# The Damping of Ocean Waves by Surface Films: A New Look at an Old Problem

# WERNER ALPERS

Fachbereich 1 (Physik), Physik des Meeres, Universität Bremen, Bremen, Federal Republic of Germany

# HEINRICH HÜHNERFUSS

Institut für Organische Chemie, Universität Hamburg, Hamburg, Federal Republic of Germany

A new theory is presented explaining why not only short surface ripples, but also longer ocean surface waves are damped by oil films floating on the sea surface. The wave attenuation by viscoelastic surface films is attributed to the Marangoni effect, which causes a strong resonance-type wave damping in the short-gravity-wave region, and to nonlinear wave-wave interaction, by means of which wave energy is transferred from the longer waves to the energy sink in the Marangoni resonance region. A viscoelastic surface film changes the free surface boundary condition in the tangential direction and thus strongly modifies the flow pattern in the boundary layer. As a consequence, wave energy is dissipated by enhanced viscous damping in the short-gravity-wave region due to large velocity gradients induced in the viscous boundary layer. Estimates of the influence of surface films on nonlinear transfer rates are given. Data on wave damping obtained in laboratory and field experiments by previous investigators are discussed in the light of the proposed theory. It is found that this theory is capable of explaining the observed strong wave damping by viscoelastic surface films. The theory predicts that in the equilibrium range of the spectrum, but outside the Marangoni resonance region, wave damping increases with wave number k as  $k^{3/2}$  and increases quadratically with wind speed (up to the limit where the film is "washed down"). The higher the elasticity of the surface film, the stronger is the wave damping.

## 1. INTRODUCTION

Since ancient times it has been well known that oil films ("slicks") spread on the surface of rough seas dampen surface waves (Aristotle, *Problematica Physica*, 23, no. 38; Plinius Secundus (the Elder), *Historia Naturalis*, vol. 2, chap. 49, 77, also chap. 106; Plutarch, *Moralis: Quaestiones Naturalis*, vol. 11, no. 12, also *Moralis: De Prima Frigido*, no. 950). There exist many historical records of oil having been used to aid rescue operations in stormy seas (see, for example, the historical reviews by *Scott* [1978]), a tacit acknowledgement that slicks considerably reduce wave breaking and the wave-induced turbulence, thus making the sea less dangerous for small boats.

However, among present-day oceanographers there exists much scepticism about the effectiveness of thin oil films in calming long ocean waves [*Scott*, 1978]. Indeed, from a physical point of view it is difficult to understand that surface films which may be only one molecular layer thick, i.e., few  $10^{-9}$  m, can have a damping effect on surface waves with wavelengths much longer than the wavelengths of capillary waves. For example, *Gottifredi and Jameson* [1968] concluded "that no known surface film could affect waves of length greater than about 1 m."

It has been argued that, by suppressing the capillary and short gravity waves, surface films reduce the aerodynamic roughness and thus the energy input from the wind [*Franklin*, 1774; *Scott*, 1978]. However, the wave system cannot respond instantaneously to a reduction of the wind input, because the dissipation of gravity wave energy requires a

Copyright 1989 by the American Geophysical Union.

Paper number 88JC04297. 0148-0227/89/88JC-04297\$05.00 considerable length of time. Clearly, according to hydrodynamic wave theory (see, for example, *Phillips* [1977, equation (3.4.25)]), normal viscous dissipation is much too weak to account for the observed strong damping of surface waves with wavelengths of the order of meters.

In 1979 the damping of long surface waves by a monomolecular surface film consisting of oleyl alcohol was measured quantitatively in a slick experiment carried out in the North Sea [*Hühnerfuss et al.*, 1983]. It was found that even waves with wavelengths of 3.2 m are significantly damped when they travel through a 1.5-km-long monomolecular surface film patch. At that time we had no explanation as to why the longer waves were also damped.

In this paper we show that the attenuation of long ocean waves by surface films consisting of surface-active material can be explained by the Marangoni effect, which causes a resonance-type damping of short gravity waves by viscoelastic films [Levich, 1940, 1962; Dorrestein, 1951; Davies and Vose, 1965; Lucassen and Hansen, 1967; Lucassen, 1968; Gottifredi and Jameson, 1968; Lucassen-Reynders and Lucassen, 1969; Lucassen-Reynders, 1985; Cini et al., 1987] and by nonlinear wave-wave interaction by means of which wave energy is transferred from longer waves to the energy sink in the short wave region [Hasselmann, 1962, 1963a, b; Hasselmann et al., 1973; Komen et al., 1984]. At this point we should mention that in the western scientific literature it has become standard practice to attach the name "Marangoni" to all effects that are induced by surface tension gradients at interfaces between two fluids. Such effects were first studied by the Italian physicist Marangoni [1872].

When studying the influence of surface films on wave damping, oceanographers have often confined their investigation to inextensible films, thereby implying that inextensible films give rise to the strongest wave damping (see, for example, *Phillips* [1977, p. 48]). But, as was already shown by *Levich* [1940] and *Dorrestein* [1951], this is not true: surface films of finite surface elasticity give rise to stronger damping.

In the past, the effect of viscoelastic films on the damping of small-wavelength capillary waves has been investigated mainly by chemists, who used this effect to study the rheological properties of surface-active materials (for a review, see *Lucassen-Reynders* [1985]). Only in the last few years has it been realized that such films can give rise to a resonance-type or anomalous damping in the shortgravity-wave region [*Cini and Lombardini*, 1978; *Lucassen*, 1982; *Hühnerfuss*, 1986; *Cini et al.*, 1987].

Experimental evidence of such anomalously high damping of surface waves in the short-gravity-wave region by monomolecular slicks was obtained in laboratory experiments as early as 1981 by *Cini and Lombardini* [1981] and by *Hühnerfuss et al.* [1981b]. Recently, this effect has also been measured by Russian investigators in the open sea [*Ermakov et al.*, 1985, 1986].

In section 2 we briefly sketch the basic underlying physics of the Marangoni wave theory. For details, the reader is referred to the book of Levich [1962] and to the papers by Lucassen-Reynders and Lucassen [1969], Cini and Lombardini [1978], and Cini et al. [1987] or to the appendix of this paper. The appendix has been added because in Levich's [1962] book, equations (121-18) and (121-19) contain a sign error (apparently a misprint) which is perpetuated throughout the literature and which has resulted in incorrect formulae for the damping coefficient appearing in many papers. In section 3 we discuss how wave energy can be transferred from the low-wave number region to the energy sink in the Marangoni resonance region by nonlinear wave-wave interaction. Experimental evidence of Marangoni damping is presented in section 4. In section 5 we compare our theoretical predictions on wave damping of long ocean waves with experimental data obtained during the Marine Remote Sensing (MARSEN) slick experiment in the North Sea in 1979 [Hühnerfuss et al., 1983]. Finally, the results and implications of the present investigation are discussed in section 6.

### 2. THE THEORY OF MARANGONI WAVE DAMPING

The resonance-type behavior of damping of water waves is connected with the fact that elastic surfaces can carry two kinds of waves, the well-known gravity-capillary waves and the Marangoni waves. The Marangoni waves are predominantly longitudinal waves in the boundary or shear layer. They are heavily damped by viscous dissipation. When these two waves are in resonance as given by linear wave theory, the surface waves experience maximum damping. The restoring force for Marangoni waves is a tangential force associated with surface tension gradients, which are determined by the viscoelastic properties of the surface film. The inertial mass of the system is given by the mass of the boundary layer, which is a thin layer extending below the surface. Its thickness d is determined by the dynamic viscosity  $\eta$  and the density  $\rho$  of the fluid, as well as by the angular frequency  $\omega$  of the wave [Phillips, 1978, p. 46]:

$$d = \left(\frac{2\eta}{\rho\omega}\right)^{1/2} \tag{1}$$

The dispersion relation for Marangoni waves can be derived from the Navier-Stokes equations together with the appropriate boundary conditions. In the case of a surface covered with a viscoelastic film the kinematical boundary condition at the free surface differs from the one for a clean surface. The viscous tangential stress does not vanish as in the case of a clean surface, but it is balanced by the tangential stress exerted on the water surface by surface tension gradients. Since the viscous stress is proportional to gradients in the velocity field, the stress associated with the viscoelastic film causes strong velocity gradients in the boundary layer.

Here we do not want to give exact derivations of the relevant formulae of Marangoni wave theory. This is deferred to the appendix. Instead, we use the analogy with longitudinal oscillations of a viscoelastic membrane to derive approximate formulae. This derivation has the advantage of providing further insight into the basic physics involved.

For a membrane with elasticity modulus  $\bar{E}$ , membrane thickness  $\bar{d}$  and mass density  $\bar{\rho}$ , the dispersion relation for the longitudinal wave mode is given by  $\omega = (\bar{E}/\bar{\rho}d)^{1/2} k$ , where  $\omega$  and k denote the radian frequency and wave number, respectively. Quite similarly, the dispersion relation for the "longitudinal" Marangoni wave reads

$$\omega_l = [(1 - i)E/\rho d]^{1/2} k_l$$
(2)

Here E denotes the dilational modulus of the surface film. It is a complex quantity which describes the surface elasticity (the real part) and the surface viscosity (the imaginary part). The factor (1 - i) enters into (2) because the restoring force due to the film elasticity has to be balanced not only by fluid acceleration but also by the viscous force within the boundary layer. It can be shown that both terms have equal amplitudes, but are out of phase by 90°.

Inserting (1) into (2) yields

$$\omega_l^3 = [(-i)E^2/(\rho\eta)]k_l^4$$
(3)

This is the well-known approximate dispersion relation for Marangoni waves first derived by *Lucassen* [1968], which is obtained from the exact hydrodynamic equations when both the gravity and the surface tension (but not surface tension gradient) terms are neglected.

If we assume that the film is purely elastic (*E* real), write  $k_l$  as  $k_l = \kappa_l + i\Delta_l$  ( $\kappa_l$  and  $\Delta_l$  real), and assume that  $\omega_l$  is real, we obtain from (3)

$$\kappa_l = \cos (\pi/8) (\rho \eta E^{-2})^{1/4} \omega_l^{3/4}$$
(4a)

$$\Delta_l = \tan \left( \pi/8 \right) \kappa_l = 0.414 \kappa_l \tag{4b}$$

From (4b) we see that the imaginary part of  $k_i$  is of the same order of magnitude as the real part, which implies that the Marangoni wave is heavily damped on the scale of one wavelength. Only at a distance of one wavelength from the source has the wave amplitude decreased to 7.4% of its original value. This is the reason why Marangoni waves escaped detection until 1968 [Lucassen, 1968]. Marangoni waves can exist only when the sea surface can support surface tension gradients. Marangoni waves are predominantly associated with horizontal particle motions and are therefore also called "longitudinal waves." The strong damping of the Marangoni waves is associated with the occurrence of strong velocity gradients within the surface boundary or shear layer which then leads to enhanced viscous dissipation.



