down from 17.90 T to zero. The temperature of the sample reached 29 K, reflecting a marked enhancement of its thermal conductivity. Also, the temperature rise during field sweeping is small compared to the experiment shown in Fig. 2. This also supports the fact that the thermal conductivity was greatly improved in the present configuration. As the applied field is decreased, the field on the superconductor gradually decreased. However, the field at the centre of the sample stayed at an initial value of 17.9 T. No sudden temperature rise occurred during the field-decreasing process, but, because the temperature increased to 30 K at 4 T, we lowered the sweeping rate to provide a safety margin. Even after the external field was removed, a field of >17 T was trapped by the superconductor (Fig. 5). We also performed similar trapped-field experiments at 78 K and 46 K (Fig. 5). The trapped-field profiles at these temperatures show saturation, with a peak field of 9.5 T for 46 K and 1.2 T for 78 K. Compared to the data at 46 and 78 K, the trapped field at 29 K is far below saturation, and hence the present bulk magnet has the potential to trap much higher fields than 17 T if a higher magnetic field is available for activation.

The static field of 17.24 T is attractive for various applications. As long as the sample temperature is kept at 29 K with a cryocooler, a bulk superconductor magnet trapping 17.24 T could be transported to any desired place. This means that a strong static field of 17.24 T limited to the bore space of the superconducting solenoid could be freely used in free space. For magnetic separation of contaminants from polluted water, pre-treatment with ferromagnetic powders is unnecessary for fields larger than 10 T. Therefore, a much simpler separation system could be made. Furthermore, the output of an electromagnetic machine is the product of electric current and magnetic field, so a strong magnetic field is beneficial for the development of high-power, compact machines. The range of a stray field is very small in bulk superconductor magnets, so the deleterious effect of stray field can be localized. We therefore believe that the present results will open the way to new applications of fields from bulk superconducting magnets.

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# The effects of surfactants on spilling breaking waves

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Breaking waves markedly increase the rates of air-sea transfer of momentum, energy and mass<sup>1-4</sup>. In light to moderate wind conditions, spilling breakers with short wavelengths are observed frequently. Theory and laboratory experiments have shown that, as these waves approach breaking in clean water, a ripple pattern that is dominated by surface tension forms at the crest<sup>5-14</sup>. Under laboratory conditions and in theory, the transition to turbulent flow is triggered by flow separation under the ripples, typically without leading to overturning of the free surface<sup>15</sup>. Water surfaces in nature, however, are typically contaminated by surfactant films that alter the surface tension and produce surface elasticity and viscosity<sup>16,17</sup>. Here we present the results of laboratory experiments in which spilling breaking waves were generated mechanically in water with a range of surfactant concentrations. We find significant changes in the breaking process owing to surfactants. At the highest concentration of surfactants, a small plunging jet issues from the front face of the wave at a point below the wave crest and entraps a pocket of air on impact with the front face of the wave. The bubbles and turbulence created during this process are likely to increase air-sea transfer.

Experiments were done in a tank of 15 m by 1.2 m with a water depth of 0.8 m. Weak spilling breakers were produced from Froude-scaled mechanically generated dispersively focused wave packets<sup>18,19</sup> with average frequencies of 1.15, 1.26 and 1.42 Hz. The breaker generation technique and wave-maker motion parameters are identical to those described in ref. 13 (in the present case, the dimensionless wave-maker amplitude is 0.0505). The wave-maker motions are repeatable to within  $\pm 0.1\%$  of their amplitude.

