J. Fluid Mech. (1999), *vol.* 382, *pp.* 331–349. Printed in the United Kingdom

The effect of surfactant on the stability of a fluid filament embedded in a viscous fluid

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(Received 16 March 1998 and in revised form 6 October 1998)

The effect of surfactant on the breakup of a viscous filament, initially at rest, surrounded by another viscous fluid is studied using linear stability analysis. The role of the surfactant is characterized by the elasticity number – a high elasticity number implies that surfactant is important. As expected, the surfactant slows the growth rate of disturbances. The influence of surfactant on the dominant wavenumber is less trivial. In the Stokes regime, the dominant wavenumber for most viscosity ratios increases with the elasticity number; for filament to matrix viscosity ratios ranging from about 0.03 to 0.4, the dominant wavenumber decreases when the elasticity number increases. Interestingly, a surfactant does not affect the stability of a filament when the surface tension (or Reynolds) number is very large.

1. Introduction

Filaments of liquids are common in engineering processes. These filaments can be formed by a jet impinging into another liquid, or, as frequently occurs in the food industry and in polymer blending, by stretching a droplet. Capillary forces due to interfacial tension make filaments unstable and cause breakup into smaller droplets. In some applications, it is desirable to stabilize a filament for as long as possible; in others, it is only necessary to realize or control the size of the droplets resulting from breakup. For instance, the size and structure of droplets, or morphology, in a blend affects the final properties. Increasingly, surfactants are added to dispersions, and compatiblizers, acting as surfactants, are added to high-molecular-weight (bio)polymer blends to control morphology. Still, the understanding of the role of surfactants during breakup of filaments is incomplete.

Lord Rayleigh (1892) first studied the stability of an infinitely long cylindrical fluid filament in an inviscid fluid. Years later, Tomotika (1935) considered the breakup of a viscous cylindrical fluid thread in another quiescent viscous fluid. Many studies have followed these classic works, but few have considered how surfactants affect this problem. Whitaker (1976) was one of the first to formulate the problem accounting for both interfacial tension gradients and interfacial viscosity due to the presence of surface-active material in a fluid filament surrounded by a gas. Interestingly, Whitaker noted that the problem is very complex and not treated correctly by previous authors – his analysis also had a sign error (see equation (60) in Whitaker 1976). More recently, Hajiloo, Ramamohan & Slattery (1987) considered the effect of interfacial viscosity on the breakup of filaments embedded in another viscous liquid; their work did not consider local fluctuations in interfacial tension. On the other hand, Palierne &

Lequeux (1991) studied the effects of surface elasticity on the breakup of a viscoelastic thread surrounded by a viscoelastic fluid for low Reynolds numbers.

The flow during the breakup of a thread is related to surfactant concentration which determines the interfacial tension driving the flow. Likewise, surfactant concentration is affected by the flow which convects the surfactant. The coupling of the surfactant concentration and the underlying flow creates interfacial tension gradients which result in an interesting range of phenomena, termed Marangoni effects (Edwards, Brenner & Wasan 1991). In fact, flux of surfactant through the interface of a filament can lead to an instability in addition to capillary instabilities (Burkholder & Berg 1974). Here, we are however interested in an interface initially in equilibrium with its surrounding phases. In this case, Marangoni effects can give elastic properties to a fluid–fluid interface, similar to those considered by Palierne & Lequeux (1991). Detailed analysis of the problem, however, requires coupling the mass and momentum transport equations not done by these authors.

Some numerical work focuses on the effect of surfactant on the breakup of droplets. Stone & Leal (1990) study the deformation and breakup of droplets covered with an insoluble surfactant at low capillary numbers. Milliken, Stone & Leal (1993) consider the formation and breakup of long slender drops with an insoluble surfactant on the surface, while Milliken & Leal (1994) study how solubility of the surfactant influences the problem. These studies illustrate much of the important physics of the problem. Surfactants tend to stabilize the droplet, i.e. disturbances grow more slowly on drops with surfactants. This stabilizing effect results from the elasticity caused by Marangoni effects, and the lower average interfacial tension due to the presence of surfactant. Nevertheless, the understanding of this problem can still benefit from further analysis considering very long filaments which may have a wide range of material parameters and are not limited to the Stokes regime.

In this paper, we study the effect of surfactant on the breakup of a viscous filament surrounded by another viscous fluid, termed the matrix, by means of linear stability analysis. The system is initially in equilibrium. The surfactant is soluble and diffuses in both the matrix and the filament. Surface diffusion of the surfactant is also considered. The only role of the surfactant is to decrease the interfacial tension. Surface viscosity is not considered. The interface has an elastic nature, but, unlike the work of Palierne & Lequeux (1991), it results only from local fluctuations in the interfacial tension due to the transport of surfactant. The growth rate and wavelength of the fastest growing disturbance are of particular interest, as they determine the time until breakup and the size of resulting droplets, respectively.

The paper is organized as follows. We first describe the relationship between interfacial tension and surface-active agents. This is followed by the modelling of the flow produced by breakup of viscous threads and the convection and diffusion of surfactant. We then perform a linear stability analysis of a viscous fluid filament surrounded by a viscous matrix, accounting for surfactant. Afterwards, in the results and discussion section, we examine the stability of the thread for various limiting cases. The final section summarizes the important results. A table of relevant dimensionless parameters is provided in § 3 to aid the reader.

2. Surfactants and interfacial tension

Before proceeding with the modelling, it is appropriate to discuss the relationship between interfacial tension and surfactant concentration. Interfacial tension, as with pressure, the three-dimensional analogue of interfacial tension, has been described by various equations of state. One such equation of state can be derived by assuming that surface adsorption can be described by a Frumkin isotherm and that the surfactant solution is ideal (Lin, McKeigue & Maldarelli 1990), yielding

$$\sigma = \sigma_c + R_g T \gamma_\infty [\ln\,(1 - \gamma/\gamma_\infty) - \tfrac{1}{2}k(\gamma/\gamma_\infty)^2]. \tag{2.1}$$

Here, σ is the interfacial tension, σ_c is the interfacial tension of a 'clean' surface, γ is the surface concentration of surfactant, γ_∞ is the maximum surfactant concentration of a unimolecular film on the surface, k is a material parameter, and R_g and T are the gas constant and temperature, respectively. For dilute concentrations, interfacial tension is related to surfactant concentration by the linear relationship

$$\sigma = \sigma_c - \gamma R_g T. \tag{2.2}$$

The above equations, and others like them, can for small perturbations from the equilibrium surfactant concentration be approximated as

$$\sigma = \sigma_0 - E_0 \left(\frac{\gamma - \gamma_0}{\gamma_0} \right). \tag{2.3}$$

Here, the subscript 0 denotes the value at the equilibrium or 'undisturbed' surfactant concentration, and E_0, the Gibbs elasticity, is

$$E_0 = - \left. \frac{\partial \sigma}{\partial \ln \gamma} \right|_{\gamma = \gamma_0}. \tag{2.4}$$

The nomenclature becomes apparent when considering the definition of surface dilatational modulus (Lucassen & van den Tempel 1972),

$$K^s \equiv \frac{\mathrm{d}\sigma}{\mathrm{d}\,\ln\,\mathscr{S}}, \tag{2.5}$$

where $\mathscr{S}$ is the area of the interface. When mass transfer into and out of the interface and surface diffusion are negligible, γ is inversely proportional to $\mathscr{S}$, and $K^s = E_0$. The mass transfer of surfactant and the Gibbs elasticity dictate the form of the surface dilatational modulus due to surfactant. There is no corresponding shear modulus in the interface due to Marangoni effects.

3. Physical model

Consider an initially quiescent infinitely long cylindrical filament of viscous fluid embedded in a viscous matrix. On the interface between the fluids is a surfactant which might be soluble in one or both of the fluids. Capillary waves form on the interface between the fluids. The underlying flow produced by the waves convects the surfactant on the interface and in the bulk, causing interfacial tension gradients which result from a non-uniform surfactant concentration on the interface. These interfacial tension gradients lead to an extra 'elastic' force which slows the formation of the waves. Still, the waves eventually break the filament.