Fig. 1. Dispersion relations of gravity-capillary and Marangoni waves (approximation based on (3)) for the case that the water surface is covered with a monomolecular film consisting of CEM3AB.

If gravity-capillary waves propagate on a water surface covered with a viscoelastic film, they give rise to local contractions and expansions of the surface film which in turn cause surface tension gradients. Thus Marangoni waves can be excited. However, the surface deformations are forced to oscillate with frequencies and wave numbers that in general are not the frequency and the wave number of Marangoni waves. Resonance will occur when the wave number of the surface wave at a given frequency is equal to that of the Marangoni wave. It is possible because the structure of the dispersion relations for gravity-capillary and Marangoni waves is such that both dispersion curves can "intersect" or approach each other. In Figure 1 the approximate dispersion relation of Marangoni waves based on (4b) is plotted together with the well-known dispersion relation of gravitycapillary waves. A dilational modulus applicable to a monomolecular film consisting of hexadecyl-trimethylammonium bromide (CEM3AB) was used in the calculations.

In this context it should be emphasized that the resonance between short gravity waves and Marangoni waves discussed herein is based upon linear wave theory, while the nonlinear resonant wave-wave interaction theory described, for instance, by *Hasselmann* [1962, 1963*a*, *b*] is a higherorder effect of weak nonlinear wave theory.

In the resonance region it no longer makes any sense to talk about two separate wave modes. The particle motions are shared by both modes. (Strictly speaking, dispersion curves cannot "intersect.") Both wave modes are affected by the enhanced viscous dissipation in the surface boundary layer due to the presence of a viscoelastic film and thus experience strong damping. The result is a resonance-type behavior of the relative damping coefficient  $y(f) = \Delta/\Delta_0$  as a function of wave number or frequency. Here  $\Delta$  and  $\Delta_0$  denote the (viscous) damping coefficients of gravity-capillary waves propagating on slick-covered and on clean surfaces, respectively.

The location of the resonance in the frequency domain can be obtained by equating the wave number of the Marangoni wave and the wave number of the gravity-capillary wave. Since in most cases of practical interest to ocean wave damping, resonant damping due to surface films occurs in the short-gravity-wave region, we use here only the dispersion relation for gravity waves

$$k_g = g^{-1} \omega_g^2 \tag{5}$$

where g denotes the acceleration of gravity and  $\omega_g$  denotes the radian frequency and  $k_g$  the wave number, of the gravity waves. The resonance frequency  $\omega_{res}$  and resonance wave number  $k_{res}$  is obtained by equating  $\kappa_l$  and  $k_g$  of (4a) and (5). This yields

$$\omega_{\rm res} = (\cos \pi/8)^{4/5} g^{4/5} \rho^{1/5} \eta^{1/5} E^{-2/5}$$
(6)

Note, however, that the maximum of  $y(f) = \Delta/\Delta_0$  is located not exactly at  $\omega_{res}$ , but rather at a slightly lower frequency because the Marangoni wave is a strongly damped wave. This effect can be compared with a forced damped harmonic oscillator, where the maximum amplitude is also encountered below the resonance frequency. Since the Marangoni wave is heavily damped, the width of the resonance must be quite broad. From (4b) we conclude that the half-power width is of the order of the resonance wave number. Thus the width of the resonance increases with increasing resonance frequency  $\omega_{res}$ .

From (6) we see that the resonance wave number decreases with increasing dilational modulus E. Therefore in order to achieve maximum damping at long wavelengths, one has to choose a surface film with large E. However, no chemical substances exist in nature with dilational moduli much larger than 0.4 N m<sup>-1</sup>. If this value is inserted into (6), we obtain as an upper limit for the resonant wavelength



Fig. 2. Relative viscous damping coefficient  $y(f) = \Delta(f)/\Delta_0(f)$ as a function of frequency for water surfaces covered with hexadecanoic acid methyl ester (PME), oleic acid (OLS), oleyl alcohol (OLA), hexadecyl-trimethylammonium bromide (CEM3AB) and triolein.

$$\lambda_{\rm res} = 2 \ \pi/k_{\rm res} = 2 \ \pi \ g/\omega_{\rm res}^2 \tag{7}$$

$$\lambda_{\rm res} \leq 1 \, {\rm m}$$

The exact resonance condition as well as the functional dependence of the damping coefficient  $\Delta$  on wave frequency  $\omega$  and complex dilational modulus  $E = |E| \exp(-i\theta)$  has been calculated by several authors [*Cini and Lombardini*, 1978; *Lucassen*, 1982; *Hühnerfuss*, 1986; *Cini et al.*, 1987]. The clean-surface damping coefficient  $\Delta_0$  is given by the Stokes equation

$$\Delta_0 = \frac{4\kappa^2 \eta \omega}{\rho g + 3\sigma \kappa^2} \tag{8}$$

where  $\kappa$  denotes the real part of the complex wave number and  $\sigma$  is the surface tension. The formula for the relative damping ratio  $y(f) = \Delta/\Delta_0$  then reads

$$y(f) = \frac{1 + X(\cos \theta - \sin \theta) + XY - Y \sin \theta}{1 + 2X(\cos \theta - \sin \theta) + 2X^2}$$
(9)

where  $\theta$  is the phase angle,

$$X = |E| \kappa^2 (2^{1/2} \omega^{3/2} (\rho \eta)^{1/2})^{-1}$$
(10)

$$Y = |E| \kappa (4\omega\eta)^{-1} \tag{11}$$

Figure 2 shows the theoretical y as a function of  $f = (2\pi)^{-1}$  $\omega$  for water surfaces covered with five different monomolecular slicks assuming the *E* and  $\theta$  values summarized in Table 1: hexadecanoic acid methyl ester (PME), oleic acid (OLS), oleyl alcohol (OLA), hexadecyl-trimethylammonium bromide (CEM3AB), and triolein (TOLG). In calculating these curves, the dispersion relation for gravity-capillary waves

$$\omega^2 = g\kappa + \frac{\sigma}{\rho}\kappa^3 \tag{12}$$

has been used to convert from wave number to frequency space.

In Table 1 the maximum of the damping coefficient,  $y_{max}$ , as well as the frequency  $f_M$  at which y(f) attains its maximum value are also given. The calculations were carried out with  $\eta = 10^{-3}$  Pa s,  $\rho = 10^3$  kg m<sup>-3</sup>, and  $\sigma = 0.073$  N m<sup>-1</sup>.

We now define the Marangoni damping time  $T_M$  as the time in which the spectral energy density at  $f = f_M$  has decayed to 1/e of its original value. More often its reciprocal value  $\alpha_M = T_M^{-1}$  is used; this value is called the damping rate. They are related to  $\Delta_M$ , which is the damping ratio defined in the spatial domain, by

$$\alpha_{M} = T_{M}^{-1} = 2c_{g}(f_{M}) \ \Delta_{M} = 2c_{g}(f_{M})y_{\max} \ \Delta_{0}(f_{M})$$
(13)

Here  $c_g(f_M)$  denotes the group velocity of the surface wave at  $f = f_M$ . The factor 2 enters into (13) because  $\Delta_M$  is conventionally defined in terms of amplitudes, not energies.

In the case of an oleyl alcohol slick, using values of  $c_g(f_M) = 0.18 \text{ m s}^{-1}$ ,  $\Delta_0(f_M) = 0.09 \text{ m}^{-1}$ , and  $y_{\text{max}} = 28$  (see Table 1), we obtain from (13)

$$\alpha_M = T_M^{-1} = 0.91 \text{ s}^{-1} \tag{14}$$

In the absence of a surface film the damping is due mainly to viscous dissipation in the bulk water, while in the presence of a viscoelastic film it is caused mainly by the viscous dissipation in the boundary layer. The elastic stress associated with the surface tension gradient  $\partial \sigma / \partial x$ , which is induced by the nonuniform horizontal displacement of the film, has to be balanced by a shear stress in the boundary layer:

$$\frac{\partial \sigma}{\partial x} = \eta \left( \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x} \right) \tag{15}$$

Here  $u_x$  and  $u_z$  denote the orbital velocities of the water particles in x (horizontal) and z (vertical) directions. The surface tension gradient is related to the horizontal displacement  $\xi$  of the surface due to the passage of a surface wave by

$$\frac{\partial \sigma}{\partial x} = E^{-1} \frac{\partial^2 \xi}{\partial x^2} \tag{16}$$

As was stated before, the surface dilational modulus E is a complex quantity. A nonvanishing phase angle implies that if the surface area is varied harmonically in time, the areas of maximum surface dilation or compression do not coincide with areas of maximum or minimum surface tensions, respectively. This means that the viscoelastic film has a finite response (relaxation) to surface area variations. Experimental verification of this effect was recently supplied by windwave tunnel experiments using a surface potential sensor carried by a wave follower [Lange and Hühnerfuss, 1984;

TABLE 1. Dilational Moduli Used in Calculating the Curves of Figure 2

Substance	E , N m <sup>-1</sup>	$\theta$ , deg	y <sub>max</sub>	f <sub>M</sub> , Hz
Hexadecanoic acid methyl ester (PME)	0.046	176	40.1	3.5
Oleic acid (OLS)	0.014	176	19.5	6.1
Olevl alcohol (OLA)	0.0225	175	27.9	4.8
Hexadeyl- trimethylammonium bromide (CEM3AB)	0.0255	177	26.3	4.6
Triolein (TOLG)	0.0115	175	18.3	6.85

These values were obtained in wave tank experiments at a temperature of about 288 K. Also given are  $y_{max}$  and  $f_M$ , defined by  $y_{max} = y$  ( $f_M$ ).

Hühnerfuss et al., 1985a]. For the five surfactants mentioned above, the phase angle is always close to 180°. This implies that at areas of maximum divergence the surface tension is largest, which is just the opposite of what one intuitively expects.

Viscoelastic films greatly enhance velocity shear in the boundary layer. The ratio of the velocity gradient at the surface in the presence of a viscoelastic film to the velocity gradient at a clean surface is approximately given by

$$r = \left(\frac{\partial u_z}{\partial x}\right)_{\text{film}} / \left(\frac{\partial u_z}{\partial x}\right)_{\text{clean}} = \frac{E}{\eta} \frac{\partial^2 \xi}{\partial x^2} / \omega \frac{\partial \xi}{\partial x} = \frac{E}{\eta} \frac{k}{\omega}$$
(17)

The last identity follows because the spatial scales of the horizontal and vertical displacements  $\xi$  and  $\zeta$  associated with the passage of a wave are the same. Inserting the values for an oleyl alcohol film floating on water and considering the 4.8-Hz surface wave where maximum damping occurs, we obtain r = 81.4. The depth of the boundary layer in this case is (see (1))  $d = 2.6 \times 10^{-4}$  m. The large increase of the velocity gradients in the boundary layer by almost 2 orders of magnitude gives rise to a drastically increased viscous dissipation in the surface layer, which in turn leads to an increase in the skin temperature.

