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Parametrically driven surface waves in surfactant-covered liquids

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Vertical vibration will excite standing waves on a liquid free surface. We perform a linear-stability analysis for viscous and viscoelastic liquids of arbitrary depth to determine the role that insoluble surfactants play in the formation of these parametrically driven surface waves. We find that in order to obtain time-periodic solutions which involve Marangoni forces in a non-trivial way, it is necessary to consider the high-Peclet number limit of the surfactant transport equation. Floquet theory is applied to the linearized governing equations to obtain a recursion relation for the temporal modes of the free-surface deflection. The recursion relation is then solved numerically to obtain the critical vibration amplitude needed to excite the surface waves, and the corresponding wavenumber. The results show that the presence of surfactants raises or lowers the critical amplitude and wavenumber depending on the spatial phase shift between the surfactant-concentration variations and surface deflections.

Keywords: instability; free surface; waves; surfactant; viscoelasticity

1. Introduction

Wave formation on a liquid free surface subject to vertical vibration has been a topic of active study since the report of Faraday nearly two centuries ago (Faraday 1831). The intricate patterns and complex dynamics displayed by these standing waves have made them a prototype for fundamental studies of spatially extended nonlinear systems (Miles & Henderson 1990; Edwards & Fauve 1994; Kudrolli & Gollub 1996; Hogrefe *et al*. 1998; Lioubashevski *et al*. 1999). An important step in understanding the behaviour of the waves involves prediction of the critical vibration amplitude at which they form. Although this problem has been well studied for inviscid (Benjamin & Ursell 1954), Newtonian (Kumar 1996) and viscoelastic liquids (Kumar 1999), the role of surfactants has not received as much attention. This issue is addressed in the present work through the use of linear-stability analysis and Floquet theory.

Surfactants may appear as contaminants in a given experiment, where their presence generally serves to lower the surface tension. However, if there are variations in surfactant concentration along a free surface, surface-tension variations will result. The latter will exert tangential stresses at the interface and drive a flow in the bulk liquid. These Marangoni flows may change the critical amplitude needed to excite standing waves, as well as the corresponding wavelength. Although existing studies acknowledge this possibility (Miles 1967; Decent 1997), they account for viscous effects in an approximate way and do not address the possibility that there may be a spatial phase shift between the surfactant-concentration variations and surface deflections. Studies of the Faraday instability that account for viscous effects in a more rigorous way (Kumar 1996, 1999) assume that the surface tension is uniform. In addition to appearing as contaminants, surfactants may be an integral part of the liquid itself. In polymer solutions, for example, a layer of polymer may adsorb at the interface and act like a surfactant (Edwards *et al.* 1991). Another valuable reason for understanding surfactant effects is the improvement of applications where vertical vibration of free surfaces plays an important role. These include materials processing in microgravity environments and ultrasonic atomization.

We present here an analysis of the role of surfactants on the formation of parametrically driven surface waves. The theory we develop is valid for viscous and viscoelastic liquids of arbitrary depth covered by a monolayer of insoluble surfactant whose time-scale for diffusion is much slower than the vibration period. The problem is formulated in § 2, Floquet theory is applied in § 3, results and a discussion are given in § 4, and concluding remarks, as well as comparisons of the present work with related previous work, are made in § 5.

2. Problem formulation

(*a*) *Governing equations*

We consider a layer of incompressible viscoelastic liquid which is uniformly covered by a monolayer of insoluble surfactant. The liquid rests on a horizontal plate which undergoes vertical sinusoidal oscillations of amplitude a and frequency ω. The vertical coordinate is denoted by z, such that the bottom of the liquid is taken to be at $z=-h$ while its undisturbed free surface is located at $z=0$. The horizontal and transverse coordinates are represented by x and y, respectively. The effects of lateral boundaries are assumed to be negligible, which is consistent with previous studies (Kumar 1996, 1999).

The equations of momentum and mass conservation are given by

$$\rho(\partial_t \boldsymbol{u} + \boldsymbol{u}\cdot\nabla\boldsymbol{u}) = -\nabla p + \nabla\cdot\boldsymbol{\tau} - \rho B(t)\boldsymbol{e}_z, \tag{2.1}$$

$$\nabla\cdot\boldsymbol{u} = 0, \tag{2.2}$$

in which $\boldsymbol{u}$ represents the velocity field, t denotes time, ρ is the density, p is the pressure, $\boldsymbol{\tau}$ is the deviatoric stress tensor, $\boldsymbol{e}_z$ is the unit vector in the z-direction, and $B(t) = g - a\cos(\omega t)$, where g is the mean gravitational acceleration. The stress tensor, τ, is expressed as follows:

$$\boldsymbol{\tau} = \eta_{\mathrm{s}}(\nabla\boldsymbol{u} + (\nabla\boldsymbol{u})^{\mathrm{T}}) + \boldsymbol{a}, \tag{2.3}$$

where η_{s} is the solvent viscosity and $\boldsymbol{a}$ is the non-Newtonian contribution to the stress tensor, which is potentially a complicated function of the velocity and its gradients. In this work, however, only linear perturbations about a quiescent base state will be considered, meaning that the displacement gradients will be small. We may then apply the linear theory of viscoelasticity to describe $\boldsymbol{a}$ (Bird *et al.* 1987):

$$\boldsymbol{a} = \int_{-\infty}^{t} G(t-t')(\nabla \boldsymbol{u} + (\nabla \boldsymbol{u})^{\mathrm{T}})\,\mathrm{d}t', \tag{2.4}$$

in which $G(t-t')$ is called the relaxation modulus.

