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The effect of soluble surfactants on liquid film flow

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Abstract. We investigate experimentally the modifications in the dynamics of liquid film flow, resulting from the addition in water of the soluble surfactants iso-propanol (IP) and Sodium Dodecyl Sulfate (SDS). Recent experiments indicate that, the primary instability of film flow in channels of finite width depends on surface tension. Using IP solutions of varying concentrations, we have shown that this dependence scales with Kapitza number. Based on the high solubility and diffusivity of iso-propanol in water, we argue that these solutions behave as pure liquids with reduced surface tension. Indeed, low-frequency inlet disturbances turn in the unstable regime into solitary humps preceded by capillary ripples, with the scaling predicted by theory for simple liquids. Aqueous solutions of SDS exhibit a remarkably different behavior, with more pronounced feature of strong damping of all inlet disturbances. The dominant structures for the entire range of inlet frequencies tested, even at surprisingly high Re, are sinusoidal traveling waves of very small amplitude.

1. Introduction

Falling liquid thin film have been studied for many years, due to their appearance in a large number of industrial systems, and environmental and biological flows. The effect of surfactants on the stability and on the flow characteristics of falling thin liquid films is also of interest, both because of industrial considerations and because understanding these effects can provide some information about the physical chemistry of interfaces.

Observations of a calming effect of surfactants (in particular oils) on free surface flows date back to historic times. In particular, there are several theoretical studies of the hydrodynamic stability of falling liquid films [1–5] indicating that surfactants can be very effective in retarding, if not completely suppressing the onset of waves. At this point though, we should mention that there are studies concluding that surface instabilities can be enhanced by assuming a soluble and volatile surfactant [6–8]. Nevertheless, we consider that the general effect of surfactants is the strong damping.

A general review of the literature regarding the effect of surfactant is presented by Lenewait *et al.* [9]. They refer to some pioneering experimental studies [10; 11] that had described the damping of surface waves on thin liquid, falling films and also to some theoretical approximations [3–5; 12]. The damping effect was treated independently by Whitaker [3] and Benjamin [12]. In order to clarify the mechanism of damping, Whitaker, by treating the surface as a two dimensional Newtonian fluid, examined the role of surface tension, surface viscosity and surface elasticity in stabilizing falling liquid films for low Reynolds numbers. The first two parameters despite the fact that they decrease the growth rates of infinitesimal disturbances are not capable of stabilizing a film. Surface elasticity gives a rise to the critical Reynolds number, below

which the flow is stable to all small disturbances. Benjamin developed a model assuming that the monomolecular layer as two-dimensional viscoelastic and insoluble fluid and he found an analytical solution of the Orr-Sommerfeld equation for long waves, i.e., small wavenumbers. Whitaker [4] continued his numerical study concerning the stability problem for soluble and insoluble surface active agents in terms of a perturbation solution of the Orr-Sommerfeld equation, without having the restriction of long waves like Benjamin. His conclusion was that the numerical [3] and the analytical solution [4] are in good agreement. Surprisingly, the analytical results for insoluble monolayers from both of [12] and [4] do not show any important difference despite the fact that their theoretical concepts are different. Anshus and Acrivos [5] using an asymptotic analysis based on the assumption of a large surface elasticity parameter (which is caused by large concentrations of surfactant), arrived at two main conclusions: first, the bifurcation Reynolds number which is obtained via a small wave number perturbation solution is indeed the critical Reynolds number for the system and second, the presence of surfactants results in a large decrease in the growth rate and a large increase in the wave length of the most rapidly amplified disturbance.

The most important result of the aforementioned studies regarding the effect of surfactants, and mainly the damping effect is that principally, surface elasticity can eliminate entirely surface waves. It owes its existence to the variation of surface tension with surface concentration, and the latter may be essentially constant if the surface equilibrates rapidly with the bulk fluid. Surface viscosity and surface diffusion are insufficient to produce a stable surface.

