A VARIATIONAL DERIVATION OF YOUNG'S EQUATION FOR THE CONTACT ANGLE

ABSTRACT

Young's equation for the contact angle in a solid-liquid-vapor system is deduced, by a straightforward variational method, as the minimum surface free energy equilibrium condition for a small mass of liquid resting on a plane insoluble solid surface. Shape variations are subject to the two constraints of uniform internal liquid pressure, to assure mechanical equilibrium, and constancy of liquid volume under the allowed variations of the shape parameters. The analysis includes a proof that the Young contact angle is not simply an extremal condition on free energy but actually a minimal condition, so that it corresponds to <u>stable</u> equilibrium for the case considered.

INTRODUCTION

In analyses of solid-liquid-vapor systems, use is frequently made of the Young equation,

$$\gamma_{23} \cos \theta = \gamma_{13} - \gamma_{12} \tag{1}$$

where γ_{23} is the surface tension of the liquid-vapor interface, θ is the contact angle, γ_{13} is the specific surface free energy of the solid-vapor interface, and γ_{12} is the specific surface free energy of the solid-liquid interface, as shown in Fig. 1a.

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Derivations of (1) are often given in a form in which γ_{12} and γ_{13} are treated as surface tensions, so that (1) is presented as if it were a condition for static mechanical equilibrium of a line-element of the locus of contact of all three phases. There are conceptual difficulties in such an approach, since γ_{12} and γ_{13} are not readily interpreted as simple surface tensions, but details of those familiar difficulties need not be examined here.

Clearly, Young's equation (1) is more comfortably validated when it is made to rest upon a derivation in which the surface energy interpretation is employed in place of surface tension. Gregg (1) displays a derivation framed in this spirit, but he ~~properly~~ takes note of a very obvious deficiency of that derivation (see below) and then cites recent discussions (2) of a curious controversy as to whether Young's relation is even valid for solid-liquid-vapor interfaces of the type shown in Fig. 1a. A proof, developed by Johnson (3) in the very general and very elegant manner of Gibbs (4), is cited by Gregg as the strongest demonstration of the validity of (1).

Johnson follows Gibbs in obtaining (1) from arguments similar to those of the principle of virtual work; but he goes beyond Gibbs to include the possibility that gravitational forces and adsorption effects are important. The purpose of the present discussion is to outline a conceptually simple derivation of (1) which also rests on considerations somewhat analogous to the principle of virtual work but which confines attention to a very specific case of considerable theoretical interest. Exactly because the following derivation of Young's equation is less general than Johnson's, its essential points are much more readily understood than those underlying his quite elegant analysis. Indeed, the principal virtue of the following may be that it will make somewhat more understandable the almost mysterious manner in which three terms emerge from the variations of three different integrals to group themselves into the integrand from which Johnson's variational argument neatly generates Young's equation.

A derivation somewhat like the one to be given below has been presented by Schwartz and Minor (5), but their method of handling the condition of constant volume seems less clear than the direct variational approach used here. Perhaps this may account for the fact that their quite valid approach has not been incorporated into recent texts like that of Gregg (1) or Davies and Rideal (6). Because the Young equation is of such basic conceptual importance, it seems desirable to have available the clearest possible mathematical derivation resting on easily grasped general principles. It is hoped that the approach developed below may fill that need and also further clarify the basically simple considerations upon which the Young equation actually rests.

The following treatment has one further virtue in that it answers an important question not examined in any of the above references, namely the question of whether the extremal condition which is satisfied by Young's relation characterizes a stable or unstable equilibrium. It is shown below that the condition is one of stability for the case considered.

AN INADEQUATE DERIVATION

Certain essential features of the derivation to be given in the next section will be better appreciated if we first examine a crucial deficiency of the type of variational derivation exhibited and criticized by Gregg (1, p. 201). In Fig. 1b, we imagine a wedge of liquid to be displaced slightly towards the right so that the liquid-vapor interface takes up the new position indicated by the dashed line BB' preserving the contact angle θ, i.e., BB' is parallel to AA'. This small displacement increases the solid-liquid interface by amount δA_{12} proportional to length AB, and concurrently decreases the solid-vapor interfacial area by that same magnitude. If we now uncritically assert that the increment of liquid-vapor interfacial area δA_{23} is proportional to length CD, so that it is given by $\delta A_{12} \cos \theta$, then we can go through the following argument that appears to constitute a variational derivation of Young's equation.