The location of the air–liquid interface is taken to be $z = \zeta(x, y, t)$, where ζ represents the surface deflection from its quiescent state. The shear stress balance at the interface is expressed by (Deen 1998)

$$\boldsymbol{t} \cdot \boldsymbol{\pi} \cdot \boldsymbol{n} = \boldsymbol{t} \cdot \nabla_{\mathrm{s}}\, \sigma, \tag{2.5}$$

$$\boldsymbol{n} \cdot \boldsymbol{\pi} \cdot \boldsymbol{n} = -\sigma\kappa. \tag{2.6}$$

Here, the dynamics of the air overlaying the liquid layer have been neglected. In (2.5) and (2.6), the tensor $\boldsymbol{\pi}$ is expressed by

$$\boldsymbol{\pi} = -(p - \rho B(t)\zeta)\boldsymbol{\delta} + \boldsymbol{\tau}, \tag{2.7}$$

in which $\boldsymbol{\delta}$ is the identity tensor, σ is the surface tension, κ is the curvature, and $\boldsymbol{t}$ and $\boldsymbol{n}$ are the tangent and normal vectors to the interface, respectively.

The kinematic boundary condition at $z = \zeta(x, y, t)$ is given by

$$(\partial_t + \boldsymbol{u}_{\mathrm{s}} \cdot \nabla_{\mathrm{s}})\zeta = w_{\mathrm{s}}, \tag{2.8}$$

where $\boldsymbol{u}_{\mathrm{s}}$ and w_{s} denote the velocity vector and its vertical component evaluated at $z = \zeta$, and $\nabla_{\mathrm{s}} = (\boldsymbol{\delta} - \boldsymbol{nn}) \cdot \nabla$ is the surface gradient operator. The equation of mass conservation for the surfactant is given by

$$\partial_t \Gamma + \nabla_{\mathrm{s}} \cdot (\boldsymbol{u}_{\mathrm{s}}\Gamma) + (\boldsymbol{u}_{\mathrm{s}} \cdot \boldsymbol{n})(\nabla_{\mathrm{s}} \cdot \boldsymbol{n})\Gamma = \mathcal{D}\nabla_{\mathrm{s}}^2 \Gamma, \tag{2.9}$$

where Γ is the surfactant surface concentration and $\mathcal{D}$ is the surface diffusion coefficient (Stone 1990). In (2.9), the second term on the left-hand side represents transport by convection, the third term represents transport due to surface dilation, while the term on the right-hand side represents diffusive transport. Finally, no-slip and no-penetration are applied at the plate:

$$w|_{z=-h} = 0 \quad \text{and} \quad \partial_z w|_{z=-h} = 0. \tag{2.10}$$

(*b*) *Scaling and linearization*

In order to render these equations dimensionless, the following scaling is chosen:

$$\boldsymbol{u} = (\omega d)\tilde{\boldsymbol{u}}, \quad (x, y, z) = h(\tilde{x}, \tilde{y}, \tilde{z}), \quad \zeta = d\tilde{\zeta}, \quad t = (1/\omega)\tilde{t}, \quad p = (\eta_{\mathrm{s}}\omega d/h)\tilde{p}, \tag{2.11}$$

where tilde denotes a dimensionless quantity. In this work, we shall assume that the ratio of the deflection amplitude to the liquid depth is $\epsilon = d/h \ll 1$. For the surfactant concentration, Γ, and surface tension, σ, we choose the following scaling:

$$\Gamma = \Gamma_{\mathrm{m}}\tilde{\Gamma} \quad \text{and} \quad \sigma = \sigma_{\mathrm{m}} + \tilde{\sigma}\mathcal{S}, \tag{2.12}$$

where Γ_{m} denotes the mean surfactant concentration and σ_{m} is the surface tension corresponding to Γ_{m}. The spreading pressure is given by $\mathcal{S} = \sigma_0 - \sigma_{\mathrm{m}}$, where σ_0

denotes the value of the surface tension for an uncontaminated liquid surface. We shall assume that the surfactant concentration is dilute enough to permit use of a linear equation of state:

$$\sigma = \sigma_0 + \left(\frac{\partial \sigma}{\partial \mathit{\Gamma}}\right)_{\mathit{\Gamma}=0} \mathit{\Gamma}. \tag{2.13}$$

We will write the relaxation modulus as $G(t-t') = (\eta_{\mathrm{p}}/\lambda)F(t-t')$, where η_{p} is the non-Newtonian contribution to the zero-shear viscosity of the liquid, λ is a characteristic relaxation time, and F is a dimensionless function.

