A method for removing surfactants from an air/water interface

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The study of heat, mass, and momentum transport across an air/water interface is an aspect of fluid mechanics where the presence of surfactant monolayers can play a significant role. Experimental studies of air/water transport typically require a method for cleaning the air/water interface so that it is free from any contaminating surfactant monolayer. This may be for the sake of running an experiment under clean surface conditions, or to clean the surface prior to deposition of a known surfactant. Herein a method is described for maintaining a clean air/water interface during conditions of finite air flow over the water surface. The unique aspect of this method is its ability to maintain clean surfaces while experiments are conducted. © *2008 American Institute of Physics.* [DOI: 10.1063/1.3053316]

I. INTRODUCTION

Transport processes that occur at an air/water interface, such as the transfer of heat, dissolved gases, and water vapor, are all important to the understanding of lakes, oceans, and rivers. These processes play a significant role in the overall balance of heat and water for the entire planet, and laboratory studies play an important role in their understanding. Most of these transport processes are affected in one way or another by the presence or absence of surfactant monolayers, and so laboratory studies of these processes are often conducted for situations where the interface is populated by a known concentration of a given surfactant, and/or for a condition where the surface is devoid of such monolayers. The latter condition is considerably more difficult to create and maintain since the air/water interface is notoriously prone to surfactant contamination even when extraordinary steps are taken to maintain laboratory cleanliness. Even for the case where surfactants are purposely introduced to an air/water interface, initially clean conditions are desired prior to surfactant deposition to prevent any deleterious effects caused by mixing the deposited monolayer with any adventitious monolayer.[1]

Many procedures have been developed over the years for maintaining a clean air/water interface. Surface scientists typically use a Langmuir trough apparatus to study monolayers wherein de-ionized water is often used. This de-ionized water is further cleaned by swiping the surface with the Teflon barriers that are used to compress monolayers. By sweeping over the entire surface with these barriers, any contaminant surfactant can be pushed over the trough edge, leaving a clean surface behind. This and other methods typically used to assure cleanliness in Langmuir trough facilities can be found in textbooks on the subject.[1,2]

Air/water transport studies require a range of facilities having characteristics significantly different from those utilized in a Langmuir trough. For example, these studies often use large volumes of water, the air and water side may be in motion, and large amplitude waves may be present. A range of methods have been developed to provide clean water surfaces for experiments of this type. These methods generally fall into one of the following categories: (i) bubble sparging wherein a bubble cloud is used to bring surfactants from the bulk toward the surface, (ii) surface swiping where a rod or laboratory wipe is used to push monolayers over the container edge, (iii) tank overflowing, and (iv) surface vacuuming where suction is used to directly aspirate surfactants from the interface.

The above approaches have been used either separately or in combination to create clean water surfaces in a variety of experimental studies of transport processes. Bubble sparging was perhaps first suggested for the preparation of clean surfaces in free surface hydrodynamics experiments by Scott,[3] who showed how the introduction of nitrogen gas through a porous glass membrane at the bottom of a water-filled cylinder could bring surfactants to the top of the column, whereupon they could be removed. This method enables the use of tap water, which is ultimately purified and can subsequently be used to create clean surfaces. Scott's approach was designed as a low cost way to create clean water that could then be transferred into another facility. However, in practice, this method has more often been implemented in the actual facility where the clean surface is needed; that is, the bubble sparging is done *in situ*.

Overflowing of the water surface can also be used to effect a clean surface. This was perhaps first employed by Röntgen[4] in 1892 in his overflowing weir, where he prepared clean water surfaces for the study of films. Saylor *et al.*[5,6] prepared clean water surfaces by first sparging the water with nitrogen gas while permitting a slight overflow so that surfactants brought to the surface were quickly removed. This procedure was followed by a swipe of the water surface using a clean glass rod. This procedure was used in their study of the statistics of the surface temperature field of water undergoing evaporation. In a study on the effect of surfactant monolayers on the formation of subsurface vortices formed from drop impacts, Saylor and Grizzard[7,8] used an overflow followed by swiping using a glass rod to ensure cleanliness. Conover and Saylor[9] utilized a laboratory tissue to swipe the water surface. This method can be especially useful if a large tissue is simply laid flat upon the entire surface to be cleaned (if possible) and then removed by pulling laterally, taking the entire water surface and any surface contaminants with the tissue. Judd *et al.*[10] studied the effect of an impinging gas jet on the surface temperature field of a water surface for clean and surfactant-covered surfaces and were able to clean the water surface by dry nitrogen sparging and tank overflow for a 1 h period while periodically swiping the water surface with a glass rod.

