Title
On Accurate Determination of Contact Angle

Authors
Concus, P.
Finn, R.

Publication Date
1991-05-01

LBL-30497

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Physics Division

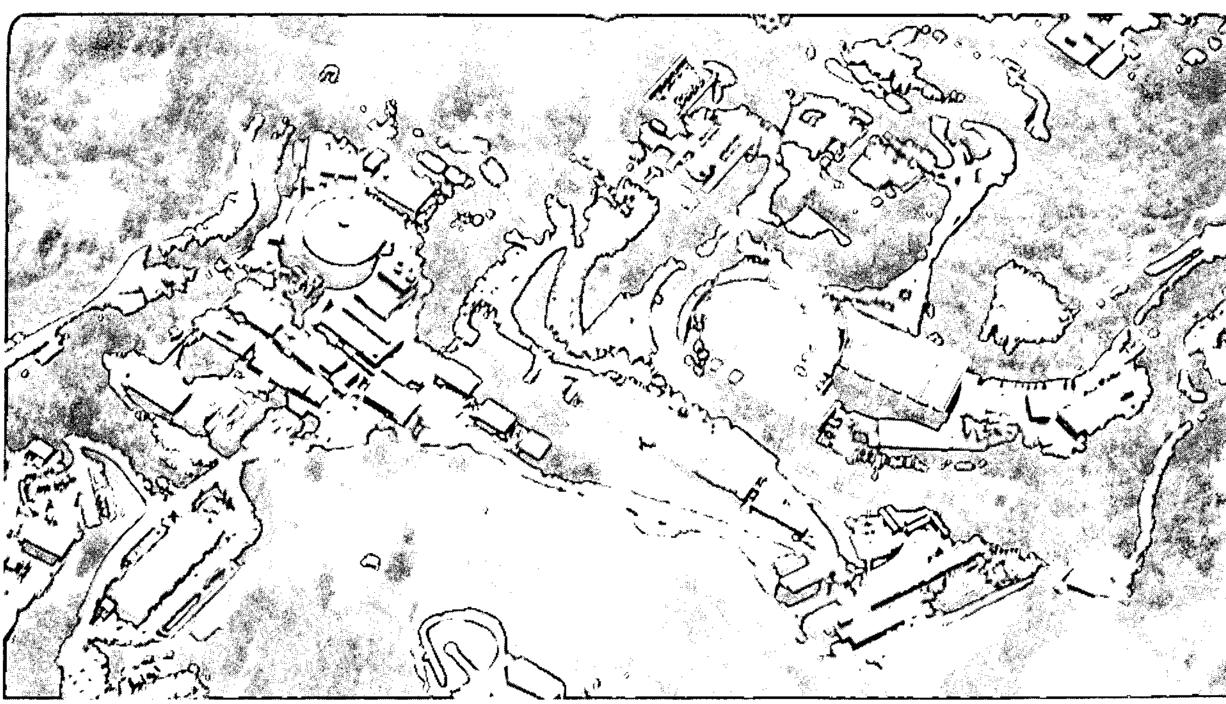
Mathematics Department

To be presented at the IUTAM Symposium on Microgravity Fluid Mechanics, Bremen, Germany, September 2–6, 1991, and to be published in the Proceedings

On Accurate Determination of Contact Angle

P. Concus and R. Finn

May 1991



Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

DISCLAIMER

LBL-30497

ON ACCURATE DETERMINATION OF CONTACT ANGLE*

Paul Concus
Lawrence Berkeley Laboratory
and
Department of Mathematics
University of California
Berkeley, California 94720

Robert Finn
Department of Mathematics
Stanford University
Stanford, California 94305

May 1991

To be presented at the
IUTAM Symposium on Microgravity Fluid Mechanics
Bremen, Germany
September 2–6, 1991
and to appear in the Proceedings

* This work was supported in part by the Mathematical Sciences Subprogram of the Office of Energy Research, U. S. Department of Energy, under Contract Number DE-AC03-76SF00098, by the National Aeronautics and Space Administration under Grant NAG3-1143, and by the National Science Foundation under Grant DMS89-02831.

ON ACCURATE DETERMINATION OF CONTACT ANGLE

Paul Concus and Robert Finn

Abstract

Methods are proposed that exploit a microgravity environment to obtain highly accurate measurement of contact angle. These methods, which are based on our earlier mathematical results, do not require detailed measurement of a liquid free-surface, as they incorporate discontinuous or nearly-discontinuous behavior of the liquid bulk in certain container geometries. Physical testing is planned in the forthcoming IML-2 space flight and in related preparatory ground-based experiments.

