing about ten ml of liquid. The view of the meniscus in the corner was typically magnified about thirty times by a binocular microscope.

All experiments were conducted in a fume hood to avoid contact with harmful vapors. Various methods were tried for cleaning the glass slides and were rated by the reproducibility of the contact-angle measurements. The method finally chosen was a three-minute ultrasonic bath in Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane). Similar trials were made for plexiglas, and the method chosen was washing in MS-260 (65% water, 5% 2-butoxyethanol, 30% various alcohols and additives).

About 100 liquids were tested. Hysteresis for advancing and receding contact lines was highly variable, ranging from 1° (1-bromobutane, several esters) to 25° (1-octanol), with most values in the range from 3° to 8° . Most liquids had mean contact angles on glass in the range from 5° to 15° . The observed contact angle for water on glass was about 35° . Some correlation was found between contact angle and chemical structure. Among the straight-chain alcohols (ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-octanol) and the straight-chain aldehydes (butanal, pentanal, heptanal), the contact angle both on glass and on plexiglas tended to increase with the number of carbon atoms in the chain. The contact angles on glass for the straight-chain ketones (2-propanone, 2-butanone, 3-pentanone, 2-octanone) were all in the range from 5.7° to 8.2° $\pm$ 20%. The glycols as a family had larger contact angles (10° to 27° on glass, 37° to 67° on plexiglas).

As with most new methods, this method had some problems. There was a conspicuous discontinuity in meniscus shape only for water, dibromomethane, benzyl formate, and butyl benzoate. The meniscus was hard to see for many liquids, no matter what lighting was tried, because the indices of refraction were close to those of glass or plexiglas. Some of the liquids, especially the glycols, are known to be hygroscopic. Their contact angles tended to decrease with time as the liquid absorbed more and more water. Some liquids were very viscous, and would not drain off the slides; examples are glycerin and triethylene glycol on glass. In fact, none of the liquids could be said to drain completely. The contact angle of a liquid could decrease significantly between the first and second readings because of wetting. The contact line was often very ragged, making it difficult to classify the profile. It was particularly difficult to estimate the contact angle for liquids with low boiling points, such as acetone or ethanol. As soon as the surface developed a sharp tip, it evaporated away. Many of the more volatile liquids would evaporate, condense on the slides a few millimeters above the contact line, and drip back down.

In view of these problems, the corner-angle method is considered at present to be a marginally usable method for measuring the contact angle. A measurement takes about ten minutes and requires about 10 ml of liquid, the solid material need not be transparent, and the method works best with liquids having a high index of refraction and a high boiling point. An apparently irreducible disadvantage of the geometry, illustrated in the second sketch, is that the criterion $\alpha + \gamma \leq \pi/2$ will always be exceeded for the rear corner before it is exceeded for the front corner, unless $\gamma > 45°$. Ideally, the two corners should be isolated by a seal, but no practical sealing method has been found. The technique is probably most useful for quick comparative tests such as determining the effect of impurities such as fluorescent dyes or the effect of a particular cleaning procedure. To improve the technique, the apparatus should be enclosed in a sealed enclosure, perhaps a glove box, so that evaporation and contamination can be controlled.

Another important interaction between the co-investigators occurred when preliminary work at Stanford on instrumentation of the proposed experiment suggested that there are important advantages in working with an internal meniscus between two liquids. A search was therefore made at Caltech to identify suitable immiscible transparent liquid pairs. No particular chemical expertise was on hand at the time, so a simplistic assumption was made that one liquid should be hydrophilic (examples are formamide and several glycols) and the other liquid should be hydrophobic (examples are brominated hydrocarbons, numerous esters, and a few alcohols and ketones).

The search, particularly for pairs that are compatible with plexiglas and perhaps other optical plastics, has also taken into account various other desirable physical and optical properties. These include low toxicity, optical clarity, chemical stability, closely matched refractive indices, low viscosity, compatibility with dye, and absence of permanent deposition of either liquid as droplets on the wall under the other liquid. Altogether, 110 candidate liquid pairs were identified, 76 of which are compatible with plexiglas. Several dozen pairs were found showing a close match in index of refraction, and a few pairs were found showing a close match in specific gravity. Two pairs had a good match in both (1,3-propanediol/diethyl maleate, and glycerol tributanoate/ethylene glycol). An optical estimate of internal contact angle on glass showed that this quantity was usually in the range from 8 to 15 degrees. Contact angles on plexiglas, where these could be measured, were usually considerably larger and were usually inverted; i.e., the interface was concave in the opposite sense to that found for glass. Details and results of this search are given in chapter 2.