Except of the stability, another interesting aspect is the effect of surfactants on the characteristics of falling liquid films in the unstable regime. Strobel and Whitaker [13] have studied experimentally the values of the wave length and wave velocity for dilute solutions of valeric and hexanoic acid for a vertical film for comparison with stability theory. They observed two interesting phenomena. The first of these was the point at which waves were first observed as a strong function of the surfactant concentration and the Reynolds number. By increasing concentration of some aliphatic acids, the distance from the top of the film to the point at which waves first appear increases. The second interesting phenomenon that they observed is the behavior of the surface velocity. The surface velocity was decreased for increased surfactant concentration and the explanation for this anomaly is that the free surface velocity is greatly retarded by the adsorption of the surface active agents.

Cero and Whitaker [14] have studied experimentally and theoretically the hydrodynamic development of thin vertical liquid films under the presence of surfactants. The surface velocity profile is strongly dependent on the surface elasticity but only mildly affected by the diffusivity of the surfactant, the equilibrium relation, and the kinetics of interfacial mass transport.

In this experimental study, we present preliminary results on the effect of soluble surface active agents on inclined liquid film flow. Our goal is to determine the critical Reynolds number of the primary instability, as well as the characteristics of the traveling waves in the unstable regime. Isopropanol aqueous solutions (IP) and SDS (Sodium Dodecyl Sulfate) surfactant solutions at various concentrations are used as surface active agents. An interesting finding is that the two agents exert a strikingly different influence on the flow. The difference is attributed to the effect of surface elasticity, which is absent with the former and present with the latter surface active agent.

2. Experimental Method

Experiments were performed in two inclined flow facilities, a 3000 mm long by 450 mm wide channel and a 800 mm long by 250 mm wide channel made of Plexiglas. Both facilities may operate with adjustable width up to the above maximum values. The experimental method used is electrical conductivity by local probes that detect temporal evolution of film thickness as described in detail by Vlachogiannis *et al.* [15]. At the inlet of the channel, a perturbation at

desired frequency is created, in the range of 0.15-1.5 Hz. A system of perturbing the entrance flow rate at desired frequency is used, based on the periodic obstruction of a by-pass liquid stream. The liquids used are Isopropanol aqueous solutions (IP) and SDS (Sodium Dodecyl Sulfate) surfactant solutions. Surface tension is measured by maximum bubble pressure, and ring method several times during an experiment to ensure that it does not change.

3. Results

Both IP and SDS are soluble surfactants. However, apart from reducing surface tension, surfactants modify the surface properties. Differences in the behavior of those surface active agents (IP is an alcohol and SDS is an anionic surfactant), that will be observed in detail at the following subsections, are interpreted in terms of surface properties, by introducing surface elasticity and surface viscosity expressed respectively as the real and imaginary component of a complex surface dilatational modulus (Lucassen-Reynders and Lucassen [16] and Lucassen [17]). The two modifications, i.e., reduction in surface tension and introduction of surface elasticity are expected to have a competing effect on interfacial disturbances, the former aggravating and the latter damping them. The addition of Isopropanol in water is expected to reduce surface tension without significant surface elasticity or viscosity, and the solution practically behaves as a pure liquid with lower surface tension. As argued by Lucassen-Reynders [16] and Lucassen [17], this behavior is a result of the considerable solubility of alcohol in water, which - in combination with the low viscosity, i.e. high diffusivity, of the aqueous solution - permits fast diffusional interchange between the surface and the bulk. Thus, surface tension gradients that would attribute visco-elastic properties to the surface are completely short-circuited, at least for the range of wave frequencies enforced in the present work.

3.1. Isopropanol Aqueous Solutions

Recent experimental findings [18] indicate an unexpected effect of the transverse dimension in channels of finite width, which renders the primary, long-wave, instability a function of surface tension. Data are correlated by the Kapitza number $Ka = \sigma/\rho g^{1/3}\nu^{4/3}$, which represents the ratio of capillary to viscous stresses; σ , ρ , ν and g , are respectively, the surface tension, density, kinematic viscosity of the fluid, and the gravitational acceleration. For example, figure 1 shows the variation with Ka of the experimentally observed critical Re (normalized with the classical prediction, $Re_{crit} = 5/6 \cot\theta$) for a channel 250 mm wide. Of particular interest to the present study is that the data for different IP solutions (2.5-70 % w.t) fall on the same curve with the core data, which are produced by changing Ka through variation of the liquid viscosity by adding in water various concentrations of glycerol. Thus, the addition of IP appears to have no other dynamic effect on the free surface, apart from reducing its surface tension.

