# THE FORMATION OF FARADAY WAVES ON A LIQUID COVERED WITH AN INSOLUBLE SURFACTANT: INFLUENCE OF THE SURFACE EQUATION OF STATE.

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Abstract— In this work the effects of relatively large amounts of insoluble surfactants on the formation and evolution of two-dimensional Faraday waves is analyzed by means of numerical experiments. To describe the functional relationship between the surface tension and the local concentration of the absorbed solute, two equations of state are used: the Frumkin and the Langmuir expressions. A linear approximation is also employed for comparison. Results obtained show that the threshold conditions for the formation of the waves depend on the nature of the surfactant; nevertheless, the differences detected diminish as the amplitude of the external excitation is augmented.

*Keywords*— free-surface, surfactants, finite-element, Faraday waves.

# I. INTRODUCTION

When a container partially filled with a liquid is vertically vibrated, stationary waves with a frequency equal to one half the frequency of the external excitation can be observed at the liquid-air interface. These waves were reported by Faraday in 1831 but it was not until 1954 that the first theoretical analysis of this problem was presented by Benjamin and Ursell. These authors studied the stability of the interface of an ideal fluid in irrotational motion, for infinitesimally small amplitudes of the free surface oscillations. They derived an infinite set of Mathieu's equation and they showed that resonance is responsible for the wavy motion. They also concluded that the system is always unstable when the frequency of the external vibration is equal to twice the natural frequency of the system, even for forcing amplitudes infinitesimally small. This unrealistic result is a consequence of the ideal behavior assumed.

Since the pioneering work of Benjamin and Ursell (1954), many theoretical and experimental contributions dealing with different aspects of the problem have been published (for a review see Miles and Henderson 1990, Miles 1993, and Perlin and Schultz, 2000). Even though the damping effect on surface waves produced by surface active agents is well known since ancient times (Franklin, 1774), very few articles are concerned with the influence of surfactants on Faraday waves. Miles (1967) performed a weakly non linear analysis in

which approximate analytical expressions for the damping coefficients of surface waves under the influence of surfactants were established. Henderson (1998) measured damping rates of the fundamental axisymmetric Faraday waves in a cylindrical container and compared the experimental values with those obtained evaluating the approximate analytical expression of Miles. She found a reasonable agreement between them even when the amplitude of the waves were large.

Kumar and Matar (2002a, b; 2004) presented three analyses about the role of insoluble surfactants on the critical oscillation amplitude required to form Faraday waves. In the first of these studies, they performed a linear stability analysis for fluids of arbitrary viscosity and depth. As a consequence of the assumptions introduced, a time-independent concentration of surfactant is the only solution compatible with the existence of Marangoni flows, this solution being possible in the limit of very high Péclet number. These authors proposed that the distribution of solute presents a spatial shift with the free surface deflections and they reported solutions using the spatial phase angle as an arbitrary parameter. The main conclusion reported is that the surfactant may either raise or lower the amplitude of the external oscillation needed to produce a wavy interface, depending on the value of the shift.

In the second article Kumar and Matar (2002b) established the magnitude of the minimum external force needed to form two-dimensional Faraday waves at the free surface of a liquid layer covered with an insoluble surfactant. The approach employed in this work is the lubrication approximation based on the assumption that the liquid thickness is very small compared to the wavelength of the disturbance. The results obtained show that the contaminated liquid layer becomes more stable as the elasticity number (i.e. the ratio between the Gibbs elasticity and the surface tension) increases; nevertheless, they predict that a clean system meeting the requirements of the approximations used can not be excited, a result that contradicts the predictions of the linear stability analysis (Kumar and Tuckerman, 1994).

In the third work, Kumar and Matar (2004) analyzed the formation of standing waves when the free surface is covered with an insoluble surfactant. They performed a full linear stability analysis of the problem in which surfactant convection is rigorously accounted for. They

evaluated both the critical vibration amplitude and the critical wave number as a function of the Marangoni number.