1. Introduction

Procedures for accurate determination of the contact angle formed between a liquid and a solid at a triple interface are developed, as an application of our general mathematical comparison principles for the equations describing capillary surfaces. Contact angles are notoriously difficult to measure, and differing procedures often lead to disparate results that are not easily reproducible. As a consequence of these difficulties, the intrinsic physical significance of an equilibrium contact angle has come into some question. Two microgravity experiments are under development for procedures that should lead to substantially improved accuracy in the respective ranges of applicability, and which we believe will shed some light on the question as to whether contact angle can properly be regarded as an intrinsic property of materials, as suggested by the classical Young-Gauss theory. Both procedures have the advantage of not requiring sophisticated instrumentation for measurements, as they depend on global instabilities (or near instabilities) that occur at values of experimental parameters corresponding to the contact angle to be measured.

The first procedure is based on a discontinuous behavior that occurs in a capillary tube whose section contains a corner. It is especially well adapted for contact angles γ between about 40° and 140°. The method can be applied whether or not gravity is present; however, observation of the discontinuity becomes more feasible, and accuracy improved correspondingly, by letting $g \to 0$.

For values of γ closer to 0° or 180° another procedure is proposed. It is based on behavior that can change very rapidly with contact angle, when g is small, although not discontinuously as above. Preliminary calculations indicate that very good accuracy should be expected; detailed confirmation will require more extensive computer calculations, which are currently being carried out for particular geometries.

2. First Method

2.1. Background. We suppose first that $g > 0$ (as in a capillary tube on the earth's surface), and $0 \leq \gamma < \frac{\pi}{2}$ (wetting liquid). We consider a vertical capillary tube, in an infinite reservoir, whose section Ω contains a wedge with opening angle 2α. We introduce a disk B_δ such that the shaded region shown in Fig. 1 lies in Ω. Let $\Delta\rho$ = density change across interface, σ = surface tension, $\kappa = g\Delta\rho/\sigma$. It is shown in [1] (see also [4] Chapter 5) that if $\alpha + \gamma \geq \frac{\pi}{2}$ then the height $u(x,y)$ of the free surface interface relative to the reservoir satisfies

$$0 < u < \frac{2}{\kappa\delta} + \delta \tag{1}$$

throughout the shaded region.

However, if $\alpha + \gamma < \frac{\pi}{2}$ then we set $k = \sin\alpha/\cos\gamma$ and find the asymptotic relation

$$u \simeq \frac{\cos\theta - \sqrt{k^2 - \sin^2\theta}}{k\kappa r} \tag{2}$$

(see Fig. 1) as $r \to 0$.

Note that (1) gives a bound that holds for all $\alpha \geq \frac{\pi}{2} - \gamma$. It does *not* depend on α in this range. Thus, if we let α decrease to $\frac{\pi}{2} - \gamma$ from larger values, the fluid height stays uniformly bounded throughout the shaded region and does not tend to infinity, even at the vertex. But according to (2), as soon as $\alpha < \frac{\pi}{2} - \gamma$ then $u \to \infty$ at P. Thus, the behavior changes discontinuously as α moves across the critical value $\frac{\pi}{2} - \gamma$.

2.2. An Example. Consider Ω as above, water in the earth's gravity field ($\kappa \approx \frac{400}{13}$), and $\delta = 0,5$ cm. Then

$$u < \frac{4 \cdot 13}{400} + \frac{1}{2} \approx 0,6 \text{ cm}$$

holds if $\alpha + \gamma \geq \frac{\pi}{2}$; but $u \to \infty$ if $\alpha < \frac{\pi}{2} - \gamma$. Thus, by changing α a fraction of a degree, the rise height can be made to jump from less than about 0,6 cm to infinity. Presumably, the jump could be observed optically or with laser beams, or by placing an electrode into the corner above the critical height. The difficulty with such an approach is that unless γ is reasonably close to $\pi/2$, the jump will be restricted to an extremely small neighborhood of P, and correspondingly measurements will be significantly affected by hysteresis, evaporation from the interface, imprecision of the corner, and irregularities in the solid surface. We thus consider a modified approach.