4 Instrumentation

Work on optical instrumentation at Stanford began in 1982. Hesselink made a preliminary study of the relative complexity and sensitivity of various optical methods, including shadowgraphy, Schlieren photography, holography, direct or holographic interferometry, scattering, refraction, reflection, and laser-induced fluorescence. A corollary consideration was the recording means, whether photographic or electronic. Some elegant optical processing techniques were investigated for holographic records, and holographic images of a test cell were produced, but this method was eventually judged to be impractical. In the event, the method recommended in 1984 for further development was laser-induced fluorescence, using one or more sheets of laser light scanned through the volume of the fluid. Images viewed along the axis of the container were to be recorded electronically. On-board data processing, if used, would be limited to reduction of data volume by edge-detection algorithms. This method was shown to be capable of a resolution of about 0.01 cm in all three space dimensions, and thus capable in principle of determining the surface curvature and the contact angle as part of the experiment. The method could also be applied to dynamic measurements.

One consequence of these developments, as already mentioned, was almost to require use of an immiscible liquid pair rather than a single liquid in equilibrium with its vapor. Even for a two-liquid system, serious optical distortions can occur inside the container if the refractive indices are not well matched. For example, if the difference in refractive index is 0.01, total reflection will occur whenever light traveling through the optically denser liquid encounters the interface at a relative angle smaller than about 7° . There is therefore a conflict between the need for a close match in index for the flight experiment and the need for a sufficient mismatch in index so that the contact angle can be measured in the laboratory. Another consideration was that a suitable fluorescent dye should be soluble in one liquid of the pair but not in the other. A suitable dye was defined to be one capable of being excited by light from a solid-state laser diode, for obvious reasons of reliability of the optical instrumentation. In practice, this last consideration was found not to be a problem.

Other contributions to the research, mostly coming from Hesselink at Stanford, included ideas about the mechanical design of the flight apparatus. Small contact angles generally require containers of large aspect ratio if a substantial fraction of the fluid volume is to be associated with the critical region for which displacement is theoretically unbounded. The difficulty of managing stretched or distorted geometries needs to be weighed against the disadvantage of using liquids having larger contact angles but having less desirable and perhaps less reproducible physical and chemical properties. In order to operate on both sides of a critical condition, the geometry should be variable or the container should be tapered, either literally or figuratively (perhaps by a programmed change in temperature). In either event, the experiment must initially define one direction to be down. One method in space might be to mount several containers on a carousel to produce artificial gravity that can be slowly and carefully reduced to zero after the container is filled and the liquids are separated. A side benefit would be the opportunity to experiment over a wide range of Bond number. A disadvantage is potential conflict between the need for rotation and the needs imposed by whatever technique is chosen for optical instrumentation.

Several possible configurations for the apparatus have been explored to achieve the objectives of the experiment. The major differences are in the placement of the optical and electronic instrumentation. Maximum flexibility is achieved by placing the optical diagnostics on the carousel and by providing an independent scan mechanism. This flexibility is achieved at the expense of complexity. A mechanically simpler system would place the optical diagnostics on a stationary platform and use the rotation of the carousel to scan the liquid volume inside the container. However, the observation period is then slaved to the spin rate of the carousel. The scan rate is slowest when the body forces are small and the interface behavior is most interesting. Other problems concern the amount of data processing to be performed in space or on the ground after the flight, the influence of the space-vehicle environment on the design, and the probable effects of launch on the apparatus. None of these problems seems to be particularly difficult.

5 Other Interactions

Peer review of this research was part of several contract renewals. These reviews more than once raised the point that a space experiment might not be necessary if a liquid pair could be found with a sufficiently close match in specific gravity. Examination of the tables in chapter 2 suggests that a suitable pair might be, for example, glycerol tributanoate (specific gravity 1.035) and 1,2-propanediol (1.036), with the specific gravity of either adjustable by dilution with small amounts of a third liquid.