The above scalings are substituted into the governing equations, boundary conditions and equation of state, which are then linearized; we henceforth drop the tilde notation. The equation of momentum conservation becomes

$$\mathcal{R}\boldsymbol{u}_t = -\nabla p + \nabla^2 \boldsymbol{u} + \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')\nabla^2\boldsymbol{u}\,\mathrm{d}t' + O(\epsilon), \tag{2.14}$$

where $\mathcal{R}$ is a modified Reynolds number expressed by

$$\mathcal{R} \equiv \frac{\rho h^2 \omega}{\eta_{\mathrm{s}}}, \tag{2.15}$$

and $\eta \equiv \eta_{\mathrm{p}}/\eta_{\mathrm{s}}$. The Deborah number, a ratio of the characteristic relaxation time to the characteristic time-scale associated with the flow, is given by

$$De \equiv \lambda\omega. \tag{2.16}$$

The continuity equation is unaltered.

The shear stress balance becomes

$$(\nabla_{\mathrm{s}}^2 - \partial_{zz})w|_{z=0} + \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')(\nabla_{\mathrm{s}}^2 - \partial_{zz})w|_{z=0}\,\mathrm{d}t' = \mathcal{M}\nabla_{\mathrm{s}}^2\sigma + O(\epsilon), \tag{2.17}$$

in which $\mathcal{M}$ is a Marangoni parameter, which represents a ratio of Marangoni stresses to viscous stresses:

$$\mathcal{M} \equiv \frac{\mathcal{S}}{\eta_{\mathrm{s}}\omega d}. \tag{2.18}$$

The normal stress balance is expressed by

$$p|_{z=0} = 2\partial_z w|_{z=0} + 2\frac{\eta}{De}\int_{-\infty}^{t} F(t-t')\partial_z w|_{z=0}\,\mathrm{d}t' + B(t)\zeta - \mathcal{C}\nabla_{\mathrm{s}}^2\zeta + O(\epsilon), \tag{2.19}$$

where $B(t)$, the dimensionless modulated gravity, is expressed by

$$B(t) = \mathcal{B} - \mathcal{A}\cos(t) \tag{2.20}$$

in which

$$\mathcal{A} \equiv \frac{\rho a h^2}{\eta_{\mathrm{s}}\omega d} \tag{2.21}$$

is the dimensionless amplitude of the sinusoidal acceleration and

$$\mathcal{B} \equiv \frac{\rho g h^2}{\eta_{\mathrm{s}}\omega d} \tag{2.22}$$

provides a measure of the significance of the mean gravitational forces. The parameter $\mathcal{C}$, given by

$$\mathcal{C} \equiv \frac{\sigma_{\mathrm{m}}}{\eta_{\mathrm{s}}\omega h}, \tag{2.23}$$

is an inverse capillary number reflecting the importance of capillarity. Note that the potential effect of Marangoni stresses on capillarity has been neglected (see Appendix A).

The kinematic boundary condition is now given by

$$\partial_t \zeta = w|_{z=0} + O(\epsilon), \tag{2.24}$$

and the equation of surfactant mass conservation is

$$\partial_t \mathit{\Gamma} = \frac{1}{Pe}\nabla_{\mathrm{s}}^2 \mathit{\Gamma} + O(\epsilon), \tag{2.25}$$

where Pe, which represents the ratio of surfactant transport by Marangoni stresses to that by surface diffusion, is expressed by

$$Pe \equiv \frac{h\omega d}{\mathcal{D}}. \tag{2.26}$$

Equations (2.10) become

$$w|_{z=-1} = 0 \quad \text{and} \quad \partial_z w|_{z=-1} = 0. \tag{2.27}$$

Following scaling, the surfactant equation of state simply becomes

$$\sigma = 1 - \mathit{\Gamma}. \tag{2.28}$$

In arriving at these equations we have performed a Taylor series expansion about $z = 0$ and, to leading order, the free-surface boundary conditions apply at $z = 0$.

(*c*) *Normal-mode decomposition*

Making use of the continuity equation, it can be shown that $\boldsymbol{e}_z \cdot \nabla \wedge \nabla \wedge \boldsymbol{u} = -\nabla^2 w$. Use of this relation permits us to write (2.14) as

$$(\mathcal{R}\partial_t - \nabla^2)\nabla^2 w - \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')\nabla^2(\nabla^2 w)\,\mathrm{d}t' = 0 + O(\epsilon). \tag{2.29}$$

The pressure, p, can be eliminated by applying ∇_{s} to the x- and y-components of (2.1), applying ∇_{s}^2 to (2.19) and using the continuity equation:

$$\begin{aligned} 2\nabla_{\mathrm{s}}^2 \partial_z w|_{z=0} &+ 2\frac{\eta}{De}\int_{-\infty}^{t} F(t-t')\nabla_{\mathrm{s}}^2 \partial_z w|_{z=0}\,\mathrm{d}t' + B(t)\nabla_{\mathrm{s}}^2\zeta - \mathcal{C}\nabla_{\mathrm{s}}^4\zeta \\ &= \mathcal{R}(\partial_t - \nabla^2)\partial_z w|_{z=0} - \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')\nabla^2 \partial_z w|_{z=0}\,\mathrm{d}t' + O(\epsilon). \end{aligned} \tag{2.30}$$