It is convenient to scale the problem such that inertia and viscous terms balance. To this effect, we define the following dimensionless variables:

$$\left. \begin{aligned} &\boldsymbol{v} = \frac{\rho R \boldsymbol{v}'}{\mu}, \quad \hat{\boldsymbol{v}} = \frac{\rho R \hat{\boldsymbol{v}}'}{\mu}, \quad P = P' \rho \left(\frac{R}{\mu} \right)^2, \quad \hat{P} = \hat{P}' \rho \left(\frac{R}{\mu} \right)^2, \\ &r = \frac{r'}{R}, \quad z = \frac{z'}{R}, \quad c = \frac{c'}{c_0}, \quad \hat{c} = \frac{\hat{c}'}{c_0}, \quad \Gamma = \frac{\gamma}{K c_0}, \quad t = \frac{\mu t'}{\rho R^2}. \end{aligned} \right\} \tag{3.1}$$

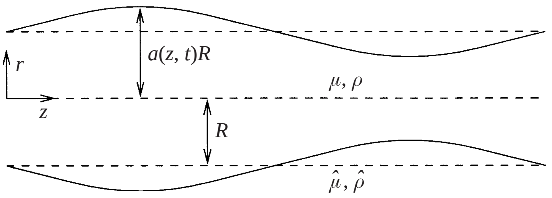

FIGURE 1. Definitions of the important parameters of a filament of viscous fluid embedded in another viscous fluid.

Here, R is the initial radius of the filament, K is the ratio of interfacial concentration to bulk concentration in the thread of surfactant at equilibrium, and μ and ρ are the viscosity and density of the fluid inside the filament, respectively. Except in the case of interfacial concentration of surfactant, the prime ($'$) denotes the variable with dimensions and that without the prime, the dimensionless parameter. The variables, with a hat signifying a variable in the matrix, are defined as follows: $\boldsymbol{v}$ is the velocity vector; P is the modified pressure – the sum of pressure and potential due to gravity (Hajiloo *et al.* 1987); c and Γ are the surfactant concentration in the bulk and on the interface, respectively; r and z are the radial and axial components of the cylindrical coordinates (see figure 1), respectively; and, t is time. The equations governing momentum and mass transfer will be written in terms of these dimensionless variables.

The flow in the filament and matrix, both incompressible Newtonian fluids, can be described by the Navier–Stokes and continuity equations:

$$\frac{\mathrm{D}\boldsymbol{v}}{\mathrm{D}t} = -\nabla P + \nabla^2 \boldsymbol{v}, \tag{3.2}$$

$$\frac{1}{N_\rho}\frac{\mathrm{D}\hat{\boldsymbol{v}}}{\mathrm{D}t} = -\nabla \hat{P} + \frac{1}{N_\mu}\nabla^2 \hat{\boldsymbol{v}}, \tag{3.3}$$

$$\nabla \cdot \boldsymbol{v} = 0 \quad \text{and} \quad \nabla \cdot \hat{\boldsymbol{v}} = 0. \tag{3.4}$$

Here, $\mathrm{D}/\mathrm{D}t$ is the material derivative, N_ρ is the ratio of the fluid density in the thread to the fluid density in the matrix, and N_μ, termed the viscosity ratio, is the ratio of viscosity inside the filament to that outside the filament. The Reynolds number for the filament, defined as $N_{Re} \equiv \rho U R/\mu$, where U is the characteristic velocity of the system, quantifies the ratio of inertia to viscous forces. Scaling capillary pressure with viscous terms gives the characteristic velocity $U = \sigma_0/\mu$. On the other hand, scaling capillary pressure with (transient) inertia terms gives the characteristic velocity $U = (\sigma_0/\rho R)^{1/2}$. Therefore, we use $N_\sigma \equiv \rho\sigma_0 R/\mu^2$, termed the surface tension number, to characterize the breakup process, and define the Reynolds number,

$$N_{Re} = \frac{N_\sigma}{1 + N_\sigma^{1/2}}. \tag{3.5}$$

This definition captures the limiting behaviour of the Reynolds number for high and low surface tension numbers. We note that the characteristic velocity should be determined by scaling capillary pressure with viscous (or inertia) terms in the matrix when N_μ (or N_ρ) $\ll 1$; however, the scalings presented earlier demonstrate the connection between the surface tension number and the Reynolds number, and the analysis is not influenced by the scaling. When the surface tension number approaches zero, the left-hand side of (3.2), which accounts for inertia in the thread, becomes negligible, and can be set to zero (see § 5).

Assuming that the Bond number is

$$Bo \equiv \frac{\Delta\rho a_g R^2}{\sigma} \ll 1, \tag{3.6}$$

where $\Delta\rho$ is the density difference between the filament and the matrix, and a_g is the acceleration due to gravity, allows us to neglect gravity and consider initially axisymmetric threads (Hajiloo *et al.* 1987). We further assume that axisymmetric disturbances grow faster than asymmetric ones.

The boundary conditions on the thread and matrix are as follows. In the matrix, far from the interface between the two fluids there is no flow, and, in the filament, the flow at the centre is bounded. That is,

$$\hat{\boldsymbol{v}} \to 0 \quad \text{as} \quad r \to \infty, \tag{3.7}$$

$$\boldsymbol{v} \quad \text{is finite at} \quad r = 0. \tag{3.8}$$

On the interface, the velocities of the fluids are equal:

$$\hat{\boldsymbol{v}} = \boldsymbol{v} \quad \text{at} \quad r = a(z,t) \tag{3.9}$$

where $a(z,t)$ is the dimensionless radial position of the interface at axial position z and time t (for the undisturbed filament $a = 1$). The stresses on the interface of the two fluids are related by

$$(\hat{\boldsymbol{T}}/N_\mu - \boldsymbol{T}) \cdot \boldsymbol{n} = N_\sigma \left(\frac{\sigma}{\sigma_0}\right) \boldsymbol{n}(\nabla_s \cdot \boldsymbol{n}) - N_\sigma \nabla_s \left(\frac{\sigma}{\sigma_0}\right) \quad \text{at} \quad r = a(z,t). \tag{3.10}$$

Here, $\boldsymbol{n}$ is the unit normal to the interface directed into the matrix, $\boldsymbol{T}$ is the dimensionless stress tensor, and ∇_s denotes the surface gradient operator, $\nabla_s = (\boldsymbol{I} - \boldsymbol{nn}) \cdot \nabla$. The local mean curvature of the surface is $\nabla_s \cdot \boldsymbol{n}$.

As demonstrated in (3.10), the flow is dependent on the interfacial tension, which is a function of surfactant concentration (see § 2). For dilute concentrations of surfactant, the convection and diffusion of surfactant in the fluids is governed by

$$\frac{\mathrm{D}c}{\mathrm{D}t} = \frac{1}{N_{Sc}} \nabla^2 c, \tag{3.11}$$

$$\frac{\mathrm{D}\hat{c}}{\mathrm{D}t} = \frac{1}{N_{\mathscr{D}} N_{Sc}} \nabla^2 \hat{c}. \tag{3.12}$$

Here, $N_{\mathscr{D}}$ is the ratio of the diffusivity of surfactant inside the thread to that inside the matrix, and N_{Sc}, referred to as the Schmidt number, is defined as $N_{Sc} \equiv \mu/\rho\mathscr{D}_\gamma$, where $\mathscr{D}_\gamma$ is the diffusivity of surfactant inside the filament.

Assuming that transport between the interface and the bulk fluids is diffusion limited – fast adsorption/desorption kinetics – the concentration of the surfactant in the bulk fluids is in equilibrium with that in the interface. The relationships between the concentrations of surfactant at the interface and in the interface are

$$\Gamma = c \quad \text{at} \quad r = a \tag{3.13}$$

and

$$\Gamma = \hat{c}/N_K \quad \text{at} \quad r = a, \tag{3.14}$$

where $N_K = K/\hat{K}$, with K and $\hat{K}$ the equilibrium ratios of surfactant concentration in the interface to surfactant in the filament and in the matrix, respectively. The isotherms are linearized; that is, the values of K and $\hat{K}$ are approximated as constants, which

$N_{El} \equiv \dfrac{\rho E_0 R}{\mu^2}$	Elasticity number	$N_{Sur} \equiv \dfrac{\mu}{\rho \mathscr{D}_s}$	Surface diffusion number
$N_K \equiv K/\hat{K}$	Equilibrium coefficient ratio	$N_\mu \equiv \mu/\hat{\mu}$	Viscosity ratio
$N_L \equiv R/K$	Interface thickness number	$N_\rho \equiv \rho/\hat{\rho}$	Density ratio
$N_{Re} \equiv \dfrac{N_\sigma}{1+N_\sigma^{1/2}}$	Reynolds number	$N_\sigma \equiv \dfrac{\rho \sigma_0 R}{\mu^2}$	Surface tension number
$N_{Sc} \equiv \dfrac{\mu}{\rho \mathscr{D}_\gamma}$	Schmidt number	$N_{\mathscr{D}} \equiv \mathscr{D}_\gamma/\hat{\mathscr{D}}_\gamma$	Diffusivity ratio