2.3. Planned Experiment. Consider a capillary tube whose section Ω is that of a "near rhombus", with opposite half-angles $\alpha_1 < \alpha_2 < \pi/4$ and boundary Σ, as indicated in Fig. 2. Let

Z denote the vertical cylinder over Ω, closed at the base. For gravity $g > 0$, consider the capillary surface $u(x, y; g)$, with contact angle γ, obtained by introducing a volume V of fluid into Z. It can be shown that if V is large enough so that the left side of (3) is positive, and if $\alpha_1 + \gamma \geq \pi/2$, then

$$\frac{V}{|\Omega|} - \frac{\delta}{\cos\gamma}\left(1 - \frac{\sqrt{k_1{}^2 - 1}}{k_1}\right) < u(x.y;\gamma) < \frac{V}{|\Omega|} + \frac{\delta}{\cos\gamma}\left(1 - \frac{\sqrt{k_1{}^2 - 1}}{k_1}\right) \tag{3}$$

throughout Ω. Here $k_1 = \sin\alpha_1/\cos\gamma$, δ = radius of inscribed circle, and $|\Omega|$ denotes the area of Ω. *This estimate holds regardless of* g. Further, there holds

$$\lim_{g \to 0} u(x, y; g) = v(x, y), \tag{4}$$

where $v(x, y)$ is the lower hemisphere of radius $\delta/\cos\gamma$ concentric with the inscribed circle and at a height such that the volume bounded over Ω is V.

Thus, if $\alpha_1 + \gamma \geq \pi/2$ the fluid stays bounded above *and* below and tends to a known spherical cap as $g \to 0$. But if $\alpha_1 + \gamma < \pi/2$, and $\alpha_2 + \gamma \geq \pi/2$, then the fluid moves into the smaller corner and forms, in an asymptotic sense, a section as shown in Fig. 3, with $R = \frac{|\Omega|}{|\Sigma|\cos\gamma}$. The area of any such section with opening half-angle α is

$$A = R^2\{\cos^2(\alpha + \gamma)\cot\alpha + \cos(\alpha + \gamma)\sin(\alpha + \gamma) - \pi/2 + \alpha + \gamma\} > 0, \tag{5}$$

and thus if the height of Z is large enough, the base Ω will become partly uncovered with decreasing gravity, the fluid moving into the smaller corner. Thus, instead of looking for the highest fluid point at the vertex P, it is better to look for the lowest point, which occurs at a known height over the center O of the inscribed circle when $g = 0$ and $\alpha_1 + \gamma \geq \pi/2$, and is thus easily accessible. The discontinuous change when $\alpha_1 + \gamma$ decreases past $\pi/2$, in conjunction with an observation of the direction of motion of the fluid (away from the larger corner and toward the smaller one), should lead to an extremely sensitive contact angle measurement without detailed measurements of the fluid free-surface in the range $\gamma > 45°$ that is admissible in the construction.

If $\gamma \leq 45°$ the above construction is not feasible, as the existence criterion will fail for the upper and lower corners. We may however replace it by the configuration of Fig. 4, in which two of the angles are replaced by arcs of the inscribed circle. The discussion remains unchanged and the relation (3) continues to apply, with Ω and Σ now taken from Fig. 4. Thus, at least in principle, contact angles in the entire range $0 < \gamma < \pi/2$ can be measured by this procedure. A practical difficulty may appear, however, in that the sectional area (5) filled out with fluid in the corner tends to zero as $\alpha \to \pi/2$, and thus the cylinder would have to be of large height in order to absorb a significant amount of the fluid into the corner at P. Correspondingly, it must be expected that the discontinuity as $\alpha_1 + \gamma$ crosses $\pi/2$ becomes physically less pronounced. These considerations are to some extent heuristic; the configuration is known exactly only when $\alpha_1 + \gamma \geq \pi/2$, $g = 0$, and does not lend itself easily to computation when $\alpha_1 + \gamma < \pi/2$. It is proposed to determine experimentally the actual range for which precise answers can be anticipated. It does however seem clear that for small values of γ (say $\gamma < 40°$) another approach should be sought, and accordingly we consider such an approach below.

