Sufficient conditions for the stability and instability of a fluid boundary subjected to local stress

2002 J. Phys. A: Math. Gen. 35 4335

(http://iopscience.iop.org/0305-4470/35/19/313)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS A: MATHEMATICAL AND GENERAL

J. Phys. A: Math. Gen. **35** (2002) 4335–4347 PII: S0305-4470(02)30526-2

Sufficient conditions for the stability and instability of a fluid boundary subjected to local stress

S J Miklavcic[1] **and P Attard**[2]

[1] Department of Science and Technology, Campus Norrköping, Linköping University, S-601 74, Norrköping, Sweden
[2] Ian Wark Research Institute, The Levels Campus, University of South Australia, Mawson Lakes, SA 5095, Australia

Received 2 November 2001, in final form 11 March 2002
Published 3 May 2002
Online at stacks.iop.org/JPhysA/35/4335

Abstract

Sufficient conditions for either stability or instability of the interface of a fluid drop subject to localized surface stresses are presented. The stated conditions pertain to the case of an axisymmetric sessile drop having a fixed contact line and subject to axisymmetric forces acting on the surface of the drop. These conditions, appearing for the first time in the literature, are in the form of pointwise inequalities. They have quite general applicability, as they do not rely on explicit knowledge of the specific nature of an externally applied surface force. Supplementary integral inequalities are also provided and discussed.

PACS numbers: 42.70.Df, 82.70.Dd

1. Introduction

Two distinctive features involved in the industrial application of flotation to water purification or to the de-inking of recycled paper, are the colloidal interaction between gas bubbles and solid microscopic particles in a colloidal dispersion, and the capture of these particles by the bubble interfaces. The underlying equilibrium interactions are basically the well-studied dispersion and electrical double-layer forces [1], here acting between the bubble and particle surfaces across the dispersion medium. On the other hand, particle capture involves three-phase contact line formation which necessitates the rupture of the bubble surface. It is natural in investigating the mechanisms of flotation, that the study of the simpler of these two aspects be undertaken first, and although by no means simple the historical development of the area does indicate such a priority.

What complicates soft body interactions is the fact that the underlying forces are modified by surface deformation occurring with the bubble. Indeed, bubble deformation itself has been offered as an explanation for the longevity of froths in highly concentrated salt solutions [2]. Actually, surface deformation is an intrinsic feature affecting colloidal interactions between all fluid entities. Not only are gas bubbles subject to deformation, oil droplets in the emulsion or microemulsion systems used in the pharmaceutical industry are also prone to shape changes as a result of surface forces. Experimental work using several different techniques [3–12] investigating different fluid interface systems, has been undertaken to quantify droplet–droplet and droplet–particle interactions. Unfortunately, it has been found that additional information is required in some of the experimental techniques in order for quantitative results to be extracted. This in itself has initiated some rather specific studies of the deformation process [13–17], looking into the characterization of a droplet surface as an elastic spring.

Among the theoretical investigations of deformation and interaction we can name the works of Denkov and co-workers [18–20] who have approached the problem of the interaction of two droplets or two bubbles by assuming complete flattening of the surfaces in the interfacial region, allowing the authors to then use traditional continuum theory between flat surfaces [1] to provide them with an approximation to the total interaction potential. However, this approach can be argued inappropriate, indeed unphysical, in cases of attractive surface forces which do not promote flattening but rather the opposite: elongation of the fluid interfaces. What is required in general is a more self-consistent treatment in which the effects of surface forces promoting fluid interface deformation are considered simultaneously with the effects of surface deformation on the equilibrium interaction. This is the approach taken in the independent studies of Miklavcic *et al* [21–23], Aston and Berg [15], Bhatt *et al* [16] and Chan *et al* [17].

Recently, the analysis of surface deformation by the colloidal interaction between fluid and solid bodies was made more rigorous with the derivation and study of the exact equation describing the equilibrium shape of a fluid drop subjected to a surface stress of colloidal origin varying over the surface of the fluid [24]. It has been shown that in the case of a fluid interface represented by the pair $(r, z(r))$, the function $z(r)$ satisfies the nonlinear differential equation

$$\left([\gamma + \sigma(r, z)]\frac{2\pi r z_r}{W(z_r)}\right)_r = 2\pi r[Gz - \lambda + \sigma_z(r, z)W(z_r)]. \qquad (1)$$

In (1) the subscripts denote differentiation with respect to either r or z, γ is the intrinsic interfacial tension, σ accounts for the local action of an externally applied stress and $G = g\Delta\rho$, where g is the acceleration due to gravity and $\Delta\rho$ is the difference in fluid densities on either side of the interface. Furthermore, for a drop of incompressible fluid of fixed volume, V_Λ, λ is a Lagrange multiplier associated with the (approximate) constraint that V_Λ be constant under external action. For a gas bubble λ represents the physical pressure difference across the interface [13, 24].

Earlier analyses [2, 15–23] employed an approximate version of (1) valid only in some regimes and for some types of interactions. Equation (1), advocated in [24] and utilized in [13, 14] by Attard and Miklavcic, is essential for the correct analysis of soft body deformation under arbitrary colloidal interactions. As an example, it correctly accounts for an inherent singularity ($\gamma + \sigma = 0$) occurring when attractive forces act, earmarking an ultimate stability limit. The approximate equations used in the past overlook such a condition. In reports [13, 14, 24], numerical solutions were given as well as integral results based on the mathematical character of the governing differential equation, and on the expected physical properties of the solution. In addition, for the benefit of experimentalists an approximate solution, the first term of a perturbation expansion about the spherical shape for the case without gravity, was derived employing the total imposed surface force as a perturbation parameter. As this total force of colloidal origin is an experimentally measurable quantity, this approximate solution can assist in indicating how the fluid interface responds to the presence of a colloidal particle as a function of the macroscopic accumulated load.

