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Mode mixing of surface waves

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Abstract. It is shown that the coupling between capillary waves and dilatational fluctuations at a liquid surface can lead to the appearance of mixed modes. Calculations are presented for various cases, and related to recent experiments.

1. Introduction

Although waves on liquid surfaces have been studied for many years [1, 2], theoretical studies continue in various directions, including the stability [3, 4] and non-linear effects of surface waves [5]. In general liquid interfaces sustain several modes of oscillation, of which two are of present concern: transverse or capillary and longitudinal or dilatational. These modes are coupled [6, 7]. However, in many recent studies this coupling has been neglected. The discovery in the framework of linear theory of certain hitherto unsuspected effects of this coupling [8, 9] suggests that this may seriously undermine such studies. We discuss these recently discovered effects and their experimental verification.

2. Background

Interfaces between two fluids supporting molecular films of amphiphiles may support many modes of fluctuation, both hydrodynamic [10, 6] and molecular [11]. However, our primary concern is with two hydrodynamic modes: capillary waves, governed by the interfacial tension (γ), and dilatational modes, governed by the dilatational modulus (ε) of the interface ($= -d\gamma/d \ln \Gamma_s$, Γ_s being the surface excess of amphiphile).

The fluctuation of the interface from the equilibrium position due to a disturbance of wave number q is $\zeta = \zeta_0 \exp i(qx + \omega t)$, the frequency ω being complex ($=\omega_0 + i\Gamma$). For the general case of a liquid–liquid interface [6, 7] the boundary conditions for the linearized Navier–Stokes equation for the interfacial waves can be written in the following form [6], which makes the coupling of the horizontal and vertical motions particularly apparent:

$$a_{zz}v_z + a_{zx}v_x/i = 0 \quad (1)$$

$$a_{xz}v_z + a_{xx}v_x/i = 0 \quad (2)$$

where

$$a_{xx} = \varepsilon q^2/\omega + i[\eta(q+m) + \eta'(q+m')] \quad (3)$$

$$a_{zz} = \gamma q^2/\omega + g(\rho - \rho')/\omega - \omega(\rho + \rho')/q + i[\eta(q+m) + \eta'(q+m')] \quad (4)$$

$$a_{zx} = \eta(q-m) - \eta'(q-m'). \quad (5)$$

Here

$$m = \sqrt{q^2 + \frac{i\omega\rho}{\eta}} \quad \text{Re}(m) > 0 \quad (6)$$

and η and ρ are the liquid viscosity and density (primed quantities for the upper fluid).

Equating the determinant of the coefficients of equations (1) and (2) to zero yields the dispersion equation for the interfacial waves. This has two roots, corresponding to capillary and dilatational waves respectively [6, 7]. Their behaviour may conveniently be approximated by

$$\omega_C = \sqrt{\gamma q^3/\rho} + i\frac{2\eta q^2}{\rho} \quad (7)$$

for the capillary waves [1] and

$$\omega_D = \frac{1}{2}(\sqrt{3} + i)(\varepsilon^2 q^4/\eta\rho)^{1/3} \quad (8)$$

for the dilatational waves [6]. The coupling between the modes modifies these approximate dispersion behaviours [6, 7]. The major effect is a resonance between the two modes, occurring when the frequencies of the modes coincide (at $\varepsilon_0/\gamma_0 \approx 0.16$), at which the capillary wave damping rises to roughly twice its value for a clean surface.

Dissipative effects within the surface can be incorporated into the formalism by expanding the surface moduli as linear response functions [10]:

$$\gamma = \gamma_0 + i\omega\gamma' \quad (9)$$

$$\varepsilon = \varepsilon_0 + i\omega\varepsilon' \quad (10)$$

where γ_0 and ε_0 are now the tension and elastic modulus, while the primed quantities represent surface viscosities. The dissipative effects represented by these surface viscosities influence the corresponding surface modes: the transverse shear surface viscosity γ' increases the dampings of the capillary waves compared to that due to the viscosity of the ambient liquid, while the dilatational surface viscosity ε' increases the damping of the dilatational modes.

3. Results and discussion

It is well known that coupled oscillators may show physically interesting behaviour, in particular mode mixing, in which behaviour characteristic of one mode changes smoothly to that characteristic of the other as some control parameter is varied [12]. At intermediate values of the control parameter we have mixed modes: the excitations cannot be definitively ascribed to one or other of the original modes. Such mode mixing is characterized by splitting of the frequencies of the modes.

In the present context, we first recall that the surface modes constitute *lossy* oscillators: both are damped by the fluid viscosity and perhaps by dissipation within the surface film. Manifest mode mixing derives from the free exchange of energy between the coupled oscillators. However, in the lossy case, if the rates of damping differ energy will flow from the less damped vibrator to the more damped one, essentially being lost to the system. Clearly this increases the rate of loss of energy of the less damped oscillator, and reduces that of the more damped one (due to energy flow from the former). The net effect is that the dampings of the two vibrators are brought together until ultimately they are the same and splitting of the real frequencies occurs [12]. We now consider the implications of this for our surface waves.