# 3. NONLINEAR WAVE-WAVE INTERACTION

## 3.1. The Action Balance Equation

The evolution of surface wave spectra can be described by the action balance equation [Hasselmann, 1960; Willebrand, 1975; Masuda, 1980, 1986; Komen et al., 1984; Phillips, 1985]:

$$\frac{dN}{dt} = \frac{\partial N}{\partial t} + (\mathbf{c}_g + \mathbf{U}) \cdot \nabla_x N = S_{\rm in} + S_{\rm nl} - S_{\rm dis} \qquad (18)$$

Here  $N(\mathbf{k}, \mathbf{x}, \mathbf{t}) = (\omega/k) F(\mathbf{k}, \mathbf{x}, \mathbf{t})$  denotes the spectral density of wave action per unit mass in wave number space,  $\nabla_{r}$  is the gradient operator in x space, and F(x, k, t) is the ocean wave height variance spectrum, which in the following we shall simply call "ocean wave spectrum." In the case of gravity waves,  $N(\mathbf{k}, \mathbf{x}, t)$  can also be written as  $N = gF/\omega$ . Likewise,  $\mathbf{c}_{g}$  denotes the group velocity, U is the velocity of the underlying current,  $\rho$  is the density of seawater, and  $\omega$  is the intrinsic angular frequency, which is related to the wave number  $k = |\mathbf{k}|$  by the dispersion relation (12).  $S_{in}$ ,  $S_{nl}$ , and  $S_{dis}$  represent source terms describing the wind input, nonlinear wave-wave interactions, and dissipation, respectively. The source terms are functions of the wave vector  $\mathbf{k}$ , the friction velocity  $\mathbf{u}_*$ , and also of the wave spectrum F. The source function  $S_{in}$  and  $S_{dis}$  are poorly known both theoretically and experimentally (for a detailed discussion see, for instance, Komen et al. [1984] or Phillips [1985]).

Useful quantities which characterize the strength of the three source terms in the spectral evolution are the transfer rates  $\alpha_{in}$ ,  $\alpha_{nl}$ , and  $\alpha_{dis}$  or the transfer times  $T = \alpha_i^{-1}$  (i = in, nl, dis). They are defined by

$$\alpha_t = T_t^{-1} = \left| \frac{S_t}{N} \right| \tag{19}$$

The nonlinear transfer function  $S_{nl}$  can be calculated from resonant wave-wave interaction theory [Hasselmann, 1962; 1963a, b; Hasselmann and Hasselmann, 1985].  $S_{nl}$  can be written as

$$\mathbf{S}_{\mathrm{nl}} = -\boldsymbol{\nabla}_k \mathbf{T}(\mathbf{k}) \tag{20}$$

where T(k) represents the net spectral flux of action through wave number space. The flux divergence in wave number space represents the net gain or loss of action spectral density at the wave number k.

In the gravity wave region the third-order (four wave) nonlinear wave-wave interaction is predominant [Valenzuela and Wright, 1976], and  $\nabla_k T(\mathbf{k})$  can be expressed as

$$-\nabla_{k} \mathbf{T} (\mathbf{k}) = \iiint Q^{2} \{ (N+N_{2}) N_{3} N_{4} - (N_{3}+N_{4}) N N_{2} \}$$
  
 
$$\cdot \delta (\omega + \omega_{2} - \omega_{3} - \omega_{4}) \delta (\mathbf{k} + \mathbf{k}_{2} - \mathbf{k}_{3} - \mathbf{k}_{4}) dk_{2} dk_{3} dk_{4}$$
(21)

Here  $N_i$  (i = 1, 2, 3) and N denote  $N(\mathbf{k}_i)$  and  $N(\mathbf{k})$ , respectively, and  $\delta$  is the Dirac delta function.  $Q^2$  is an interaction coefficient which depends on  $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4$ , and  $\mathbf{k}$ . It is largest when the low wave numbers are all comparable in magnitude and are parallel. Computer programs have been developed for calculating the nonlinear energy transfer in spectral regions up to  $k = 2.5 k_p$ , where  $k_p$  denotes the wave number of the spectral peak (see, for example, *Hasselmann* and Hasselmann [1985]). In this spectral region the nonlinear energy transfer is very sensitive to the spectral shape. However, in our investigation we need to know the nonlinear energy transfer in the equilibrium range, in which k is usually larger than 2.5  $k_p$ .

In the equilibrium range of the spectrum, estimates of the nonlinear energy transfer have been given by *Kitaigorodskii* [1983] and *Phillips* [1985]. This is the range where the wave numbers are substantially larger than  $k_p$  and much smaller than those which are influenced by capillarity and molecular viscosity. In this wave number range the spectrum can be described by the form [*Toba*, 1973; *Phillips*, 1985]

$$F = \beta \, u_* \, k^{-7/2} \tag{22}$$

where k denotes the modulus of k. The proportionality factor  $\beta$  is a constant which has to be determined experimentally. According to Phillips and Kitaigorodskii, the interaction coefficient  $Q^2$  in this range is approximately proportional to  $k^6$ .

The nonlinear interaction or energy transfer is structured in such a way that the energy gain at a fixed spectral point kis independent of, but the loss is proportional to, the value of the spectrum at k [Hasselmann, 1962]. Thus resonant wavewave interaction tends to level down peaks and fill in dips in the wave spectrum such that the spectral energy is more uniformly distributed over all wave numbers. The nonlinear transfer resembles a diffusion process in wave number space which drives the spectrum toward equilibrium. The more the spectrum is distorted owing to Marangoni damping, the larger is the transfer rate by nonlinear interaction.

A functional form describing the rate of action or energy input from the wind,  $S_{in}$ , has been proposed by *Phillips* [1985] and is given by

$$S_{\rm in} = \beta N(k) = M(\cos \varphi)^{2p} \left[ \frac{u_*}{c} \right]^2 \omega N(\mathbf{k})$$
(23)

where c is the phase velocity of the wave component,  $\varphi$  is the angle between the wave vector and the wind, p is the



Fig. 3. Frequency spectra of wind waves measured in the wind wave tank of the University of Hamburg (fetch is 15 m) for a slick-covered (CEM3AB) and a clean surface. The wind speed at a reference height of 0.5 m was  $U_{ref} = 8$  m s<sup>-1</sup>. The dotted line represents the relative damping curve y(f) with the ordinate on the right-hand side [from Hühnerfuss et al., 1987].

index in the directional distribution of  $F(\mathbf{k})$ , and M is a numerical factor, which has to be determined experimentally. According to *Phillips* [1985] and *Plant* [1982], reasonable estimates for M and p are  $M = 4 \times 10^{-2}$  and p = 0.5.

Mitsuyasu and Honda [1986] have shown that (23) is also applicable when the water surface is covered with a slick. However, in this case the relationship between wind speed and friction velocity u is different from the relationship applicable to a slick-free surface. In wind wave tank experiments, Hühnerfuss et al. [1981b] found that  $u_*$  is about 20% lower for a water surface covered with methyl oleate than for a clean surface.

The dissipation source function  $S_{dis}$  describes the dissipation of wave action due to wave breaking and viscous damping. In the Marangoni resonance region the energy dissipation is caused primarily by viscous dissipation. Visual observation of sea surfaces covered with surface films clearly shows that wave breaking is effectively absent in the short-gravity-wave region and that the breaking of longer waves is strongly reduced. The attenuation of these waves is caused mainly by nonlinear energy transfer to waves with shorter wavelengths, which dissipate the energy by enhanced viscous dissipation due to Marangoni damping.

# 3.2. Nonlinear Transfer Rates

In order to explain the damping of ocean waves with wavelengths in the meter range by monomolecular slicks, a phenomenon which was observed in earlier experiments [Hühnerfuss et al., 1981a, 1983], we must show that nonlinear wave-wave interaction can transfer energy sufficiently fast from these wave components to the Marangoni damping region. Obviously, normal viscous damping is much too slow to explain the strong damping of these long waves (the decay time for a 0.7-Hz wave due to viscous damping is 36 hours!). Indeed, it was shown by *Hasselmann et al.* [1973] that the time evolution of wave spectra is determined mainly by nonlinear wave-wave interactions. The nonlinear interaction establishes a balance between the input and dissipation

source functions. It involves a delicate adjustment of the spectral shape and the nonlinear transfer.

If the wave spectrum is distorted in the short-gravity-wave region by Marangoni damping, the wave system reacts with an adjustment of the nonlinear energy transfer such that the wave spectrum is driven toward equilibrium. This can be achieved only by an increase in the energy transfer in the direction of the Marangoni dip. In principle, the energy transfer can be calculated by solving (18) numerically with an initial spectrum which includes an undistorted Marangoni dip (similar to the one shown in Figure 3). This has been attempted by using a Siemens 7.800 mainframe computer. Though these computations clearly show an increase of the nonlinear transfer, they are not accurate enough to render reliable quantitative results. This is because the storage capacity of the computer was not adequate for numerical calculations to be carried out for a sufficiently fine spectral grid.

From theoretical considerations we expect that at wave numbers much smaller than the Marangoni resonance wave number but much larger than the peak wave number, the nonlinear transfer rate is of the same order of magnitude in the case of a slick-covered surface as for a slick-free surface. This is because in this wave number region the intrinsic dynamics of the waves are essentially unaltered by the presence of a slick. However, the nonlinear energy transfer is indirectly affected, because a slick gives rise to a spectral form which in the equilibrium range is steeper than the Phillips spectrum. The wave field tries to restore equilibrium by increasing the nonlinear energy transfer rate.

Estimates of the transfer rates due to nonlinear wavewave interaction in the equilibrium range of the spectrum have been given by *Kitaigorodskii* [1983] and *Phillips* [1985]. According to *Phillips* [1985] the processes of energy input from the wind, nonlinear energy transfer, and loss by wave breaking are all of importance in the equilibrium range and have comparable magnitudes. Phillips' expressions for the action spectral flux divergence and the spectral action den-

sity read (see equations (2.4), (2.10), (2.20), and (3.1) of Inserting (29) into (28) yields Phillips [1985])

$$\alpha_{\rm nl} = \left| \frac{-\nabla_k T(\mathbf{k})}{N} \right| = G\omega(\cos \varphi)^{2p} \left[ \frac{u_*}{c} \right]^2$$
(24)

where G is a dimensionless constant, which, according to Phillips (1985), has the same order of magnitude as the nondimensional constant M in the wind input source term (23). Inserting the dispersion relation for gravity waves

$$\omega = (gk)^{1/2} \tag{25}$$

into (24) and setting p = 0.5 yields

$$\alpha_{\rm nl} = G \ g^{-1/2} k^{3/2} \ u_*^2 \cos \varphi \tag{26}$$

Now we want to get an estimate of the increase in the nonlinear energy transfer rate in the presence of a slick. If the energy flux to the Marangoni damping region by nonlinear wave-wave interaction is smaller than the energy dissipation by Marangoni damping, the Marangoni dip cannot be filled in. In this case, the wave spectra obtained by the wave number domain measurements, e.g., by radar backscattering, should delineate the Marangoni dip. With increasing wind stress the nonlinear transfer rate increases, and thus so does the energy flux. We therefore predict that the depth of the Marangoni dip decreases with increasing wind stress. If the wind stress exceeds a critical value  $u_{*c}$ , the Marangoni dip should disappear completely. In this case, nonlinear interaction is sufficiently fast to transfer enough wave energy from longer waves to the Marangoni damping region to balance the enhanced viscous dissipation.