Despite the progress that has been made and the generally increasing experimental interest in studying soft-bodied, deformable systems [3–12], there remains a gap in our theoretical knowledge which the present paper seeks to fill. A hitherto unaddressed question is whether the solutions one obtains to the governing deformation equation, say by using numerical methods, actually represent stable equilibrium droplet or bubble shapes. That is to say, while a solution to (1) may exist and, subject to appropriate boundary conditions, be unique (see [25] for a mathematical discussion of existence and uniqueness), there exists little information on which one can establish whether an interfacial profile actually corresponds to a physically viable fluid drop or bubble. This question lies at the heart of the second feature crucial to the success of flotation, that of bubble rupture and particle capture. Whether or not a predicted deformed bubble surface is stable is equivalent to asking whether or not interfacial rupture occurs. In this paper we focus attention on the stability characteristics of solutions to (1) representing the shape of a free fluid boundary under local stress, and establish conditions which are sufficient for rupture or alternatively sufficient for the preservation of the surface. Our approach is based on a study of the second variation of a free energy functional. The first variation of this functional gives the Euler–Lagrange equation (1), above. Without placing too restrictive demands on the functional, we derive quite general conditions guaranteeing either stability or instability, based on a comparison with a simple eigenvalue problem. Our results in the form of inequalities are derived without reference to a specific physical case. Thus, by means of the criteria presented here, the stability or instability state of a profile in an actual instance can be readily established.

2. Stability and instability conditions

Equation (1) is the Euler–Lagrange equation corresponding to the first variation of a free energy functional (see [24] for details and also [26] for more general cases):

$$E = \gamma A_\Lambda + G \int_{V_\Lambda} \tilde{z}\, \mathrm{d}V - \mu A_\Sigma + \int_\Lambda \sigma\, \mathrm{d}S. \tag{2}$$

This thermodynamic potential contains both volume and surface energy contributions for a fluid drop of finite volume, V_Λ, interfacial area, A_Λ, and density difference, $\Delta\rho$, with respect to a bulk continuum phase, in a uniform gravitational field. The drop is sessile on a horizontal substrate, occupying a circular region of area $A_\Sigma = \pi R_c^2$ with a contact radius, R_c. The terms in (2) are, respectively, the surface energy of the fluid drop surface in contact with the bulk liquid, the gravitational energy arising from the density difference between interior and exterior fluids, the energy of contact of the drop with the solid substrate, Σ, and finally, the surface energy associated with the interaction of the drop with a neighbouring body. σ is a nonuniform, axisymmetric surface free energy density. The remaining physical constant, $\mu = \gamma \cos\alpha$, where α is the contact angle measured from within the drop. In the case of a gas bubble, as opposed to a fluid drop, equation (2) must be modified to account for the thermodynamic state of the gaseous phase. The appropriate modification is described in [13, 24]. Here, we shall adhere to the incompressible fluid droplet case for which a finite volume is assumed. The discussion and conclusions below are not altered in considering the gas system.

The profile, hereafter called the equilibrium profile, z, that minimizes (2) is sought. In searching for the minimum it is important to specify the class of functions, $\tilde{z}$, that represent viable candidates for a physical profile. It is only from within this class that the equilibrium profile can be found. Equation (1) is satisfied by the profile, z, a member of the class of axisymmetric profiles that enclose the given volume, V_Λ. Traditionally, however, one follows the equivalent but simpler approach of specifying that the equilibrium profile, $\tilde{z} = z$, gives the unconditional minimum of the constrained thermodynamic potential

$$\mathcal{F} = E - \lambda(V - V_\Lambda) \tag{3}$$

where λ is a Lagrange multiplier associated with the volume constraint [24, 27]. The minimization of $\mathcal{F}$ is now performed with respect to functions satisfying only the boundary conditions

$$\begin{cases} \tilde{z}_r(0) = 0 \\ \tilde{z}(R_c) = 0 \end{cases} \tag{4}$$

for some finite positive scalar $R_c < \infty$. These boundary conditions pertain to the physical case of an axisymmetric drop maintaining a fixed contact line on the substrate, $z = 0$, i.e. a pinned sessile drop.

Let us denote by η, functions belonging to the set

$$\Omega_r = \{\eta \in C^\infty((0, R)) : \eta_r(0) = \eta(R_c) = 0\}.$$

As indicated, this set contains functions of r that are smooth (in the infinitely differentiable sense), that satisfy the condition of axisymmetry, and whose extreme extent makes contact with the substrate at $r = R_c$. Clearly, an arbitrary $\tilde{z}$ belonging to the class of allowed functions can be expressed in the form $\tilde{z} = z + \epsilon\eta$, where $\eta \in \Omega_r$ and ϵ is a parameter.

In the remainder of this paper we shall assume the existence of the equilibrium profile, z, and analyse its stability properties.

Before proceeding further we remark that σ appearing in (2) is a surface energy per unit area, acting over the surface of the drop. In the present scenario it arises as a result of the noncontact interaction between the two colloidal bodies which, as is well known [1], is manifested as a force between the two interfaces segregating the three media. σ is the surface energy density corresponding to this surface stress (force per unit area). By definition, σ will vary over the interface, being largest in magnitude in the region between the bodies and decaying rapidly away from the apex, since the colloidal interactions that are involved are short range.