All of the experiments reported here were done with a single tank of filtered tap water over a period of 8 d. Rhodamine 6G, a fluorescent dye, was mixed with the water at a concentration of

0.5 p.p.m. for visualization purposes. The main surfactant used in this work was the soluble surfactant sodium dodecyl sulphate (SDS), although other surfactants (from bacteria, impurities in the chemicals and other sources) would have been present as well. Measurements were done with relatively clean water (data set CLEAN) and five different concentrations of surfactants (data sets 1, 2, 3, 4a and 4b). The bulk concentration of SDS (C) corresponding to each data set is given in Fig. 1. The SDS concentrations in data sets 4a and 4b are equal, but the measurements were taken 3 d apart (see Methods). The purpose of the experiments is to correlate the wave behaviour with *in situ* measurements of dynamic surface properties rather than the specific chemicals that create these surface properties.

The presence of soluble surfactants in the bulk creates, through adsorption of surfactant molecules, an ambient surface excess concentration of surfactant ( $\Gamma_a$ ; ref. 16). To characterize the dynamical properties of the water surface, the surface pressure isotherm, the equilibrium (Gibbs) surface elasticity and the surface viscosity (the sum of the surface shear and dilational viscosities) were measured *in situ* for each data set (1 to 4b; Fig. 1). The ambient surface tension ( $\sigma_a$ ) is plotted against the log of *C* in Fig. 1a. The data fall on a single straight line with the ambient surface tension decreasing as the bulk concentration increases, as is typical of surfactants<sup>16</sup>; however, the measured values are not the same as those found in tests with pure SDS and distilled water<sup>17</sup>. The ambient surface tension at the highest SDS concentration was the same for data sets 4a and 4b.

Figure 1b shows plots of the surface pressure isotherms for each data set. The isotherm for data set CLEAN shows a constant surface pressure ( $\pi = \sigma_c - \sigma$ , where  $\sigma_c$  is the surface tension of clean water and  $\sigma$  is the local surface tension at the measuring device) of zero down to a compression of 75% ( $A/A_0 = 0.25$ , where  $A/A_0$  is the

normalized surface area in a Langmuir trough that surrounds the surface tension measuring device; see Methods). (It was found that breakers generated in this case behaved in the same manner (see below) as breakers generated in cases with lower values of  $\Gamma_a$ .) In the presence of SDS, the surface pressure increases monotonically from a non-zero initial value as the surface area is compressed. The two surface pressure curves for the highest concentration (data sets 4a and 4b) are the same at low surface compression, but the curve for data set 4b has a much higher slope for  $A/A_0 < 0.3$  (-1.2 in the semi-log plot). The slope of these curves is called the static elasticity.

The equilibrium elasticity  $E_0$  and surface viscosity  $\mu_s$  are plotted against the bulk concentration of SDS in Fig. 1c, d, respectively. Both quantities decrease as the bulk concentration of SDS increases. At the highest bulk concentration, the equilibrium elasticity is about the same on the two measurement days, whereas the surface viscosity shows a marked increase on the last day of the experiment (data set 4b). The measured values of ambient surface pressure and elasticity are within the range of field measurements in some coastal regions<sup>20,21</sup>.

The histories of the crest shape of the breaking waves were recorded in each data set. As has been reported previously<sup>9,10,13</sup>, in clean water a bulge forms on the forward face of the wave crest as it steepens and capillary waves form upstream of the leading edge (called the toe) of the bulge (Fig. 2a). (In crest-fixed coordinates, the upstream direction is to the left of the crest.) When the toe becomes sharp (small radius of curvature), the flow separates, the toe begins to move down the wave face (Fig. 2b) and a turbulent flow ensues<sup>15</sup>. As the toe moves down the wave face, ripples are generated between the toe and the crest (not shown in Fig. 2), and these ripples propagate backwards over the crest in crest-fixed coordinates. There is no plunging jet formation and impact, or any other overturning of the free surface.