In a previous work, we numerically investigated the elastic effects of an insoluble surfactant on the formation and evolution of two-dimensional Faraday waves (Ubal *et al.*, 2004). The numerical experiments carried out, establish the minimum value of the external force required to form standing waves of a given wavelength as a function of the elasticity of the surface active agent. We show the existence of a temporal phase shift between the motion of the liquid in the bulk and along the interface; this phase shift is related to the magnitude of the external force needed to excite the system.

In all the works mentioned above, it is assumed that the surface tension is a linear function of the concentration of the adsorbed surfactant, a hypothesis that is reasonable when both the free surface deflection and the interfacial concentrations of the surface active agents are small.

In the present study we numerically analyze the effects of an insoluble surfactant on two dimensional Faraday waves without the limitations associated to the use of a linear equation of state for surface tension. Therefore, we can compute solutions for larger values of the free surface amplitude and larger amounts of solute absorbed; moreover, we are able to predict the conditions under which a linear equation of state underestimates or overestimates the threshold conditions for surface wave generation. We use two thermodynamic equations that can be derived from the Langmuir and Frumkin isotherms (see, for instance, Edwards *et al.*, 1991). Results computed with them and with their linear approximations are presented and discussed.

# II. MATHEMATICAL FORMULATION

#### A. Governing equations

We consider a layer of an incompressible Newtonian liquid covered by a monolayer of an insoluble surfactant. The liquid is lying on the horizontal (x, z) plane, and its height at rest is  $H_0$ . The viscosity  $(\mu)$  and density  $(\rho)$  of the liquid are constant, and the air above it is inviscid. The pressure of the gas phase is the reference pressure of the system and is taken equal to zero.

Initially, a 2-D perturbation of amplitude  $\varepsilon H_0$  and wave number k is imposed to the free surface and the time evolution of the disturbance is followed. The extension of the domain in the x-direction is equal to one half the wavelength of the initial perturbation imposed; therefore, lateral boundaries are symmetry planes and the wavy motion developed is mirrored at both sides of the domain. Under these conditions the free surface is described by a function of one spatial coordinate and time: h(t, x).

The reference frame adopted is attached to the solid boundaries which oscillate with frequency  $\omega$  and amplitude  $a_0$ ; therefore, the externally induced acceleration is

added to gravity. The equations of momentum and mass conservation are

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p + \frac{1}{Re} \nabla \cdot \left[ \nabla \mathbf{v} + (\nabla \mathbf{v})^T \right] + \frac{1}{Fr} \left[ F \cos(2\pi t) - 1 \right] \mathbf{j}, \tag{1}$$

$$\nabla \cdot \mathbf{v} = 0 , \qquad (2)$$

where  $Re=\rho\omega\pi H_0^2/2\mu\alpha^2$  is the Reynolds number,  $Fr=\omega^2H_0/4\pi\alpha g$  is the Froude number, and  $F=a_0\omega^2/g$  gives the ratio between the external imposed force and gravity force. The characteristic scales adopted are  $\pi/k=\pi H_0/\alpha$  for lengths,  $2\pi/\omega$  for time,  $\omega H_0/2\alpha$  for velocities, and  $\rho(\omega H_0/2\alpha)^2$  for pressures and stresses. The initial perturbation imposed to the free surface is

$$h(0,x) = \alpha/\pi \left[ 1 - \varepsilon \cos \pi x \right], \ 0 \le x \le 1. \tag{3}$$

The boundary conditions required by Navier-Stokes equation are summarized in Fig. 1 where u and v are the x and y components of the velocity vector, respectively. At the bottom wall the non-slip condition is imposed while at the lateral planes, symmetry is required.

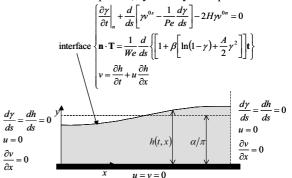


Fig. 1. Schematic representation of the flow domain, boundary conditions, and coordinate system adopted.