In the following we suppose $\sigma = \sigma(r, \tilde{z})$ to be a smooth function, although in practice all that is required is that σ be differentiable twice. In terms of a nonparametric representation of the profile, $\{(r, \tilde{z}(r))\}$, the free energy functional of $\tilde{z}$ can be written in the one-dimensional integral form

$$\begin{aligned} \mathcal{F} = & \int_0^{R_c} f(r, \tilde{z}(r), \tilde{z}_r(r))\, \mathrm{d}r \\ & = \gamma \int_0^{R_c} 2\pi r W(\tilde{z}_r(r))\, \mathrm{d}r + G \int_0^{R_c} \pi r \tilde{z}(r)^2\, \mathrm{d}r - \lambda \int_0^{R_c} 2\pi r \tilde{z}(r)\, \mathrm{d}r \\ & \quad + \int_0^{R_c} 2\pi r W(\tilde{z}_r(r)) \sigma(r, \tilde{z}(r))\, \mathrm{d}r \end{aligned}$$

where $W(\tilde{z}_r) = \left(1 + \tilde{z}_r^2\right)^{1/2}$ and $\tilde{z}_r = \mathrm{d}\tilde{z}/\mathrm{d}r$.

The terms $-\mu A_\Sigma$ and $-\lambda V_\Lambda$ in (2) and (3) are important for determining z. However, these terms play neither an active nor an explict role in establishing the stability properties of z and thus can be dropped from the analysis at this point. It should also be remarked that the form of (1) and of the functional $\mathcal{F}$, as well as the representation $\{(r, \tilde{z}(r))\}$, implicitly assumes that the sessile drop does not possess a vertical tangent anywhere along its profile. That is, $z(r)$ is a single-valued function of r; the representation is injective. An implicit constraint that must therefore be satisfied by the system is that the contact angle which the drop makes with the substrate cannot exceed $\pi/2$. Other representations which can account for the more general situation, not appropriate to this nonparametric description, can be defined as outlined in [24, 26].

The energy density is

$$f(r, \tilde{z}, \tilde{z}_r) = 2\pi r W(\tilde{z}_r) h(r, \tilde{z}) + G\pi r \tilde{z}^2 - 2\pi r \lambda \tilde{z} \tag{5}$$

with $h = \gamma + \sigma$. Treating f as a smooth (since σ is smooth) function of three independent variables, $f = f(r, u, v)$, we deduce the following second partial derivatives of f with respect to u and v:

$$\begin{cases} f_{vv} = \dfrac{2\pi r h(r, u)}{(1 + v^2)^{3/2}} \\ f_{uu} = 2\pi r G + 2\pi r h_{uu}(r, u)(1 + v^2)^{1/2} \\ f_{uv} = \dfrac{2\pi r v h_u(r, u)}{(1 + v^2)^{1/2}}. \end{cases} \tag{6}$$

Note that $f_{uv} = 0$ and $f_{uu} = 2\pi r G$ in the case $h \equiv \gamma$, which occurs in the absence of any external source of surface stress. From (6) we draw the important conclusion, used often in the analysis below, that $f_{vv} > 0$ for all $r \in (0, R_c]$ provided $h > 0$. This last condition will be trivially satisfied for positive stresses (repulsive interactions) and will be satisfied even for negative stresses (attractive interactions) which are bounded in magnitude by the intrinsic surface tension of the drop, i.e. $0 \leqslant |\sigma| < \gamma$.

Since $\mathcal{F}$ is the integral of the smooth function f, then $\mathcal{F}$ will be a smooth function of the parameter ϵ defined above,

$$g(\epsilon) := \mathcal{F}[z + \epsilon\eta].$$

The vanishing of the first variation of the functional, $\mathcal{F}$ [27],

$$\delta\mathcal{F} = \epsilon \left(\frac{\partial \mathcal{F}}{\partial \epsilon} \bigg|_{\epsilon=0} \right) = \epsilon g'(0) = 0$$

is a necessary condition to be satisfied by z. This leads to (1). The second variation of $\mathcal{F}$ determines whether or not z is a minimizing profile. That is, the second variation establishes whether the equilibrium profile is stable or unstable with respect to perturbations. Stability is guaranteed if the second variation

$$\delta^2\mathcal{F} = \frac{\epsilon^2}{2} \left(\frac{\partial^2 \mathcal{F}}{\partial \epsilon^2} \bigg|_{\epsilon=0} \right) = \frac{\epsilon^2}{2} g''(0)$$

is positive definite for all perturbations to z. If it is negative for any perturbation, then the profile is considered unstable.

Performing the indicated differentiation and further manipulations [26] we find that the second variation of $\mathcal{F}$ can be expressed as the integral

$$\delta^2\mathcal{F} = \frac{\epsilon^2}{2} \int_0^{R_c} \left(f_{z_r z_r} \eta_r^2 + \left(f_{zz} - \left(f_{z z_r} \right)_r \right) \eta^2 \right) \mathrm{d}r. \tag{7}$$

In this equation and those below we take for granted that the energy density, f, is evaluated at the equilibrium profile, z. It is from (7) that stability and instability conditions can be deduced. We present these sequentially in order to distinguish their regimes of applicability. Our principal findings are in the form of *pointwise* inequalities, which may arguably be of greatest use to researchers in the field. However, it turns out that in each case supplementary conditions in the form of *integral* inequalities can be presented which have potential use in physical interpretations.