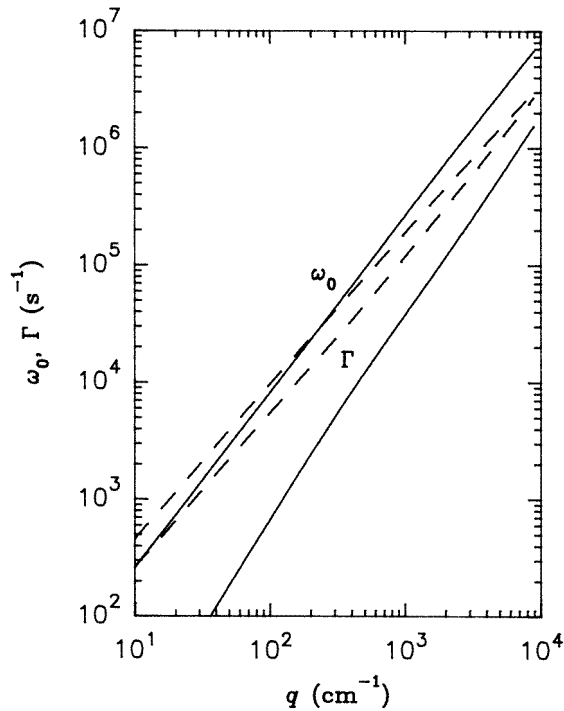


Figure 1. The q -dependence of ω_C and ω_D , found by solving the dispersion equation for $\gamma_0 = 70 \text{ mN m}^{-1}$, $\varepsilon_0 = 12 \text{ mN m}^{-1}$, other properties being as for water. Full lines represent the capillary wave behaviour, dashed lines that of the dilatational waves.

The dispersion behaviours of the two surface modes are shown in figure 1 for a typical liquid surface. Typical capillary and dilatational behaviours as suggested by equations (7) and (8) are clearly apparent. Slight deviations from the expected power-law dependences, particularly apparent in the damping, arise from approach to the resonance between the modes. The two damping values are not equal, so manifest mode mixing cannot immediately occur. In particular the dilatational wave damping exceeds that of the capillary waves, as is usually the case. Thus to cause the appearance of mode mixing, Γ_C must be increased or Γ_D must be decreased.

Now, as stated above, γ' increases the capillary wave damping, causing the Γ values of the two modes to converge, so the coupling has greater effect. As γ' increases above a critical value this can lead to manifest mode mixing [8].

This is more readily apparent when the standard dispersion graph (as figure 1) is replotted with frequencies normalized by the approximate capillary wave frequency and Γ values normalized by the approximate capillary wave damping (equation (7)). When replotted thus, capillary wave-like behaviour should correspond to normalized ω_0 and Γ of order unity, and be roughly independent of q , whereas dilatational wave-like behaviour will vary with q and differ significantly from unity in magnitude, due to the inappropriate normalization.

Figure 2 shows the normalized surface wave dispersion behaviour for a value of γ' sufficient to induce mode mixing. Note the change in behaviour of both frequencies and damping constants at q just above 1000 cm^{-1} . That normalized ω_0 which at low q is

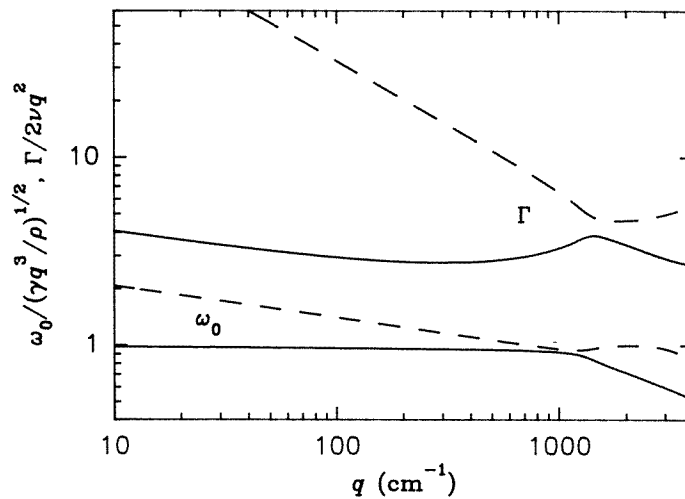


Figure 2. Manifest mode mixing of the surface waves induced by γ' above a critical value. Surface properties used in computation were $\gamma_0 = 65 \text{ mN m}^{-1}$, $\gamma' = 4 \times 10^{-5} \text{ mN s m}^{-1}$, $\varepsilon_0 = 15 \text{ mN m}^{-1}$. See the text for discussion.

constant and about unity suddenly changes to follow the downward trend shown at lower q by the other frequency, and vice versa. The tendency of one Γ value to increase with q (reflecting the effect of γ' on the capillary mode) similarly swaps from one mode to the other. Clearly the full line represents behaviour which is capillary wave-like at low q and dilatational wave-like at high q , the dashed line just being the opposite. Thus increasing the capillary wave damping via the transverse shear surface viscosity γ' can indeed lead to mode mixing of the surface waves.