The behavior of IP solutions as simple liquids, characterized only by their surface tension, is further reinforced from observations of the traveling waves formed beyond the instability threshold. Indeed, looking at the time-signals in the right column of figure 2 (to be discussed below), it becomes evident that low-frequency, unstable disturbances evolve into solitary humps with well-defined precursor ripples. It is recalled that surface tension determines the characteristics of the solitary waves, developing on the free surface of simple liquids, by balancing the gravity-induced inertia of the liquid humps with the capillary force that arises from the wrinkling of the surface into a series of precursor ripples [19]. These ripples generate sufficient capillary pressure to drain fluid out from the crest, and in this way stabilize the solitary humps [20].

Figure 2 contains time-signals, resulting from imposition of a low-frequency (0.16 Hz) inlet disturbance on the flow of pure water (left column) and IP solution (right column). The flow rates are normalized in terms of the reduced Reynolds number, δ , which is defined as $\delta = Re^{11/9}5Ka^{1/3}3^{7/9}$, and introduces the destabilizing and dispersive effects of inertia at

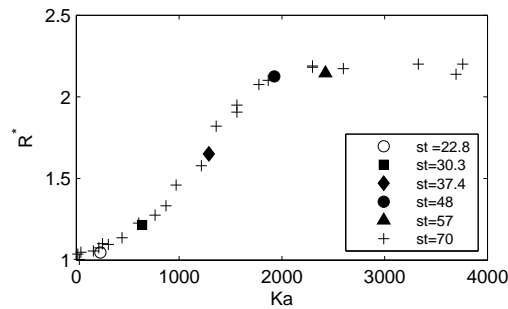


Figure 1. Normalized $Re R^*$ as a function of Ka for several fluids. Surface tension is in mN/m and the value of $70 mN/m$ corresponds to glycerol solutions of various concentrations. Channel inclination for all the data is $\theta = 3^\circ$

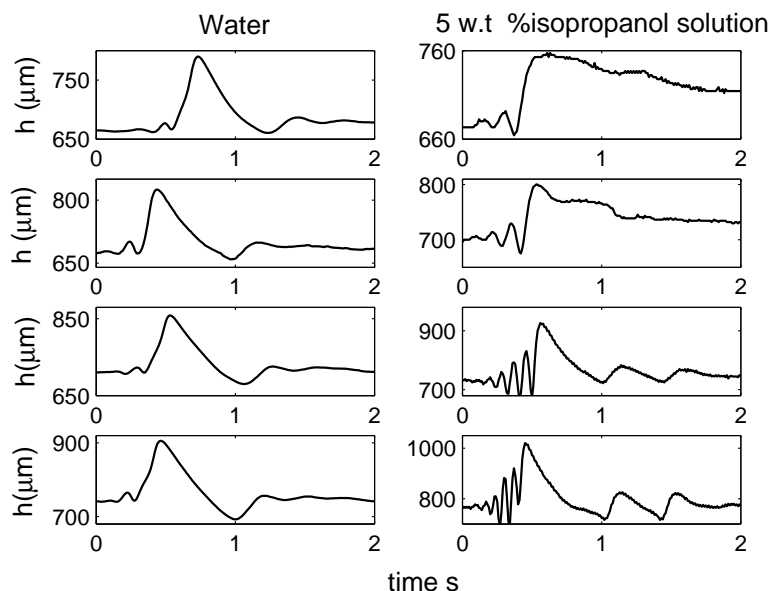


Figure 2. Comparison at same δ between water (first column) and 5% w.t IP solution (second column). The corresponding δ for each line is 18, 20, 25, 28

higher flow rates [21]. A comparison of the left and right column in figure 2, indicates that capillary ripples are higher and better formed in the IP solutions, as compared to plain water, although the former has a lower surface tension than the latter (48 mN/m versus nominally 70 mN/m). This is attributed to the well-known anomalous behavior of water [8], caused by erratic surface absorption of various impurities and leading to irreproducible results. Because of the above, the properties of capillary ripples are more reliably determined from the IP solutions, and this is a side-benefit of the present work. A characteristic size of the ripples observed for various isopropanol solutions may be defined according to figure 3, and this size correlates very satisfactorily with δ for a wide range of Ka , as indicated in figure 4. Ka 2424 refers to 2.5% w.t IP while 1929, 1962 and 235 correspond to 5, 15 and 70% w.t respectively. Thus, at the same Re , higher values of Ka lead to more pronounced ripples. An increase in Ka may result either from raising the surface tension or from lowering the viscosity.