This is indeed observed in wind wave tank experiments, as will be discussed later. Therefore we hypothesize that the nonlinear transfer rate in the presence of a slick, which we write as

$$\alpha_{nl}^{s} = \alpha_{nl} + \Delta \alpha_{nl} \tag{27}$$

has the same functional dependence on wind stress and wave number as does the nonlinear transfer rate  $\alpha_{nl}$  for a slick-free surface (see (24)). However, for a slick-covered surface the wave spectrum  $F^{s}(k)$  is slightly steeper because the short waves are damped more strongly than the long waves. This leads to an increase in the nonlinear transfer rate because the wave system responds to a deviation from equilibrium by an increase in the nonlinear energy transfer. Therefore our estimates of the nonlinear transfer rates, which are based on equilibrium spectra, constitute lower limits.

We assume that the additional energy flux  $\Delta \varepsilon$  through the spectrum caused by the Marangoni dip is constant in the equilibrium range for a given wind stress. The condition for constant energy flux  $\Delta \varepsilon(k)$  through the spectrum is (see Kitaigorodskii [1983, equation (8)]

$$\varepsilon(k) = gF(k)k^2 \Delta \alpha_{\rm nl}(k) = \Delta \varepsilon_0 = \text{const}$$
(28)

Here F(k) denotes the wave spectrum integrated over angles and  $k = |\mathbf{k}|$ . We assume further that the dependence of  $\Delta \varepsilon_0$ on wind stress is the same as for the spectral flux in the case of a slick-free surface as given by Kitaigorodskii [1983, equation (45)] and Phillips [1985, equations (2.10) and (2.20)],

$$\Delta \varepsilon_0 \propto u_*^3 \tag{29}$$

$$\Delta \alpha_{\rm nl} \propto \beta^{-1} g^{-1/2} k^{3/2} u_*^2 \tag{30}$$

Thus  $\Delta \alpha_{nl}$  has the same dependence on k and  $u_*$  as does  $\alpha_{nl}$ . We can now relate  $\Delta \alpha_{nl}$  at  $k = k_1$  and  $u_* = u_{*1}$  to  $\Delta \alpha_{nl}$  at k  $= k_2$  and  $u_* = u_{*2}$  by

$$\Delta \alpha_{\rm nl}(k_1, \, u_{*1}) = \left[\frac{k_1}{k_2}\right]^{3/2} \left[\frac{u_{*1}}{u_{*2}}\right]^2 \, \Delta \alpha_{\rm nl}(k_2, \, u_{*2}) \qquad (31)$$

It must be stressed that these equations apply only in the equilibrium range of the spectrum where no internal wave number scale exists. This implies that (30) and (31) are valid only outside the Marangoni resonance region when the wave spectrum exhibits a Marangoni dip. However, these equations should also apply in the Marangoni resonance region when above a certain wind stress  $u_{*c}$ , the Marangoni dip is filled in owing to a large flux of wave energy into the Marangoni resonance region by nonlinear wave-wave interaction. In this case the Marangoni resonance region loses its characteristic wave number scale, which is given by the width of the Marangoni dip. Thus in this case, this wave number region can also be included in the equilibrium range of the spectrum. However, the slope of the spectrum is slightly modified.

The disappearance of the Marangoni dip occurs for wind stresses larger than  $u_{*c}$ , which can be determined experimentally, for example, in wind-wave tank experiments. The critical wind stress  $u_{*c}$  depends on the physicochemical properties of the surface film. In the case of an oleyl alcohol film, Feindt [1985] found in a wind wave tank experiment that the Marangoni dip disappears at  $u_{*c} = 0.50 \text{ m s}^{-1}$ . (This value corresponds to his reference wind speed of 12 m s<sup>-1</sup> (see section 4.1).)

Thus at the wind stress  $u_* = u_{*c}$ , Marangoni damping is balanced by the nonlinear energy transfer, if the following identity holds at the center of the Marangoni dip where k = $k_M$ :

$$\Delta \alpha_{\rm nl}(k_M, \, u_{*c}) = \alpha_M \tag{32}$$

Inserting (32) into (31) yields

$$\Delta \alpha_{\mathsf{nl}} (k, u_*) = \alpha_M \left[ \frac{k}{k_M} \right]^{3/2} \left[ \frac{u_*}{u_{*c}} \right]^2$$
(33)

This is the principal equation of this section. Equation (33) makes it possible to calculate the increase of the nonlinear energy transfer rate  $\Delta \alpha_{nl}$  (or the damping rate) due to the presence of a slick at any wave number k and wind stress  $u_*$ in the equilibrium range of the spectrum.

The constants appearing in (33) are the Marangoni damping rate  $\alpha_M$ , the Marangoni resonance wave number  $k_M$ , and the critical wind stress  $u_{*c}$  at which the nonlinear energy transfer has reached the level where it just balances Marangoni damping. Both  $\alpha_M$  and  $k_M$  can easily be calculated from Marangoni wave theory if the physico-chemical properties of the surface film are known. Also,  $u_{*c}$  can in principle be calculated by using nonlinear wave-wave interaction wave theory.

An alternative way of determining  $u_{*c}$  is by experiment, for instance, by measuring the wave spectrum of a slickcovered water surface as a function of wind speed in a wind wave tank. As an example we calculated  $\Delta \alpha_{nl}$  for a water surface covered with an oleyl alcohol film  $(k_M = 2\pi/0.068$ m<sup>-1</sup>,  $\alpha_M = 0.9$  s<sup>-1</sup>,  $u_{*c} = 0.50$  m s<sup>-1</sup>) at the wave number k $= 2\pi/3.2$  m<sup>-1</sup> and at the wind stress  $u_* = 0.16$  m s<sup>-1</sup>, corresponding to  $U_{10} = 5.5$  m s<sup>-1</sup> ( $U_{10}$  is the wind speed at a height of 10 m; see section 5). With these values inserted into (33) we obtain

$$\Delta \alpha_{nl} = 2.9 \times 10^{-4} \text{ s}^{-1}$$

which corresponds to an interaction time of  $T_{nl} = (\Delta \alpha_{nl})^{-1} = 58$  min.

It is interesting to compare this estimate of the increase of the nonlinear transfer rate  $\Delta \alpha_{nl}$  with an estimate of the nonlinear transfer rate  $\alpha_{nl}$  for a clean surface. In *Kitaigorodskii*'s [1983] paper one can find such an estimate. Combining his equations (13), (45), and (63) and setting  $U_a = 30$  $u_*$ , one obtains

$$\alpha_{\rm nl} = (1.5 - 9.9) \times 10^{-2} g^{-1/2} k^{3/2} u_*^2 \qquad (34)$$

With  $k = 2\pi/3.2 \text{ m}^{-1}$  and  $u_* = 0.16 \text{ m s}^{-1}$  inserted, the nonlinear transfer rate becomes

$$\alpha_{\rm nl} = (3.4 - 22) \times 10^{-4} \, {\rm s}^{-1} \tag{35}$$

corresponding to a nonlinear transfer time of

$$T_{\rm nl} = \alpha_{\rm nl}^{-1} = (7.5 - 49.5) \,\,{\rm min}$$
 (36)

Thus  $\Delta \alpha_{nl}$  is in this case smaller than  $\alpha_{nl}$  by a factor of 0.13 to 0.85.

Now we want to get an estimate of how the wave spectrum is deformed by Marangoni damping. Let us denote the quantities that refer to slick-covered surfaces by the index sand those that refer to the clean surface by the index 0. First we note that to first order, the source functions on the right-hand side of (18) balance each other. We obtain for the clean and the slick-covered surfaces

$$S_{in}^{0} + S_{nl}^{0} - S_{dis, v}^{0} - S_{dis, b}^{0} = 0$$

$$S_{in}^{s} + S_{nl}^{s} - S_{dis, v}^{s} - S_{dis, b} = 0$$
(37)

Here we have split the dissipation source function  $S_{dis}$  into two parts:  $S_{dis, v}$  describes the dissipation due to viscous dissipation, and  $S_{dis, b}$  is the dissipation due to wave breaking.  $S_{dis, v}^0$  and  $S_{dis, v}^s$  are well known theoretically and are proportional to  $F_0$  and  $F_s$ , respectively [*Phillips*, 1977]

$$S_{\text{dis, }\nu}^{0} = -2 \ \Delta_0 F_0 \tag{38}$$
$$S_{\text{dis, }\nu}^{s} = -2 \ \Delta F_s$$

From (37) and (38) we obtain

$$\frac{F_0}{F_s} = \frac{\Delta}{\Delta_0} \frac{S_{\rm in}^s + S_{\rm nl}^s - S_{\rm dis, b}^s}{S_{\rm in}^0 + S_{\rm nl}^0 - S_{\rm dis, b}^0}$$
(39)

In the Marangoni damping region the first factor in (39), the ratio  $y(f) = \Delta/\Delta_0$ , is a strong function of wave number k or frequency f (see Figure 2), while the second term presumably depends only weakly on these variables. As a consequence, the ratio  $F_0/F_s$  should show the same functional dependence on k or f as does  $\Delta/\Delta_0$ . This is indeed observed, as we shall show in the next section.

The source functions appearing in the second factor in (39) are, with the exception of  $S_{nl}^0$ , poorly known. However, according to *Phillips* [1985], all three source functions  $S_{nn}^0$ ,  $S_{nl}^0$  and  $S_{dis, b}^0$  have the same order of magnitude in the equilibrium range of the wave spectrum. The source functions  $S_{in}^s$  and  $S_{dis, b}^o$  of a slick-covered water surface are presumably small in the Marangoni damping region, such that the remaining term  $S_{nl}^s$  determines the value of the numerator in the second factor in (39). Since  $\alpha_{nl}^s > \alpha_{nl}^0$ ,  $S_{nl}^s$ must also be larger than  $S_{nl}^0$ . This implies that the denominator is larger than the numerator. Thus the peak in the  $F_0/F_s$ curve must be smaller than the peak in the  $\Delta/\Delta_0$  curve, which is also observed.

#### 4. EXPERIMENTAL EVIDENCE OF MARANGONI DAMPING

## 4.1. Laboratory Experiments

It seems that *Cini and Lombardini* [1981] were the first to demonstrate experimentally that the ratio of the short-wave attenuation of water covered with a monomolecular film to that of pure water exhibits a maximum as a function of frequency. They studied the attenuation of mechanically generated sinusoidal waves in a small wave tank. Since they used monochromatic waves, nonlinear interactions were absent in their experiment. They showed that the measured wave attenuation agrees quite well with the one calculated from Marangoni theory.