TABLE 1. Dimensionless parameters.

is valid for small fluctuations about the equilibrium or dilute concentrations. We further note that K is a length scale reflecting the ‘thickness’ of the interface, and is referred to as the adsorption depth (Lin *et al.* 1990). Transport of the surfactant in the interface is governed by (Stone & Leal 1990)

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\Gamma \boldsymbol{v}_s) + \Gamma (\nabla_s \cdot \boldsymbol{n})(\boldsymbol{v} \cdot \boldsymbol{n}) = \frac{1}{N_{Sur}} \nabla_s^2 \Gamma + j_n. \tag{3.15}$$

Here, $\boldsymbol{v}_s$ is the dimensionless surface tangential velocity, j_n is the dimensionless net flux of surfactant into the interface, and $N_{Sur} \equiv \mu/\rho\mathscr{D}_s$, where $\mathscr{D}_s$ is the surface diffusivity of surfactant. This surface transport equation consists of the flux into the interface, the usual convection and diffusion terms, plus $\Gamma(\nabla_s \cdot \boldsymbol{n})(\boldsymbol{v} \cdot \boldsymbol{n})$, which accounts for interfacial expansion due to flow normal to the surface (Stone 1990).

The dimensionless parameters introduced in this section are defined in table 1.

4. Linear stability analysis

To further our understanding of breakup, we consider the response of a filament to small disturbances. Disturbances to the interface are represented in terms of Fourier components; the radial position of the interface is

$$a(z,t) = 1 + \epsilon \mathrm{e}^{\omega t} \cos(kz). \tag{4.1}$$

Here, ϵ is the amplitude of the disturbance, ω is the dimensionless growth rate of the disturbances and k, the dimensionless wavenumber, is $2\pi R/\lambda$, where λ is the wavelength of the disturbance. The assumption of small disturbances to the interface, incorporated by linear stability analysis, requires that the amplitude of the disturbance is much less than the undisturbed radius of the thread, i.e. $\epsilon \ll 1$.

We expand the velocity, pressure, and surface and bulk concentrations of surfactant in orders of ϵ about the base, zero-order, solutions for an undisturbed static thread at equilibrium, yielding

$$\boldsymbol{v} = \epsilon \boldsymbol{v}_1 + O(\epsilon^2), \tag{4.2}$$

$$P = P_0 + \epsilon P_1 + O(\epsilon^2), \tag{4.3}$$

$$\Gamma = 1 + \epsilon \Gamma_1 + O(\epsilon^2), \tag{4.4}$$

$$c = 1 + \epsilon c_1 + O(\epsilon^2). \tag{4.5}$$

Similar expansions hold for the variables in the matrix. As the filament and the matrix are initially quiescent, the zero-order solutions to surface and bulk concentrations of surfactant are the equilibrium concentrations, and the base solution to velocity is zero. The base pressure difference between the phases is

$$P_0 - \hat{P}_0 = N_\sigma \tag{4.6}$$

which comes from the leading order of (3.10).

The problem is reformulated in terms of the streamfunction, ψ, defined by

$$v_{1r} = \frac{1}{r}\frac{\partial \psi}{\partial z}, \quad v_{1z} = -\frac{1}{r}\frac{\partial \psi}{\partial r}, \tag{4.7}$$

where v_{1r} and v_{1z} are the radial and axial components of $\boldsymbol{v}_1$, respectively. This streamfunction satisfies the continuity equation (3.4) to $O(\epsilon)$. The Navier–Stokes equations, neglecting terms of $O(\epsilon^2)$ and higher, are written as

$$\left(\frac{\partial}{\partial t} - \mathrm{L}^2\right)\mathrm{L}^2\psi = 0 \tag{4.8}$$

for the fluid inside the filament, and as

$$\left(\frac{1}{N_\rho}\frac{\partial}{\partial t} - \frac{1}{N_\mu}\mathrm{L}^2\right)\mathrm{L}^2\hat{\psi} = 0 \tag{4.9}$$

for the fluid outside the filament, where

$$\mathrm{L}^2 \equiv \frac{\partial^2}{\partial r^2} - \frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}. \tag{4.10}$$

Note that pressure does not appear in the above streamfunction formulation of the Navier–Stokes equation.

The streamfunction formulations of the Navier–Stokes equations with the boundary condition (4.1) can be satisfied by

$$\psi = f(r)\mathrm{e}^{\omega t}\cos(kz) \quad \text{and} \quad \hat{\psi} = \hat{f}(r)\mathrm{e}^{\omega t}\cos(kz). \tag{4.11}$$

Substituting (4.11) into (4.8) and (4.9) yields

$$(\omega - \bar{\mathrm{L}}^2)\bar{\mathrm{L}}^2 f = 0 \tag{4.12}$$

and

$$(\omega/N_\rho - \bar{\mathrm{L}}^2/N_\mu)\bar{\mathrm{L}}^2\hat{f} = 0 \tag{4.13}$$

with

$$\bar{\mathrm{L}}^2 \equiv \frac{\mathrm{d}^2}{\mathrm{d}r^2} - \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r} - k^2. \tag{4.14}$$

These fourth-order ordinary differential equations are forms of the Orr–Sommerfeld equation, with an analytical solution consisting of modified Bessel functions (Tomotika 1935). The solution to equation (4.12), noting that the flow is bounded at $r = 0$, has the form

$$f = A_1 r I_1(kr) + A_2 r I_1(k_1 r) \quad \text{with} \quad k_1 = (k^2 + \omega)^{1/2}. \tag{4.15}$$

Here, I_n is the modified Bessel function of the first kind, and order n, where n is an integer, and A_1 and A_2 are constants to be evaluated with the boundary conditions. Likewise, the solution to (4.13), noting that the fluid velocity approaches zero as $r \to \infty$, has the form

$$\hat{f} = \hat{A}_1 r K_1(kr) + \hat{A}_2 r K_1(k_2 r) \quad \text{with} \quad k_2 = (k^2 + \omega N_\mu/N_\rho)^{1/2}. \tag{4.16}$$

Here, K_n is the modified Bessel function of the second kind, and order n.

To within $O(\epsilon^2)$, the boundary conditions on the interface can be applied at $r = 1$. We note that solving for higher than $O(\epsilon)$ terms requires expanding the boundary conditions at the interface about $r = 1$. Accordingly, substituting the streamfunction (4.7), the form for the streamfunction (4.11), and equations (4.15) and (4.16) into the boundary condition (3.9) gives

$$A_1 I_1(k) + A_2 I_1(k_1) - \hat{A}_1 K_1(k) - \hat{A}_2 K_1(k_2) = 0 \tag{4.17}$$

from the axial component of the velocities, and

$$A_1 k I_0(k) + A_2 k_1 I_0(k_1) + \hat{A}_1 k K_0(k) + \hat{A}_2 k_2 K_0(k_2) = 0 \tag{4.18}$$

from the radial component of the velocities.