For a liquid layer where the effect of lateral boundaries is negligible, ζ, w and $\mathit{\Gamma}$ may be expressed in terms of the following normal modes:

$$\left.\begin{aligned} \zeta(x,y,t) &\to \zeta(t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}, \\ w(x,y,z,t) &\to w(z,t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}, \\ \mathit{\Gamma}(x,y,t) &\to \mathit{\Gamma}(t)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}}, \end{aligned}\right\} \tag{2.31}$$

where $\boldsymbol{k}$ is the real-valued wave vector in the (x,y)-plane and $\boldsymbol{x}$ is the planar coordinate vector such that $\nabla_{\mathrm{s}}^2 \to -k^2$. Substitution of (2.31) into (2.17), (2.24), (2.27), (2.29) and (2.30) yields

$$[\mathcal{R}\partial_t - (\partial_{zz} - k^2)](\partial_{zz} - k^2)w - \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')(\partial_{zz}^2 - k^2)^2 w \,\mathrm{d}t' = 0 + O(\epsilon), \tag{2.32}$$

$$\partial_t \zeta = w|_{z=0}, \tag{2.33}$$

$$(k^2 + \partial_{zz})w|_{z=0} + \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')(k^2 + \partial_{zz})w|_{z=0}\,\mathrm{d}t' - \mathcal{M}k^2\mathit{\Gamma} = 0 + O(\epsilon), \tag{2.34}$$

$$\begin{aligned}(\mathcal{R}\partial_t - \partial_{zz} + 3k^2)\partial_z w|_{z=0} - \frac{\eta}{De}\int_{-\infty}^{t} F(t-t')(\mathcal{R}\partial_t - \partial_{zz} + 3k^2)\partial_z w|_{z=0}\,\mathrm{d}t' \\ + k^2 B(t)\zeta + \mathcal{C}k^4\zeta = 0 + O(\epsilon),\end{aligned} \tag{2.35}$$

$$\partial_t \mathit{\Gamma} + \frac{k^2}{Pe}\mathit{\Gamma} = 0 + O(\epsilon), \tag{2.36}$$

$$w|_{z=-1} = 0 \quad \text{and} \quad \partial_z w|_{z=-1} = 0. \tag{2.37}$$

Note that $\nabla_{\mathrm{s}}^2\sigma$ has been replaced by $k^2\mathit{\Gamma}$ using (2.28) and (2.31). Equations (2.32)–(2.37) will be used with Floquet theory to investigate the linear-stability characteristics of the problem.

3. Floquet theory

Since the vibration is time-periodic and appears as a coefficient of ζ in (2.35), the response of the standing waves should also be time-periodic according to Floquet theory. However, (2.36) indicates that the surfactant concentration decays exponentially on a time-scale inversely proportional to Pe. Thus, the time-periodic solution to (2.36) is $\mathit{\Gamma} = 0$, which corresponds to a constant surfactant concentration. There are no Marangoni flows with this solution because the surface tension is spatially uniform. As we wish to study the effects of Marangoni flows on time-periodic solutions, we hereby consider the high-Pe limit of (2.36). In this limit, the time-periodic solutions of (2.36) include those for which the surfactant concentration varies spatially, but not temporally. The resulting surface-tension variations will drive a Marangoni flow which should affect the onset of the waves. Recognizing that the Peclet number can also be expressed as $Pe = \epsilon h^2\omega/\mathcal{D}$—and using typical values of $h = 1$ cm, $\omega/2\pi = 60$ Hz and $\mathcal{D} = 10^{-5}$ cm^2 s^{-1}—we see that $Pe \gg 1$ even for relatively small values of ϵ. This indicates that the high-Pe limit of (2.36) is of physical relevance to many situations of interest.

We begin by expressing $\zeta(t)$ and $w(z,t)$ by

$$\zeta(t) = \mathrm{e}^{(s+\mathrm{i}\alpha)t}\sum_{n=-\infty}^{\infty}\zeta_n \mathrm{e}^{\mathrm{i}nt}, \tag{3.1}$$

$$w(z,t) = \mathrm{e}^{(s+\mathrm{i}\alpha)t} \sum_{n=-\infty}^{\infty} w_n(z)\mathrm{e}^{\mathrm{i}nt}, \tag{3.2}$$

where s and α are real valued. The value of α determines whether the surface waves respond subharmonically ($\alpha = \frac{1}{2}$) or harmonically ($\alpha = 0$) to the vibration.