To establish the boundary conditions at the interface, we presume that the free surface is a material surface; therefore, the kinematic condition applies

$$\frac{\partial h}{\partial t} + u \frac{\partial h}{\partial x} = v. \tag{4}$$

Besides, the free surface is Newtonian and inviscid, so that the dimensional surface stress tensor  $\mathbf{T}^{(S)}$  is  $\mathbf{T}^{(S)} = \sigma(\mathbf{I} - \mathbf{n}\mathbf{n})$ , where  $\mathbf{I}$  is the identity tensor,  $\mathbf{n}$  is the outwardly directed unit vector normal to the interface, and  $\sigma$  is the gas-liquid surface tension that is a function of the amount of surfactant  $(\rho^S)$  locally adsorbed; thus, the interfacial balance of stresses results

$$\mathbf{T} \cdot \mathbf{n} = \frac{1}{We} \frac{d}{ds} (\overline{\sigma} \mathbf{t}), \overline{\sigma} = \frac{\sigma}{\sigma}.$$
 (5)

In Eq. (5),  $We=\pi\rho\omega^2H_0^3/4\alpha^3\sigma_F$  is the Weber number,  $\sigma_F$  is the surface tension of the corresponding "clean" system, and  $\mathbf{t}$  is the unit vector tangent to the free surface pointing in the direction of increasing arc-length s. If there are not surfactants on the interface, Eq. (5) will simplify to the boundary condition usually imposed to the free surface. On the other hand, in the presence of surfactants, this equation must be complemented with an appropriate equation of state that specifies the dependence of the interfacial tension on surfactant concentration. In this work, the expressions adopted can be derived from the Frumkin isotherm; that is,

$$\overline{\sigma} = 1 + \beta \left[ \ln(1 - \gamma) + \frac{A}{2} \gamma^2 \right]. \tag{6}$$

In Eq. (6),  $(\overline{\sigma}-1)$  represents the local variation in surface tension relative to the interfacial tension of a clean interface.  $\beta = RT\rho_{\infty}^{\ S}/\sigma_F$  is the elastic number, R being the perfect gas constant, T the absolute temperature and  $\rho_{\infty}^{\ S}$  the maximum concentration of solute that can be absorbed on the interface; and  $\gamma$  is the dimensionless interfacial concentration of surfactant measured in units of  $\rho_{\infty}^{\ S}$ .

Finally, in this expression, A is a parameter that measures the degree of non-ideality of the interface; A is positive or negative for cohesive or repulsive interactions between the surfactant molecules, respectively. The Langmuir equation of state is a special case of Eq. (6) that supposes the interface to be ideal; that is, A = 0. It is also worth noting that Eq. (6) reduces to the commonly used linear equation of state

$$\overline{\sigma} = 1 - \beta \gamma \tag{7}$$

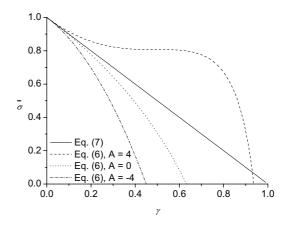
in the dilute limit,  $\gamma$  << 1. Although Eq. (7) has been used in all previous works concerning this problem, it is easy to verify that it is only valid in the limit of very low concentrations of surfactant. In fact, the curves illustrated in Fig. (2) corresponding to the evaluation of Eq. (6) with A equal to 0, 4 and -4, put into evidence that non linear effects can be important when the initial surface coverage is relatively low.

Since the interfacial tension is a function of the local concentration of the surface active agent adsorbed at the interface, the system of governing equations must be complemented with the interfacial mass balance of surfactant; for an insoluble contaminant, this equation is (Stone, 1990)

$$\left(\frac{\partial \gamma}{\partial t}\right)_{n} + \frac{\partial}{\partial s} \left[ \gamma v^{0s} - \frac{1}{Pe} \frac{\partial \gamma}{\partial s} \right] - \gamma 2H v^{0n} = 0, \quad (8)$$

where  $v^{0s}$  and  $v^{0n}$  are the tangential and normal components of the interfacial velocity, respectively, H is the dimensionless curvature of the interface, and  $Pe=2\alpha^2D^S/\pi\omega H_0^2$  is the surface Péclet number;  $D^S$  being the interfacial diffusivity of the solute.