At the same time, Hühnerfuss et al. [1981b] noted in wind wave tank experiments with slicks that the wind wave spectra often exhibit a dip in the short-gravity-wave region. Figure 3 shows frequency spectra of wind waves measured with a wave staff in the wind wave tank of the University of Hamburg for the case of a slick-covered surface (monomolecular CEM3AB film) and a clean water surface. The reference wind speed was  $U_{ref} = 8 \text{ m s}^{-1}$ , and the fetch was 15 m. This wind speed  $U_{ref}$  is the wind velocity measured at a reference height of 0.50 m above water level. The relationship between  $U_{ref}$  and the friction velocity  $u_*$  derived from wind profile measurements [Lange and Hühnerfuss, 1978; Feindt, 1985] is in the case of a clean surface

$$u_* = 0.053 U_{\rm ref}$$
 (40)

and in the case of a film-covered surface approximately

$$u_{*s} = 0.042 U_{\text{ref}}$$
 (41)

For most monomolecular surface films we have  $u_{*s} = 0.8 u_{*}$ .

The dotted line in Figure 3 represents the relative damping coefficient  $y(f) = \Delta(f)/\Delta_0(f)$  as calculated from Marangoni theory with |E| = 0.0255 N m<sup>-1</sup> and  $\theta = 177^\circ$ . It has its maximum very close to the center of the Marangoni dip [see Hühnerfuss et al., 1987].

Figure 4 shows frequency spectra measured in the same wind wave tank [*Feindt*, 1985] with the water surface covered with a CEM3AB surface film for three different wind speeds. As can be seen from this plot, the depth of the Marangoni dip is greatest at  $U_{ref} = 8 \text{ m s}^{-1}$ . It decreases with increasing wind speed and vanishes at  $U_{ref} \ge 12 \text{ m s}^{-1}$ . This wind speed is about 1 m s<sup>-1</sup> below the wind speed at which the surface film is disrupted by wave breaking and "washed down." The disappearance of the slick from the surface is also evident from visual observations and from radar backscattering experiments carried out by *Feindt* [1985] in the



Fig. 4. Frequency spectra of wind waves measured in a wind wave tank with the water surface covered with a CEM3AB film for three different wind speeds  $U_{ref}$  [from *Feindt*, 1985].

wind wave tank in Hamburg. Figure 5 shows the X band (9.8 GHz) radar cross section of a clean water surface and of surfaces covered with hexadecanol (CEA), oleyl alcohol (OLA), and CEM3AB, as a function of wind speed. In this experiment the incidence angle was 54°, and measurements were carried out at VV polarization (vertical transmission and vertical reception). At this incidence angle the radar backscattering can be described by Bragg scattering theory [Valenzuela, 1978]. According to this theory the radar cross section is proportional to the spectral energy density at the Bragg wave number, which in this case was 331 m<sup>-1</sup>. From Figure 5 we see that the radar cross sections for the clean and slick-covered surfaces become equal if  $U_{ref} = 13 \text{ m s}^{-1}$ . This means that at this wind speed the slick is "washed down" by wave breaking.

## 4.2. Open Ocean Experiments

To our knowledge, Cini et al. [1983] were the first to report Marangoni damping in wave spectra measured in polluted sea areas in the Gulf of Genoa, Italy. However, clear evidence of Marangoni damping on slick-covered ocean waves was first presented by Ermakov et al. [1985, 1986]. They carried out slick experiments from a platform in the Black Sea, USSR, in 1982 and 1983. These investigators used olein (technical grade oleic acid) and vegetable oil as surfactants. The dimensions of their slicks were small, typically 10 m. Figure 6 shows as an example the spectral energy depression by olein for a low wind speed case ( $U \sim$  $1 \text{ m s}^{-1}$ ) as a function of frequency. These frequency spectra were obtained from wave measurements performed by a resistive-type wave gauge. Note, however, that in the open ocean the short-wave frequencies are subject to significant Doppler-shifting by the orbital motion of the long waves (see discussion in section 5). Only at low sea states, such as were encountered in the experiment by Ermakov et al., the root-mean-square Doppler shift is so small that the Marangoni dip can still be delineated in frequency spectra. These measurements, as well as other measurements performed by Ermakov et al. [1986], show that with increasing wind speed the maximum of  $F_0/F_s$  decreases and the frequency at which this maximum occurs shifts toward higher frequencies.



Fig. 5. Wind wave tank measurements of the radar cross section of a clean water surface (circles), and of water surfaces covered with hexadecanol (CEA, triangles), oleyl alcohol (OLA, pluses), and CEM3AB (crosses) as a function of wind speed, for incidence angle of 54°, and VV polarization [from *Feindt*, 1985].

Radar backscattering measurements carried out by Singh et al. [1986] also delineate resonance-type Marangoni damping [Alpers and Hühnerfuss, 1988]. Singh et al. measured the depression of the normalized radar cross section (NRCS) by an oil slick simultaneously at 5.7 GHz (C band) and 13.3 GHz ( $K_u$  band) from an airplane as a function of incidence angle  $\vartheta$ . In the range of incidence angles where the radar backscattering is dominated by Bragg scattering the variation of the NRCS depression with incidence angle can be related to the depression of spectral energy density in wave number space k.

According to Bragg scattering theory the NRCS is proportional to the spectral energy density of the surface waves at the wave number  $|\mathbf{k}| = 2 |\mathbf{k}_0| \sin \vartheta$  in look direction of the antenna. Here  $|\mathbf{k}_0|$  denotes the radar wave number. Thus by varying  $\vartheta$  and/or the radar wave number  $|\mathbf{k}_0|$ ,  $F_0/F_s$  can be measured as a function of wave number  $\mathbf{k}$ . Furthermore, by



Fig. 6. Spectral energy depression  $F_0/F_s$  by an olein surface slick patch of 10-m length as a function of frequency for a wind speed of about 1 m s<sup>-1</sup> [after *Ermakov et al.*, 1986] (dotted curve; left-hand ordinate) and damping curve y(f) calculated by means of the Marangoni wave theory (E = 0.030 N m<sup>-1</sup>;  $\theta = 176^{\circ}$ ) (solid curve; right-hand ordinate).



Fig. 7. Depression of spectral energy density of short waves by crude oil as function of wave number for low wind speeds (3-6 m s<sup>-1</sup>). The data are derived from the C band and  $K_{\mu}$  band radar backscatter measurements of Singh et al. [1986].

changing the azimuth angle of the radar antenna, the directional dependence of  $F_0/F_s$  can also be determined. Figure 7 shows the depression of spectral energy density of short waves by crude oil as a function of wave number at low wind speeds (3-6 m/s). This curve was derived from C and  $K_{\mu}$ band radar data obtained by Singh et al. (flight line 5, September 16, 1983). It clearly exhibits the typical Marangoni-type behavior. Alpers and Hühnerfuss [1988] have conjectured that Marangoni damping is also active in this case, because surface-active compounds spread from thick oil centers and form numerous small monomolecular slick patches interdispersed in the vicinity of crude oil spills. Surface-active compounds are always encountered in crude oil as impurities [Hühnerfuss et al., 1989]. It can be concluded from the location of the peak in the spectral energy depression curve (Figure 7) that the surface-active material spreading from the crude oil centers is a medium damping surface-active compound resembling triolein, which is secreted by plankton or fish ("fish oil").

The experimental data discussed above clearly delineate the resonance-type Marangoni damping. It is surprising that this damping escaped detection for such a long time.

## 5. EXPERIMENTAL EVIDENCE OF LONG-WAVE DAMPING

Quantitative measurements of long-ocean-wave damping by large slicks were carried out by *Hühnerfuss et al.* [1983] during the Marine Remote Sensing Experiment (MARSEN) in 1979 in the North Sea. During this experiment a monomolecular oleyl alcohol film of approximately  $1.5 \text{ km} \times 1.5$ km was laid on the sea surface by disseminating small chunks of frozen oleyl alcohol from a helicopter. The tidal current and the wind drift moved the slick toward the platform. It took the slick little more than half an hour to drift through the position of the platform. The frequency spectra were measured inside and outside the slick area by a wave staff at the German research platform *Nordsee*. Records of 29-min duration were used for calculating the wave spectra, because such long time series are required to achieve acceptable statistical significance of the spectral estimates. The frequency resolution in the frequency range 0.06-1 Hz was 0.09 Hz, and the number of degrees of freedom was 162.

The frequency spectra of the short waves with frequencies between 2 and 20 Hz were also measured by a wave staff. However, a Marangoni dip could not be delineated. This is expected because the frequency of the short waves is subject to Doppler shifting by the orbital velocity  $\mathbf{u}_{orb}$  of the long waves. Since the Doppler shifts are positive as well as negative, the Marangoni dip is smeared out in the frequency spectrum. We expect that the Marangoni dip can hardly be delineated in the frequency spectrum if the rms Doppler shift is larger than the half width  $(\delta f)_{res}$  of the Marangoni resonance region

$$\langle (\delta f_d)^2 \rangle^{1/2} = \lambda_{\text{res}}^{-1} \langle (\mathbf{u}_{\text{orb}})^2 \rangle^{1/2} \ge (\delta f)_{\text{res}}$$
(42)

This equation may be approximated by

$$\langle (\delta f_d)^2 \rangle^{1/2} = 2\pi^3 g^{-1} \lambda_{\text{res}}^{-1} f_0^3 H_s \ge (\delta f)_{\text{res}}$$
(43)

where  $H_s$  denotes the significant wave height and  $f_0$  is the frequency of the dominant wave. For a Pierson-Moskowitz spectrum,  $\langle (\mathbf{u}_{orb})^2 \rangle^{1/2}$  can be calculated exactly, and condition (42) reads

$$\langle (\delta f_d)^2 \rangle^{1/2} = 0.064 \ \lambda_{\text{res}}^{-1} \ U_{19.5} \ge (\delta f)_{\text{res}}$$
 (44)

Here  $U_{19.5}$  denotes the wind speed at a height of 19.5 m, which is related to the significant wave height by  $H_s = 0.21$  $g^{-1} U_{195}^2$ . If we insert the values applicable to the MARSEN experiment ( $\lambda_{res} = 0.067$  m,  $U_{19.5} = 5.5$  m s<sup>-1</sup>,  $H_s = 1.5$  m, and  $f_0 = 0.35$  Hz), we obtain from (43)

$$\langle (\delta f_d)^2 \rangle^{1/2} = 6.0 \text{ Hz}$$
 (45)

and from (44)

$$\langle (\delta f_d)^2 \rangle^{1/2} = 5.3 \text{ Hz}$$
 (46)

Both values are larger than the half width  $(\delta f)_{res}$  of the Marangoni resonance for oleyl alcohol, which is about 2 Hz. This explains why the Marangoni dip could not be delineated in the measured frequency spectra during the MARSEN slick experiment.