Substitution of equation (3.2) into equation (2.32) yields

$$(\mathrm{D}^2 - q_n^2)(\mathrm{D}^2 - k^2)w_n(z) = 0, \tag{3.3}$$

where $\mathrm{D} \equiv \mathrm{d}/\mathrm{d}z$ and the q_n are given by

$$q_n^2 = k^2 + \frac{\mathcal{R}(s + \mathrm{i}(\alpha + n))}{\nu_n}, \tag{3.4}$$

in which $\nu_n = 1 + (\eta/De)I_n$, wherein the integral I_n is expressed by

$$I_n \equiv \int_0^\infty F(\tau)\mathrm{e}^{-(s+\mathrm{i}(\alpha+n))\tau}\,\mathrm{d}\tau; \tag{3.5}$$

here $\tau = t - t'$. Equation (3.3) suggests a solution for $w_n(z)$ of the form (if $s + \mathrm{i}(\alpha+n) \neq 0$)

$$w_n(z) = P_n\cosh(kz) + Q_n\sinh(kz) + R_n\cosh(q_nz) + S_n\sinh(q_nz). \tag{3.6}$$

Noting that $\varGamma$ is now a time-independent quantity, we substitute (3.2) into (2.34) to obtain

$$\left(1 + \frac{\eta}{De}\right)I_n(\partial_{zz} + k^2)w_n(0) - \bar{\mathcal{M}}k^2\varGamma = 0, \tag{3.7}$$

where

$$\bar{\mathcal{M}} = \frac{\mathcal{M}(1 - \mathrm{e}^{-2\pi(s+\mathrm{i}(\alpha+n))})}{2\pi(s + \mathrm{i}(\alpha + n))}. \tag{3.8}$$

Substituting (3.6) into (3.7) yields

$$[2k^2P_n + (k^2 + q_n^2)R_n]\nu_n - \bar{\mathcal{M}}k^2\varGamma = 0, \tag{3.9}$$

while substitution of equations (3.1) and (3.6) into equation (2.33) yields

$$P_n + R_n = \frac{\nu_n(q_n^2 - k^2)}{\mathcal{R}}\zeta_n. \tag{3.10}$$

It then follows that

$$P_n = \frac{\nu_n}{\mathcal{R}}(q_n^2 + k^2)\zeta_n - \frac{\bar{\mathcal{M}}k^2}{\nu_n(q_n^2 - k^2)}\varGamma \tag{3.11}$$

and

$$R_n = -\frac{2\nu_n}{\mathcal{R}}k^2\zeta_n + \frac{\bar{\mathcal{M}}k^2}{\nu_n(q_n^2 - k^2)}\varGamma. \tag{3.12}$$

Substitution of equation (3.6) into equations (2.37) yields

$$\begin{aligned} P_n\cosh(k) - Q_n\sinh(k) + R_n\cosh(q_n) - S_n\sinh(q_n) &= 0, \\ -kP_n\sinh(k) + kQ_n\cosh(k) - q_nR_n\sinh(q_n) + q_nS_n\cosh(q_n) &= 0. \end{aligned}$$

Making use of the result $\cosh^2(q_n) - \sinh^2(q_n) = 1$, it then follows that

$$Q_n = \frac{q_n R_n - P_n[k\sinh(k)\sinh(q_n) - q_n\cosh(k)\cosh(q_n)]}{q_n\sinh(k)\cosh(q_n) - k\sinh(q_n)\cosh(k)}, \tag{3.13}$$

$$S_n = -\frac{kP_n + R_n[k\cosh(k)\cosh(q_n) - q_n\sinh(k)\sinh(q_n)]}{q_n\sinh(k)\cosh(q_n) - k\sinh(q_n)\cosh(k)}. \tag{3.14}$$

Substitution of equation (3.6) into equation (2.35) yields

$$\begin{aligned}\nu_n[Q_n(k(q_n^2 - k^2) + 2k^3) + S_n(q_n(q_n^2 - k^2) + q_n(3k^2 - q_n^2))] \\ + \mathcal{B}k^2\zeta_n + \mathcal{C}k^4\zeta_n = \tfrac{1}{2}k^2\mathcal{A}(\zeta_{n+1} + \zeta_{n-1}).\end{aligned} \tag{3.15}$$

Substitution of equations (3.11)–(3.14) into equation (3.15) finally yields

$$A_n\zeta_n + B_n\varGamma = \tfrac{1}{2}\mathcal{A}(\zeta_{n+1} + \zeta_{n-1}), \tag{3.16}$$

wherein

$$A_n = \frac{\begin{array}{l}[k^2\mathcal{B} + \mathcal{C}k^4 - \nu_n^2((4k^3/\mathcal{R})q_n(q_n^2 + k^2) \\ \qquad -(k/\mathcal{R})[C_n\cosh(k)\cosh(q_n) - D_n\sinh(k)\sinh(q_n)]])]\end{array}}{k^2(q_n\sinh(k)\cosh(q_n) - k\sinh(q_n)\cosh(k))}, \tag{3.17}$$

$$B_n = \bar{\mathcal{M}}k\frac{[E_n(1 - \cosh(k)\cosh(q_n)) + F_n(\sinh(k)\sinh(q_n))]}{q_n\sinh(k)\cosh(q_n) - k\sinh(q_n)\cosh(k)}, \tag{3.18}$$

in which

$$\begin{aligned}C_n &= q_n(q_n^4 + 2q_n^2k^2 + 5k^4), \\ D_n &= k(q_n^4 + 6q_n^2k^2 + k^4), \\ E_n &= q_n\frac{(q_n^2 + 3k^2)}{(q_n^2 - k^2)}, \\ F_n &= k\frac{(3q_n^2 + k^2)}{(q_n^2 - k^2)}.\end{aligned}$$

If $s + \mathrm{i}(\alpha + n) = 0$, then $w_0(z) = 0$ and we take $A_0 = (\mathcal{B}k + \mathcal{C}k^3)$ and $B_0 = 0$.