Condition 1 (Stability)**.** *A sufficient condition for $z(r)$ to be a stable equilibrium profile is that*

$$\Phi(r) := \frac{\left(f_{zz} - \left(f_{zz_r}\right)_r\right)}{f_{z_r z_r}} \geqslant 0 \qquad r \in [0, R_c]. \tag{8}$$

Proof. In this proof and in the two following we rely on the fact that $f_{z_r z_r} > 0$ for all $r \in (0, R_c]$, and on the assumption that the integrand in the second variation

$$g''(0) = \int_0^{R_c} \left(f_{z_r z_r}\eta_r^2 + \left(f_{zz} - \left(f_{zz_r}\right)_r\right)\eta^2\right) \mathrm{d}r$$

is single-signed in the respective cases of interest. Application of the mean-value theorem gives, for some $\rho \in [0, R_c]$,

$$g''(0) = f_{z_r z_r}(\rho) \int_0^{R_c} \eta_r^2 + \frac{\left(f_{zz} - \left(f_{zz_r}\right)_r\right)}{f_{z_r z_r}}\eta^2 \, \mathrm{d}r.$$

Therefore,

$$g''(0) = f_{z_r z_r}(\rho) \int_0^{R_c} \eta_r^2 + \Phi(r)\eta^2 \, \mathrm{d}r > 0$$

for all $\eta \neq 0$, if $\Phi(r) > 0$ for all $r \in [0, R_c]$. □

Note that the pointwise inequality $\Phi(r) > 0$ implies the integral inequality

$$\int_0^{R_c} 2\pi r W(r) h_{zz}(r, z) \, \mathrm{d}r + \pi R_c^2 G \geqslant 0 \tag{9}$$

where use has been made of the derivatives in (6).

More interesting results arise in the case when $\Phi(r) < 0$ over at least part of the interval. In such cases, sufficient conditions for *either* stability *or* instability can be established.

Condition 2 (Stability)**.** *Let $\lambda_1 > 0$, λ_2 be constants satisfying the inequality*

$$-\lambda_1 = \min_{r \in [0, R_c]} \Phi(r) \leqslant \Phi(r) \leqslant \max_{r \in [0, R_c]} \Phi(r) = \lambda_2 \tag{10}$$

where $\Phi(r)$ is defined as in (8). If $\lambda_1 < \pi^2 \big/ 4R_c^2$, then $z(r)$ is a stable equilibrium profile.

Here, $-\lambda_1$ and λ_2 represent the minimum and maximum values of $\Phi(r)$, respectively, over the range of r values. The condition therefore states that if the minimum value of $\Phi(r)$ is strictly greater than $-\pi^2 \big/ 4R_c^2$, where R_c is the contact radius, then the minimizing profile found as a solution to the Euler–Lagrange equation (1) will be stable. Note that in condition 2, the maximum value of Φ need not be specified.

Proof. As stated, we insist that

$$f_{z_r z_r} = \frac{2\pi r h(r, z)}{\left(1 + z_r^2\right)^{3/2}} > 0 \qquad r \in (0, R_c]$$

and write again

$$g''(0) = \int_0^{R_c} f_{z_r z_r} \left(\eta_r^2 + \frac{\left(f_{zz} - \left(f_{zz_r}\right)_r\right)}{f_{z_r z_r}}\eta^2\right) \mathrm{d}r.$$

Provided the content of the brackets is single-signed, an application of the mean-value theorem gives, for some $\rho \in [0, R_c]$,

$$\begin{aligned} g''(0) &= f_{z_r z_r}(\rho) \int_0^{R_c} \eta_r^2 + \Phi(r)\eta^2 \, \mathrm{d}r \\ &\geqslant f_{z_r z_r}(\rho) \left[\int_0^{R_c} \eta_r^2 \, \mathrm{d}r - \lambda_1 \int_0^{R_c} \eta^2 \, \mathrm{d}r \right] \\ &= f_{z_r z_r}(\rho) \int_0^{R_c} \eta^2 \, \mathrm{d}r \left[\frac{\int_0^{R_c} \eta_r^2 \, \mathrm{d}r}{\int_0^{R_c} \eta^2 \, \mathrm{d}r} - \lambda_1 \right] \qquad \eta \neq 0 \\ &\geqslant f_{z_r z_r}(\rho) \int_0^{R_c} \eta^2 \, \mathrm{d}r \left[\min_{\Omega_r/\{0\}} \frac{\int_0^{R_c} \eta_r^2 \, \mathrm{d}r}{\int_0^{R_c} \eta^2 \, \mathrm{d}r} - \lambda_1 \right] \\ &= f_{z_r z_r}(\rho) \, \|\eta\|_2^2 \, (\mu - \lambda_1) \end{aligned} \tag{11}$$

where

$$\mu = \min_{\Omega_r/\{0\}} \frac{\int_0^{R_c} \eta_r^2 \, \mathrm{d}r}{\int_0^{R_c} \eta^2 \, \mathrm{d}r} = \min_{\Omega_r/\{0\}} \left(\frac{I_1}{I_2} \right) > 0 \tag{12}$$

and where $\|\cdot\|_2^2 := \int |\cdot|^2 \, \mathrm{d}r$ is the integral norm, and the minimum in (12) is with respect to all functions belonging to the set Ω_r that are not identically zero. The minimum value of this ratio of positive integrals can be obtained via a variational calculation. Suppose $\zeta \in \Omega_r$ is the function giving the minimum value to I_1/I_2, then a necessary condition it must satisfy is that

$$\begin{aligned} \delta \left(\frac{I_1}{I_2} \right) &= \frac{I_2 \delta I_1 - I_1 \delta I_2}{I_2^2} = \frac{1}{I_2} \left(\delta I_1 - \left(\frac{I_1}{I_2} \right)_{\min} \delta I_2 \right) \\ &= \frac{1}{I_2} (\delta I_1 - \mu \delta I_2) = 0 \end{aligned} \tag{13}$$

where

$$\delta I_2 = \int_0^{R_c} \frac{\mathrm{d}}{\mathrm{d}\epsilon} (\zeta + \epsilon \eta)^2 \bigg|_{\epsilon=0} \mathrm{d}r$$