Now we turn to the damping of the long waves. Figure 8 shows the ratio  $F_s/F_0$  as a function of frequency in the range 0.06–1 Hz. The error bar refers to 90% confidence limit. The wind speed during the experiment measured by a cup anemometer on the platform at a height of 46 m above sea level was 5–6 m s<sup>-1</sup>, the significant wave height was 1.5 m, the peak frequency of the wind wave spectrum was 0.35 Hz, the air temperature was 286.1 K, and the water temperature was 287.1 K.

From Figure 8 we see that for  $f \ge 0.7$  Hz corresponding to a wavelength of  $\lambda \ge 3.2$  m, a statistically significant decrease in the spectral energy density is observed. In the frequency range between 0.7 Hz and 1 Hz, the spectral energy has decreased to about  $0.80 \pm 0.15$  of the energy of a pure water surface.

Unfortunately, in this experiment we could not measure the damping ratio of the waves as a function of the distance traveled in the slick. During the record of 29-min duration, some waves (the ones recorded first) had almost traveled



Fig. 8. Reduction of spectral energy density of ocean waves by an oleyl alcohol film patch of approximately 1.5 km length, for wind speed of 5–6 m s<sup>-1</sup> and significant wave height of 1.5 m. The error bars (90% confidence limits) indicate that wave attenuation becomes statistically significant at about 0.7 Hz.

through the whole slick patch of 1.5 km length and others (the ones recorded last) hardly traveled at all. Almost the total time period during which the slick drifted through the position of the platform was used to calculate the spectrum. Thus the effective length of the slick patch relevant to determining the wave damping was around 750 m. The time for a 0.7-Hz wave to travel through an ocean patch of 750-m length is

$$t_s = 750 \text{ m/}c_{g} = 11.4 \text{ min}$$
 (47)

where  $c_g$  is the group velocity of the 0.7-Hz wave ( $c_g = 1.1 \text{ m s}^{-1}$ ).

The damping rate  $\Delta \alpha_{nl}$  can be calculated from the equation

$$\exp\left(-\Delta\alpha_{\rm nl}t_s\right) = F_s/F_0 \tag{48}$$

Inserting  $t_s = 11.4$  min and  $F_s/F_0 = 0.80$ , we obtain for the 0.7-Hz wave

$$\Delta \alpha_{\rm nl}(0.7 \text{ Hz}) = 3.3 \times 10^{-4} \text{ s}^{-1}$$
(49)

This value corresponds to a characteristic damping time of

$$T_{\rm nl} = (\Delta \alpha_{\rm nl})^{-1} = 51 \, \rm min$$

which is very close to the theoretical estimate of 58 min obtained in section 3.2.

## 6. DISCUSSION

Much experimental evidence exists that demonstrates that surface-active material accumulated on the surface of the sea increases the damping of short surface waves (ripples). However, contrary to common belief, not the inextensible films but the viscoelastic ones exert the strongest damping on the short surface waves. (For a more quantitative comparison between the "inextensible" and the "viscoelastic" case the reader is referred to the paper by *Hühnerfuss et al.* [1981*a*]). When the surface waves are in (linear) resonance with Marangoni waves, i.e., when the frequencies and wave numbers of both wave modes coincide, the relative damping coefficient reaches a maximum. For many viscoelastic films, maximum damping is encountered in the short-gravity-wave region.

The resonance-type damping gives rise to a dip (the "Marangoni dip") in the energy spectrum in this wave number region. The Marangoni dip has been delineated by wave spectra measured in the frequency domain by a wave staff in a wind wave tank [Hühnerfuss et al., 1981b]. In the open ocean it can be delineated in frequency domain measurements only when the rms Doppler shift by the orbital motion of the long ocean waves is sufficiently small, i.e., when condition (31) is fulfilled. This situation was encountered in the experiments of *Ermakov et al.* [1985, 1986]. For the special case of an oleyl alcohol film and a fully developed wind sea this means that for wind speeds roughly above 2 m s<sup>-1</sup> it becomes difficult to delineate the Marangoni dip in the frequency spectrum.

However, this restriction does not hold for measurements in the wave number domain. Such measurements can be performed by radar backscattering at oblique incidence angles where Bragg scattering holds [Alpers and Hühnerfuss, 1988] or by photographic techniques [Cini et al., 1983]. The data of Singh et al. [1986] indicate that the resonance-type depression of the spectral energy density in the short-gravity-wave region can be delineated in wave number space even at wind speeds between 10 and 14 m s<sup>-1</sup>. However, the damping effect vanishes when the film is "washed down," i.e., when it has disappeared from the sea surface. Wind wave tank experiments show that in the presence of surface films with very strong wave damping ability this happens for  $u_* \ge 0.6$  m s<sup>-1</sup>, which should correspond to a wind speed at a height of 10 m of about  $U_{10}$ =  $18 \text{ m s}^{-1}$  in the open ocean. Slicks with a medium or low wave-damping ability exhibit less intensive intermolecular forces between the film-forming substances and are thus "washed down" already at wind speeds  $U_{10}$  considerably less than 18 m s<sup>-1</sup>. In particular, biogenic slicks, which consist of a mixture of surface-active compounds, may sometimes already disappear from the sea surface at  $U_{10} \approx$  $7-10 \text{ m s}^{-1}$ .

Marangoni damping leads to a deformation of the spectral form in the short-gravity-wave region. The wave system responds to such deviations from equilibrium with an increase in the energy flux towards higher wave numbers. Thus energy is drawn from the waves with low wave numbers, which leads to damping of longer water waves. For example, in a field experiment in the North Sea in 1979, Hühnerfuss et al. [1983] found that gravity waves of 3.2-m wavelength were significantly damped when traveling through a 1.5-km slick patch consisting of oleyl alcohol. At that time we had no explanation for the measured damping of such long waves by the monomolecular slick. In this paper we have presented theoretical estimates of the damping time based on the theories of Kitaigorodskii [1983] and Phillips [1985] on the energy balance in the equilibrium range of the spectrum. The damping time of the 3.2-m wave is estimated to be 51 min in this field experiment, while the theoretical estimate is 58 min. This time is about 1.2 to 7 times lower than the clean surface nonlinear interaction time at this spectral range. We interpret this result as a confirmation that Marangoni damping together with nonlinear wave-wave interaction can explain the observed strong damping of medium long gravity waves by viscoelastic surface films.

According to our theory, the rate of energy transfer increases quadratically with wind speed. This is consistent with wave staff measurements carried out in a wind wave tank [Feindt, 1985] and with airborne radar backscatter measurements carried out over the ocean [Singh et al., 1986]. An increase in the nonlinear transfer from low to high wave numbers results in a shallower Marangoni dip and leads to an increase in the long-wave damping. Thus the higher the wind speed, the stronger is the damping of the long waves by the slick.

In addition to increasing of nonlinear energy transfer by the Marangoni dip, a surface film also decreases the wind input such that the wind stress is about 20% less than it is for a clean surface [ $H\ddot{u}hnerfuss\ et\ al.$ , 1981b]. Wave breaking also diminishes, and thus dissipation due to this effect decreases.

However, the main mechanism responsible for long-wave damping remains nonlinear wave-wave interaction. At high wind speeds, slick patches a few hundred meters in diameter can be very effective in damping waves of a few meters wavelength. The result is a strong reduction in wave breaking such that a stormy sea becomes much less dangerous for small boats or for offshore structures.

Viscoelastic surface films could be applied in rescue operations at sea or at oil rigs for protecting them against the impact of wave breaking. A few liters of surface-active material disseminated from a helicopter upwave from the distressed ship would suffice to calm the sea sufficiently. Oil rigs could be protected by surrounding them at distances of several kilometers by a chain of buoys which are capable of releasing surface active material by remote control in the case of dangerous sea states. The same method could be applied for protecting the coast by anchoring a chain of buoys, on which surface-active material is stored, several kilometers off the coastline.

Though the damping effect of viscoelastic films increases with wind speed, it should be kept in mind that the damping effect disappears at high sea states when the film is "washed down." For slicks with very strong wave-damping ability, this should take place at friction velocities  $u_*$  above 0.6 m s<sup>-1</sup> corresponding to values of  $U_{10}$  around 18 m s<sup>-1</sup>. However, usually this happens at wind speeds  $U_{10} = 10 - 13$ m s<sup>-1</sup>, and in the case of biogenic slicks it happens at even lower wind speeds  $U_{10} \leq 10$  m s<sup>-1</sup>.

Surfactants best suited for calming a stormy sea are those which have a large dilational modulus E, i.e., those which have a high elasticity.

# Appendix: Derivation of Basic Formulae of Marangoni Wave Theory

Both surface and Marangoni waves are solutions of the Navier-Stokes equation describing the dynamics of a fluid, in this case, water. Marangoni waves exist only when the surface is covered with a viscoelastic film. Surface waves exist when the surface is clean as well as when it is covered by a viscoelastic film.

In this investigation we confine ourselves to plane wave solutions of the Navier-Stokes equation. Then all quantities depend only on two space variables, x and z. The z-axis is chosen normal to the unperturbed water surface pointing into the air. The Navier-Stokes equation describing the time and space evolution of the velocity field  $\mathbf{u} = (u_x, u_z)$  then reads

$$\rho \frac{\partial u_x}{\partial t} = -\frac{\partial p}{\partial x} + \eta \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right] u_x$$
(A1)
$$\rho \frac{\partial u_z}{\partial t} = -\frac{\partial p}{\partial z} - \rho g + \eta \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial z^2} \right] u_z$$

Here, p denotes the pressure within the water, g is the acceleration of gravity,  $\rho$  is the density, and  $\eta$  is the dynamic viscosity of water. In (A1) the advection term has been neglected, implying that only waves of small amplitudes are considered (linear wave approximation).

The (kinematical) boundary conditions at the free surface for the tangential and normal stress components read

$$\frac{\partial \sigma}{\partial x} - \tau_{xz} = 0 \tag{A2a}$$

$$\sigma \frac{\partial^2 \zeta}{\partial x^2} + p - \rho g \zeta - p_a - \tau_{zz} = 0$$
 (A2b)

Here  $\sigma$  denotes the surface tension,  $\zeta$  is the surface elevation,  $p_a$  is the atmospheric pressure, and  $\tau_{ij}$  (i, j = x, z) is the stress tensor describing the viscous friction within the fluid

$$\tau_{ij} = \eta \left[ \frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right]$$
(A3)

These boundary conditions differ from the ones applicable to a clean surface only by the first term in (A2a), which is zero in the case of a clean water surface. Thus a viscoelastic film changes the tangential boundary condition such that the viscous stress  $\tau_{xz}$  no longer vanishes at the free surface. Now the viscous stress has to be balanced by the tangential stress exerted on the water surface by surface tension gradients. Since the viscous stress is proportional to gradients in the velocity field, the strain associated with the viscoelastic film causes strong velocity gradients in a layer adjacent to the surface. The occurrence of such strong velocity gradients is the reason for enhanced viscous dissipation and therefore enhanced damping of surface waves by viscoelastic films.