More relevant to the instrument described herein is the fourth category of methods described above where monolayers are removed by applying suction to the water surface. Such a process is described by Davies and Vose,[11] who enhanced the method by first sprinkling ignited talc onto the water surface and then removing the talc via suction through a capillary tube.[12] Asher and Pankow[13] removed surfactants in their study of carbon dioxide transport due to mechanically generated turbulence by vacuuming the water surface using a Pasteur pipette connected to a peristaltic pump. These authors also used helium bubble sparging, followed by surfactant removal using rayon lens paper. McKenna and McGillis[14] used a surface aspiration method to clean water surfaces when studying oxygen transport across an air/water interface due to oscillating grid-generated turbulence. Jähne *et al.*[15] used surface suction to skim surfactants from a circular wind/water tank to control the degree of surface contamination, and Zappa and co-workers[16,17] used surface vacuuming to clean air/water surfaces in their study on the effect of microscale wave breaking on air/water gas exchange.

In many laboratory studies of air/water transport processes, a flow of air is imposed over a nominally flat air/water interface to simulate wind flowing over a small lake, pond, or reservoir. The authors are currently engaged in such work, where experiments can be several hours in duration. Typical use of the surface cleaning methods described above involves surfactant removal at the beginning of the experiment, after which the actual experiment is conducted. However, even in very clean laboratory conditions, the existence of particles in the air having a multiplicity of origins will inevitably result in the deposition of enough surface active material to reform a contaminant monolayer. Hence, even if the above methods are used to create a clean water surface, these surfaces will become contaminated in a period of time, which, in our experience, is of the order of tens of minutes; other authors suggest this occurs in about 1 h.[1] Hence, a method is required, which provides *continuous* cleaning, thereby removing monolayers as they happen to form. In the presence of air flow, a laboratory tissue or wipe cannot be used for obvious reasons without shutting down the airflow, causing a range of problems. Bubble sparging could conceivably be continuously run during the course of an experiment, but the bubble sparging process would itself affect transport in a significant way, preventing one from simulating environmental conditions where bubbles do not play a role. The use of a vacuum aspirator that is manually swept across the whole surface of the water would not be acceptable, since the user handling the probe would interfere with the flow of air

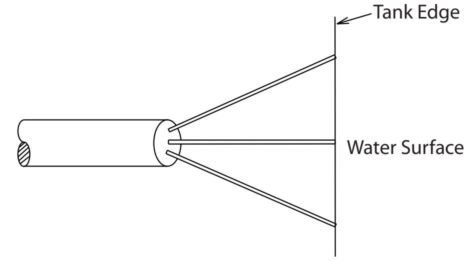

FIG. 1. The surfactant tube rake viewed from above, showing the three microbore tubes, connected to a larger diameter tube.

over the water surface. An overflowing weir of any type would continuously remove a significant quantity of water from the tank, which would result in problems due to the changing mass of the liquid undergoing transport. Of course this water could be returned to the tank, however, the return flow would serve to mix the water bulk. In studies of natural convection, or even forced convection, this mixing would affect the transport being studied, causing erroneous results. Moreover, the use of an overflowing weir could impose a significant water surface velocity, which could again affect the transport across the air/water interface.

Herein we describe a method that enables one to continuously maintain a clean water surface under finite wind speed conditions over a flat air/water interface using a modification of the vacuum aspiration method. Specifically, a rake of very small tubes is placed at the downstream edge of the tank, positioned in such a way that they remove only the very top portion of the air/water interface, and alternatively remove air and water at a high frequency, so that the actual interface is effectively removed. The method is tested in an air/water tunnel where the rake is located at the downstream edge of the water tank, thereby taking advantage of the tendency of the monolayers to be pushed by the wind toward the rake. The method provides a water surface, free from monolayers for an essentially unlimited period of time. In the sample experiments presented here, this method established a clean surface, while removing a quantity of water, small enough to avoid errors in the measurement of heat transfer rates.