If θ is the equilibrium value of the contact angle, then a vanishingly small net change δF of total surface free energy F must accompany the above-specified variations as those variations are shrunk to infinitesimal magnitude, inasmuch as a system in equilibrium occupies a state of minimal free energy, i.e., $\delta F = 0$. The stipulation that, at equilibrium, the variation of F shall vanish requires, if $\delta A_{23} = \delta A_{12} \cos\theta$,

$$\delta F = \gamma_{12}\delta A_{12} - \gamma_{13}\delta A_{12} + \gamma_{23}\delta A_{12}\cos\theta = 0 \qquad (2)$$

Since this must be true for any small variation δA_{12}, we may divide through by that factor and thereby we seem to obtain Young's equation (1).

The foregoing is, however, quite unacceptable for the following reason (1): We have simply asserted, without any proof, that the increment of liquid-vapor interfacial area is given by $\delta A_{23} = \delta A_{12} \cos\theta$; that is, δA_{23} is simply declared to be proportional to length BC. But why could we not have said, almost with more apparent justification, that the increment of liquid-vapor interfacial area is proportional to BD? As soon as the latter question is posed, we recognize that we have not put down enough restrictions (constraints) on our problem to warrant any valid assertions as to the magnitude of the increment of liquid-vapor interfacial area. We sense that, in order to specify properly the quantity δA_{23}, we must know what is happening, during our virtual displacement, to parts of the liquid not even exhibited in Fig. 2. Our difficulty arises from what Gray (2) has aptly termed "the fallacy of the semi-infinite interface." Briefly, we must specify much more clearly, and translate into mathematical form, certain additional integral constraints that characterize the specific problem we seek to investigate.

A VARIATIONAL DERIVATION FOR A SPECIAL CASE

In many problems, especially those of heterogeneous nucleation (see, e.g., 7, p. 54), we often deal with a small mass of liquid lying on a plane solid insoluble surface, so it is of interest to submit that important specific case to variational analysis. We shall specify that gravitational effects are negligible. The latter assumption is true to excellent approximation in the nucleation problem, as well as in all other cases where only tiny patches of liquid are involved. The "sessile drop" problem, by contrast, is one in which gravitational flattening is quite significant because of large masses of liquid involved, so we exclude it from present consideration and take comfort in knowing that the generality of Johnson's (3) proof assures us that Young's equation also holds in such circumstances. We also exclude adsorption effects, so that surface tensions become identical in significance with surface free energies (3).

We seek the equilibrium shape and contact angle for this special case. We can assert immediately that, in order that mechanical equilibrium shall exist, one obvious requirement is that (in the assumed absence of gravity) the internal pressure within the fluid mass must be everywhere the same, lest motions develop in non-equilibrium manner. But because we can certainly regard the external pressure as essentially constant over our vapor-liquid interface, and because the increment of pressure in crossing the latter interface from the vapor to the liquid side is controlled by γ_{23} and the local mean interfacial curvature, according to a familiar relation, we see that uniformity of internal pressure will require that the liquid-vapor interface be a portion of a sphere. (The only exceptions to this conclusion will apply in cases that are not of sufficiently general interest to warrant discussion here.) Thus we now further specify that the liquid always lies as a <u>spherical cap</u> on the solid, with one and the same radius of curvature r for all portions of its liquid-vapor interface. The magnitude of that radius will, of course, be considered to vary as we carry out our virtual variations of cap-shape, but we agree to restrict attention to varied shapes that are in all cases spherical segments, in order that uniform internal pressure is always maintained in keeping with requirements of mechanical equilibrium.

The preceding sphericity stipulation is the first one of our two constraints, the second being that the volume V of the liquid mass shall be invariant as we vary r and θ. Referring to the sketch of Fig. 2, we might start with a cap represented by the solid profile with radius r and contact angle θ, and press it down until its radius became everywhere $r + \delta r$ and its contact angle changed to $\theta + \delta\theta$ (smaller than θ, since here $\delta\theta$ would be negative). During this variation of configuration from one spherical cap form to another, our second constraint dictates simply that $\delta V = 0$. As is readily seen from Fig. ~~3~~ 2, such variations will entail some variation δA_{23} of the spherical liquid-vapor interface and concomitant variation δA_{12} of the plane liquid-solid interface.