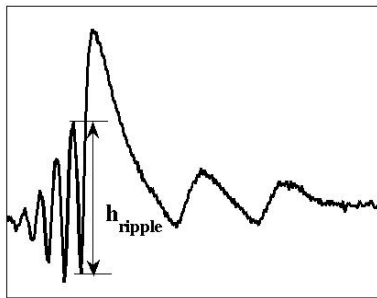


Figure 3. Definition of the size of the ripples as h_{ripple} .

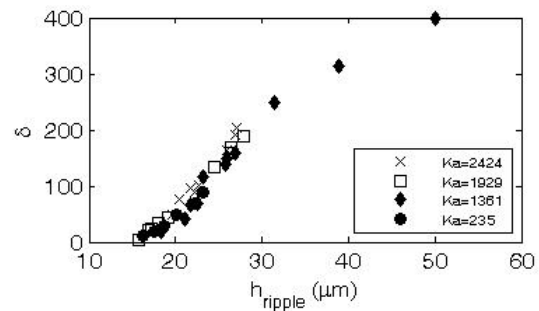


Figure 4. h_{ripple} as a function of δ for various IP solutions.

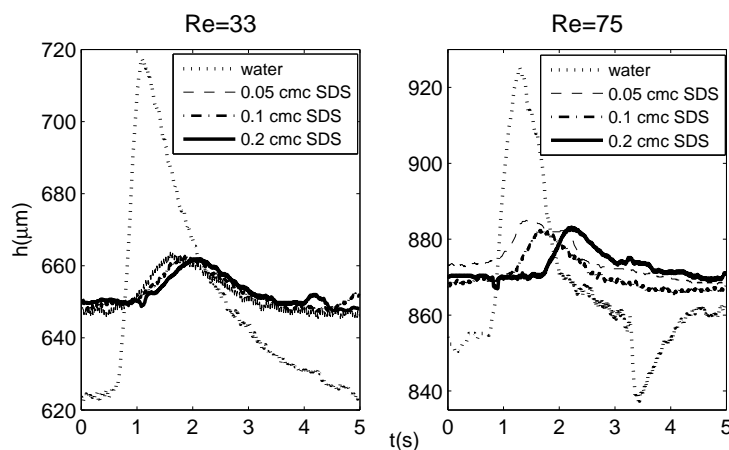


Figure 5. Time series of liquid film height for water, 0.05, 0.1, 0.2 CMC SDS solution at Reynolds numbers 33 and 75. Channel inclination is $\theta = 2^\circ$ and inlet disturbances have frequency $f=0.167$ Hz. In all subsequent plots, we represent by dotted line water signals, by dashdot, dashed and solid lines 0.05, 0.1, 0.2 CMC SDS solutions respectively.

3.2. SDS Aqueous Solutions

Experiments were conducted at SDS surfactant concentrations 0.05, 0.1 and 0.2 of the critical micelle concentration (CMC). The CMC of SDS surfactant was determined experimentally by Duangprasert *et al.* [22] as 2.75 g/L, from measurements of electrical conductivity and surface tension. We have also confirmed this value by measuring the variation in surface tension with increasing SDS concentration. A first observation refers to the very drastic attenuation of inlet disturbances for all tested solutions of SDS. Relevant results are shown in figure 5, where time-signals for pure water and SDS solutions are recorded at a location just 50 mm downstream of the film entrance. It is noted that, in all cases shown, the periodic change in flow rate imposed by the by-pass electro-valve is the same, i.e. the different patterns of film thickness variation correspond to different accommodations by the liquids of the same changes in flow rate. This behavior is evidently related to modifications in the establishment of the flow caused by the surfactant, which were attributed to surface elasticity by Cerro & Whittaker [14].