Symmetry boundary conditions must be satisfied at both ends of the interface implying that  $\partial \gamma/\partial s = \partial h/\partial s = 0$ .



**Fig. 2.** Surface tension versus surface coverage evaluated with Eqs. (6) and (7) with  $\beta = 1$ .

Next, we briefly summarize the numerical technique employed to solve the system of governing equations and boundary conditions.

### B. Numerical technique

The Galerkin/finite-element method is used to obtain the spatial discrete version of the governing equations (1), (2), (4), and (8) with their boundary conditions, while the free surface location is traced with the aid of a suitable parameterization (Kheshgi and Scriven, 1984).

The flow domain is tessellated into quadrilateral elements and each element is mapped isoparametrically onto a unit square; this transformation applied to all the elements defines the computational domain in which the free surface is a coordinate line. Mixed interpolation is used to approximate the velocity and pressure fields. The interfacial concentration of surfactant is interpolated by the one-dimensional specialization of the biquadratic basis functions used to approximate the velocities.

The weighted residuals of the governing equations are built in the usual form; thus a set of ordinary differential equations is obtained. This set is reduced to a set of nonlinear ordinary equations by means of a finite-difference predictor-corrector scheme and it is solved using a Newton loop. The size of the time step is controlled using Crisfield's method.

The criteria adopted to select an appropriate finite element mesh are the following:

- There is one boundary layer near the solid wall and another one near the interface; consequently, the mesh is refined in these regions.

- Numerical oscillations associated to large Péclet values should be negligible.
- Errors in the surfactant mass balance should be bounded to a small amount; typically the cumulative error between the first and the last time step of a simulation is less than 2%.

From the numerical experiments performed, we concluded that a mesh with 140 elements was appropriated to follow the evolution of the free surface and the interfacial concentration of surfactant in almost all the situations presented in this work. In fact, only in few opportunities a more refined mesh was employed.

A complete discussion of the numerical algorithm employed and a detailed description of the numerical tests performed are reported elsewhere. (Ubal *et al.* 2003, 2004).

#### III. RESULTS AND DISCUSSION

As we have already mentioned in the Introduction, in this work we are primarily concerned with insoluble surfactants of different nature and the effects they have on the formation of the waves. More specifically, we compare the behavior of the system under the influence of Langmuir and Frumkin surfactants. Also, we consider the linear form of these equations in order to explore the range of validity of this approximation.

For this purpose, we carried out numerical simulations for a particular set of the dimensionless parameters:

$$\alpha^2 Re = 39.478$$
,  $\alpha^3 We = 4.429$ ,  $\alpha Fr = 3.206$ , (9)

which corresponds to the following typical values of the physical variables

$$\rho$$
=1000 $kg/m^3$ ,  $\mu$ =25×10<sup>-3</sup>  $Pa$   $s$ ,  
 $\sigma_F$ =70×10<sup>-3</sup>  $N/m$ ,  $H_0$ =10<sup>-3</sup> $m$ ,  $\omega$ =200 $\pi$   $s$ <sup>-1</sup>.

These parameters were employed in the simulations of both a contaminated surface and a system free of surfactant. In addition, when a surface active agent is present, the following value for the Péclet number —that corresponds to a typical value of the surface diffusion coefficient ( $D^S$ =2.5×10<sup>-9</sup>  $m^2/s$ )—was specified

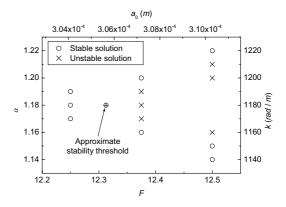
$$\alpha^2 Pe = 394784.$$
 (10)

The numerical solutions presented in this section are organized as follows. First, we select a particular wave number ( $\alpha$ ) in order to define a reference case for the numerical experiments. Then we analyze the influence of the amount of surfactant adsorbed at the interface on the critical conditions required to form standing waves of wave number  $\alpha$ ; this study is carried out using Eq. (6) with A equal to 0, 4 and -4. Finally, the effect of increasing the amplitude of the external force on these systems is studied.