Our derivation is to be based primarily on the equilibrium principle that small variations about the equilibrium form shall lead to vanishingly small variations of total surface free energy, i.e., $\delta F = 0$, subject to the two constraints of always-spherical liquid-vapor interface and invariant liquid volume. In interests of notational simplification, we now introduce the "contact parameter" m, defined as

$$m = \cos \theta \tag{3}$$

so that we shall hereafter speak of variations of m rather than of θ. To carry through the above-outlined program, we must first find explicit expressions for V, A_{12}, and A_{23} in terms of r and m, and then we must form the variations of each of those three quantities. But because the second of our constraints requires $\delta V = 0$, it is clear that we shall be able to obtain from that condition some general relation joining δr and δm, namely equation (8) below. Use of the latter relation will then permit us to eliminate from our expressions for δA_{12} and δA_{23} either δr or δm (we shall below arbitrarily take δr as our independent variation, eliminating δm). Our basic equilibrium requirement, $\delta F = 0$, which we shall at first express quite generally in terms of the area-variations, can then be put into a form in which every term will contain the factor δr. But δr represents an arbitrary, non-zero variation, so that factor can be divided out of the equation $\delta F = 0$, leaving us with some condition on m that will specify our equilibrium condition (Young's relation, as we shall see).

By straightforward integrations, we can immediately take the first of the above-outlined steps, obtaining the following three geometric relationships for spherical caps:

$$V = \frac{\pi r^3}{3} (2 + m)(1 - m)^2 \tag{4}$$

$$A_{12} = \pi r^2 (1 - m^2) \tag{5}$$

$$A_{23} = 2\pi r^2 (1 - m) \tag{6}$$

Our first constraint has now been imposed; we limit attention, via (4-6), to variational changes preserving sphericity of the liquid-vapor interface. To impose our second constraint, we form the variation of (4) and equate it to zero to obtain:

$$\delta V = \pi r^2[(2+m)(1-m)^2]\delta r + \frac{\pi r^3}{3}[(1-m)^2 - 2(2+m)(1-m)]\delta m = 0 \tag{7}$$

But condition (7) permits us now to express δm in terms of δr, yielding:

$$\delta m = \frac{(2 + m)(1 - m)\delta r}{(1 + m)r} \tag{8}$$

as our volume-conserving relation between m- and r-variations.

It is to be noted carefully that (8) constitutes a key relationship in our variational analysis. In absence of any interrelationship like (8), we would be admitting into consideration entirely arbitrary pairs of variations $(\delta m, \delta r)$. But almost all of these would lead to either volume increases or decreases, so they would fail to describe the problem we seek to analyze, namely the problem of the equilibrium shape attained by some given volume of liquid dropped onto a specified plane substrate.

Equation (8) restricts the allowed family of variations (δm, δr) to that desired subset which satisfies our requirement of constancy of V.

Next we form the general expression for the total surface free energy F. (Note that it was characteristic of our previously-outlined inadequate variational derivation that we had such an incompletely specified system that we could not have written down any explicit expression for F; all we could do was to write down what appeared to be an expression for δF.) Taking as a convenient zero-reference state that in which the solid is everywhere in contact with the vapor in absence of any liquid deposit, we may write:

$$F = \gamma_{23} A_{23} + \gamma_{12} A_{12} - \gamma_{13} A_{12}$$

whence the variation of F is given in general by

$$\delta F = \gamma_{23} \delta A_{23} + (\gamma_{12} - \gamma_{13}) \delta A_{12} \ . \tag{9}$$

But from (5) and (6) we can form the spherical-cap variations

$$\delta A_{12} = 2\pi r(1 - m^2)\delta r - 2\pi r^2 m \delta m \tag{10}$$

$$\delta A_{23} = 4\pi r(1 - m)\delta r - 2\pi r^2 \delta m \ , \tag{11}$$

and we next restrict these by introducing the volume-conserving relation (8) between δm and δr, yielding

$$\delta A_{12} = 2\pi r \delta r(1 - m)/(1 + m) \tag{12}$$

$$\delta A_{23} = 2\pi r \delta r m(1 - m)/(1 + m) \tag{13}$$

If we now substitute (12) and (13) into (9), we get for the first variation of F, in our constant-volume spherical-cap case, the expression

$$\delta F = 2\pi r\delta r(1 - m)/(1 + m)\left\{m\gamma_{23} + \gamma_{12} - \gamma_{13}\right\} \qquad (14)$$