II. EXPERIMENTAL

The heart of the instrument presented here is illustrated in Fig. 1, which shows the surfactant tube rake. This rake consists of three 0.38 mm inside diameter (ID) microbore tubes (Cole-Parmer solvent/hydrocarbon quality). These three microbore tubes were connected to a 1.5 mm ID tube using silicone sealant (GE RTV 118). All three capillary tubes were oriented in the same plane at an angle of 30° to each other. As shown in Fig. 2 the tube rake assembly was connected to a peristaltic pump (Cole-Parmer L/S economy analog pump) via 3.0 mm ID tubing. The peristaltic pump provided the suction needed to remove monolayers. One end of the pump was connected to the tube rake, while the other end delivered the aspirated water/surfactant mixture to a waste beaker. We note that while only three microbore tubes are illustrated in Fig. 1, more tubes can be included in the

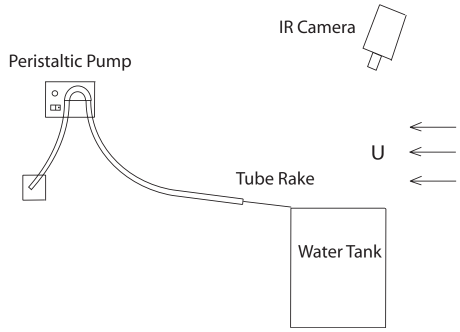

FIG. 2. Experimental facility used to test the surfactant tube rake shown in Fig. 1. The rake is located at the downstream end of the glass tank and at the air/water interface.

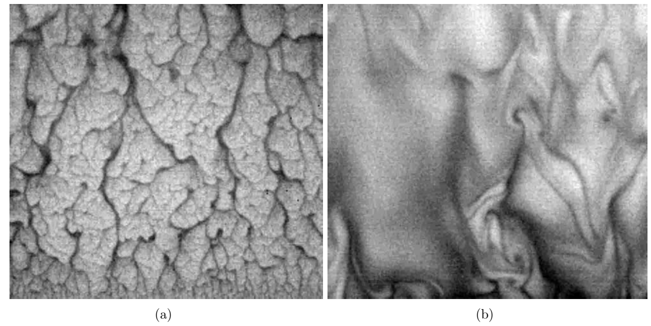

FIG. 4. IR images of a water surface at a wind speed $U=2$ m/s. (a) The water surface is free of surfactants. (b) The water surface is completely covered with a surfactant monolayer. In both images the heat flux leaving the tank is approximately 625 W/m^2. The flow of air is from the bottom of the image to the top.

rake to provide more rapid surfactant removal if so desired. In some of our works, we utilized as many as five tubes, but considerably more could be included.

Figure 2 shows a portion of the wind/water tunnel that was used to test the surfactant rake shown in Fig. 1. The rake was installed on the downstream side of the water tank, at the tunnel exit. Although not shown in Fig. 2, a Plexiglas wind tunnel is mounted on the water tank. A blower, motor, and motor controller at the entrance to the wind tunnel (also not shown) provide wind speeds ranging from $U=0-5$ m/s. A top view of the water tank and rake is presented in Fig. 3.

The goal of the surfactant rake system is to create a clean water surface under finite wind speed conditions. To demonstrate the efficacy of the rake in achieving this goal, an infrared (IR) camera was utilized to identify the existence of surfactant monolayers on the surface, thereby determining if they were effectively removed by the rake. Surfactant monolayers are easily visualized in IR imagery, as demonstrated by Saylor.[18] This is because the elasticity imparted on the water surface by surfactants reduces the small scale structure normally present in a turbulent flow. As long as there is a finite temperature difference between the air and the water, this reduction in small scale structure is seen in the surface temperature field, which is essentially what is recorded in an IR image of a water surface. Two sample IR images, both obtained at the same wind speed, are shown in Fig. 4, where Fig. 4(a) is for a clean water surface, and Fig. 4(b) has a surfactant monolayer on the surface. The difference in the degree of small scale structure is obvious. In Fig. 4 the images are either completely clean or completely surfactant covered. The qualitative difference between these two images is used later in this paper to identify surfactant-covered and surfactant-free regions existing simultaneously on the same surface. The camera used in this work was an Inframetrics Thermacam model SC 1000 focal plane array camera with a 255×239 pixel sensor sensitive to the 3.4–5 μm wavelength band.

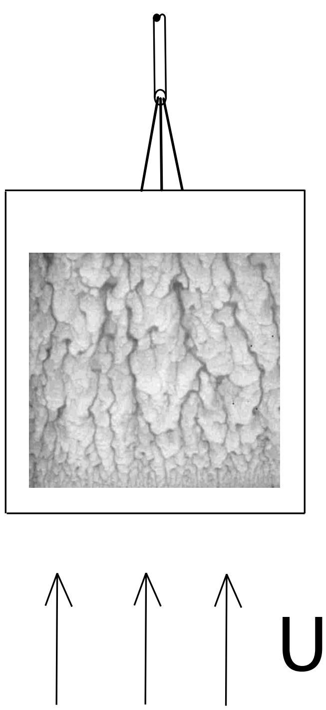

FIG. 3. Top view of the experimental facility showing the surfactant rake and the water tank. A sample IR image is superimposed on the surface of the water showing the region that was imaged.