#### A. Selection of the reference case

In order to determine a base case for the analysis, we conducted a first set of numerical simulations in a system free of surfactant; that is,  $\beta=0$ . The results obtained are summarized in Fig. 3, where crosses and circles represent the outcome of each numerical experiment. Every simulation starts with the liquid at rest, the free surface slightly perturbed from the horizontal flat state according to (3) with  $\varepsilon$  =0.001, and a uniform concentration of surfactant ( $\gamma = \gamma_0 / S_0$ ,  $S_0$  being the initial dimensionless interfacial length and  $\gamma_0 = \rho_0^S / \rho_\infty^S$ ;  $\rho_0^S$ is the initial concentration of surfactant adsorbed on the interface). In this figure, crosses denote unstable solutions while circles denote stable ones. The criterion adopted for this classification is the following: when the amplitude initially imposed to the free surface decays to zero, the numerical experiment is considered stable, otherwise it is catalogued as unstable.

The unstable solutions shown in Fig. 3 define a region in which the oscillation of the free surface has a frequency equal to one half the frequency of the external vibration and a wavelength equal to  $2\pi/k$  (in dimensional units). Under these conditions, there exists a particular wave number ( $\alpha_C$ ) that requires a minimum excitation amplitude ( $F_C$ ) to raise a wavy motion. The point marked with  $\oplus$  ( $F_C$ =12.31,  $\alpha_C$  =1.18) represents the approximate critical conditions for wave generation. This particular wave number together with the set of dimensionless numbers (9) and (10) define the reference set (RS) that will be employed in the numerical experiments carried out in this work to study the influence of the surface active agents on the generation of the waves.



**Fig. 3.** Stability map in the F- $\alpha$  plane for a clean system characterized by (9).

# B. Effect of the initial surface coverage on $F_C$

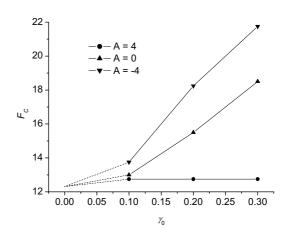
In this section we analyze the influence of the initial surface coverage  $\gamma_0$  on the minimum vibration amplitude required to form the standing waves.

We fixed  $\beta$  equal to 1—i.e. a typical value for the elasticity number— and we computed solutions for RS and several values of the initial surface coverage  $\gamma_0$ , in order to detect the minimum amplitude needed to produce the waves. In all the cases considered, we employed Eq. (7) and Eq. (6) with A equal to 0, 4 and -4, these last two values represent a surfactant with strong cohesive and repulsive interactions, respectively (Johnson and Borhan, 1999).

As we have mentioned in the Introduction, the damping effect that films of insoluble surfactant have on surface waves is well known since a long time ago. When a wavy motion is established and the Péclet number is large, the liquid moving from the valley toward the crest of the wave convects surfactant to this region creating a positive concentration gradient directed from the trough toward the crest of the wave. This gradient gives rise to a non zero tangential component of the traction vector along the interface (see Eq. (5)) pointing toward the region of larger interfacial tension (lower concentration of the surface active solute). These tensions, that are known as Marangoni tensions, try to restore a uniform concentration of surfactant by pulling the interface in the opposite direction to the motion of the bulk damping, in this way, the surface waves.

Therefore, as the amount of surfactant adsorbed at the interface increases one should expect larger values of the minimum external amplitude needed to form the waves, whenever a larger amount of surfactant implies larger elastic effects ( $d\overline{\sigma}/d\gamma$ ). It can easily be verified (see Eq. (6) and Fig. 2) that this quantity depends upon the type of surfactant adsorbed at the interface; consequently, the dynamic behavior of the system for a Langmuir or a strongly repulsive surfactant will be different compared to the behavior of a strongly cohesive one.