3. Second Method

We consider a section Ω bounded by two circular arcs, as shown in Fig. 5. We normalize the smaller radius to be unity, and consider the problem of finding a capillary surface over Ω in zero gravity, with contact angle γ on the walls over Σ. We introduce a circular arc of radius $R = \frac{|\Omega|}{|\Sigma| \cos\gamma}$ as shown. Again, we discuss the case of a wetting liquid. Using methods introduced in [3] (see also [4] Chapter 6), it can be proved that for all (large enough) ρ, there is a critical γ_0 with $0 < \gamma_0 < \pi/2$, such that the problem has (under suitable normalization) a bounded solution over Ω when $\gamma > \gamma_0$, but such that the fluid disappears to infinity in the shaded region when $\gamma \leq \gamma_0$. In this case the change is not discontinuous as before, but indications are that it will be "nearly discontinuous", in the sense that for decreasing γ the height will stay bounded until γ is very close to γ_0, and then increase rapidly in the shaded region. Accurate indications of the nature of the change are being obtained by numerical solution of the capillary free-surface equation.

Figs. 6-8 depict the dependence of γ_0 and of d on ρ for varying values of α, and of γ_0 on α for varying ρ. It is seen that even for very small γ_0, the rates of change of γ_0 with respect to ρ and α can be made small, so that errors in construction of the apparatus will not lead to large errors in the measured contact angle γ_0.

4. Experimental Considerations

4.1. First Method. Preliminary experiments, using glycerol and fluorinert in rhombic containers of acrylic plastic, were carried out by D. Langbein in parabolic flight, and are described in [5]. One sees in all cases the marked effect of the discontinuity as the critical angle is crossed; however for fluorinert the effects of residual accelerations are significant, while glycerol, in view of its larger viscosity, did not have sufficient time during the 20 seconds at zero g to achieve its equilibrium configuration. The proposed experiments to be carried out in space flight will permit a much longer time duration. Residual accelerations will also then be much smaller, and equilibrium configurations should be achievable with liquids of widely varying viscosity and density. If contact angle is indeed an intrinsic property of materials (as we expect it to be) then it should be feasible by the proposed procedures to obtain reproducible measurements to considerably greater accuracy than has heretofore been possible. In this connection, we note an earlier "kitchen sink" experiment conducted by T. Coburn in the medical school of Stanford University, which used the discontinuous dependence property in a terrestrial gravity environment essentially along the lines of Example 2.2 above to establish the contact angle of water with acrylic plastic as about 78°, see [1] or Chapter 5 of [4]. The experiment was repeated recently by M. Weislogel under more controlled terrestrial conditions, who obtained 80° to a repeatable accuracy of 2°, see [2]. Our estimate that γ should exceed 40° for accurate results is based on past experience and is tentative; neither exact nor calculated solutions are presently available. We believe that the estimate errs on the side of caution. Nevertheless, for significantly smaller angles, we consider the second method, as described above and below, to have in the long range more promise.

4.2. Second Method. The configuration is directly amenable to computer calculation for $\gamma > \gamma_0$; it poses some difficulties but is within range of modern methods. The main emphasis in our current calculations is on determining the dependence on γ of rise height in the shaded region of Fig. 5, as $\gamma \searrow \gamma_0$. It is anticipated that for the geometries of principal interest, the height will change very slowly until γ enters a small interval around γ_0, and then shoot rapidly upward toward infinity. If this occurs as expected, an extremely effective method for getting contact angle measurements for most angles that occur physically will have been found. The final details of design will depend strongly on the results of the calculations. Similar information could in principle be obtained by preliminary experiments, as has been done for the first method above, and could be used to corroborate the computer calculations.

5. Space Flight

The experiments discussed here are scheduled for the International Microgravity Laboratory IML-2 space flight in 1994 as part of a joint investigation with D. Langbein, T. M. Haynes, and U. Hornung.

References

[1] P. Concus and R. Finn, *On capillary free surfaces in a gravitational field.* Acta Math. **132** (1974) 207–224.

[2] P. Concus, R. Finn, and M. Weislogel, *Drop-tower experiments for capillary surfaces in an exotic container.* Paper AIAA 91-0107, 29th Aerospace Sciences Meeting, Reno, NV, USA, Jan. 1991.

[3] R. Finn, *A subsidiary variational problem and existence criteria for capillary surfaces.* J. Reine Angew. Math. **353** (1984) 196–214.

[4] R. Finn, *Equilibrium Capillary Surfaces.* Grundlehren **284**, Springer-Verlag, New York, 1986.

[5] D. Langbein, R. Grossbach, and W. Heide, *Parabolic flight experiments on fluid surfaces and wetting.* Appl. Microgravity Tech. **2** (1990) 198–211.