with $\eta \in \Omega_r$ arbitrary. A similar expression exists for δI_1. The variational problem (13) is thus equivalent to the integral equation

$$\int_0^{R_c} (\zeta_r \eta_r - \mu \zeta \eta) \, \mathrm{d}r = 0 \quad \Longrightarrow \quad \int_0^{R_c} (-\zeta_{rr} - \mu \zeta) \eta \, \mathrm{d}r + \int_0^{R_c} \frac{\mathrm{d}}{\mathrm{d}r} (\zeta_r \eta) \, \mathrm{d}r = 0$$

where the second equality has been obtained by integrating by parts. The second integral on the right vanishes upon invoking the properties of ζ and η. As $\eta \in \Omega_r$ was chosen arbitrarily (or, strictly speaking, by the Dubois–Reymond lemma [28]), the minimization problem is equivalent to the eigenvalue problem

$$\begin{cases} \zeta_{rr} + \mu \zeta = 0 \\ \zeta_r(0) = \zeta(R_c) = 0 \end{cases}$$

which clearly has sinusoidal solutions. The boundary conditions result in the eigenvalue equation

$$\cos \left(\mu^{\frac{1}{2}} R_c \right) = 0$$

which has solutions

$$\mu^{\frac{1}{2}} R_c = \pm\pi/2, \pm 3\pi/2, \pm 5\pi/2, \ldots$$

or, for integers $n \geqslant 1$,

$$\mu_n = \frac{(2n-1)^2\pi^2}{4R_c^2}.$$

The least possible value occurs when $n = 1$:

$$\mu = \min_n \mu_n = \mu_1 = \frac{\pi^2}{4R_c^2}.$$

Consequently, if $\lambda_1 < \mu = \pi^2/4R_c^2$, then from (11) we have stability. □

If the criteria of condition 2 are met and in particular $\lambda_1 < \pi^2/4R_c^2$, then the predicted stable equilibrium profile, z, also satisfies the integral inequality,

$$\frac{\pi^2}{4R_c^2} E_s + \pi R_c^2 G + \int_0^{R_c} 2\pi r W(r)\, h_{zz}(r, z)\, \mathrm{d}r > 0 \tag{14}$$

where

$$E_s = \int_0^{R_c} 2\pi r W(r) h(r, z)\, \mathrm{d}r \tag{15}$$

is the total surface energy of the stressed drop. Condition (14) can be established by noting that the inequality

$$\lambda_1 < \frac{\pi^2}{4R_c^2}$$

is equivalent to the inequality

$$-\frac{\pi^2}{4R_c^2} < -\lambda_1 < \Phi(r)$$

valid pointwise. That is, using (6)

$$-2\pi r(G + h_{zz}W) + \left(\frac{2\pi r z_r h_z}{W}\right)_r < \frac{\pi^2}{4R_c^2}\frac{2\pi r h}{W^3} < \frac{\pi^2}{4R_c^2} 2\pi r h W$$

for all $r \in [0, R_c]$. This last inequality is easily seen to be true since $W = \left(1 + z_r^2\right)^{1/2} \geqslant 1$. Upon integration over the interval $(0, R_c)$, we arrive at the integral inequality

$$-\int_0^{R_c} 2\pi r W(r) h_{zz}\, \mathrm{d}r - \pi R_c^2 G + \left[\frac{2\pi r z_r h_z}{W}\right]_{r=0}^{r=R_c} < \frac{\pi^2}{4R_c^2}\int_0^{R_c} 2\pi r W(r) h\, \mathrm{d}r.$$

The third term on the left-hand side vanishes since h is effectively nonzero only within a bounded region centred on the apex of the drop.

Unfortunately, the integral condition, (14), does not hold the status of a sufficient condition for stability equivalent to the pointwise condition, $-\pi^2/4R_c^2 < -\lambda_1 < \Phi(r)$. While a sufficient condition in integral form, corresponding to this pointwise condition, can be mathematically established (but is less meaningful physically); the integral inequality (14) itself cannot be considered as such. In fact, without further analytical justification, (14) can at best represent a necessary condition for stability.

In a manner similar to the proof of condition 2, we can establish a sufficient condition for *instability* of an equilibrium profile, $z(r)$. Note first that for stability we have established that the second variation must be positive for all possible perturbations to the equilibrium profile.

If the variation is negative for a particular perturbation, then the system (the drop) is unstable. This is a fact we exploit in the following.

Condition 3 (Instability)**.** *Let* $\lambda_1, \lambda_2 > 0$ *be constants satisfying the inequality*

$$-\lambda_1 = \min_{r\in[0,R_c]} \Phi(r) \leqslant \Phi(r) \leqslant \max_{r\in[0,R_c]} \Phi(r) = -\lambda_2 < 0.$$

Then, a sufficient condition for instability of the equilibrium profile, $z(r)$*, is* $\lambda_2 > \pi^2\big/4R_c^2$.

Here, $-\lambda_1$ and $-\lambda_2$ represent the minimum and maximum values of $\Phi(r)$. This time it is assumed that the maximum, $-\lambda_2$, is less than zero. The condition states that if the maximum is strictly less than $-\pi^2\big/4R_c^2$, then the equilibrium profile solving the Euler–Lagrange equation (1) will be unstable.