The results of the numerical solutions computed are reported in Fig. 4. One should note that  $\gamma_0 \approx 0$ , represents a limit case in which the amount of surfactant adsorbed is negligible and consequently,  $\overline{\sigma} \rightarrow 1$ ; therefore, the value of  $F_C$  corresponds to the situation in which the concentration of surfactant is nearly zero (infinite dilution),  $\beta$  being equal to 1. The solutions illustrated in this figure show that  $F_C$  increases with the initial surface coverage when A is equal to 0 or -4, as expected. On the other hand, for A=4,  $F_C$  slightly increases with  $\gamma_0$  when this quantity is between 0 and 0.1, and from this point it remains almost constant within the range of initial surface coverage considered in this analysis.



**Fig. 4.** Influence of the initial surface coverage on  $F_C$  for  $\beta = 1$ , and A equal to 0, 4 and -4. The other parameters of the system correspond to RS.

In order to understand the trends of the curves illustrated in Fig. 4, one should notice that for a fixed surfactant coverage Eq. (6) predicts larger values of  $\left| d\overline{\sigma}/d\gamma \right|$  when A is equal to 0 (ideal surfactant) or negative (repulsive interactions between the surfactant molecules) than for a positive A (attractive interactions between the surfactant molecules). The isotherms depicted in Fig. 2 for A equal -4 and 0, show that this quantity increases rapidly with  $\gamma$ , and consequently, the surface tension diminishes fast as the concentration of surfactant is augmented. On the other hand, the curve corresponding to A=4, shows that  $\left| d\overline{\sigma}/d\gamma \right|$  is almost zero when the surface coverage is smaller than 0.7; therefore, the surface tension is almost insensitive to changes in concentration within this range of surfactant concentration .

According to the above remarks, it is easy to understand why  $F_C$  increases with the amount of surfactant adsorbed at the free surface in a system covered with either an ideal surfactant (Langmuir) or a surfactant with strong repulsive interactions (Frumkin with A=-4). Moreover, the larger values presented by  $|d\overline{\sigma}/d\gamma|$  in the last case are responsible for the higher external forces required to form the waves.

When the deviation from the ideal behavior (A=0) is due to large attractive forces between the surfactant molecules,  $\left| d\overline{\sigma}/d\gamma \right|$  is small (see Fig. 2); therefore,  $F_C$  slightly increases from the value corresponding to infinite dilution, as the results in Fig. 4 indicate.

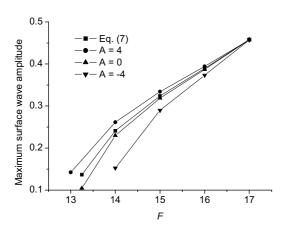
Next, we analyze the effects of increasing F beyond its critical value on the dynamic behavior of a system covered with a Langmuir or a Frumkin surfactant that presents either repulsive or cohesive interactions.

# C. Evolution of the interfacial variables for increasing external amplitude and a fixed surface coverage.

It is interesting to study the dynamic behavior of the system when the external force is larger than the minimum value needed to form the waves, and the surfactant adsorbed on the interface is a Langmuir or a Frumkin surfactant.

To this end, we computed solutions for F between  $F_C$  and 17, when the parameters of the system stand for the RS,  $\beta = 1$ , and the relationship between surface tension and the concentration of surfactant corresponds to either the Langmuir equation or the Frumkin equation with A = 4 and A = -4. Also, in order to detect the limits of validity of the linear approximation, we computed solutions with Eq. (7).

In Fig. 5, the time-periodic maximum amplitude of the free surface oscillation is illustrated as a function of F, for the different types of surfactants considered in this work.



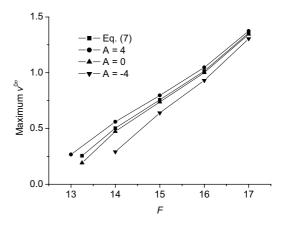
**Fig. 5.** Values of the free surface maximum amplitude as a function of F, for three types of surfactants (A equal to 0, -4 and 4),  $\gamma_0 = 0.1$ , and  $\beta = 1$ . The other parameters of the system correspond to RS. Results computed with Eq. (7) are also included.