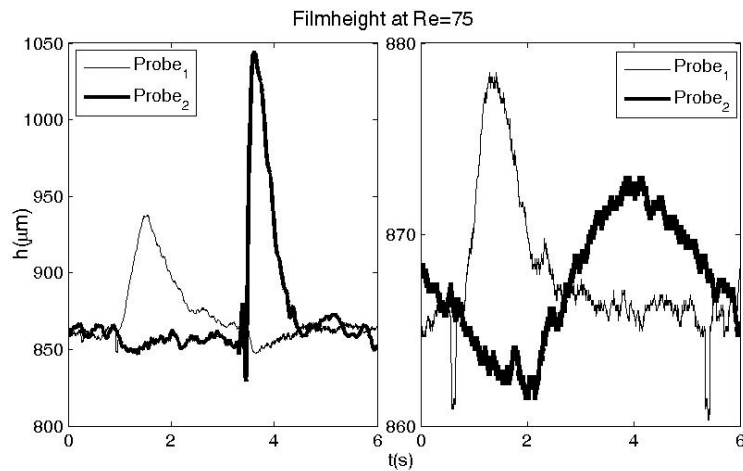


Figure 6. Time series of liquid film height for water and 0.05 CMC SDS solution at Reynolds numbers 75. *Probe₁* and *Probe₂* are located 50 and 550 mm from the film entrance. Channel inclination is $\theta = 2^\circ$ and inlet disturbances have frequency $f=0.167$ Hz. In both plots, the thin lines represent the upstream and thick lines the downstream signal. Note the large difference in scales between the two plots

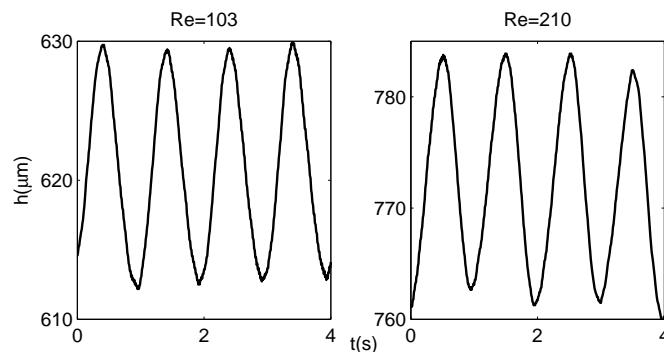


Figure 7. Examples of sinusoidal travelling waves at 7 degrees inclination angle recorded 550 mm from the film entrance, perturbation frequency $f=1$ Hz and surfactant concentration 0.1 CMC

As a consequence of the above, downstream evolution of the disturbances in pure water and in SDS solutions is strikingly different. Representative time-signals are shown in figure 6, taken at distances 50 mm and 550 mm from the film entrance, and corresponding to a fairly large value of Re . In the case of pure water, disturbances grow in size, and at the same time steepen and develop front-running ripples. This is the typical evolution towards formation of solitary waves. On the contrary, in the case of the solution, with SDS concentration equal to 0.05 CMC, disturbances decline and become smoother, approaching a sinusoidal shape. Incidentally, we note that the downstream signal is rather noisy, because the height of the disturbance is already very low. This provides also an indication of the accuracy of the measuring technique.

The development of the flow towards sinusoidal waves of very small amplitude, irrespective of the inlet disturbance frequency, is a general trend confirmed for all SDS solutions. Indeed,