In order to solve these equations, we have to relate the surface tension gradient  $\partial \sigma / \partial x$  to the horizontal displacement  $\xi$  of the surface due to the passage of a surface wave and to such rheological properties of the film as elasticity and viscosity. Strictly speaking, however, the intrinsic rheological properties of the film coupled to the medium on which the surface film floats.

A varying surface stress leads to changes in area and shape of a surface element. In this investigation we take into account only changes in surface area and neglect changes in shape (see, for example, *Lucassen-Reynders*, 1985]). This amounts to retaining only the dilational stress part of the surface stress tensor and neglecting the shear stress part.

For small deformations, the change in surface tension  $\Delta\sigma$  is then related to the relative change in area  $\Delta A/A$  by

$$\Delta \sigma = E \, \frac{\Delta A}{A} \tag{A4}$$

where E is the surface dilational modulus. In general, E is a complex quantity, which conventionally is written as

$$E = |E| \exp(-i\theta) = E_d + i\omega\eta_d$$
 (A5)

 $E_d$  is called the surface dilational elasticity, and  $\eta_d$  is the surface dilational viscosity. A nonvanishing phase angle  $\theta$  implies that if the surface area is varied harmonically in time, the areas of maximum surface dilation or compression do not coincide with areas of maximum or minimum surface tension, respectively. This means that the viscoelastic film has a finite response (relaxation) to surface area variations. For linear waves the tangent of this phase lag  $\theta$  is proportional to wave frequency  $\omega$ .

For small-amplitude waves the relative change in surface area of a surface element of area A is, to first order, given by [Lucassen-Reynders and Lucassen, 1969]

$$\frac{\Delta A}{A} = \frac{\partial \xi}{\partial x} \tag{A6}$$

where  $\xi$  is the horizontal displacement of the surface element due to the orbital motion associated with the passage of a surface wave.

Thus the kinematical boundary conditions (A2a) and (A2b) read

$$E\frac{\partial^2 \zeta}{\partial x^2} - \eta \left[\frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial x}\right] = 0$$
 (A7*a*)

$$\sigma \frac{\partial^2 \zeta}{\partial x^2} + p - p_a - 2 \ \eta \frac{\partial u_z}{\partial x} = 0$$
 (A7b)

For an incompressible viscous fluid, solutions of the Navier-Stokes equation can be obtained by writing the velocity field **u** as a sum of an irrotational field and a divergence-free field. In the case considered here where all quantities depend on two variables only, the irrotational field can be described by a potential function  $\Phi$  and the divergence-free field by a vorticity function  $\Psi$ , which satisfy the equations

$$\Delta \Phi = 0 \tag{A8a}$$

$$\rho \, \frac{\partial \Psi}{\partial t} - \, \eta \Delta \Psi = 0 \tag{A8b}$$

Thus we can write u as

$$\mathbf{u} = \operatorname{grad} \, \Phi + \operatorname{curl} \, \Psi \tag{A9}$$

or in components

$$u_x = \frac{\partial \phi}{\partial x} - \frac{\partial \Psi}{\partial z}$$
 (A10*a*)

$$u_z = \frac{\partial \Phi}{\partial z} - \frac{\partial \Psi}{\partial x} \tag{A10b}$$

Note that the velocity field of a fluid without viscosity ( $\eta = 0$ ) can be characterized solely by a potential function  $\Phi$ . The vorticity function  $\Psi$  describes the modification of the flow field due to viscosity.

Harmonic wave solutions of (A1) can be written as

$$\Phi = C e^{kz} e^{i(kx + \omega t)} \tag{A11}$$

$$\Psi = Be^{mz} e^{i(kx + \omega t)}$$
(A12)

where k, m, and  $\omega$  are complex quantities, which are related by

$$m^2 = k^2 + i\omega\rho/\eta \tag{A13}$$

because  $\Psi$  has to satisfy (A8b). Inserting (A11) and (A12) into the dynamical boundary conditions (A7a) and (A7b), expressing the pressure p in (A7b) by

$$p = -\rho \,\frac{\partial \Phi}{\partial t} \tag{A14}$$

taking the time derivative of the resulting equations (A7*a*) and (A7*b*), and replacing  $\zeta$  according to the kinematic boundary condition at the free surface (neglecting the advective term) by

$$\dot{\zeta} = \frac{\partial \Phi}{\partial t} \tag{A15}$$

yields two homogeneous equations for C and B.

Solutions exist if the determinant vanishes (see equations (17) and (18) of *Lucassen* [1968]):

$$+ 2 i\eta\omega k^{2} + Ek^{3} + \eta\omega(m^{2} + k^{2}) - iEmk^{2} + i\rho gk - i\rho\omega^{2} - 2\eta\omega k^{2} + i\sigma k^{3} \sigma gk^{2} + 2i\eta\omega mk + \sigma k^{3} = 0$$
(A16)

For a fixed  $\omega$ , this equation has two solutions. One solution describes surface waves, and the other describes the Marangoni waves.

Note that (A1) contains a friction term which implies that the solutions are damped waves. Therefore k has to be a complex quantity. Conventionally, k is written as

$$k = \kappa - i\Delta \tag{A17}$$

where the real part  $\kappa$  represents the wave number and the imaginary part  $\Delta$  represents the damping coefficient.

The surface wave solutions of (A16) have been investigated by computer calculations which show that the wave number  $\kappa$  is practically independent of *E*. To a good approximation,  $\kappa$  obeys the dispersion relation (12) applicable to a fluid with a clean surface. However, the damping coefficient  $\Delta$  strongly depends on *E*. In certain frequency regions,  $\Delta$  can attain values which are ten to several hundred times larger than the damping coefficient  $\Delta_0$  for viscous fluids with a clean surface.  $\Delta/\Delta_0$  is not a monotonic function of *E*. It has a maximum at an intermediate *E*.

As an illustration of these formulae, we consider the propagation of a wave with a frequency of 4.8 Hz corresponding to a wavelength of 0.068 m in water with dynamical viscosity of  $\eta = 10^{-3}$  Pa s. Inserting these values together with  $\rho = 10^3$  kg m<sup>-3</sup> and  $\sigma = 73 \times 10^{-3}$  N m<sup>-1</sup> into (8) yields for a clean water surface

$$\Delta_0 \approx 0.1 \text{ m}^{-1} \tag{A18}$$

Thus the distance  $D_0$  at which the amplitude of a wave with a wavelength of 0.068 m wave has decayed to 1/e of its original value is in the case of a clean water surface

$$D_0 = \Delta_0^{-1} \approx 10 \text{ m} \tag{A19}$$

Now let the water surface be covered with a surface film with dilational modulus |E| = 0.0225 N m<sup>-1</sup>, and phase angle  $\theta = 175^{\circ}$ . This is the value applicable to oleyl alcohol (Z-9-octadecen-1-o1) as measured in wave damping experiments in a wind wave tank [*Hühnerfuss*, 1986]. With these values we obtain f = 4.8 Hz and  $\Delta/\Delta_0 = 28$ . Therefore the

distance at which the amplitude of a wave of 0.068-m wavelength has decayed to 1/e of its original value becomes in this case

$$D = (\Delta_0 / \Delta) D_0 = 0.36 \text{ m}$$
 (A20)

This means that the wave amplitude has decayed to 1/e of its original value only after about five wavelengths.

The distance at which the square of the amplitude had decayed to 1/e of its original value is then D/2. We now define a characteristic damping time  $T_M$  as the time in which the spectral energy has decayed to 1/e of its original value. Since the energy propagates with the group velocity  $v_g$ , we obtain

$$T_M = D/2v_g \tag{A21}$$

Our example yields  $T_M \approx 1$  s because  $v_g$  for a 4.8-Hz wave is 0.18 m/s. This is about 5 times the wave period.

 $\Delta/\Delta_0$  is a function of both the dilational modulus *E* and the wave number  $\kappa$ . It has a maximum both as a function of *E* as well as a function of  $\kappa$ . From equations (2), (8), and (9) of *Lucassen* [1982] we infer that in the gravity wave region

$$\left[\frac{\Delta}{\Delta_0}\right]_{\max} \propto \kappa^{-3/4} \tag{A22}$$

This means that the maximum attainable increase in wave damping due to a surface film increases with water wavelength. Furthermore, we infer from equation (10) of *Lucassen* [1982] that the dilational modulus required for obtaining maximum damping in the gravity wave region depends on  $\kappa$ in the following way (assuming  $\theta = 0$ ):

$$E_{\rm max} \propto \kappa^{-5/4}$$
 (A23)

From this equation we see that for obtaining maximum damping at long wavelengths, one has to choose a surface film with large E. However, no chemical substances exist in nature with dilational moduli E much larger than 0.4 N m<sup>-1</sup>. If E = 0.4 N m<sup>-1</sup> is inserted into (9), one obtains maximum wave damping at a frequency corresponding to a wavelength of approximately 1 m. Thus surface chemistry puts a constraint on maximum wave damping. Waves with wavelengths above 1 m cannot be damped strongly by the Marangoni effect (except for wind waves; see section 3).

Monomolecular surfactants have E values typically in the range of  $10^{-3} - 5 \times 10^{-2}$  N m<sup>-1</sup> [Hühnerfuss, 1986]. Maximum damping occurs for these surfactants in the centimeter to decimeter range. The relative damping coefficient at maximum damping in this wavelength regime lies typically between 10 and 100. Furthermore, the ratio of the maximum damping coefficient  $\Delta_{max}$  to the wave number  $\kappa$  is related to  $\kappa$  by [see Lucassen, 1982, equation (8)]

$$\frac{\Delta_{\max}}{\kappa} \propto \kappa^{3/4}$$
 (A24)

This means that the shorter waves decay over fewer wavelengths by Marangoni damping than do the longer waves.

The penetration depth d' of the vorticity function  $\Psi$  is defined by

$$d' = |\operatorname{Re} m|^{-1} \tag{A25}$$

Since  $k \ll m$ , we obtain from (A13)

$$d' = (\eta/\rho\omega)^{1/2} \tag{A26}$$

where d' is related to the thickness d of the boundary layer, defined in (1), by

$$d = 2^{1/2} d'$$
 (A27)

Inserting the values applicable to oleyl alcohol floating on the water surface ( $f_M = 4.8$  Hz,  $\rho = 10^3$  kg m<sup>-3</sup>, and  $\eta = 10^{-3}$  Pa s), we obtain

$$d \approx 2.6 \times 10^{-4} \text{ m} \tag{A28}$$

The penetration depth of the vorticity function defines the thickness of the sea surface skin layer. According to (A26), the thickness of this layer decreases with increasing wave number:

$$d' \propto \kappa^{-1/4} \tag{A29}$$

Acknowledgments. We thank R. Cini (Florence, Italy), P. P. Lombardini (Turin, Italy), and S. A. Ermakov (Gorki, USSR) for several enlightening discussions concerning Marangoni wave theory, and we thank K. Hasselmann (Hamburg), O. M. Phillips (Baltimore, Maryland), and H. Masuko (Tokyo) for their valuable comments on nonlinear wave-wave interactions in the equilibrium range of the spectrum. This work was supported by the Bundesministerium für Forschung und Technologie under grant 01QS86174 and by the European Community through the "Stimulation Action," contract ST2J-0155-1-D.