Results depicted in Fig. 5, show that the maximum amplitude of the oscillation when the external force is fixed is larger when A=4 and it is smaller for A=-4. Also, the predictions of the linear model are very similar to those computed with Langmuir equation, an expected result if one takes into account that the surface coverage considered is relatively low. As we have already mentioned, the damping effect of a surface active agent on the surface waves is primarily due to the Marangoni traction whose magnitude depends on  $\left| d\overline{\sigma} / d\gamma \right|$ . For the case under analysis, this variable is smaller when A=4 and it is larger for A=-4, while the values corresponding to the linear approximation (7) and to A=0 are very similar (see Fig. 2).

It is interesting to note, that the differences observed between the models are larger near the onset, including those between the Langmuir expression and the linear approximation (7), even for the small surface coverage considered here. All the curves merge at F=17, pointing out that when the external force is large the effects of the surfactant on the system are practically negligible.

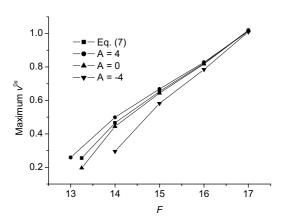
The generation of the waves results from the competition between capillary, viscous, inertia, Marangoni, and external forces. Capillary and Marangoni forces are related to the type of surfactant adsorbed at the interface. Their values depend on surface tension and surface elasticity that in turns depends on the interfacial concentration gradients generated by interfacial convection and interfacial deformation. On the other hand, inertia forces depend directly on the velocity. Therefore, it is interesting to analyze the maximum value of the time-periodic surface velocity in all the examples reported in Fig. 5.

In Figs. 6 and 7 we illustrate the normal and tangential components of the interfacial velocity as a function of F, respectively. As it is shown, the magnitude of these variables increases as F is augmented; moreover, all the curves follow a similar trend to that observed in Fig. 5 for the free surface amplitude. The differences are larger near the onset and they diminish as the external acceleration is increased. For a fixed F, the larger velocities are detected for a surfactant with molecules attracting each other and the smaller ones are presented by a surface active agent whose molecules repel each other. Also, the values computed for a Langmuir surfactant are very close to those computed with the linear approximation (7).



**Fig. 6.** Maximum values of the normal component of the interfacial velocity, as a function of F, for three types of surfactants (A equal to 0, -4 and 4),  $\gamma_0 = 0.1$ , and  $\beta = 1$ . The other parameters of the system correspond to RS. Results computed with Eq. (7) are also included.

A careful inspection of the flow field (not shown here) indicates that the magnitude of the normal component of the surface velocity typifies well the magnitude of this variable in the whole domain. Thus, for an increase of the surface velocities with F as is depicted in Figs 6 and 7, one might expect the inertia forces to become rapidly dominant over the remaining forces. In particular, their magnitude should grow large enough to make negligible any difference in the Marangoni forces. This explains why all the curves corresponding to both the magnitude of the interfacial velocity (Figs. 6 and 7) and the amplitude of the free surface waves (Fig. 5) tend to merge when the excitation amplitude is high.



**Fig. 7.** Maximum values of the tangential component of the interfacial velocity, as a function of F, for three types of surfactants (A equal to 0, -4 and 4),  $\gamma_0 = 0.1$ , and  $\beta = 1$ . The other parameters of the system correspond to RS. Results computed with Eq. (7) are also included.

On the contrary, near the onset of the instability the velocities are small, and even small differences in Capillary and Marangoni forces associated to the characteristics of the surfactant considered, should be noticeable there.

#### IV. CONCLUDING REMARKS

In this work we numerically analyze the influence of the equation of state relating surface tension and local interfacial concentration of surfactant on the formation of Faraday waves.

The numerical technique employed, which uses the Galerkin/finite element method combined with a suitable parametrization of the free surface for the spatial discretization, and a second order predictor-corrector scheme to march in time proved to be well suited for our purposes.

The numerical experiments carried out show that the commonly employed linear relationship between surface tension and interfacial concentration of surfactant, is only valid in the very dilute case. In fact, the results obtained, show differences associated to the type of surfactant present in the system when the initial surface coverage is as low as 0.1. These differences diminish when the amplitude of the external vibration imposed to the system increases, and they become negligible above a certain value of this parameter.

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