The stress balance on the interface, due to the surfactant, is relatively complex. Equation (3.10) is expressed in terms of normal and tangential components. The $O(\epsilon)$ balance of the normal stresses at the interface can be written

$$P_1 - \hat{P}_1 + \frac{2}{N_\mu}\left(\frac{\partial^2 \hat{\psi}}{\partial r \partial z} - \frac{\partial \hat{\psi}}{\partial z}\right) - 2\left(\frac{\partial^2 \psi}{\partial r \partial z} - \frac{\partial \psi}{\partial z}\right) = -N_\sigma (1 - k^2) \mathrm{e}^{\omega t} \cos(kz) + N_\sigma \left(\frac{\sigma_1}{\sigma_0}\right) \tag{4.19}$$

in which σ_1 is the $O(\epsilon)$ solution to interfacial tension, and the tangential stress balance can be written

$$\frac{1}{N_\mu}\left(\frac{\partial \hat{\psi}}{\partial r} - \frac{\partial^2 \hat{\psi}}{\partial r^2} + \frac{\partial^2 \hat{\psi}}{\partial z^2}\right) - \left(\frac{\partial \psi}{\partial r} - \frac{\partial^2 \psi}{\partial r^2} + \frac{\partial^2 \psi}{\partial z^2}\right) = -N_\sigma \frac{\partial}{\partial z}\left(\frac{\sigma_1}{\sigma_0}\right). \tag{4.20}$$

In order to properly define the interfacial tension in the above stress balances, we determine the local concentration of surfactant on the interface. Substituting the expansions (4.5) and (4.2) into (3.11) and (3.12) leads to the $O(\epsilon)$ expression

$$\frac{\partial c_1}{\partial t} = \frac{1}{N_{Sc}} \nabla^2 c_1 \tag{4.21}$$

for the fluid inside the thread, and

$$\frac{\partial \hat{c}_1}{\partial t} = \frac{1}{N_{\mathscr{D}} N_{Sc}} \nabla^2 \hat{c}_1 \tag{4.22}$$

for the fluid outside the thread in the matrix. Equations (4.1) and (4.11) indicate that we should seek a solution to concentration in the thread with the form

$$c_1 = g(r) \mathrm{e}^{\omega t} \cos(kz). \tag{4.23}$$

Substituting this relationship into (4.21) gives the ordinary differential equation

$$\frac{\mathrm{d}^2 g}{\mathrm{d} r^2} + \frac{1}{r}\frac{\mathrm{d} g}{\mathrm{d} r} - (k^2 + \omega N_{Sc}) g = 0 \tag{4.24}$$

for $g(r)$. Since c_1 is bound at $r = 1$, the concentration of the surfactant inside the thread is

$$c_1 = B I_0(mr) \mathrm{e}^{\omega t} \cos(kz) \quad \text{with} \quad m = (k^2 + \omega N_{Sc})^{1/2}, \tag{4.25}$$

where B is a constant. The concentration of the surfactant outside the thread can be found, by the same approach as above with the constraint $\hat{c}_1 \to 0$ as $r \to \infty$, to be

$$\hat{c}_1 = \hat{B} K_0(\hat{m} r) \mathrm{e}^{\omega t} \cos(kz) \quad \text{with} \quad \hat{m} = (k^2 + \omega N_{\mathscr{D}} N_{Sc})^{1/2}. \tag{4.26}$$

The remaining boundary conditions for the surfactant concentration are

$$c_1 = \hat{c}_1/N_K \quad \text{at} \quad r = 1 \tag{4.27}$$

and the surface transport equation (3.15), applied on the interface between the fluids. The $O(\epsilon)$ contribution to (3.15), after substituting Fick's law for j_n, the net diffusive flux into the interface from the thread and the matrix, can be written in dimensionless form as

$$\frac{\partial \Gamma_1}{\partial t} + \frac{\Gamma_0}{a_0} v_{1r} + \Gamma_0 \frac{\partial v_{1z}}{\partial z} - \frac{1}{N_{Sur}} \frac{\partial^2 \Gamma_1}{\partial z^2} = -\left(\frac{N_L}{N_{Sc}}\right) \frac{\partial c_1}{\partial r} + \left(\frac{N_L N_K}{N_{Sc} N_{\mathscr{D}}}\right) \frac{\partial \hat{c}_1}{\partial r}. \tag{4.28}$$

Here, N_L is the ratio of the filament radius to adsorption depth (R/K), and the leading-order solutions for surface concentration (Γ_0) and thread radius (a_0) are included in the equation for clarification, although both are unity. Recalling (3.13), we determine that

$$\frac{\partial c_1}{\partial t} + v_{1r} + \frac{\partial v_{1z}}{\partial z} - \frac{1}{N_{Sur}} \frac{\partial^2 c_1}{\partial z^2} = -\left(\frac{N_L}{N_{Sc}}\right) \frac{\partial c_1}{\partial r} + \left(\frac{N_L N_K}{N_{Sc} N_{\mathscr{D}}}\right) \frac{\partial \hat{c}_1}{\partial r} \text{ at } r = 1. \tag{4.29}$$

The boundary conditions (4.27) and (4.29) allow us to evaluate the constants B and $\hat{B}$, and determine the surfactant concentration. After determining the surfactant concentration in the filament, the interfacial concentration of surfactant is found to be

$$\Gamma_1 = -k\left(\frac{\mathrm{d}f}{\mathrm{d}r} - f\right)\left(\omega + \frac{k^2}{N_{Sur}} + \frac{mN_L}{N_{Sc}}\frac{I_1(m)}{I_0(m)} + \frac{\hat{m}N_L N_K}{N_{Sc}N_{\mathscr{D}}}\frac{K_1(\hat{m})}{K_0(\hat{m})}\right)^{-1} \mathrm{e}^{\omega t} \sin(kz). \tag{4.30}$$

The length scale for the surfactant fluctuation diffusion into the filament, referred to as the penetration depth, ℓ, is

$$\ell \sim (\mathscr{D}_\gamma \tau_B)^{1/2}, \tag{4.31}$$

where τ_B, the time scale of breakup, is $(N_\mu + 1)\hat{\mu}R/\sigma_0$ or $R((N_\rho + 1)\hat{\rho}R/\sigma_0)^{1/2}$ for low or high surface tension numbers, respectively. For many surfactants in fluids $\mathscr{D}_\gamma \sim 10^{-5}$–$10^{-6}$ cm^2 s^{-1} (Whitaker 1976; Hajiloo *et al.* 1987; Lin *et al.* 1990; Lucassen & van den Tempel 1972), and, thus, the penetration depth is much less than the radius of the thread in many industrial problems. In this case, m, which characterizes R/ℓ, is large, and $I_1(m)/I_0(m)$ and $K_1(\hat{m})/K_0(\hat{m})$ approach unity. (Expansions for the modified Bessel functions can be found in Abramowitz & Stegun (1964).) Whitaker 1976 proposed a slightly different argument yielding a similar approximation for low penetration depths. Accordingly, when the penetration depth is much less than the radius of the thread, the interfacial concentration of surfactant can be approximated as

$$\Gamma_1 = \frac{-k\left(\mathrm{d}f/\mathrm{d}r - f\right)}{\omega + k^2/N_{Sur} + mN_L/N_{Sc} + \hat{m}N_L N_K/N_{Sc}N_{\mathscr{D}}} \mathrm{e}^{\omega t} \sin(kz). \tag{4.32}$$

From here on, the interfacial concentration of surfactant will be represented by this equation to simplify the analysis and highlight the important physics of the problem; however, a more detailed study only involves substituting (4.30) for (4.32).

Examination of (4.32) shows that diffusion into and out of the matrix phase has roughly the same effect on the stability of the filament as diffusion into and out of the filament phase – the main difference lying in physical constants. Thus, the problem is essentially the same if the surfactant is only soluble in the filament or only soluble in the matrix. We note, however, that this similarity results from the assumption that $\ell \ll R$, and the absence of convection of surfactant in the bulk, which is not part of the $O(\epsilon)$ problem. In the remainder of this paper, the surfactant will be assumed to be soluble in only the filament, i.e. $N_K \to 0$, to reduce the number of parameters. Hence, the interfacial tension, determined by substituting (4.32) into (2.3), is

$$\frac{\sigma}{\sigma_0} = 1 + \epsilon \left(\frac{E_0}{\sigma_0} \right) k \left(\frac{\mathrm{d}f}{\mathrm{d}r} - f \right) \kappa(\omega, k) \mathrm{e}^{\omega t} \ \sin\,(kz) + O(\epsilon^2), \tag{4.33}$$

where

$$\kappa(\omega, k) \equiv \left(\omega + k^2/N_{Sur} + mN_L/N_{Sc} \right)^{-1} \tag{4.34}$$

describes the elastic nature of the interface. More complete understanding of $\kappa(\omega, k)$ is obtained by noting that surface dilatational modulus and interfacial tension are related by (Palierne & Lequeux 1991)

$$\sigma - \sigma_0 = \tfrac{1}{2} \int_{-\infty}^{t} K^s(t - t') \dot{\gamma}_{\alpha\alpha} \mathrm{d}t', \tag{4.35}$$

where $\dot{\gamma}_{\alpha\alpha}$ is the trace of the surface rate-of-strain tensor (Edwards *et al.* 1991 provides a review of surface tensors). Evaluation of $\dot{\gamma}_{\alpha\alpha}$ and further mathematical analysis shows that

$$E_0 \kappa(\omega, k) = \int_0^{\infty} K^s(t') \mathrm{e}^{-\omega t'} \mathrm{d}t' + O(\epsilon^2). \tag{4.36}$$

That is, $\kappa(\omega, k)$ describes the response of the interface to disturbances which grow exponentially (Palierne & Lequeux 1991). Note that as the bulk or surface diffusivity goes to infinity, i.e. N_{Sc} or $N_{Sur} \to 0$, the interface becomes effectively inelastic. Equation (4.36) also demonstrates that K^s is not a material parameter, as it is dependent upon the disturbance.