**Figure 1** Measurements of dynamic surface properties. Six sets of measurements are shown with various bulk concentrations (*C*, in mol I<sup>-1</sup>) of SDS. Open triangles, *C* = 0 (data set CLEAN); open diamonds, *C* =  $1.6 \times 10^{-5}$  (data set 1); filled circles, *C* =  $6.0 \times 10^{-5}$  (data set 2); filled triangles, *C* =  $1.94 \times 10^{-4}$  (data set 3); filled squares, *C* =  $4.17 \times 10^{-4}$  (data set 4a); open squares, *C* =  $4.17 \times 10^{-4}$  (data set 4b). Data set 4b was taken 3 d after data set 4a without adding or removing SDS from the tank. **a**, Ambient surface tension,  $\sigma_a$  (mN m<sup>-1</sup>), versus *C*. The line is a least squares fit of the experimental data. **b**, Surface pressure,  $\pi$  (mN m<sup>-1</sup>), versus the log of the normalized water surface area (*A*/*A*<sub>0</sub>) in a Langmuir trough that surrounds the surface tension measuring device. **c**, Gibbs elasticity, *E*<sub>0</sub> (mN m<sup>-1</sup>), versus *C*. **d**, Surface viscosity,  $\mu_s$  (mN s m<sup>-1</sup>), versus *C*.



**Figure 2** Two images of a breaking wave in 'clean' water. The wave-packet frequency is 1.15 Hz. The wave propagates from right to left. The breaker is highly repeatable and each image is from a different experimental run. The width of each image is 12.5 cm in the plane of the light sheet. In each image, the edge between the upper dark region and the lower wavy light region is the wave crest profile at the centreline of the tank where the laser light sheet intersects the wave surface. The variation of the light intensity below this edge is due to the non-uniform intensity of the underwater portion of the light sheet, which is produced by refraction as it enters the curved water surface and by viewing the glowing dye in the light sheet through the curved water surface between the camera and the light sheet. A detailed description of these effects is given in ref. 13. **a**, The ripple pattern forms at the crest. **b**, The toe begins to move down the wave face.

This process changes in the presence of SDS in several ways. As the concentration of SDS is increased, the capillary waves decrease in amplitude and number, the size of the bulge shrinks, and the ripples generated between the toe and the crest during the spilling process diminish. In the first experiment at the highest SDS concentration (data set 4a), the capillary waves disappear and a bulge forms with a very steep front near the toe. At this point, the toe moves down the wave face in a manner much like that found in the clean water case described above, and the wave breaks without overturning of the free surface.

In the second experiment at the highest SDS concentration (data set 4b), the wave behaviour changed markedly. Four images of one of the breakers are shown in Fig. 3. The wave-maker motion is identical to that for the breaker shown in Fig. 2. The bulge still forms initially, but without a sharp toe and without capillary waves ahead



of the toe (Fig. 3a). The bulge is fairly uniform along the crest (that is, in the direction perpendicular to the plane of the image). After a short time period, a two-dimensional jet with a thickness of about 5 mm emerges from the bulge near the toe (Fig. 3b). The roughness of the jet may be the result of a cross-stream instability found in the jets of plunging breakers in clean water<sup>22</sup>. The jet ejects forward (Fig. 3c) and re-enters the front face of the wave. As the jet hits the front face of the wave, it entraps a tube of air and a splash projects forward from the impact point (Fig. 3d). The surface motion is more violent than that for a wave generated by the same wave-maker motion in clean water. Images from high-speed movies of the breakers were analysed to obtain the crest profile at each instant. Figure 4a shows the crest profile history of a single breaking wave with an average wave-packet frequency of 1.15 Hz. The jet motion and splashing can be seen more easily from this history record.

Breakers were measured for all three wave-packet frequencies (three waves at 1.42 Hz, three waves at 1.26 Hz, and six waves at 1.15 Hz) in data set 4b. At each frequency, the wave breaks in a different position in the tank. The small jet appears in all of these breaking events and always with an initial thickness of about 5 mm. Figure 4c and d, respectively, show the relative horizontal (x) and vertical (z) distances (that is, relative to the highest point of the wave crest; see Fig. 4b for the coordinate system) of the jet tip (defined as the point where the slope of the water surface relative to the horizontal changes sign) as a function of time (t). It should be mentioned that the jet tip as defined above is not necessarily a material point.