#### References

- Alpers, W., and H. Hühnerfuss, Radar signature of oil films floating on the sea surface and the Marangoni effect, J. Geophys. Res., 93, 3642–3648, 1988.
- Cini, R., and P. P. Lombardini, Damping effect of monolayers on surface wave motion in a liquid, J. Colloid Interface Sci., 65, 387-389, 1978.
- Cini, R., and P. P. Lombardini, Experimental evidence of a maximum in the frequency domain of the ratio of ripple attenuation in monolayered water to that in pure water, J. Colloid Interface Sci., 81, 125-131, 1981.
- Cini, R., P. P. Lombardini, and H. Hühnerfuss, Remote sensing of marine slicks utilizing their influence on wave spectra, *Int. J. Remote Sens.*, 4, 101-110, 1983.
- Cini, R., P. P. Lombardini, C. Manfredi, and E. Cini, Ripple damping due to monomolecular films, J. Colloid Interface Sci., 119, 74-80, 1987.
- Davies, J. T., and R. W. Vose, On the damping of capillary waves by surface films, Proc. R. Soc. London, Ser. A, 286, 218-234, 1965.
- Dorrestein, R., General linearized theory of the effect of surface films on water ripples, *Proc. K. Ned. Akad. Wet. Ser. B*, 54, 260-272, 350-356, 1951.
- Ermakov, S. A., A. R. Panchenko, and T. G. Talipova, Damping of high-frequency wind waves by artificial surfactant films (in Russian), *Izv. Akad. Nauk. SSSR Fiz. Atmos. Okeana*, 21, 76–82, 1985. (Engl. transl., *Izv. Acad. Sci. USSR Atmos. Oceanic Phys.*, 21, 54–58, 1985.
- Ermakov, S. A., A. M. Zujkova, A. R. Panchenko, S. G. Salashin, T. G. Talipova, and V. I. Titov, Surface film effect on short wind waves, Dyn. Atmos. Oceans, 10, 31-50, 1986.
- Feindt, F., Radar-Rückstreuexperimente am Wind-Wellen-Kanal bei sauberer und filmbedeckter Wasseroberfläche im X-Band (9.8 GHz), Hamb. Geophys. Einzelschr. Reihe Al Nr. 75 224 pp., Univ. Hamburg, Hamburg, Federal Republic of Germany, 1985.
  Franklin, B., On the stilling of waves by means of oil, Philos.
- Trans., 64, 445–460, 1774. Gottifredi, J. C., and G. J. Jameson, The suppression of windgenerated waves by a surface film, J. Fluid Mech., 32, 609–618,
- 1968. Hasselmann, K., Grundgleichungen der Seegangsvorhersage, Schiffstech. Z., 191–195, 1960.
- Hasselmann, K., On the nonlinear energy transfer in a gravity wave spectrum, 1, General theory, J. Fluid Mech., 12, 481-500, 1962.

1S

- Hasselmann, K., On the nonlinear energy transfer in a gravity wave spectrum, 2, Conservation theorems, wave-particle analogy, irreversibility, J. Fluid Mech., 15, 273-281, 1963a.
- Hasselmann, K., On the nonlinear energy transfer in a gravity wave spectrum, 3, Evaluation of the energy flux and swell-sea interation for a Newmann spectrum, J. Fluid Mech., 15, 385–398, 1963b.
- Hasselmann, K., et al., Measurements of wind-wave growth and swell decay during the Joint North Sea Wave Project (JON-SWAP), Dtsch. Hydrogr. Z., 8, suppl. A, 1-95, 1973.
- Hasselmann, S., and K. Hasselmann, Computations and parameterizations of the nonlinear energy transfer in a gravity-wave spectrum, 1, A new method for efficient computations of the exact nonlinear transfer integral, J. Phys. Oceanogr., 15(11), 1369-1377, 1985.
- Hühnerfuss, H., The molecular structure of the system water/ monomolecular surface film and its influence on water wave damping, Habilitationsschrift, Fachber. Chem., Univ. Hamburg, Hamburg, Federal Republic of Germany, 1986.
- Hühnerfuss, H., W. Alpers, W. L. Jones, P. A. Lange, and K. Richter, The damping of ocean surface waves by a monomolecular film measured by wave staffs and microwave radars, J. Geophys. Res., 86, 429-438, 1981a.
- Hühnerfuss, H., W. Alpers, P. A. Lange, and W. Walter, Attenuation of wind waves by artificial surface films of different chemical structure, *Geophys. Res. Lett.*, 8, 1184–1186, 1981b.
- Hühnerfuss, H., W. Alpers, W. D. Garrett, P. A. Lange, and S. Stolte, Attenuation of capillary and gravity waves at sea by monomolecular organic surface films, J. Geophys. Res., 88, 9809–9816, 1983.
- Hühnerfuss, H., P. A. Lange, and W. Walter, Relaxation effects in monolayers and their contribution to water wave damping, 1, Wave-induced phase shifts, J. Colloid Interface Sci., 108, 430– 441, 1985a.
- Hühnerfuss, H., P. A. Lange, and W. Walter, Relaxation effects in monolayers and their contribution to water wave damping, 2, The Marangoni phenomenon and gravity wave attenuation, J. Colloid Interface Sci., 108, 442-450, 1985b.
- Hühnerfuss, H., W. Walter, P. A. Lange, and W. Alpers, Attenuation of wind waves by monomolecular sea slicks by the Marangoni effect, J. Geophys. Res., 92, 3961-3963, 1987.
- Hühnerfuss, H., W. Alpers, and F. Witte, Layers of different thicknesses in mineral oil spills detected by grey level textures of real aperture radar images, Int. J. Remote Sens., in press, 1989.
- Kitaigorodskii, S. A., On the theory of the equilibrium range in the spectrum of wind-generated gravity waves, J. Phys. Oceanogr., 13, 816–827, 1983.
- Komen, G. J., S. Hasselmann, and K. Hasselmann, On the existence of a fully developed wind-sea spectrum, J. Phys. Oceanogr., 14, 1271-1285, 1984.
- Lange, P., and H. Hühnerfuss, Drift response of monomolecular slicks to wave and wind action, J. Phys. Oceanogr., 8, 142-150, 1978.
- Lange, P. A., and H. Hühnerfuss, Horizontal surface tension gradients induced in monolayers by gravity wave action, J. Phys. Oceanogr., 14, 1620–1628, 1984.
- Levich, V. G., The damping of waves by surface-active materials (in Russian), *Zh. Eksp. Teor. Fiz.*, 10, 1296–1304, 1940. (Engl. transl., *Acta Physicochim. URSS*, 14, 307–328, 1941.)
- Levich, V. G., *Physicochemical Hydrodynamics*, Prentice-Hall, Elmsford Park, N.J., 1962.

- Lucassen, J., Longitudinal capillary waves, 1, Theory, Trans. Faraday Soc., 64, 2221-2229, 1968.
- Lucassen, J., Effect of surface-active material on the damping of gravity waves: A reapraisal, J. Colloid Interface Sci., 85, 52-58, 1982.
- Lucassen, J., and R. S. Hansen, Damping of waves on monolayercovered surfaces, II, Influence of bulk-to surface diffusional interchange on ripple characteristics, J. Colloid Interface Sci., 23, 319-328, 1967.
- Lucassen-Reynders, E. H., Surface elasticity and viscosity in compression/dilation, in *Aniomic Surfactants, Physical Chemistry of Surfactant Action*, edited by E. H. Lucassen-Reynders, pp. 173-216, Dekker, New York, 1985.
- Lucassen-Reynders, E. H., and J. Lucassen, Properties of capillary waves, Adv. Colloid Interface Sci., 2, 347-395, 1969.
- Marangoni, C., Sul principio della viscosità superficiale dei liquidi stabili, Nuovo Cimento, Ser. 2, 5/6, 239-273, 1872.
- Masuda, A., Nonlinear energy transfer between wind waves, J. Phys. Oceanogr., 10, 2082-2093, 1980.
- Masuda, A., Nonlinear energy transfer between random gravity waves, in *Wave Dynamics and Radio Probing of the Ocean Surface*, edited by O. M. Phillips and K. Hasselmann, pp. 41-57, Plenum, New York, 1986.
- Mitsuyasu, H., and T. Honda, The effects of surfactant on certain air-sea interaction phenomena, in *Wave Dynamics and Radio Probing of the Ocean Surface*, edited by O. M. Phillips and K. Hasselmann, pp. 95–115, Plenum, New York, 1986.
- Phillips, O. M., The Dynamics of the Upper Ocean, 2nd ed., 336 pp., Cambridge University Press, New York, 1977.
- Phillips, O. M., Spectral and statistical properties of the equilibrium range in wind-generated gravity waves, J. Fluid Mech., 156, 505-531, 1985.
- Singh, K. P., A. L. Gray, R. K. Hawkins, and R. A. O'Neil, The influence of surface oil on C-band and K<sub>u</sub>-band ocean backscatter, IEEE Trans. Geosci. Remote Sens., GE-24, 738-744, 1986.
- Scott, J. C., The historical development of theories of wave-calming using oil, *Hist. Technol.*, 3, 163–186, 1978.
- Toba, Y., Local balance in the air-sea boundary process, 3, J. Oceanogr. Soc. Jpn., 29, 209-220, 1973.
- Valenzuela, G. R., Theories for the interaction of electromagnetic and oceanic waves—A review, Boundary Layer Meteorol., 13, 61–85, 1978.
- Valenzuela, G. R., and J. W. Wright, The growth of waves by modulated wind stress, J. Geophys. Res., 81, 5795-5796, 1976.
- Van den Tempel, M., and R. P. van de Riet, Damping of waves by surface-active materials, J. Chem. Phys., 42, 2769–2777, 1965.
- Willebrand, J., Energy transport in a nonlinear and inhomogeneous random gravity wave field, J. Fluid Mech., 70, 113-126, 1975.
- Wu, H.-Y., E.-Y. Hsu, and R. L. Street, Experimental study of nonlinear wave-wave interaction and white-cap dissipation of wind-generated waves, Dyn. Atmos. Oceans, 3, 55-78, 1979.

H. Hühnerfuss, Institut für Organische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 2000 Hamburg 13, Federal Republic of Germany.

(Received July 5, 1988; accepted October 18, 1988.)

W. Alpers, Fachbereich 1 (Physik), Physik des Meeres, Universität Bremen, 2800 Bremen 33, Federal Republic of Germany.