To test the rake, the tank was filled with filtered tap water at a temperature of ~40 °C, the rake was positioned at the air/water interface, the peristaltic pump was turned on, and the blower was turned on and set to a fixed wind speed. Positioning of the surfactant rake was critical to the effective removal of surfactants. The open end of the capillary tubing was placed in such a way that air and water are alternately pulled into the tubing. When positioned properly a slight buzzing sound can be detected emanating from the tubes. When this buzzing sound is detected, neither pure water nor pure air is being aspirated but rather a rapidly alternating mixture of both. When in this position, as shown in the next section, surfactant monolayers are effectively removed from the water surface. The loss of water from the tank due to aspiration under these "buzzing" conditions ranged from 408–580 ml/h for the test runs conducted for this paper.

Here we investigated wind speeds ranging from 1 to 4 m/s. Surfactant cleaning was achieved in 8–10 min at 1 m/s and in 2–3 min at 4 m/s. These cleaning rates were obtained for experiments where some preliminary cleaning steps were first conducted, which included cleaning the water tank with methanol (spectrophotometric grade 99+% Sigma/Sigma-Aldrich), bubble sparging the water with nitrogen for 20–30

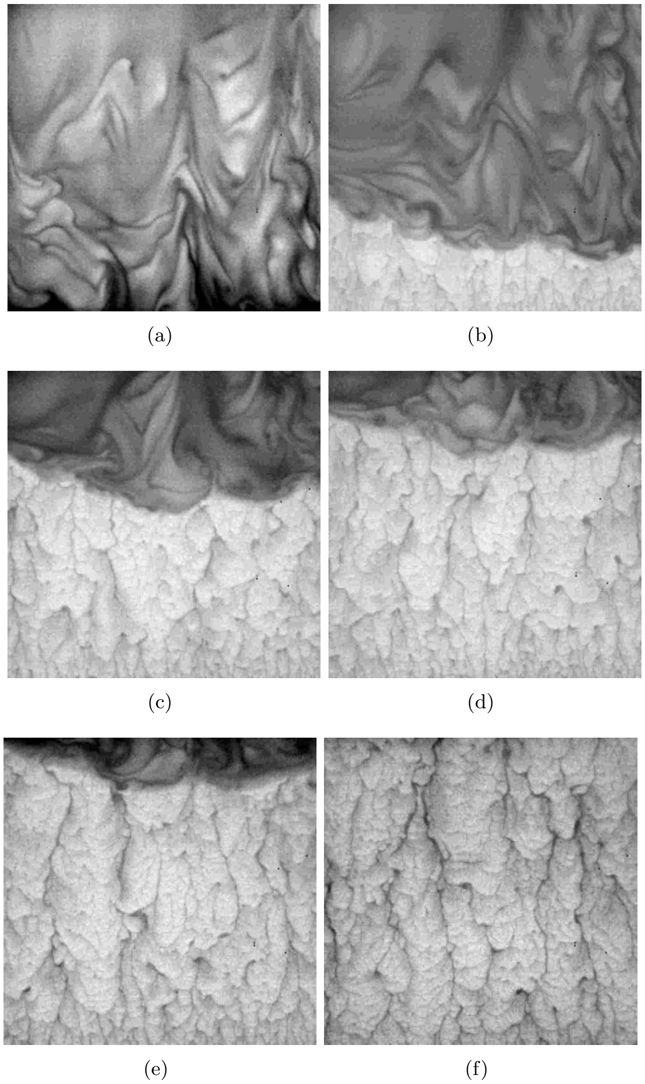

FIG. 5. IR imagery of the water surface during the cleaning process for a wind speed $U=3$ m/s. (a) Before cleaning. Time after initiation of cleaning: (b) $t=56$ s, (c) $t=117$ s, (d) $t=147$ s, (e) $t=165$ s, and (f) $t=325$ s.

min, and then swiping the water surface with a laboratory tissue. These procedures were not necessary, however, but only reduced the time needed to completely clean the water surface once the surfactant rake was applied.

In the experiments conducted here, the water tank was initially filled to the rim. As time passed, evaporation and water removal through the rake resulted in slight reductions in the water height. Accordingly, the rake was mounted on a vertical traverse, and the position of the rake was adjusted periodically to ensure that surfactants were being properly removed.