The particular spherical cap that is the equilibrium configuration must be that which satisfies the necessary, but not sufficient (see below) condition $\delta F = 0$ for arbitrary small variations δr about equilibrium; so imposing this condition we see that (14) implies three possible solutions. Two are of no present interest, namely the meaningless solution $r = 0$ and the quite real and meaningful asymptotic case $m = 1$. But the third solution to the conditional equation $\delta F = 0$ is of obvious interest in our analysis, namely the condition

$$m = (\gamma_{13} - \gamma_{12})/\gamma_{23} \qquad (15)$$

which, in view of definition (3) is seen to be identical to equation (1), Young's relation.

STABILITY ANALYSIS

Inspection of the analysis leading to (15) reveals that it shows only that (15) is a condition for the existence of an extremum (or, still more precisely, existence of a stationary value) of F in the variational neighborhood of the particular spherical-cap configuration satisfying the Young relation. An equilibrium analysis is not complete until it has shown (as above) not only that the first derivative of F vanishes at the claimed equilibrium configuration, but also that the second derivative of F with respect to the independently varied parameter is positive (i.e., that we are actually at a minimum of F) in the neighborhood of the claimed equilibrium condition.

To establish this, we must form the second derivative, i.e., second variation, of F from the general expression (14), and evaluate it at the equilibrium configuration by substituting into the general form of that second variation the particular condition (15). Care must be taken, in differentiating (14), to recognize that m is there to be treated as an implicit function of r. Keeping this in mind, one obtains:

$$\frac{\delta^2 F}{\delta r^2} = 2\pi\left(\frac{1-m}{1+m}\right)[m\gamma_{23} + \gamma_{12} - \gamma_{13}] + 2\pi r\,\frac{\delta}{\delta r}\left(\frac{1-m}{1+m}\right)[m\gamma_{23} + \gamma_{12} - \gamma_{13}]$$

$$+ 2\pi r\left(\frac{1-m}{1+m}\right)\left(\sigma_{23}\,\frac{\delta m}{\delta r}\right) \qquad (16)$$

But in the neighborhood of our claimed equilibrium configuration, Young's equation in the form (15) imposes the condition that the first two terms on the right of (16) vanish in that neighborhood because the quantity inside the square brackets is zero. (In anticipation of that ~~obliteration~~ simplification, the r-differentiation of the quantity $(1 - m)/(1 + m)$ is shown in (16) only in indicated operational form, without actually carrying out the somewhat involved and unnecessary operation.) Thus we are left with only the third term on the right. On using (8), we can finally reduce (16) to the form not only that the first derivative of F vanishes at the claimed equilibrium configuration, but also that the second derivative of F with respect to the independently varied parameter is positive (i.e., that we are actually at a minimum of F) in the neighborhood of the claimed equilibrium condition.

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$$\frac{\delta^2 F}{\delta r^2} = 2\pi\left(\frac{1-m}{1+m}\right)\left[m\gamma_{23} + \gamma_{12} - \gamma_{13}\right] + 2\pi r\,\frac{\delta}{\delta r}\left(\frac{1-m}{1+m}\right)\left[m\gamma_{23} + \gamma_{12} - \gamma_{13}\right]$$

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It will be recalled that the crucial deficiency of the incomplete type of variational analysis exhibited by Gregg and examined briefly above is that it leads to Young's relation only if δA_{23} equals $\delta A_{12} \cos\theta$. We may now ask whether the above analysis can settle that point for the spherical-cap case. We find that it can, for from (12) and (13) we see that, for all volume-conserving variations we shall have $\delta A_{23} = m\delta A_{12} = \delta A_{12} \cos\theta$, the moot relation. What had been uncertain under the inadequate specification of that analysis becomes quite definite when the surface free energy of the entire system is considered, in keeping with the point that Gray (2) has stressed in his comments on the fallacy of the semi-infinite interface.