Having determined the form of the interfacial tension, we return to the remaining boundary conditions (4.19) and (4.20), which are the shear and normal stress balances on the interface between the fluids. To completely simplify the normal stress condition, the pressure difference between the fluids and the kinematic condition are necessary. The z-components of the Navier–Stokes equation for the filament (3.2) and for the bulk (3.3) allow us to determine that

$$P_1 - \hat{P}_1 = \frac{1}{k} \left[\frac{1}{N_\mu r} \left(\bar{\mathrm{L}}^2 + r^{-2} - \frac{N_\mu}{N_\rho} \omega \right) \frac{\mathrm{d}\hat{f}}{\mathrm{d}r} - \frac{1}{r} \left(\bar{\mathrm{L}}^2 + r^{-2} - \omega \right) \frac{\mathrm{d}f}{\mathrm{d}r} \right] \mathrm{e}^{\omega t} \ \sin\,(kz). \tag{4.37}$$

The kinematic condition on the interface, having the form, $v_{1r} = \mathrm{D}a/\mathrm{D}t$, can be written to $O(\epsilon)$ as

$$\psi = \frac{\omega}{k} \mathrm{e}^{\omega t} \ \sin\,(kz) \tag{4.38}$$

applied at $r = 1$. Substituting (4.11) and (4.37) into (4.19) and (4.20), and applying (4.38) yields

$$\begin{aligned} &\frac{1}{N_\mu} \left[\frac{\mathrm{d}^3 \hat{f}}{\mathrm{d}r^3} - \frac{\mathrm{d}^2 \hat{f}}{\mathrm{d}r^2} + \left(1 - 3k^2\right) \frac{\mathrm{d}\hat{f}}{\mathrm{d}r} + 2k^2 \hat{f} \right] \\ &\quad - \left[\frac{\mathrm{d}^3 f}{\mathrm{d}r^3} - \frac{\mathrm{d}^2 f}{\mathrm{d}r^2} + \left(1 - 3k^2\right) \frac{\mathrm{d}f}{\mathrm{d}r} + 2k^2 f \right] - \omega \left(\frac{1}{N_\rho} \frac{\mathrm{d}\hat{f}}{\mathrm{d}r} - \frac{\mathrm{d}f}{\mathrm{d}r} \right) \\ &\quad = N_\sigma \frac{k^2 \left(1 - k^2\right)}{\omega} f + N_{El} \kappa(\omega, k) k^2 \left(\frac{\mathrm{d}f}{\mathrm{d}r} - f \right) \end{aligned} \tag{4.39}$$

for the normal stress balance, and

$$\frac{1}{N_\mu}\left(\frac{\mathrm{d}\hat{f}}{\mathrm{d}r}-\frac{\mathrm{d}^2\hat{f}}{\mathrm{d}r^2}-k^2\hat{f}\right)-\left(\frac{\mathrm{d}f}{\mathrm{d}r}-\frac{\mathrm{d}^2f}{\mathrm{d}r^2}-k^2f\right)=-N_{El}\kappa(\omega,k)k^2\left(\frac{\mathrm{d}f}{\mathrm{d}r}-f\right) \tag{4.40}$$

for the tangential stress balance. Here, $N_{El} \equiv \rho E_0 R/\mu^2$ is termed the elasticity number. The left-hand sides of (4.39) and (4.40) describe the stress differences between the fluids, and the right-hand sides are terms resulting from the interfacial tension. Using (4.15)–(4.18) allows us to rewrite (4.39) and (4.40) in the more manageable forms

$$\begin{aligned} &A_1\left[2\left(1/N_\mu-1\right)k^3I_0(k)-\omega kI_0(k)+N_\sigma k^2\left(1-k^2\right)I_1(k)/\omega\right]\\ &\quad+A_2\left[2\left(1/N_\mu-1\right)k^2k_1I_0(k_1)-\omega I_1(k_1)+N_\sigma k^2\left(1-k^2\right)I_1(k_1)/\omega\right]\\ &\quad+\hat{A}_1\left[-\omega kK_0(k)/N_\rho\right]+\hat{A}_2\left[\omega K_1(k_2)/N_\rho\right]=0 \end{aligned} \tag{4.41}$$

and

$$\begin{aligned} &A_1\left\{N_{El}\kappa(\omega,k)\left[kI_0(k)-I_1(k)\right]\right\}+A_2\left\{\omega I_1(k_1)\right.\\ &\quad\left.+N_{El}\kappa(\omega,k)\left[k_1I_0(k_1)-I_1(k_1)\right]\right\}+\hat{A}_1\left[-2\left(1/N_\mu-1\right)k^2K_1(k)\right]\\ &\quad+\hat{A}_2\left[-2\left(1/N_\mu-1\right)k^2K_1(k_2)-\omega K_1(k_2)/N_\rho\right]=0. \end{aligned} \tag{4.42}$$

Equations (4.17), (4.18), (4.41) and (4.42) define a system of linear homogeneous equations. Thus, there is a non-trivial solution for this capillary wave growth problem if and only if the determinant of the 4 × 4 matrix composed of the coefficients of A_1, A_2, $\hat{A}_1$ and $\hat{A}_2$ in the aforementioned four homogeneous equations equals zero. We determine that the dispersion relation for these capillary waves is

$$\begin{aligned} &\omega^2\{G(k)M(k_1,k)/N_\rho^2+\left[F(k)F(k_1)+G(k)G(k_2)+2F(k)G(k)\right]/N_\rho\\ &\quad+F(k)O(k_2,k)\}+2\left(1/N_\mu-1\right)\omega k^2\{\left[1-2F(k)\right]O(k_2,k)\\ &\quad+\left[1+2G(k)\right]M(k_1,k)/N_\rho\}-4\left(1/N_\mu-1\right)^2k^4M(k_1,k)O(k_2,k)\\ &\quad+N_{El}\kappa(\omega,k)k^2\{\omega\left[1+F(k)F(k_1)-2F(k)\right]O(k_2,k)\\ &\quad+\omega\left[1+G(k)G(k_2)+2G(k)\right]M(k_1,k)/N_\rho\\ &\quad-2\left(1/N_\mu-1\right)k^2M(k_1,k)O(k_2,k)\}=N_\sigma k^2\left(1-k^2\right)\{O(k_2,k)\\ &\quad+M(k_1,k)/N_\rho+N_{El}\kappa(\omega,k)k^2M(k_1,k)O(k_2,k)/\omega\} \end{aligned} \tag{4.43}$$

in which

$$M(k_1,k)=F(k_1)-F(k)\quad\text{and}\quad F(k)=kI_0(k)/I_1(k), \tag{4.44}$$

$$O(k_2,k)=G(k_2)-G(k)\quad\text{and}\quad G(k)=kK_0(k)/K_1(k). \tag{4.45}$$

Equation (4.43) relates the initial growth rate, ω, to the wavenumber, k, of the Fourier component of a disturbance to the interface. Components with a negative growth rate decay, while those with a positive growth rate grow. The maximum (or fastest) growth rate and the wavelength of the maximum growth rate, termed the dominant growth rate and dominant wavelength, respectively, are frequently used to characterize the breakup of a filament.

5. Results and discussion

We validate the dispersion relation (4.43) by comparison with other limiting forms. The limiting case of the Stokes problem, or negligible inertia terms, with N_σ (and $N_\sigma N_\mu^2/N_\rho$, which characterizes the Reynolds number in the matrix) approaching zero, can be solved with the same approach as used in §4 for the full Navier–Stokes equation. The analysis, which is omitted, shows that the dispersion relation for the Stokes problem is similar to the dispersion relation from Palierne & Lequeux (1991), which assumes that the interface has dilatational and shear moduli – the forms of the moduli are left undetermined. The two relations are the same if the surface dilatational modulus in Palierne & Lequeux (1991) is defined such that (4.36) holds, and the surface shear modulus is zero.