For $\mathcal{M} = 0$, (3.16) takes the form of a recursion relation for the ζ_n. This recursion relation can be truncated at a particular value of n and a matrix eigenvalue problem can be formed (Kumar & Tuckerman 1994). The solution of this eigenproblem (by standard numerical methods) for $s = 0$ yields the neutral stability curves, from which the critical vibration amplitude and corresponding wavenumber can be found. To employ a similar strategy for $\mathcal{M} \neq 0$, an expression is needed to relate $\varGamma$ to ζ_n. A reasonable assumption is that variations in the surfactant concentration will occur when the surface is deformed. This motivates us to take

$$\varGamma = \gamma\zeta_n\mathrm{e}^{\mathrm{i}\phi}. \tag{3.19}$$

Here, γ is a coupling constant and ϕ is a phase angle between the variations in surfactant concentration and surface deflection. According to (3.19), each temporal mode of the surface deflection is associated with a corresponding concentration variation. Equation (3.19) also allows for the fact that the surface and concentration disturbances may not be in phase spatially. The constant γ can be absorbed into the Marangoni number, while ϕ can be varied to study the effects of phase shifts.

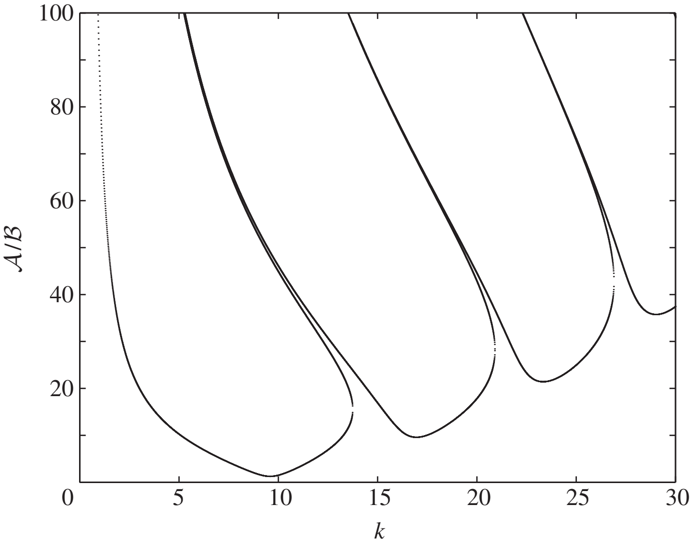

Figure 1. Tongue-like neutral stability curves in the k–$\mathcal{A}$-plane. The tongues alternately correspond to subharmonic and harmonic responses of the interfacial waves to the forcing, with the tongue closest to the $\mathcal{A}$-axis corresponding to a subharmonic response. These curves correspond to the case where $\mathcal{B} = 26$, $\mathcal{R} = 3770$, $\mathcal{C} = 0.8$, $\mathcal{M} = 0$ and $\eta = 0$.

4. Results and discussion

The critical vibration amplitude and corresponding wavenumber can be determined from the neutral stability curves, as noted above. The neutral curves form a series of tongue-like regions in the k–$\mathcal{A}$-plane, with each tongue alternately corresponding to a subharmonic or harmonic response. A typical set of these curves is shown in figure 1, and the critical amplitude and wavenumber are given by the location of the tongue tip closest to the k-axis.

For inviscid liquids, all the tongue tips touch the k-axis (Benjamin & Ursell 1954). This indicates that the standing waves can be excited by arbitrarily small amplitudes, and that a unique wavenumber is not selected at instability onset. The presence of viscosity pushes all the tongue tips off the k-axis, leaving the first subharmonic tongue closest to the k-axis (figure 1). This corresponds to a situation where the waves respond subharmonically to the vibration frequency. Harmonic responses in Newtonian liquids are possible if the liquid depth is sufficiently shallow (Kumar 1996). This has the effect of damping out long-wavelength disturbances, and pushes the tip of the first subharmonic tongue to a higher value of $\mathcal{A}$ than that of the first harmonic tongue. In viscoelastic liquids, harmonic surface responses can occur if η is sufficiently large and the Deborah number is $O(1)$ (Müller & Zimmermann 1999; Kumar 1999). This appears to be a consequence of the fact that viscoelastic liquids can behave like elastic solids and are thus capable of sustaining Rayleigh-like surface waves.

Figure 2 shows how the presence of surfactants affects the critical amplitude and wavenumber for parametrically driven surface waves. For simplicity, we consider Newtonian liquids ($\eta = 0$) and fix $\mathcal{B} = 26$, $\mathcal{R} = 3770$ and $\mathcal{C} = 0.8$, which are representative parameter values. For this set of parameters, the surface response is