**Figure 3** Images of a surfactant-dominated breaking wave generated in a manner identical to the wave in Fig. 2. The breaker is highly repeatable and each image is from a different experimental run. The width of the images is 12.5 cm in the plane of the light sheet. The dynamic properties of the water free surface correspond to data set 4b. Note that the jet does not issue from the highest elevation of the wave as it would in a typical plunging breaker in clean water. **a**, The bulge forms with a weak toe and without capillary waves ahead of the toe. **b**, The jet forms. **c**, The jet follows a parabolic trajectory. **d**, The jet hits the front face of the wave, creating a secondary splash ahead of it.

**Figure 4** Geometrical properties of the jet. The surfactant conditions correspond to data set 4b. **a**, Crest profile history of a single breaking wave, such as the one shown in Fig. 3. The bottom curve is the first wave profile, and each successive profile is plotted 1.0 mm above the previous one for clarity. The time between each profile is 3.33 ms. b, A single wave profile and the trajectory of the tip of the jet. The broken line is a parabola fitted to the experimental data. **c**, **d**, Horizontal and vertical distances, respectively, of the tip of the jet relative to the highest point of the wave crest versus time. The unbroken lines in **d** are parabolas fitted to the data. The wave-maker motion parameters for the three waves shown are  $f_0 = 1.42 \text{ Hz}$  (open circles),  $f_0 = 1.26 \text{ Hz}$  (open diamonds),  $f_0 = 1.15 \text{ Hz}$  (open triangles), where  $f_0$  is the average wave-packet frequency<sup>13</sup>.

The jet position relative to the crest is nearly fixed for the first 0.03 s. The total jet length at impact ( $\sim$ 0.1 s later) is only  $\sim$ 1 cm, whereas the wavelength of the gravity wave is on the order of 1 m. The vertical trajectories (z versus t) are parabolic with an absolute acceleration (that is, relative to the laboratory reference frame) of  $6.4 \pm 0.8 \,\mathrm{m \, s^{-2}}$  in all of the waves. The discrepancy between this value and the acceleration of gravity might be due to temporal variations in jet tip shape induced by surface tension. At the instant of impact with the front face of the wave, the absolute vertical velocity of the jet tip is  $34.0 \pm 1.4$ ,  $25.1 \pm 2.5$  and  $18.9 \pm 3.2 \text{ cm s}^{-1}$  for the wave frequencies of 1.15, 1.26 and 1.42 Hz, respectively. By contrast, the relative horizontal velocity of the jet, which is constant while the vertical trajectory is parabolic, is  $10.7 \pm 1.1 \text{ cm s}^{-1}$  at all three frequencies. Numerical simulations of weak breaking events without surface tension<sup>23</sup> have also shown the appearance of a small plunging jet. In the calculations, however, the jet issues from the highest point on the wave.

The measurements indicate that the behaviour of the breaker depends on the various surface dynamic properties in a complex way. Comparison of the wave behaviour and surface properties between data sets 4a and 4b indicates that the appearance of the small plunging jet coincides with high surface viscosity and high static surface elasticity at high surface compression. The difference in either quantity between the two cases would produce a marked change in the distribution of stress in the surfactant film at the crest. The change in elasticity is expected to be important because high surface compression is known to occur at the crests of steep waves<sup>24,25</sup>. These effects are being explored further by carrying out similar experiments with other soluble surfactants.