Alternatively, the dispersion relation for Stokes flow can be derived from (4.43) with an approach similar to that of Tomotika (1935). Noting that in the Stokes limit $\omega \sim N_\sigma$, we expand $F(k_1)$ and $G(k_2)$ into Taylor series:

$$F(k_1) \approx F(k) + \frac{F'(k)}{2k}\omega + \cdots \tag{5.1}$$

and

$$G(k_2) \approx G(k) + \frac{G'(k)}{2k}\frac{N_\mu}{N_\rho}\omega + \cdots . \tag{5.2}$$

Substituting (5.1) and (5.2) into (4.43) and neglecting terms higher than $O(\omega)$ yields

$$\begin{aligned}\omega_s \Bigg\{ &\frac{1}{N_\mu}\left(1-\frac{1}{N_\mu}\right)\left[G^2(k)-1-k^2\right]kF'(k) + \left(1-\frac{1}{N_\mu}\right)\left[F^2(k)-1-k^2\right]kG'(k) \\ &+\frac{1}{N_\mu}\left[G(k)+F(k)\right]^2 + \left(\frac{E_0}{\sigma_0}\right)\frac{\kappa_s(\omega_s,k)}{2}\left(1+k^2\right)\left[kG'(k)+\frac{1}{N_\mu}kF'(k)\right]\Bigg\} \\ &= \frac{(1-k^2)}{2}\left[kG'(k)+\frac{1}{N_\mu}kF'(k)+\left(\frac{E_0}{\sigma_0}\right)\frac{\kappa_s(\omega_s,k)}{2}kG'(k)kF'(k)\right],\end{aligned} \tag{5.3}$$

where

$$\omega_s \equiv \omega/N_\sigma \quad \text{as} \quad N_\sigma \to 0, \tag{5.4}$$

$$\kappa(\omega_s,k) \equiv \left(\omega_s + \frac{k^2}{N_{Sur}N_\sigma} + \frac{N_L}{N_{Sc}N_\sigma}(k^2+N_{Sc}N_\sigma\omega_s)^{1/2}\right)^{-1}, \tag{5.5}$$

$$kF'(k) = k^2 - F^2(k) + 2F(k) \tag{5.6}$$

and

$$kG'(k) = G^2(k) - k^2 + 2G(k). \tag{5.7}$$

This dispersion relation is identical to that derived by starting from the Stokes equations. We note that it is not uniformly valid in k, because inertia terms become important as k^2 becomes small, on the order of N_σ (or $N_\sigma N_\mu^2/N_\rho$). In most circumstances, the error in (5.3) is inconsequential, because both ω_s (from (5.3)) and ω/N_σ (from (4.43) with $N_\sigma \to 0$) approach zero as $k \to 0$; two possible exceptions, both with non-zero ω_s at $k = 0$, are threads with $N_\mu = 0$ and $N_\mu \to \infty$ without interfacial elasticity. Examination of these two cases in the limit of small wavenumbers shows that the Stokes dispersion relation for $N_{El} = 0$ is uniformly valid for $N_\mu = 0$, but it breaks down for $N_\mu \to \infty$ when $k^2 \sim N_\sigma$. Figure 2 compares the growth rate for a surfactant-free thread with $N_\mu \to \infty$ determined from the Stokes dispersion relation (5.3) with that determined from the full dispersion relation (4.43). Further study of

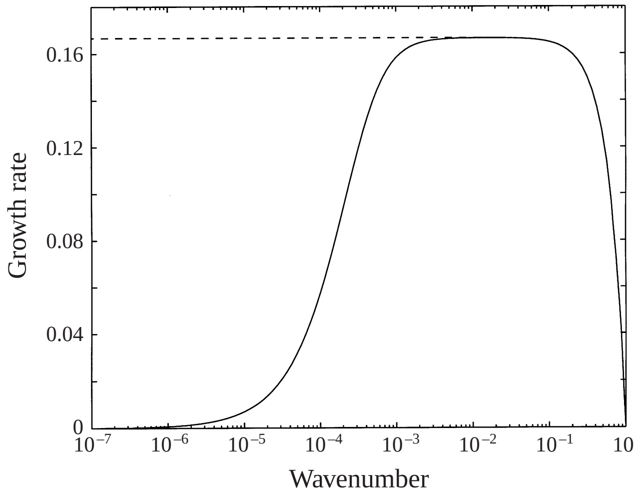

FIGURE 2. Dimensionless growth rate ω/N_σ, versus dimensionless wavenumber, k, for N_ρ and $N_\mu \to \infty$ and $N_{El} = 0$. The solid line represents ω/N_σ from (4.43) with $N_\sigma = 10^{-6}$, while the dashed line represents ω_s, from (5.3). The Stokes solution for ω_s breaks down when $k^2 \sim N_\sigma$.

the two dispersion relations at intermediate values of N_μ, and N_{El} ranging from 0 to infinity, reveals that the difference between the two relationships decreases as N_μ decreases and/or N_{El} increases. As Palierne & Lequeux (1991) did not determine the dilatational modulus for surfactant-rich interfaces and only considered the response of a surface dilatational modulus described by a Newtonian viscosity, we show the stability of a thread predicted by (5.3), i.e. both N_σ and $N_\sigma N_\mu^2/N_\rho$ approaching zero, for different elasticities and diffusivities in figure 3.

Marangoni effects resulting from gradients in surfactant concentration damp the growth rate of disturbances to a thread. Figure 3(*a*) shows that the dimensionless growth rate decreases as the elasticity number, N_{El}, which characterizes the importance of surfactant, increases. The dominant wavelength is also influenced by surfactant (see figure 3*b*). In most cases, the dominant wavenumber increases with N_{El}. However, for a narrow band of viscosity ratios, ranging from about 0.03 to 0.4, the dominant wavenumber decreases as N_{El} increases – the effect however is relatively minor. Also, the influence of surfactant is greatest when the viscosity ratio is very high or very low. These results differ from those of Milliken *et al.* (1993) which show that the average length of a disturbance, for $N_\mu = 1$, is larger when surfactant is present. There are a couple of explanations for this difference. First, Milliken *et al.* (1993) consider the breakup of droplets in which the concentration of surfactant in the interface before the disturbance begins to grow is non-uniform. Second, since Milliken *et al.* (1993) study the breakup of long slender droplets without disturbances on the interface, the breakup in their work might be dominated by end effects; their simulations show breakup starting at the ends of the drops and proceeding towards the centres.

Diffusivity of the surfactant relaxes the surface elasticity of the thread (see figure 3*c*–*f*). The elasticity of the interface results from the tendency of the surfactant to return to a uniform distribution across the interface. If diffusivity is high the distribution of the surfactant remains nearly uniform, and the effective elasticity of the interface decreases. That is, as N_{Sc} or $N_{Sur} \to 0$ the interface behaves like a 'clean' interface with an interfacial tension of σ_0. Here, we note that it is more accu-