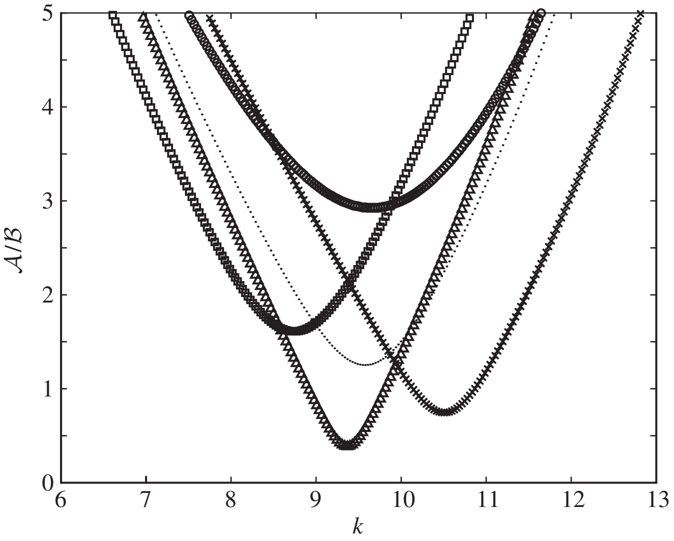

Figure 2. The tip of the first subharmonic tongue for $\mathcal{M} = 0$ (dots) and $\mathcal{M} = 10$ with $\phi = 0$ (circles), $\phi = \pi/2$ (crosses), $\phi = \pi$ (triangles) and $\phi = 3\pi/2$ (squares). The vertical axis is the ratio of the vibration amplitude ($\mathcal{A}$) to the gravitational parameter ($\mathcal{B}$). For these plots, $\mathcal{B} = 26$, $\mathcal{R} = 3770$ and $\mathcal{C} = 0.8$.

subharmonic, and only the tip of the first subharmonic tongue is shown in figure 2. When Marangoni forces are present and there is no phase shift ($\phi = 0$), the critical amplitude increases and the wavenumber increases slightly. Increasing the phase angle to $\phi = \pi/2$ decreases the critical amplitude and increases the critical wavenumber relative to the $\mathcal{M} = 0$ case. The amplitude is lowered further for $\phi = \pi$, and the wavenumber is slightly smaller than for the $\mathcal{M} = 0$ case. At $\phi = 3\pi/2$, the wavenumber decreases further and the amplitude increases to a value larger than would exist in the absence of Marangoni forces.

The behaviour of the critical amplitude with respect to the phase angle can be explained fairly easily. When the concentration disturbances are in phase with the surface deflections ($\phi = 0$), regions of high surfactant concentration will occur at the wave crests while regions of low surfactant concentration will occur at the wave troughs. Due to the surface-tension differences that these concentration variations produce, Marangoni flows will be generated which pull liquid away from the crests and into the troughs. This will tend to inhibit wave formation, and this is reflected in the larger value of the critical amplitude relative to the $\mathcal{M} = 0$ case. When the concentration disturbances are completely out of phase with the surface deflections ($\phi = \pi$), regions of low surfactant concentration will occur at the wave crests while regions of high surfactant concentration will occur at the wave troughs. The resulting Marangoni flows will pull liquid into the crests and away from the troughs. This will tend to enhance wave formation, and this is reflected in the smaller value of the critical amplitude relative to the $\mathcal{M} = 0$ case. For intermediate values of the phase angle, the observed values of the amplitude lie between the two extreme cases. Interestingly, the largest wavenumber shifts occur for the two intermediate cases ($\phi = \pi/2, 3\pi/2$) rather than for the two extreme cases ($\phi = 0, \pi$).

Table 1. *Comparison of critical amplitudes*
($\mathcal{B} = 26$, $\mathcal{R} = 3770$, $\mathcal{C} = 0.8$, $De = 0$.)

	$\mathcal{A}/\mathcal{B}$		
η	($\mathcal{M} = 0$)	($\mathcal{M} = 10$)	ratio
0	1.2	3.0	2.50
5	6.0	7.2	1.20
10	9.8	10.6	1.08
20	15.6	16.2	1.04
50	26.5	26.8	1.01

We now discuss the effect of liquid viscoelasticity by considering one of the simplest forms of the relaxation modulus, the single-mode Maxwell model (Bird *et al*. 1987; Larson 1988):

$$F(\tau) = \mathrm{e}^{-\tau/De}. \tag{4.1}$$

With this expression, ν_n take the form

$$\nu_n = 1 + \frac{\eta}{1 + De[s + \mathrm{i}(\alpha + n)]}. \tag{4.2}$$

For $De \gg 1$, $\nu_n = 1$ and viscoelasticity has no effect. For $De \ll 1$, $\nu_n = 1+\eta$, meaning that the liquid behaves in a Newtonian manner but with an enhanced viscosity. We have performed several runs in which η is varied with $De = 0$, $\mathcal{M} = 0$ or 10 and $\phi = 0$ (all other parameters had the same values as listed earlier). Comparison of the results for $\mathcal{M} = 0$ with those for $\mathcal{M} = 10$ at different values of η indicates that although the critical amplitude is larger for $\mathcal{M} = 10$, Marangoni forces have a weaker effect as η increases (table 1). This is expected since the viscosity of the liquid increases with η, and the increased viscous forces oppose the Marangoni forces. For $De \sim 1$, the effect of viscoelasticity depends on the value of η. When $\eta \sim 1$ and $\mathcal{M} = 0$, the critical amplitude for $De \sim 1$ will be lower compared with the $De = 0$ case at fixed η (Raynal *et al*. 1999; Kumar 1999). This is because the real part of ν_n, which is proportional to the energy dissipation in the system, is smaller when $De \neq 0$. In this regime, the presence of Marangoni forces will have the same qualitative effects as seen for Newtonian liquids. When $\eta \gg 1$ with $De \sim 1$ and $\mathcal{M} = 0$, the favoured surface response may become harmonic rather than subharmonic (Kumar 1999; Müller & Zimmermann 1999; Wagner *et al*. 1999). However, since this is the regime in which the liquid viscosity is large, the presence of Marangoni forces will not have as strong an effect as for the regime where $\eta \sim 1$.