It should be remarked that it is not quite proper usage to speak of derivations of the present type as being based on the principle of virtual work, for the argument is not couched in terms of virtual work done by specified forces during specified virtual displacements. Indeed, our prime objective in approaching the derivation of the Young equation in the manner illustrated above was to avoid speaking of any surface tension forces and to carry out our entire analysis instead in terms of surface energies. We formed an integral expression for the total surface free energy of our system and demanded that a certain constrained variation of that integral must vanish at equilibrium for energy-minimum reasons. Thus the above is properly termed a variational argument but not an argument resting on the principle of virtual work, despite the obviously close relation of these two approaches.

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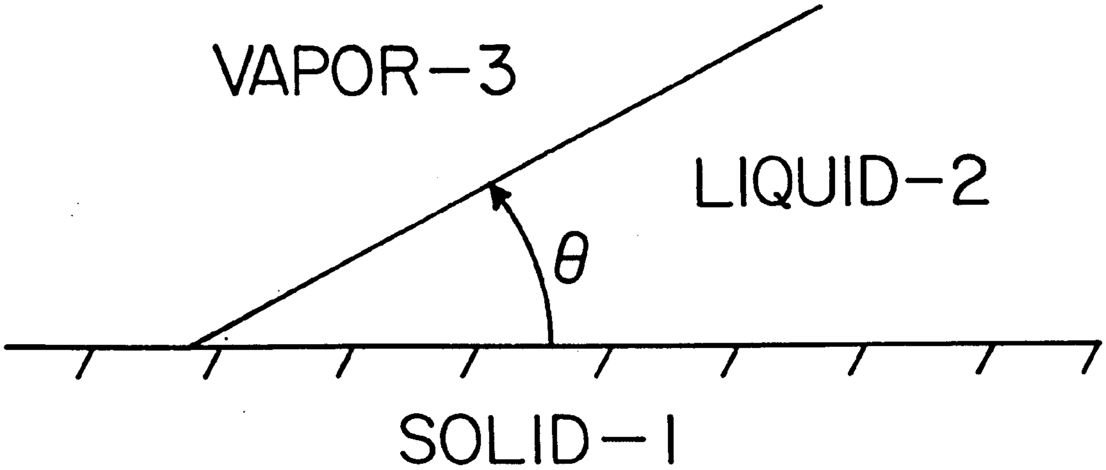
LIST OF FIGURES AND CAPTIONS