Proof. As before we define

$$g''(0) = \int_0^{R_c} f_{z_r z_r}\left(\eta_r^2 + \frac{\left(f_{zz} - \left(f_{zz_r}\right)_r\right)}{f_{z_r z_r}}\eta^2\right) \mathrm{d}r = \int_0^{R_c} f_{z_r z_r}\left(\eta_r^2 + \Phi(r)\eta^2\right) \mathrm{d}r.$$

Provided $f_{z_r z_r} > 0$ (as will be the case with most physical systems encountered in practice) and that the remainder of the integrand is single-signed, an application of the mean-value theorem gives, for some $\rho \in [0, R_c]$,

$$\begin{aligned} g''(0) &= f_{z_r z_r}(\rho) \int_0^{R_c} \eta_r^2 + \Phi(r)\eta^2 \,\mathrm{d}r \\ &\leqslant f_{z_r z_r}(\rho)\left[\int_0^{R_c} \eta_r^2 \,\mathrm{d}r - \lambda_2 \int_0^{R_c} \eta^2 \,\mathrm{d}r\right] \\ &= f_{z_r z_r}(\rho) \int_0^{R_c} \eta^2 \,\mathrm{d}r \left[\frac{\int_0^{R_c} \eta_r^2 \,\mathrm{d}r}{\int_0^{R_c} \eta^2 \,\mathrm{d}r} - \lambda_2\right] \qquad \eta \neq 0. \end{aligned} \tag{16}$$

Accordingly, if the right-hand side of (16) is negative for any $\eta \in \Omega_r$ then the equilibrium profile is unstable. Therefore, for instability, it is sufficient that

$$\lambda_2 > \frac{\int_0^{R_c} \zeta_r^2 \,\mathrm{d}r}{\int_0^{R_c} \zeta^2 \,\mathrm{d}r} = \min_{\Omega_r/\{0\}} \frac{\int_0^{R_c} \eta_r^2 \,\mathrm{d}r}{\int_0^{R_c} \eta^2 \,\mathrm{d}r} = \mu$$

where $\zeta \in \Omega_r$ is the perturbation giving the minimum value of the integral ratio. That is, for instability it is sufficient that λ_2 be larger than the least possible value of the ratio of these integrals. A variational calculation leads once more to the possible discrete eigenvalues

$$\mu_n = \frac{(2n-1)^2\pi^2}{4R_c^2} \qquad n \geqslant 1$$

from which we deduce that $\lambda_2 > \pi^2\big/4R_c^2 = \mu_1$ is sufficient to ensure instability. □

As a corollary, we can establish the following integral condition associated with the unstable profile:

$$\frac{\pi^2}{4R_c^2(1+K^2)^2} E_s + \int_0^{R_c} 2\pi r W(r) h_{zz}(r, z) \,\mathrm{d}r + \pi R_c^2 G < 0 \tag{17}$$

where K is a positive constant having the property that $0 \leqslant |z_r| < K$, for all $r \in [0, R_c]$, and E_s is as defined in (15). This follows directly. Let $K > 0$ exist such that $0 \leqslant |z_r| < K$, for all $r \in [0, R_c]$. The equivalence

$$\lambda_2 > \frac{\pi^2}{4R_c^2} \quad\Longleftrightarrow\quad \Phi(r) < -\lambda_2 < -\frac{\pi^2}{4R_c^2} \qquad r \in [0, R_c]$$

establishes the pointwise inequality,

$$2\pi r(G + h_{zz}W) - \left(\frac{2\pi r z_r h_z}{W}\right)_r < -\frac{\pi^2}{4R_c^2}\frac{2\pi r h}{W^3}$$

for all $r \in [0, R_c]$. Integrating over the interval $(0, R_c)$ we find that this, in turn, implies the integral inequality

$$\pi R_c^2 G + \int_0^{R_c} 2\pi r W(r) h_{zz}\,\mathrm{d}r - \left[\frac{2\pi r z_r h_z}{W}\right]_{r=0}^{r=R_c} < -\frac{\pi^2}{4R_c^2}\int_0^{R_c}\frac{2\pi r h}{W^3}\,\mathrm{d}r$$
$$< -\frac{\pi^2}{4R_c^2}\min_{r\in(0,R_c)}\left[\frac{1}{W^4(r)}\right]\int_0^{R_c} 2\pi r h W(r)\,\mathrm{d}r$$

since the functions involved are continuous over the interval, $(0, R_c)$. The stated corollary follows upon defining $K = \max|z_r|$ and setting the third term on the left-hand side to zero for those functions h restricted to a bounded region centred on the apex of the drop. As in the discussion following condition 2, equation (17) itself is not a condition equivalent to the inequality $\lambda_2 > \pi^2/4R_c^2$ which ensures instability. Equation (17) will, however, be satisfied by the unstable profile whenever $\lambda_2 > \pi^2/4R_c^2$ is in effect.

3. Discussion and concluding remarks

The results presented here have direct application to an axisymmetric sessile drop with pinned three-phase contact line, seated on a horizontal substrate. Despite its special nature, this one case should be the easiest to reproduce experimentally. Ducker *et al* [3], for example, used the atomic force microscope technique to study the interaction of a colloidal particle (colloidal probe) with a pinned bubble. Hartley *et al* [12] used the same technique in the case of a liquid oil droplet.

The three pointwise conditions we have introduced are represented schematically in figure 1. Note that the figure as well as the criteria stated in the text suggest that condition 1 is a special case of condition 2 (and can be derived from it by a redefinition of the limits, λ_1 and λ_2). However, condition 1 is stated explicitly as it leads to the stricter inequality, (9), and as it is referred to in the discussion below. As the pointwise inequalities in conditions 1–3 require only that the profile function, $z(r)$, and its slope, $z_r(r)$, be known, these conditions have considerable utility for case studies. Effectively, to demonstrate stability or instability for a particular system one need only produce a figure such as this schematic. With regard to the integral inequalities, (9), (14) and (17), the different terms appearing are 'macroscopic'. However, only two of these are in terms of quantities that are immediately identifiable. The first is a gravity term, $G\pi R_c^2$, which can be positive, negative, or zero depending on the fluid density difference, $\Delta\rho$. The second is a term involving the total surface energy, E_s, defined in equation (15), which unfortunately can be difficult to determine directly through experiment. Less certain is the integral term involving the derivative function, h_{zz}. As yet it is not clear to us what physical interpretation this term should be given. It is possible that for further analysis it may be necessary to use estimates of the surface energy density, σ, in individual cases.