Finally, we comment on the robustness of our results to surfactant concentrations which are non-dilute. In the non-dilute regime, a nonlinear equation of state is generally needed to describe the relationship between surfactant concentration and surface tension (Edwards *et al*. 1991). However, since our analysis is concerned with small departures from an equilibrium state, a nonlinear equation of state could be linearized around the mean surfactant concentration. This would produce an additional parameter in the problem, namely the local slope of the surfactant concentration–surface tension relationship. The additional parameter would not alter the qualitative nature of our results since it simply controls the magnitude of the Marangoni forces. The results will also be robust to changes in $\mathcal{C}$, which sets the mean surface tension.

5. Concluding remarks

We have analysed the role of insoluble surfactants on the formation of parametrically driven surface waves. To obtain time-periodic solutions of the linearized governing equations where Marangoni forces play a non-trivial role, it was necessary to consider the high-Pe limit of the surfactant transport equation. Application of Floquet theory enabled us to obtain a recursion relation for the Fourier modes of the free-surface deflection, which was then solved to obtain the critical vibration amplitude and corresponding wavenumber. The results show that the presence of surfactants will either increase or decrease the critical amplitude depending on the spatial phase shift between the surfactant-concentration variations and the surface deflections. In addition, the critical wavenumber will also change.

It is important to discuss the relationship of our work to previous work involving the effects of surfactants on standing waves. In general, surface waves on a liquid will be subject to damping from four sources (Miles 1967; Decent 1997):

(i) viscous dissipation in the bulk of the liquid;

(ii) viscous dissipation at the bottom and side walls of the liquid container;

(iii) viscous dissipation due to motion of the meniscus (contact-line damping); and

(iv) viscous dissipation due to Marangoni flows at the free surface (Craik 1982).

Miles (1967) neglected (i) and used boundary-layer methods to account for (ii)–(iv) in order to derive a linear damping coefficient for surface waves. Using a similar approach, Decent (1997) worked out a cubic damping coefficient for Faraday waves. Experiments to study the effects of surfactants on contact-line damping in both the linear and nonlinear regime of the Faraday instability were carried out by Jiang *et al*. (1996). Numerical simulations and perturbation analysis were also performed using the equations of motion for an inviscid fluid and accounting for damping by a single coefficient in the free-surface boundary condition. Our work accounts for (i) and damping at the bottom wall in a complete way for the linear regime of the instability, and neglects (iii) and damping at the side walls. We also demonstrate that Marangoni flows need not have a damping effect, and indeed can make it easier to excite the instability if the concentration disturbances are sufficiently out of phase with the surface deflections.

The results of this work should be useful for understanding the behaviour of surface waves in applications where vertical vibration plays a key role, including microgravity materials processing and ultrasonic atomization. In addition, our analysis could easily be extended to consider the behaviour of liquid sheets, which serve as a model for soap films (Kumar 2001), and to larger surfactant concentrations for which nonlinear equations of state are required. The techniques we use may also be helpful in analysing Marangoni effects brought about by temperature gradients (Birkh *et al*. 2001).

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Appendix A.

Here we illustrate the argument for neglecting the potential effect of Marangoni stresses on capillarity. Scaling the capillary term in the normal stress balance we obtain

$$\sigma\kappa = \frac{(\sigma_{\mathrm{m}} + \tilde{\sigma}\mathcal{S})}{\eta_{\mathrm{s}} h\omega}\tilde{\zeta}_{xx}, \tag{A 1}$$

where, for the sake of simplicity, we have only considered the streamwise direction. If we now consider dilute concentrations of surfactant, such that the spreading coefficient is small, $\mathcal{S}/\sigma_{\mathrm{m}} \sim \epsilon s$, where $s \sim O(1)$, then equation (A 1) becomes

$$\begin{aligned} \sigma\kappa &= \frac{\sigma_{\mathrm{m}}}{\eta_{\mathrm{s}} h\omega}(1 + \epsilon s\tilde{\sigma})\tilde{\zeta}_{xx} \\ &= \left(\frac{\sigma_{\mathrm{m}}}{\eta_{\mathrm{s}} h\omega}\right)\tilde{\zeta}_{xx} + O(\epsilon). \end{aligned} \tag{A 2}$$

We define $\mathcal{C} \equiv \sigma_{\mathrm{m}}/\eta_{\mathrm{s}} h\omega$ to finally obtain

$$\sigma\kappa = \mathcal{C}\tilde{\zeta}_{xx} + O(\epsilon). \tag{A 3}$$

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