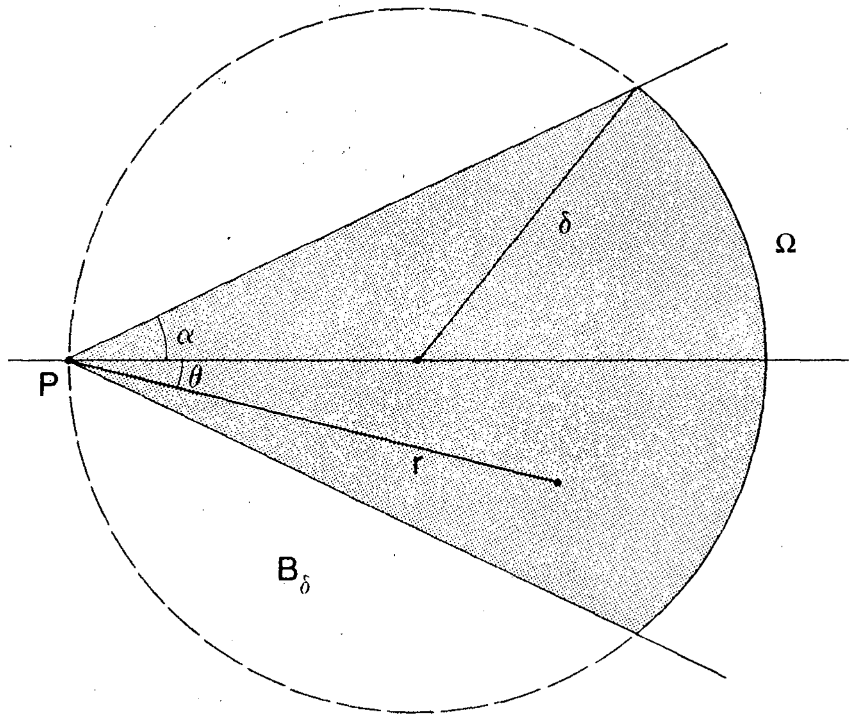


Figure 1. Wedge domain; coordinates.

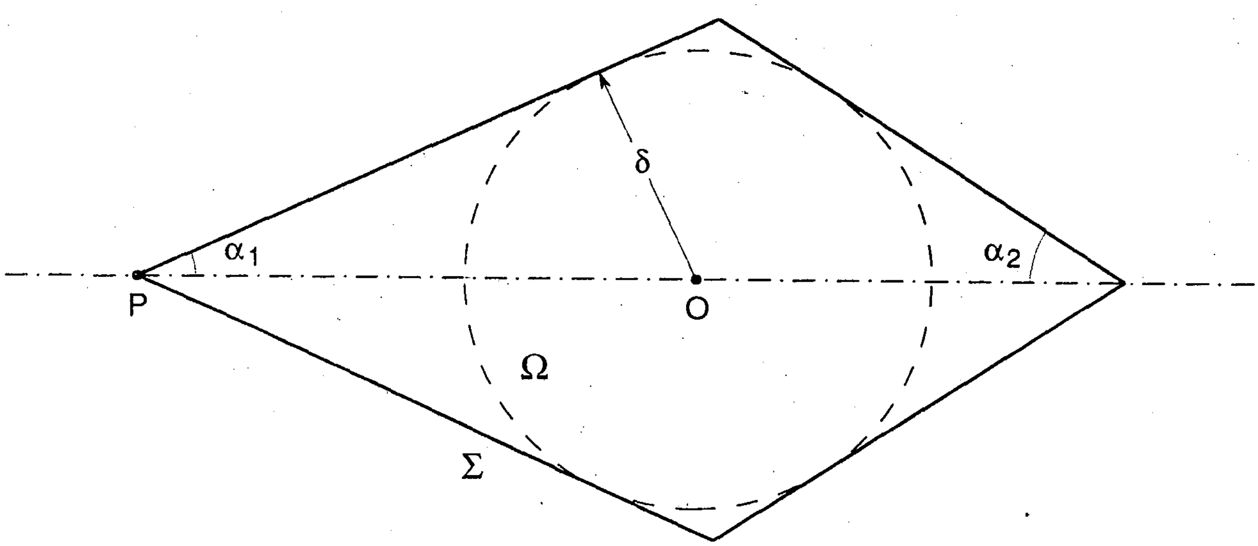


Figure 2. Near-rhombus. Case 1: $\alpha_1 < \alpha_2 < \pi/4$.