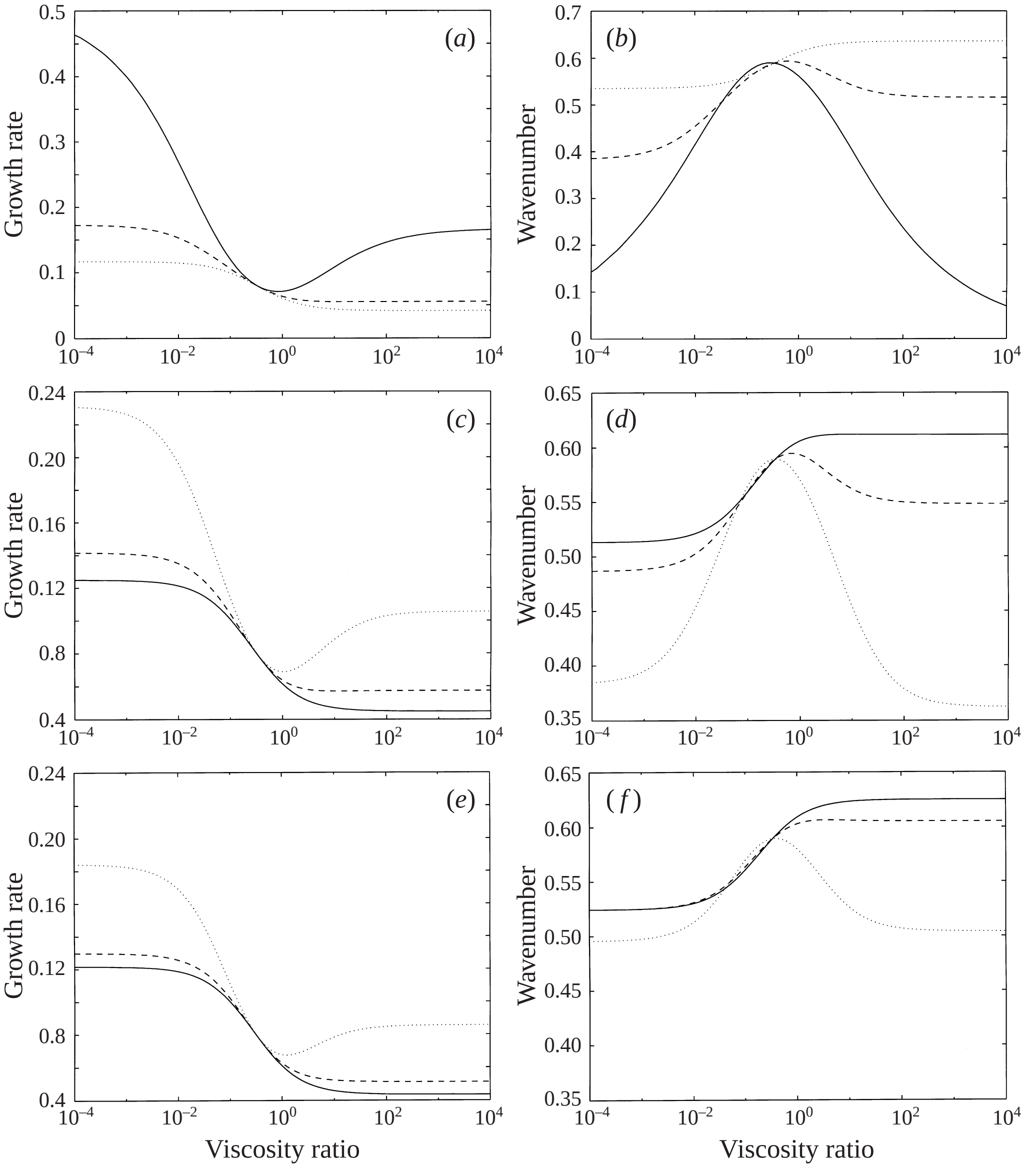

FIGURE 3. Dominant dimensionless growth rate and dimensionless wavenumber versus viscosity ratios for Stokes flow (N_σ and $N_\sigma N_\mu^2/N_\rho \to 0$), and various Gibbs elasticities and diffusivities. The density ratio does not influence the Stokes problem. The dimensionless growth rate is plotted as $\omega_s(1+N_\mu)/N_\mu$ to scale the problem with the higher of the two viscosities. (*a*) Dominant growth rate for $N_L = 0$ and $N_{Sur} \to \infty$. The solid, dashed and dotted lines are for $N_{El}/N_\sigma = 0$, 1, and 10^3, respectively. (*b*) The dominant wavenumber for the same parameters as in (*a*). (*c*) Dominant growth rate for $N_L = 1$, $N_{Sur} \to \infty$ and $N_{El}/N_\sigma = 10$. The solid, dashed and dotted lines are for $N_{Sc}N_\sigma N_\mu/(1+N_\mu) = 10$, 1, and 0.1, respectively. (*d*) The dominant wavenumber for the same parameters as in (*c*). (*e*) Dominant growth rate for $N_L = 0$ and $N_{El}/N_\sigma = 10$. The solid, dashed and dotted lines are for $N_{Sur}N_\sigma N_\mu/(1+N_\mu) = 10$, 1, and 0.1, respectively. (*f*) The dominant wavenumber for the same parameters as in (*e*).

rate to describe interfacial tension with equation (4.30) when the Schmidt number is low, but equation (4.32) qualitatively captures the behaviour. The difference between the effect of surface diffusion and bulk diffusion on the stability of a thread can be seen in figure 3(*c–f*). Two parameters, N_L and N_{Sc}, characterize the diffusion of the surfactant in the bulk, while there is only one parameter for surface diffusion, N_{Sur}. A low N_L implies the surfactant is preferentially positioned on the interface. Generally, $N_{Sur} \sim N_{Sc}$, and the importance of bulk diffusion increases and decreases with N_L. However, relaxation of the interface due to surface diffusion scales with k^2/N_{Sur} and is less important for unstable disturbances which possess low wavenumbers. Hence, we expect that diffusion in the bulk is more important than surface diffusion. As shown in figure 3(*c–f*), surface diffusion is frequently less important than bulk diffusion, but can play an important role when $N_L \rightarrow 0$. According to the Frumkin isotherm (Lin *et al.* 1990), N_L is small for dilute surfactant concentrations; however, N_{El} is also relatively small at dilute concentrations.

The preceding discussion focuses on Stokes flow – low N_σ. Here, we consider systems with inertia, or moderate to high values of N_σ. The limiting case of a filament with a non-zero N_σ in a gas was considered by Whitaker (1976). We cannot directly compare our dispersion relation with that of Whitaker owing to the previously mentioned sign error. However, we can correct the sign error and compare this modified result for a liquid filament in a gas with our result for N_ρ and $N_\mu \rightarrow \infty$. This exercise shows that equation (4.43) agrees with the modified result of Whitaker, further validating our dispersion relation.

Examination of the dispersion relation (4.43) reveals some of the behaviour of the filament. Like in Tomotika's (1935) classic problem without surfactant, threads are unstable for $\lambda > 2\pi R$, and stable for $\lambda < 2\pi R$. The dispersion relation can be written, for the limiting case of $N_{El} \rightarrow 0$, as

$$\begin{aligned}
&\omega^2\{G(k)M(k_1,k)/N_\rho^2 + [F(k)F(k_1) + G(k)G(k_2) + 2F(k)G(k)]/N_\rho \\
&\quad + F(k)O(k_2,k)\} + 2\left(1/N_\mu - 1\right)\omega k^2\{[1 - 2F(k)]\,O(k_2,k) \\
&\quad + [1 + 2G(k)]\,M(k_1,k)/N_\rho\} - 4\left(1/N_\mu - 1\right)^2 k^4 M(k_1,k)O(k_2,k) \\
&= N_\sigma k^2\left(1 - k^2\right)\{O(k_2,k) + M(k_1,k)/N_\rho\} \qquad (5.8)
\end{aligned}$$

and, for the limiting case of $N_{El} \rightarrow \infty$, as

$$\begin{aligned}
&\omega^2\{[1 + F(k)F(k_1) - 2F(k)]\,O(k_2,k) + [1 + G(k)G(k_2) + 2G(k)]\,M(k_1,k)/N_\rho\} \\
&\quad -2\omega\left(1/N_\mu - 1\right)k^2 M(k_1,k)O(k_2,k) = N_\sigma k^2\left(1 - k^2\right)M(k_1,k)O(k_2,k). \qquad (5.9)
\end{aligned}$$

When $N_{El} \rightarrow 0$, the thread is essentially surfactant free. On the other hand, when $N_{El} \rightarrow \infty$, the tangential stress condition (4.20) becomes $\partial\Gamma_1/\partial z = 0$. Physically, the surface elasticity due to Marangoni effects is so strong that the $O(\epsilon)$ part of the fractional rate of surface expansion, $\nabla_s \cdot \boldsymbol{v}_1$ at $r = 1$, equals zero. This is possible because the total surface area of the filament remains constant in the $O(\epsilon)$ problem. Higher-order contributions to the fractional rate of surface expansion are not zero. The tangential stress boundary condition can be expressed as

$$\frac{\partial v_{1z}}{\partial z} + v_{1r} = 0 \quad \text{at} \quad r = 1 \qquad (5.10)$$

and the last term in the normal stress boundary condition (4.19) drops out, because σ_1 is zero. Thus, as postulated by Whitaker (1976) for a viscous filament in a gas, in

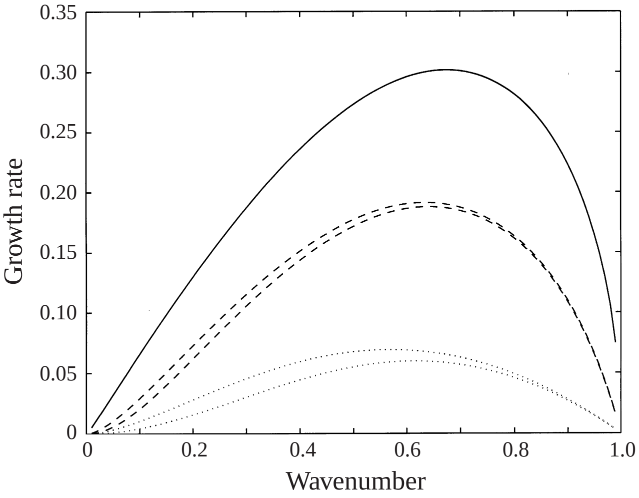

FIGURE 4. Dimensionless growth rate, ω/N_{Re}, versus dimensionless wavenumber, k, for the dispersion relation in the limits of $N_{El} \rightarrow 0$ and ∞, with $N_\rho = N_\mu = 1$. The dotted, dashed and solid lines show the growth rates for $N_\sigma = 1$, 100, and 10^6, respectively. The faster growth rates are for $N_{El} \rightarrow 0$, or (5.8), and the slower growth rates are for $N_{El} \rightarrow \infty$, or (5.9). Note that the two limiting forms for $N_\sigma = 10^6$ match to within six significant figures, and thus the two solid lines completely overlap.

the two limiting cases for N_{El} the stability of the thread becomes independent of the Gibbs elasticity.