The existing theory stipulates a value of zero for the Bond number B, defined as

$$B = \frac{g \Delta\rho L^2}{\sigma} = \frac{g}{g_0} \frac{\Delta\rho}{\rho_0} \left[\frac{g_0 \rho_0 L^2}{\sigma} \right] \tag{2}$$

where g is apparent gravity, $\Delta\rho$ is difference in density, L is a characteristic scale of the apparatus, σ is surface tension, and the subscript 0 refers to terrestrial values. For a terrestrial experiment with a single liquid under its vapor, g/g_0 is unity and $\Delta\rho/\rho_0$ is close to unity. For a space experiment, g/g_0 can presumably be reduced to $O(10^{-4})$. To reach the same small Bond number on the ground, other things being equal, $\Delta\rho/\rho_0$ would have to be reduced to $O(10^{-4})$ by use of a suitable liquid pair. This value is beyond the ordinary limit of resolution in measurement of density for either liquid, and it implies that the temperature has to be very precisely controlled. Moreover, no method suggests itself for varying the Bond number substantially during such a terrestrial experiment. Small changes in Bond number, even including a change in sign, might be achieved if the temperature is controlled and the two liquids have sensibly different volume coefficients of expansion (whether or not this is the case for the liquid pair named above, or for other candidate liquid pairs, is not known at present). Because the characteristic thermal diffusion time will be of the order of minutes to hours, it is likely for any terrestrial experiment in which temperature is an independent variable that the same difficulties with density inhomogeneities and slow convection currents will be encountered that characterize several other experiments in the PACE program, particularly experiments aimed at quantitative study of critical-point phenomena. Experiments on earth might well turn out to be as complex and as expensive as experiments in space.

From the experimental point of view, it is another difficulty in the theory that the geometry and the contact angle are the primary data. In practice, it is the apparent gravity g that is at the disposal of the experimenter. Available evidence from recent numerical computations suggests that the striking surface behavior predicted for critical configurations can be observed even if the Bond number is not strictly zero. In order to achieve a more precise understanding of physical phenomena observed in a real apparatus, therefore, it was proposed to conduct the experiments with one or more systems that are demonstrably well behaved for non-zero Bond number but approach the limiting singular behavior as the Bond number approaches zero. This objective can be best achieved in space by control of g/g_0 through programmed imposition and removal of a body force associated with rotation. This procedure also provides an opportunity to observe any hysteresis as the direction of motion of the interface is reversed. The direction of rotation can itself be reversed if there is any reason to believe that the effects of angular acceleration are not negligible, or cannot be adequately compensated for by programming the orientation of the container.

In 1986, after the Challenger accident, a PACE science review board consisting almost entirely of physicists recommended that the present proposed experiment be dropped from the program. One of the reasons given was that the static mathematical theory is sound and also sufficiently complete so that space experiments are not needed. The investigators disagree sharply. They thought and still think that space experiments should be designed to produce accurate quantitative data on dynamic configurations of the internal interface. The analytical results at present are based on a static theory. They predict conditions under which a global change in the surface configuration must occur. The theory thus provides essential guidance on the question of geometry. However, presently available analytical results do not predict the dynamic nature of this change, and no such complete description is currently in sight. The equations considered so far amount to a boundary condition of constant surface curvature and constant contact angle for much more complex non-linear dynamic equations that apply when the fluid is moving. Moreover, the contact-angle boundary condition is then highly uncertain, since there exists no acceptable theory for conditions near a moving contact line. Even if no attempt is made in an experiment to observe the internal motion of the liquid, dynamic data on surface configuration can therefore provide a challenge to theory for a long time to come. In fact, the existence of such dynamic data at the end of a space experiment can be taken as a direct measure of success or failure. A corollary conclusion is that flight experiments in simulated free fall, or experiments in a drop tower, are unlikely to be successful in the sense just defined, because the necessary instrumentation probably could not be accommodated.