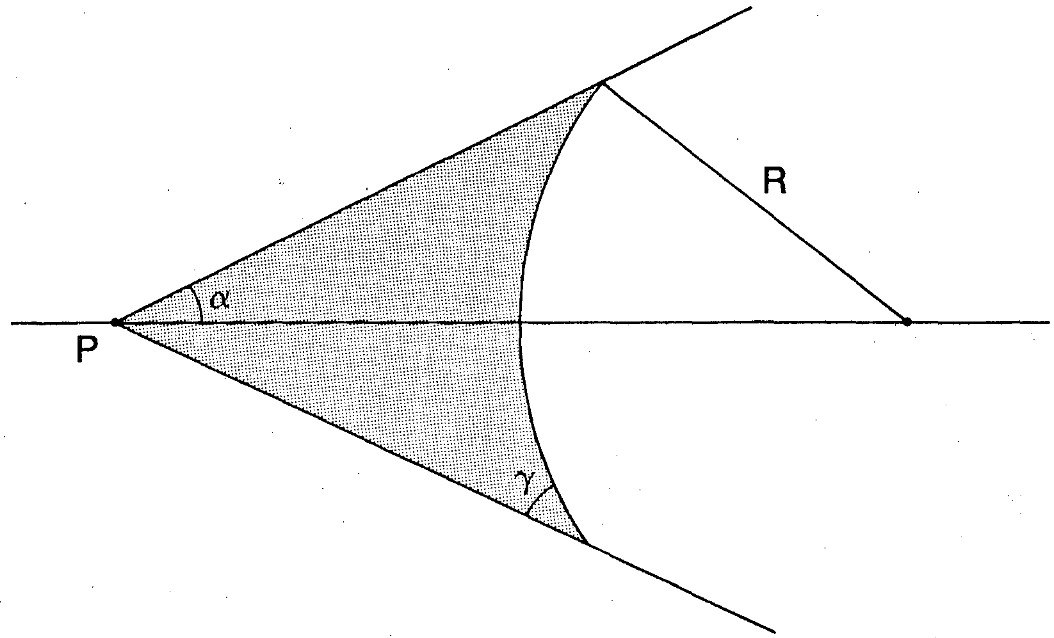


Figure 3. Fluid filling corner, $\alpha + \gamma < \pi/2$.

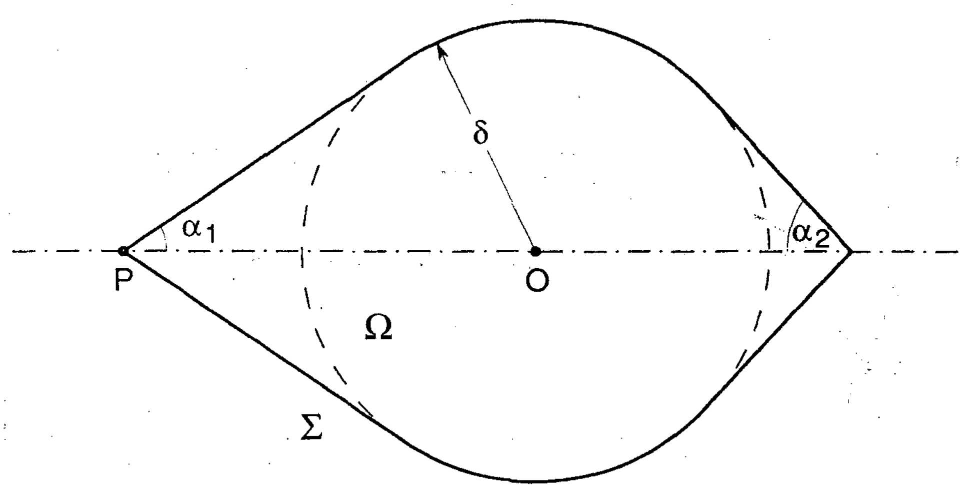


Figure 4. Near-rhombus. Case 2: $\alpha_1 < \alpha_2,\ \ \alpha_2 > \pi/4$.