Can changes affecting the dilatational wave damping similarly lead to mode mixing? ε' increases the Γ_D , rendering mode mixing less, rather than more, feasible. However, if, as suggested by certain recent theories [3, 4], certain processes within the system reduce the dilatational wave damping then mixing might occur. Unfortunately not all of the parameters of these theories are well established, making it difficult to do realistic computations of the surface wave dispersion. However, we can approximate the effects of a reduction in Γ_D by invoking $\varepsilon' < 0$ in the standard dispersion equation [9]. The two Γ values will then converge, causing the coupling to have greater effect. Again manifest mode mixing can be induced if $|\varepsilon'|$ exceeds a critical value [9].

Figure 3 shows the normalized frequency and damping values for the two modes. Before discussing the evident mixing, we first remark that the negative ε' decreases the dilatational wave damping by an amount which rises with q until eventually Γ_D goes negative: the dilatational waves have become unstable (ω_D becomes unrealistic at a somewhat larger q). Clearly the linear theory sketched above must eventually break down, but it suffices to indicate the occurrence of mode mixing. Returning to the figure, we see that the initially capillary wave-like damping, varying gently with q and of magnitude about 5, crosses over to dilatational wave-like behaviour, turning to go negative for $q \gtrsim 1500 \text{ cm}^{-1}$. Similarly, it is the q -dependent dilatational wave-like frequency which recovers and continues beyond this q -value with magnitude about unity, as expected for capillary waves.

The physical parameters used in these computations were chosen to illustrate the effects,

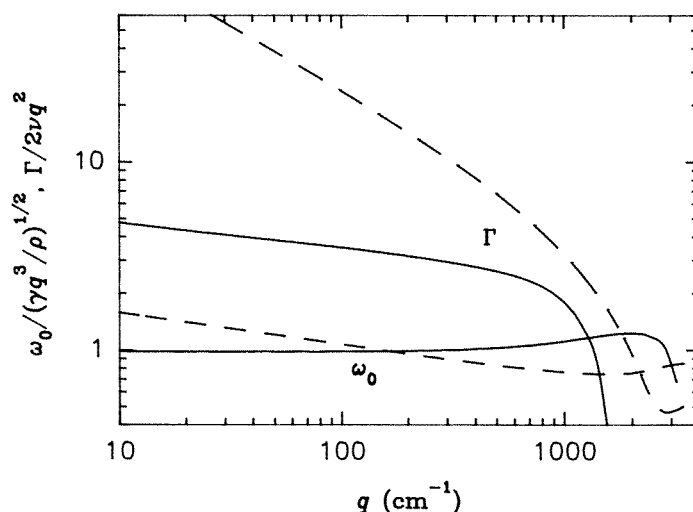


Figure 3. Mode mixing of the surface waves induced by a negative ε' of magnitude above a critical value. Surface properties used in computation were $\gamma_0 = 65 \text{ mN m}^{-1}$, $\varepsilon_0 = 10 \text{ mN m}^{-1}$, $\varepsilon' = -2 \times 10^{-5} \text{ mN s m}^{-1}$. See the text for discussion.

rather than for specific applicability to any experiment. Such computations show that the coupling between the capillary and dilatational waves can have results which have not hitherto been appreciated. There are clear differences between the two routes to mode mixing.

In experiments on solutions of various ionic surfactants the measured capillary wave behaviour diverges from normal expectation [13, 14]. For example, for aqueous solutions of the cationic surfactant cetyltrimethylammonium bromide ω_0 and Γ systematically departed from theoretical predictions at high q [13]. The effects were largest at about 0.04 mM, for which a discontinuous increase in Γ at $q \approx 1500 \text{ cm}^{-1}$ coincided with a decrease in ω_0 . Careful comparisons with predictions for the routes to mode mixing clearly showed that the data were consistent with the route to mixing associated with a reduction in the dilatational wave damping in these soap solutions, due to processes not incorporated in the standard theory [6, 7]. Data for other concentrations, while not exhibiting manifest mode mixing, were consistent with the effects of strong mode coupling due to such a reduction in Γ_D .

4. Conclusions

The coupling of waves on liquid surfaces has been shown to lead to unexpected consequences, including mode mixing. These effects have been confirmed experimentally. The discovery of such effects of the coupling emphasizes that it cannot be neglected, as has often been done in considerations of surface mode stability.

Acknowledgment

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