The sufficient condition, $\lambda_1 < \pi^2/4R_c^2$, for stability leads naturally to a necessary condition for instability. That is, instability $\Longrightarrow \lambda_1 > \pi^2/4R_c^2$. From this and a corresponding observation of condition 3, it is clear that there exists a grey area associated with the interval

$$-\lambda_1 < -\pi^2/4R_c^2 < -\lambda_2$$

in which our statements of stability and instability are no longer useful. One consequence of this is that conditions 1–3 cannot offer any information about the stability–instability transition,

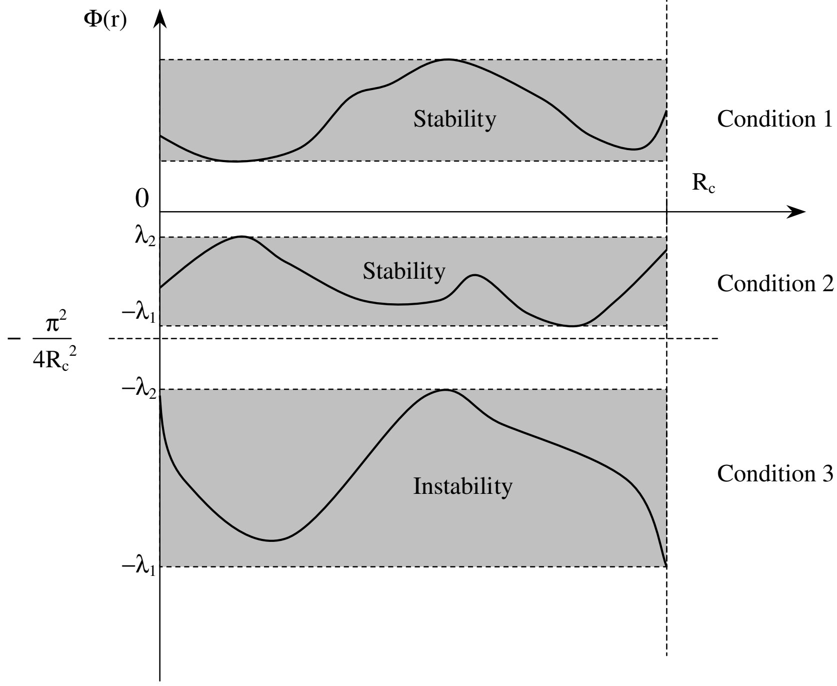

Figure 1. A schematic illustration of the relation between the minimum and maximum values of the function $\Phi(r)$ and the eigenvalue $\mu_1 = \pi^2/4R_c^2$, covering the three possibilities corresponding to conditions 1–3.

which is also of interest. Our analysis, thus, sheds light not only on the existence of extremes where either stability or instability is ensured, it also indicates where further studies, possibly involving other methods, should focus attention.

In the latter respect it is interesting to briefly compare the analysis followed here with two other approaches. Firstly, equation (7) can be expressed in the bilinear form

$$\delta^2 F = \frac{\epsilon^2}{2} \int_0^{R_c} \boldsymbol{x}^T \mathbf{A} \boldsymbol{x} \, \mathrm{d}r \qquad (18)$$

where the vector $\boldsymbol{x}^T = (\eta, \eta_r)$ and $\mathbf{A}$ is a diagonal matrix with nonzero components $\left(f_{zz} - \left(f_{zz_r}\right)_r\right)$ and $f_{z_r z_r}$. The eigenvalues of $\mathbf{A}$ are these functions themselves and are therefore r-dependent. The stability question can then be crudely phrased in terms of the minimum and maximum values of these functions over the interval $(0, R_c)$. Since we already assert that $f_{z_r z_r} > 0$, stability is guaranteed if $\min\left(f_{zz} - \left(f_{zz_r}\right)_r\right) > 0$ (the minimum taken over the r-interval). Instability on the other hand arises when at least one of these eigenvalues is negative. Consequently, if $\max\left(f_{zz} - \left(f_{zz_r}\right)_r\right) < 0$ then $z(r)$ is an unstable profile (a saddle point instability). The first of these is the special (weaker) case of condition 1 above. The second is consistent with our condition 3, but is much less informative. This crude approach is therefore much more limited than the one advocated in this paper.

Another approach, the Ritz method, is based on the idea of adopting explicit forms for the perturbation functions $\eta \in \Omega_r$, each depending on a finite number of parameters that are subsequently optimized [29]. With these one can obtain numerical approximations to the eigenvalues of the linear (self-adjoint) operator associated with $\delta^2 F$ [26]:

$$L_z \eta = -\left(f_{z_r z_r} \eta_r\right)_r + \left(f_{zz} - \left(f_{zz_r}\right)_r\right) \eta \qquad \text{for} \quad \eta \in \Omega_r. \qquad (19)$$

This approach is quite useful in that it normally provides a good estimate for the smallest eigenvalue, whose sign will indicate stability or instability. However, the estimate obtained is often dependent on the choice of explicit perturbation function (or sequence of functions) $\eta \in \Omega_r$, and is always larger than the true eigenvalue. Consequently, if the estimate is positive it may still not be possible to establish conclusively whether the given profile is stable or unstable, as the true eigenvalue may actually be negative. On the other hand, if one obtains a negative estimate for the smallest eigenvalue, then instability is certain with the estimate being a useful bound. The main disadvantages of the Ritz method are thus twofold. First, explicit test functions must be chosen, with the eigenvalue estimate being dependent on the choice. Second, instability cannot be ensured unless the estimate is negative, and no sufficient condition for stability can be provided at all. In contrast, the approach adopted here fulfils the aim of providing sufficient conditions for either stability or instability, without any of the uncertainties inherent in the Ritz method. The conditions we have derived are quite general, being unassociated with a particular system and independent of the choice of perturbation functions. Another, though less important, consideration is that, in contrast to the Ritz method, no further analysis need be undertaken to test conditions 1–3.