### Methods

#### Water preparation

The procedures for water preparation are as follows. Before the measurements, the tank and piping system were cleaned with highly chlorinated tap water, rinsed and filled with roughly 14,0001 of filtered tap water. The chlorine concentration was increased to 10 p.p.m., and the water was skimmed and filtered for 2 d. Just before the experiments, the chlorine concentration was reduced to nearly zero by adding an appropriate amount of hydrogen peroxide. The fluorescent dye rhodamine 6G (95% purity) was then mixed with the water at a concentration of 0.5 p.p.m. for visualization purposes. Immediately after mixing the dye in the tank, a set of measurements of surface properties and breaker profiles were taken (data set CLEAN). After the measurements, the soluble surfactant SDS (99% purity) was added to the tank water and the measurements were repeated on the following day (data set 1). This procedure (adding SDS at the end of the day and taking measurements on the following day) was repeated three more times over the next 3 d to obtain three additional data sets, 2, 3 and 4a, corresponding to the three increasing SDS concentrations, respectively. At the highest SDS concentration, measurements were also taken 3 d after data set 4 (data set 4b).

It is important to realize that even with the above water treatment procedures, these experiments were not done with solutions of pure water and SDS. The dye and SDS probably contain other surfactants, the water is not distilled, and additional surfactants probably enter the tank by various paths. Also, once the chlorine concentration is reduced to nearly zero, which is done to preserve the dye and SDS, bacteria in the tank begin to grow. After they reach a critical concentration, they increase exponentially in number<sup>26</sup>. Bacteria are a type of plankton and are known to produce surface-active organic material as by-products of their respiration<sup>27</sup>. It is speculated that the change in surface properties between data sets 4a and 4b is due to these organic surfactants.

#### Surface property measurements

Surface property measurements were done with equipment and techniques that are similar to those used in bench-top experiments<sup>28–30</sup>. The measurement system is centred on an *in situ* Langmuir trough. The trough is essentially a set of Teflon barriers arranged in a rectangular shape (80 cm by 30 cm) that is lowered into the tank to the point where it isolates a small portion of the water surface with area  $A_0$ . One of 30-cm barriers can be moved parallel to the water surface by means of a servo-motor system, thus changing the enclosed area in the trough. The surface pressure isotherms are measured by monitoring the surface tension (measured with a Whilhelmy plate) while compressing the surface area (*A*) around the plate with the movable barrier over a period of about 2 min. Surface pressure is measured to an accuracy of  $\pm 0.2$  mN m<sup>-1</sup>.

The equilibrium (Gibbs) surface elasticity  $E_0$  and surface viscosity  $\mu_s$  were determined from measurements of the wavelength and decay rate of longitudinal (compressive) surface waves that were generated by oscillating the movable barrier at frequencies ranging from 0.2 to 1.5 Hz. The longitudinal waves were measured with a capillary propagation technique similar to the one described in refs 28–30. The standard errors in the measurements of  $E_0$  and  $\mu_s$  are  $\pm 1.06$  mN m<sup>-1</sup> and  $\pm 0.15$  mN s m<sup>-1</sup>. The measurements indicated that the effect of surfactant diffusion was negligible.

#### Wave profile measurements

Surface profile measurements were obtained from movies taken at 300 frames s<sup>-1</sup> with a high-speed black-and-white digital camera (Vision Research, Phantom VI). Each image consists of a 512-by-512 array of pixels with 256 grey levels. The images shown in Figs 2 and 3 were obtained in an identical manner but with the high-speed camera replaced by a high-resolution digital colour camera (Nikon D1x). The illumination for both sets of images consists of a light sheet from an Nd:YAG laser. The light sheet is 1 mm thick at the water surface and oriented vertically, along the centre plane of the tank. The cameras view the intersection of the light sheet and the water surface from the side looking down with an angle of about 5° from the horizontal. A long-pass colour filter was placed in front of the camera lens to prevent the laser light from entering the camera; the light source for the images was the glowing fluorescent dye in the light sheet. The camera and the illumination system were mounted on an instrument carriage that is driven by a servo-motor and controlled by the same computer that controls the wave-maker. The carriage was set to travel along the tank with the crest of the breaking wave so that the movies were taken in crest-fixed coordinates. More detailed descriptions of these techniques are given in ref. 13.

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