Figure 4 shows the behaviour of the two limiting cases of N_{El}. We note that as $N_\sigma \rightarrow 0$ the growth rate becomes proportional to interfacial tension, and that as $N_\sigma \rightarrow \infty$ the growth rate becomes proportional to the square root of interfacial tension. Therefore, we plot ω/N_{Re}. Threads with a high elasticity are more stable than threads with no elasticity, i.e. ω decreases as N_{El} increases. However, the difference between the limiting forms, (5.8) and (5.9), decreases as the surface tension number increases. In fact, as shown in figure 4, the dilatational elasticity of the surface does not affect the stability of the interface when $N_\sigma \rightarrow \infty$. This behaviour for threads with high surface tension numbers, illustrated in figure 4, holds for all other investigated values of N_μ and N_ρ, provided that $N_\sigma N_\mu^2/N_\rho \gg 1$.

When the dimensionless groups N_σ and $(N_\sigma N_\mu^2/N_\rho)$ become very large, the system is practically inviscid. In the inviscid system with surfactant, a disturbance in tangential velocity on the surface of the filament, resulting from Marangoni effects and undamped by viscous terms, immediately corrects for concentration gradients which would normally prevail due to the local stretching and contraction of the interface during breakup. As a result, surfactant concentration remains uniform during breakup. Furthermore, the disturbance to the surface tangential velocity does not propagate into the inviscid fluids. Thus, surfactants only influence the stability of inviscid systems by lowering σ_0; dilatational surface elasticity does not affect inviscid systems.

In most cases, surfactants tend to shorten the dominant wavelength. However, as shown in figure 3 for the Stokes problem, this behaviour is not universal. Figure 5 shows the effect of increasing N_{El} on the dominant wavenumber for a moderate N_σ and N_μ, and a range of N_ρ. For this case and $N_\rho > 10^{-2}$, the dominant wavenumber first decreases then increases as N_{El} increases from zero to infinity.

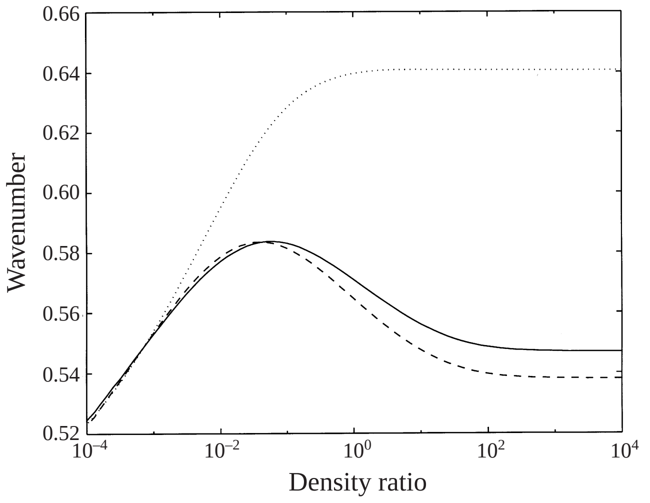

FIGURE 5. Dominant wavenumber versus dimensionless density ratio, N_ρ, for $N_\sigma = 10$, $N_\mu = 10$, $N_L = 0$ and $N_{Sur} \to \infty$. The solid, dashed and dotted lines are for $N_{El} = 0$, 1, and 10^6, respectively.

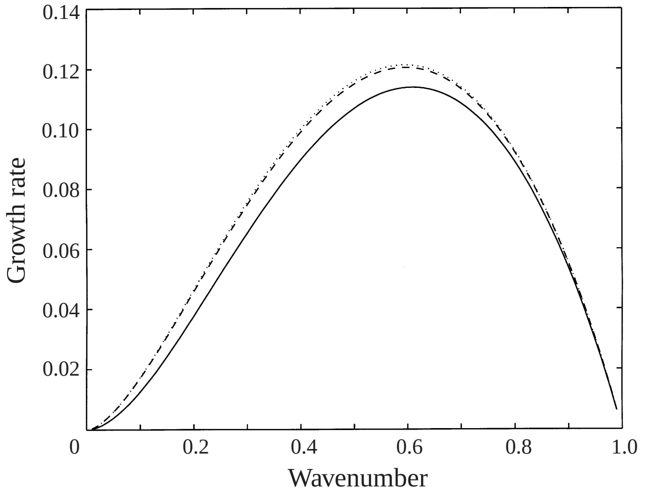

FIGURE 6. Dimensionless growth rate, ω/N_{Re}, versus dimensionless wavenumber, k, for $N_\sigma = N_{El} = 10$, $N_\mu = N_\rho = 1$, $N_L = 1$ and $N_{Sur} \to \infty$. The solid, dashed and dotted lines are for $N_{Sc} = 1$, 0.1, and 0.01, respectively.

Figure 6 shows the growth rate of disturbances on threads with an intermediate surface tension number and an intermediate elasticity number for various Schmidt numbers. The growth rate is bound by the limiting cases of no surfactant and a surfactant which does not diffuse. We caution however that while growth rate versus wavenumber is bound by the limiting cases the dominant wavenumber is not necessarily bound by the limiting forms. Nevertheless, figure 6 shows that one need not know diffusivity and adsorption depth to predict some of the effects of the surfactant.

6. Conclusion

We have determined the dispersion relation for a viscous fluid filament embedded in another viscous fluid with surfactant via linear stability theory. The surfactant, which only serves to lower interfacial tension, diffuses in the filament and the matrix, and in the fluid–fluid interface. To obtain the solution, which is valid for small disturbances, we have assumed that the system is initially in equilibrium.

Several parameters influence the stability of the thread (see the table of dimensionless parameters in § 3). As expected, the analysis shows that surfactants stabilize a filament by lowering the interfacial tension, and by giving the interface a dilatational modulus. The surface elasticity resulting from Marangoni effects is not a material parameter, and is dependent on Gibbs elasticity, diffusion in the bulk fluids and interface, adsorption depth, and the disturbance. As expected, diffusion in the interface and in the bulk relax the elastic nature of the interface. Surface diffusivity is less important than bulk diffusivity, except at low surfactant concentrations, low N_L.

The influence of surfactant on the dominant wavelength is less intuitive. Most often, the dominant wavelength decreases with increasing Gibbs elasticity. This indicates that droplets resulting from breakup of a filament are smaller when surfactant is present. However, in the Stokes regime, for a small range of viscosity ratios ($N_\mu \sim 0.03$–0.4) the dominant wavelength increases with Gibbs elasticity. Systems with moderate surface tension numbers exhibit similar behaviour. In dispersions, surfactants are used to control the size of the droplets by their influence on stretching and deformation of droplets, and on coalescence. Our results demonstrate that surfactants also affect the size of droplets resulting from breakup; however, the effect of surfactants is less important for viscosity ratios between 0.1 and 3 – which includes many practical systems – than for more extreme viscosity ratios.

Furthermore, two interesting conclusions can be drawn by examining the limiting forms of the dispersion relation. The behaviour of a filament with $N_{El} \to 0$ and that of a filament with $N_{El} \to \infty$ are both independent of the Gibbs elasticity. More interesting, the stability of a filament is not affected by surfactant when the surface tension number is very large.

This work was supported by the European Commission within the FAIR Project CT97 3022.

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