III. RESULTS AND DISCUSSION

Sample IR images are presented in Figs. 5(a)–5(f) showing the process of surfactant removal using the surfactant rake. The wind direction is from bottom to top in each of the IR images presented in Fig. 5. In these images, the grayscale convention is such that warm regions are bright and cool regions are dark. The location of the rake is not visible in the image as it is positioned just downstream of the imaged location, as shown in Fig. 3. Figure 5(a) was obtained before providing suction to the rake, and a contaminating monolayer is present over the entire surface. This monolayer is due to whatever surfactants are naturally present in the filtered tap water. In Fig. 5(b), suction has been provided to the rake for 56 s, and two distinct regions are seen in the image. The upstream region is a clean location characterized by significant small scale structure, while a surfactant-covered region exists downstream characterized by a dearth of small scale structures. These two regions are very similar to the clean and surfactant-covered sample images shown in Fig. 4. As noted above, Saylor[18] demonstrated that the change in the qualitative appearance between these two regions is indicative of a boundary between a clean and surfactant-covered region. This boundary is referred to as a Reynolds ridge,[19] and IR images of such Reynolds ridges have been obtained by Phongikaroon *et al.*[20] The two region structure is seen in Figs. 5(b)–5(e) as well.

In Fig. 5(f) there is only a clean surface, as all of the surfactant has been removed. Although not shown, subsequent images were all clean and could be maintained clean indefinitely. It is noted that, in Figs. 5(b)–5(e), the surfactant-covered region is closest to the rake despite the fact that the rake is removing surfactant. This is because the wind is continuously pushing any existing monolayers toward the rake, i.e., the downstream location. The images presented in Fig. 5 are for a wind speed of 3 m/s. The qualitative progression of the structures appears similarly at different wind speeds, although the amount of time required for cleaning decreases with wind speed. It is noted that the clean surface seen in Fig. 5(f) is maintained only as long as suction is applied to the rake. Without suction, contaminating surfactants, presumably from the air or water, accrue on the surface, resulting in a growing monolayer.

The instrument presented herein is used by the authors in investigations of heat transfer across air/water interfaces, among other things. In this specific application, a tank filled with warm water is allowed to cool down and the heat transfer rate is measured according to the equation

$$q = \rho c_p V \frac{dT}{dt}, \tag{1}$$

where q is the heat transfer rate from the water to the air, ρ and c_p are the density and specific heat of water, respectively, V is the water volume, T is the temperature of the water bulk, and t is time. This method relies on a known volume of water in the tank. As noted in the previous section, for the conditions investigated here, the surfactant rake removed water from the tank at a rate of 408–580 ml/h. If not accounted for, the heat flux error caused by this loss of water would range from 1.5% to 2.2% (the tank volume in these experiments was 27 l). This is not a large error, and of course by correcting for the loss it can be eliminated.

As noted above, a strength of the present method is that the quantity of liquid removed is small, and therefore, a return of this liquid to the bulk can be avoided without significant errors. It is noted that there may be experiments where having a return flow would not affect the results in a deleterious way and hence an overflowing weir method might work well. However, even for this case, the rake method presented here would perform better than an overflowing weir method for the following reason. For an overflowing weir, the layer of liquid, which overflows the tank edge, must be sufficiently thick to overcome the surface tension force of the meniscus. Hence, the overflow velocity and flow rate may be large. This will result in a significant surface velocity at the water surface. This is not the case with the rake method presented here, since the surface tension force is overcome by the suction force provided to the rake. This force can be large enough to overcome the surface tension force of water while simultaneously removing a small amount of liquid by positioning the rake so that it pulls intermittent slugs of liquid and gas (at high frequency).

The effect of surfactants on waves is a topic of significant interest. As noted in Sec. I, the method presented here was developed for a flat air/water interface. However it is possible that the method presented here could be used in a study of water waves if the tube rake is positioned within the oscillation range of the wavy surface. In this situation, the rake would cross the air/water interface twice for every wave period. Presumably, some quantity of surfactant would be removed during each of these crossing events. Whether this would remove enough surfactant to maintain a clean surface is left as future work. It is also possible that too much of the water bulk might be removed in such a wavy implementation, and this issue would have to be dealt with as well.

In addition to the application for which the present method was tested, it may find applicability in several other areas of free surface hydrodynamics. Namely, it will be of use in any free surface hydrodynamics experiment where a clean surface is desired and there is finite wind speed. Some examples include the study of submerged jets, where the surface signature (e.g., the IR signature) is significantly affected by the presence or absence of a surfactant monolayer and there is a need to clean the water surface to determine the behavior for both the clean and surfactant-covered cases, and the study of drop impacts on water surfaces, where the impact phenomena, which are observed (bubble formation, drop splashes, etc.) are affected by the presence of absence of a monolayer; and channel flows, where transport is again affected by the surface conditions, clean or surfactant covered.

ACKNOWLEDGMENTS

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