Fig. 1	a)	Definition sketch for contact angle in a solid-liquid-vapor system.
	b)	Small variation of a liquid wedge on a solid.
Fig. 2		Volume-preserving shape-variation of a spherical cap on a plane substrate.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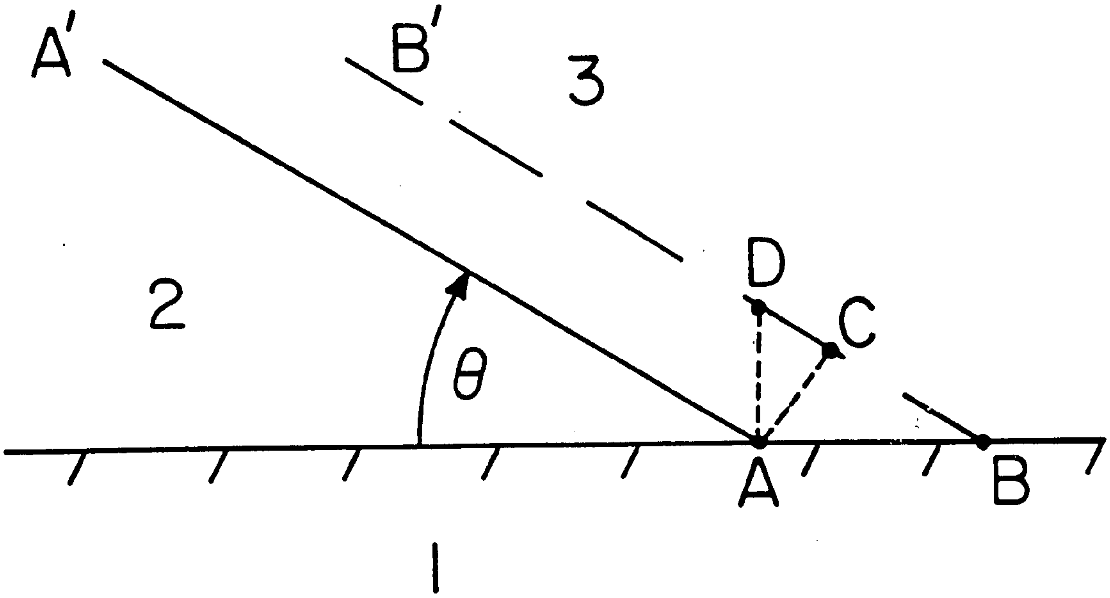
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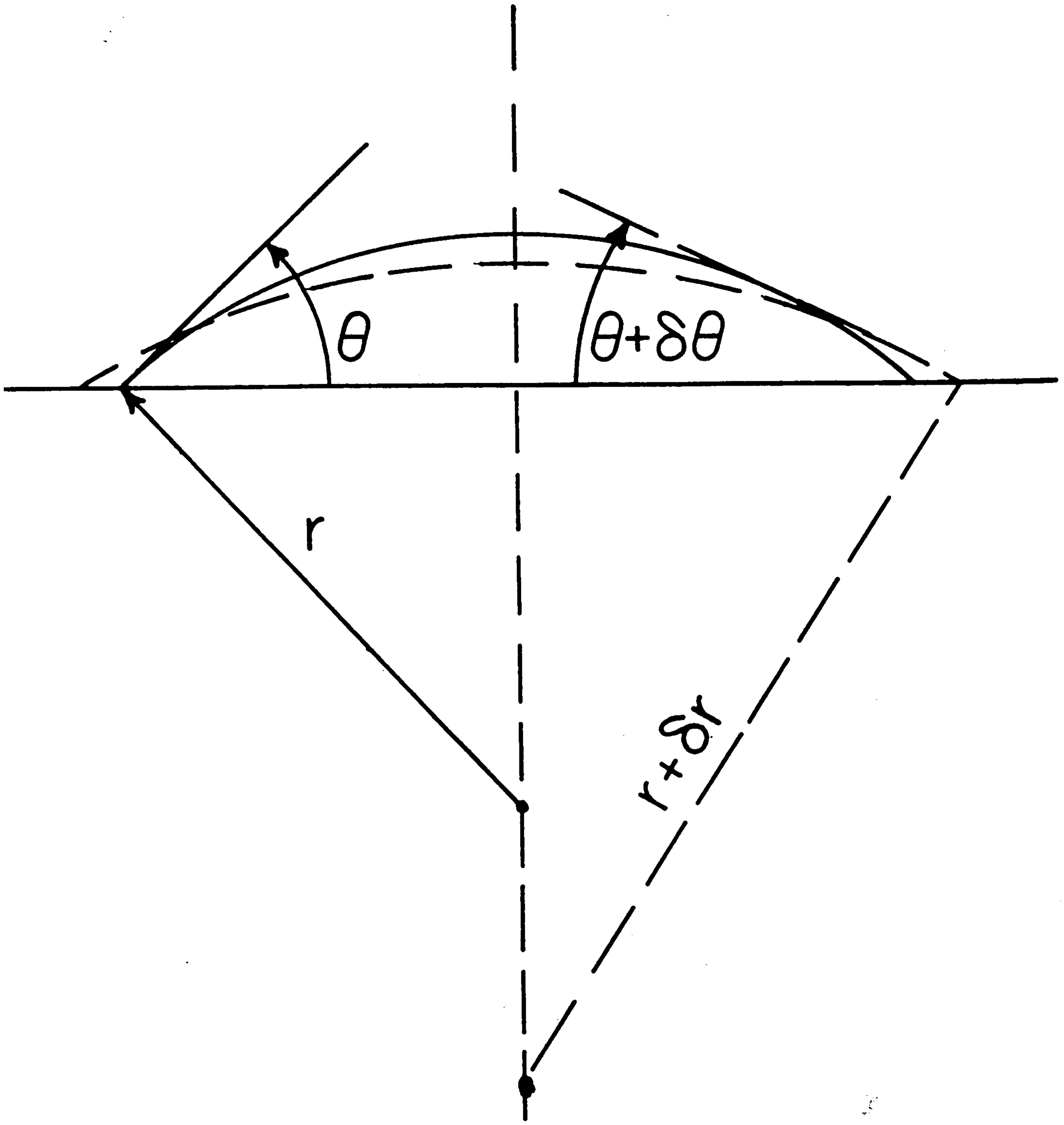
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