In a separate report [26] more general considerations than those taken up here have been addressed. An example concerns the possibility of an axisymmetric equilibrium profile becoming unstable when perturbed *asymmetrically*, even though stable to axisymmetric disturbances. That is, there is the possibility that axisymmetric perturbations are not the most unstable ones. While it is not yet clear whether definitive statements such as those given here can be made in the more general situation, due to several additional factors, it would be reasonable to expect from physical grounds that axisymmetric perturbations be the more unstable ones in cases involving attractive colloidal interactions. For repulsive colloidal interactions either axisymmetric or asymmetric disturbances can induce instability first. Further studies, however, need be undertaken in order to say whether any definitive statements can be made in general.

To our knowledge this is the first occasion on which sufficient conditions for equilibrium stability or instability have been put forward in the context of colloidal interactions with fluid droplets. This is in contrast to the fluid dynamic field in which stability studies of a vast variety of flow situations have been performed [30, 31]. However, some well-established basic concepts in dynamic stability are clearly applicable to the current problem, and have thus been employed in this paper. In a future paper implications of the conditions introduced here will be examined in detail through application to specific problems. In that report we shall also take the opportunity of comparing the present results with more traditional stability investigation methods based on analyses of the eigenvalues of the linear operator (19), including the approaches mentioned above (see also [32]).

Acknowledgment

We thank Vladimir Kozlov for valuable discussions.

References

[1] Israelachvili J N 1992 *Intermolecular and Surface Forces* (New York: Academic)
[2] Miklavcic S J 1996 *Phys. Rev.* E **54** 6551
[3] Ducker W A, Xu Z and Israelachvili J N 1994 *Langmuir* **10** 3279
[4] Butt H-J 1994 *J. Colloid Interface Sci.* **166** 109
[5] Evans E, Ritchie K and Merkel R 1995 *Biophys. J.* **68** 2580

[6] Fielden M L, Hayes R A and Ralston J 1996 *Langmuir* **12** 3721
[7] Horn R G, Bachmann D J, Connor J N and Miklavcic S J 1996 *J. Phys.: Condens. Matter* **8** 9483
[8] Basu S and Sharma M M 1996 *J. Colloid Interface Sci.* **181** 443
[9] Mulvaney P, Perera J M, Biggs S, Grieser F and Stevens G W 1996 *J. Colloid Interface Sci.* **183** 614
[10] Snyder B A, Aston D E and Berg J C 1997 *Langmuir* **13** 590
[11] Preuss M and Butt H-J 1998 *Langmuir* **14** 3164
[12] Hartley P G, Grieser F, Mulvaney P and Stevens G W 1999 *Langmuir* **15** 7282
[13] Attard P and Miklavcic S J 2001 *Langmuir* **17** 8217
[14] Attard P and Miklavcic S J 2002 *J. Colloid Interface Sci.* **247** 255
[15] Aston D E and Berg J C 2001 *J. Colloid Interface Sci.* **235** 162
[16] Bhatt D, Newman J and Radke C J 2001 *Langmuir* **17** 116
[17] Chan D Y C, Dagastine R R and White L R 2001 *J. Colloid Interface Sci.* **236** 141
[18] Denkov N D, Petsev N D and Danov K D 1993 *Phys. Rev. Lett.* **71** 3326
[19] Danov K D, Petsev N D, Denkov N D and Borwankar R 1993 *J. Chem. Phys.* **99** 7179
[20] Petsev N D, Denkov N D and Kralchevsky P A 1995 *J. Colloid Interface Sci.* **176** 201
[21] Miklavcic S J, Horn R G and Bachmann D J 1995 *J. Phys. Chem.* **99** 16357
[22] Bachmann D J and Miklavcic S J 1996 *Langmuir* **12** 4197
[23] Miklavcic S J 1998 *Phys. Rev.* E **57** 561
[24] Miklavcic S J and Attard P 2001 *J. Phys. A: Math. Gen.* **34** 7849
[25] Miklavcic S J 2002 *ITN Research Report Series* LiTH-ITN-R-2002-1 (ISSN 1650-2612)
[26] Miklavcic S J 2001 *ITN Research Report Series* LiTH-ITN-R-2001-11 (ISSN 1650-2612)
[27] Courant R and Hilbert D 1965 *Methods of Mathematical Physics* vol 1 (New York: Wiley) ch 4
[28] Renardy M and Rogers R C 1992 *An Introduction to Partial Differential Equations* (New York: Springer)
[29] Lakin W D and Sanchez D A 1982 *Topics in Ordinary Differential Equations* (New York: Dover)
[30] Chandrasekhar S 1981 *Hydrodynamic and Hydromagnetic Stability* (New York: Dover)
[31] Drazin P G and Reid W H 1982 *Hydrodynamic Stability* (Cambridge: Cambridge University Press)
[32] Basaran O A and Scriven L E 1990 *J. Colloid Interface Sci.* **140** 10