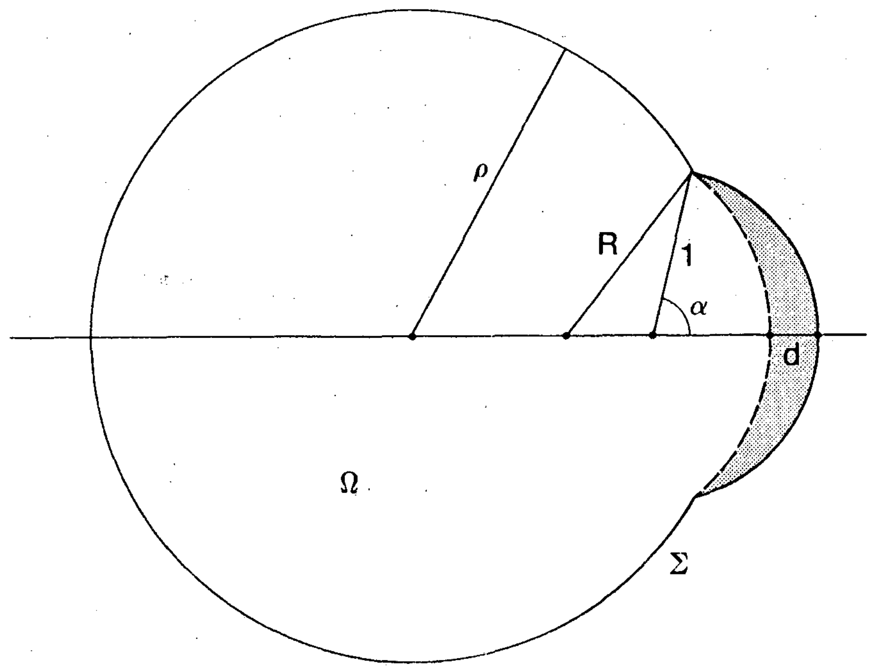


Figure 5. Two circle domain.

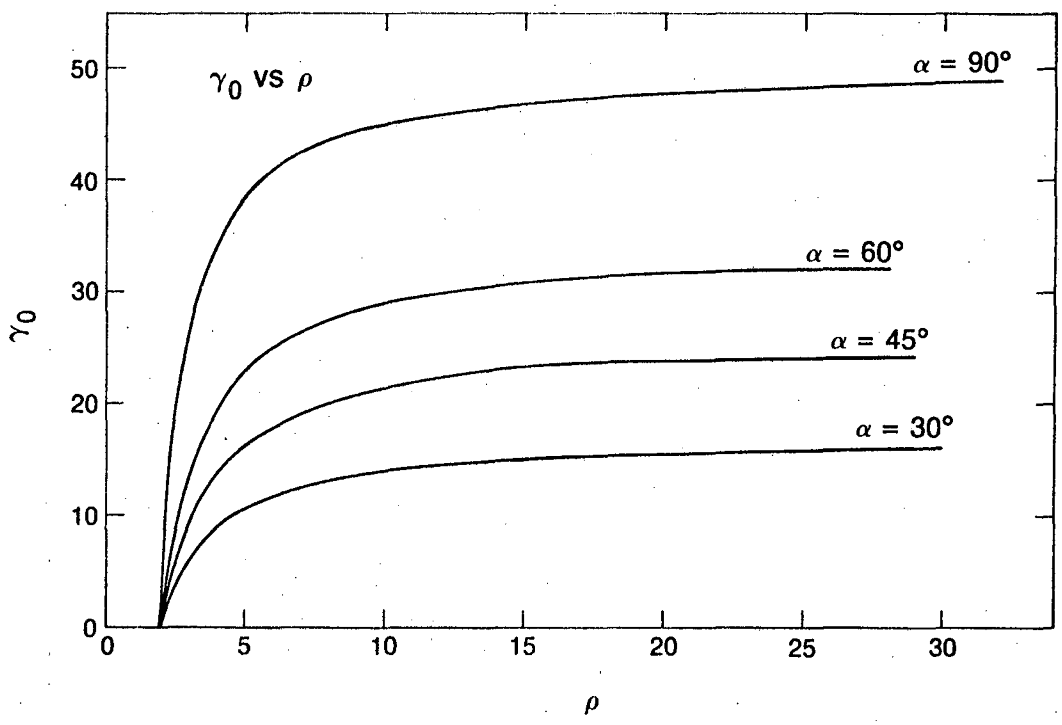


Figure 6.