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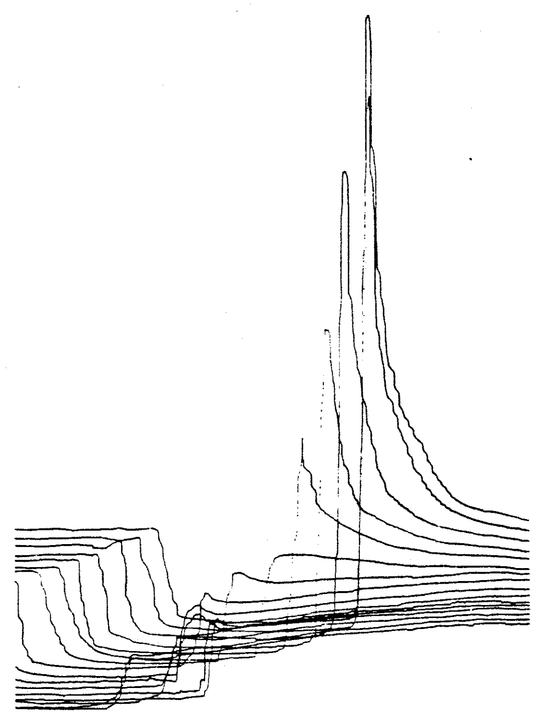
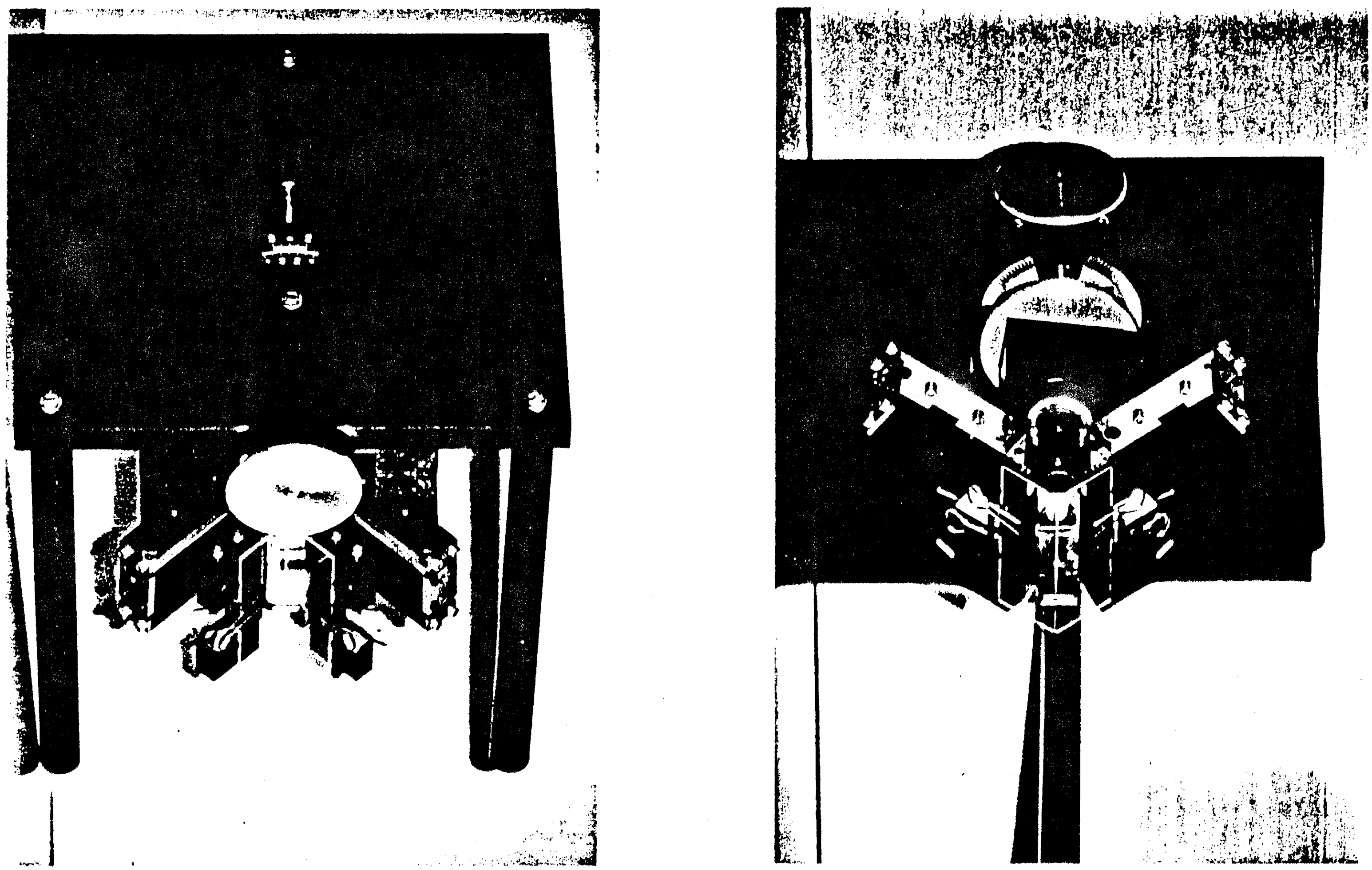


Figure 1. Measurement of the static contact angle of acetone on a glass plate by the refraction method. Horizontal coordinate is space; vertical coordinate is light intensity. Plate angle varies from 1.6 degrees (top trail) to 16.6 degrees (bottom trail).



Front/top view

Front/bottom view

Figure 2. Two views of the apparatus used to measure contact angle by application of the corner criterion of Concus and Finn (1974). (M. Yoda, private communication).