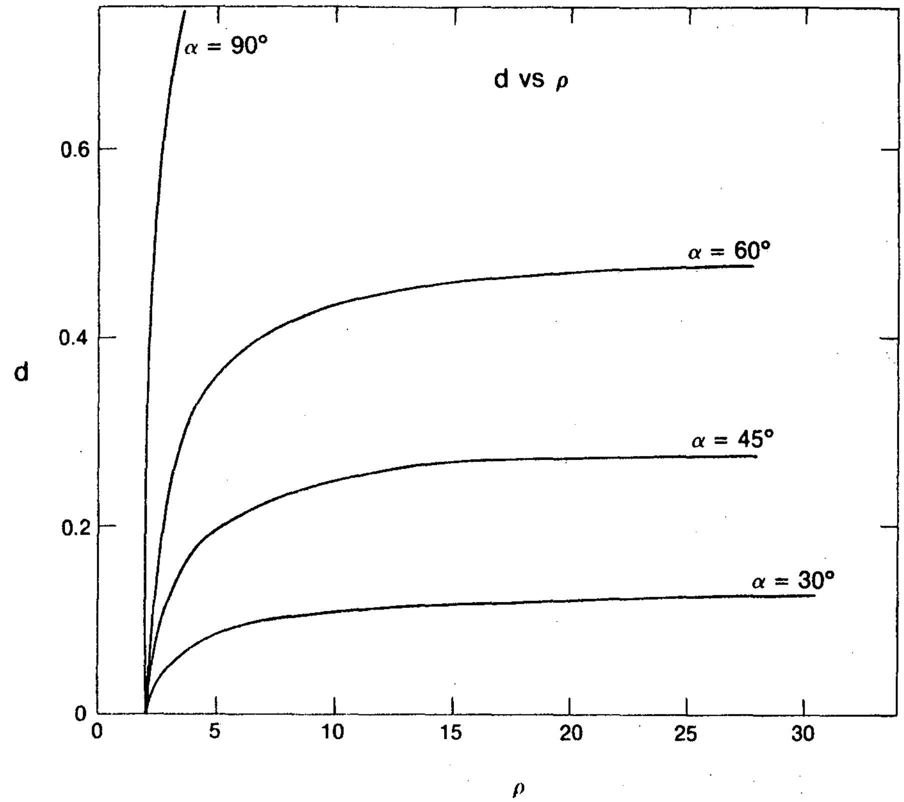


Figure 7.

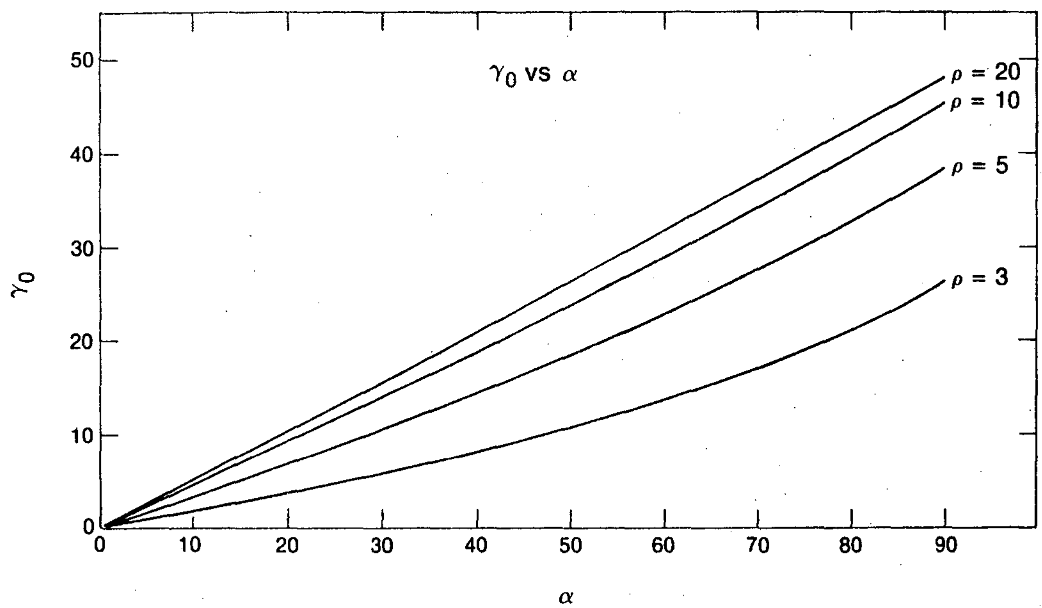


Figure 8.

LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
INFORMATION RESOURCES DEPARTMENT
BERKELEY, CALIFORNIA 94720