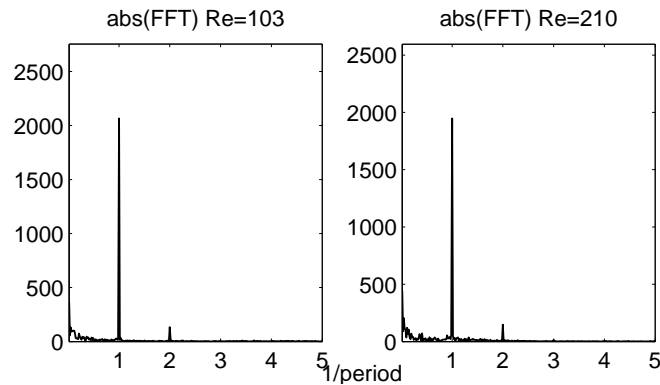


Figure 8. FFT of the corresponding signals of figure 7

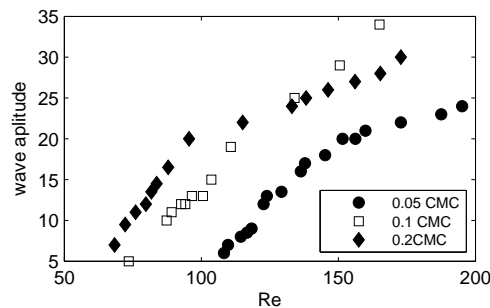


Figure 9. The amplitude of the waves measured in μm for surfactant concentrations 0.05, 0.1, 0.2 cmc at 7 degrees with perturbation frequency $f=1$ hz 550 mm from the film entrance

we have not observed steepening of inlet disturbances and formation of ripples even at the highest Re tested. Relevant results are shown in figure 7 (time-signal) and 8 (Fast Fourier Transform). A nearly monochromatic wave pattern is observed for all cases recorded in the figure. This behavior is tentatively attributed to the effect of surface elasticity, and is presently under intense investigation. It is hoped that future modeling will provide a way of relating observed wave characteristics to the visco-elastic properties of the free surface.

Finally, in an effort to determine the primary instability of the film with surfactant solution, we investigate the effect of Re on the amplitude of the traveling waves, as recorded at the downstream location of our small channel. Such results are presented in figure 9, and provide a first indication that the primary threshold may be determined, and that it probably lies at much higher Re than predicted by the classical result, valid for Newtonian liquids and long-wave disturbances. The dependence between the wave amplitude, the downstream distance, the perturbation frequency and the surfactant concentration is being investigated.

4. Summary

We examine the modifications in the dynamics of liquid film flow, resulting from the addition in water of the soluble surfactants iso-propanol (IP) and Sodium Dodecyl Sulfate (SDS). Results for IP are correlated taking into account only the reduction in surface tension, i.e. the system behaves as a simple liquid. Desired side-benefit is the clearer formation of precursor ripples, which are shown to scale with the reduced Reynolds number δ . Aqueous solutions of SDS exhibit a remarkably different behaviour, with more pronounced feature the strong damping of all inlet disturbances. The dominant structures for the entire range of inlet frequencies tested, even at

surprisingly high Re , are sinusoidal travelling waves of very small amplitude. We are presently conducting experiments in the large flow facility, in order to test if these small amplitudes correspond to stationary conditions or evolve further. We are also testing more systematically the variation of wave properties with inlet frequency, in order to identify potential resonance interactions caused by the elasticity of the free surface.

Acknowledgments

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References

- [1] Yih C S 1963 *Phys. Fluids* **6** 321
- [2] Lin S P 1967 *Phys. Fluids* **10** 308–313
- [3] Whitaker S 1964 *Ind. Eng. Chem. Fund.* **3** 132–142
- [4] Whitaker S and Jones L O 1966 *AIChE J.* **12** 421–431
- [5] Anshus B E and Acrivos A 1967 *Chem. Eng. Sci.* **22** 389–393
- [6] Ji W and Setterwall J 1994 *J. Fluid Mech.* **278** 297
- [7] Kim K J, Berman N S and Wood B 1996 *Int. J. Refrig.* **19** 322
- [8] Nordgren M and Setterwall F 1996 *Int. J. Refrig.* **19** 310
- [9] Leneweit G, Roesner K G and Koehler R 2003 *J. Colloid Interface Sci.* **260** 349–360
- [10] Emmert E E and Pigford R L 1954 *chem. Eng. Prog.* **80** 87–93
- [11] Tailby S R and Portalski S 1961 *Trans. Inst. Chem.* **39** 328–336
- [12] Benjamin T B 1964 *Arch. Mech. Stos.* **16** 615
- [13] Strobell W J and Whitaker S 1969 *AIChE J.* **15** 527–532
- [14] Cerro R L and Whitaker S 1971 *J. Colloid Interface Sci.* **37** 33–51
- [15] Vlachogiannis M, Samandas A, Leontidis V and Bontozoglou V 2010 *Phys. Fluids* **22** 012106
- [16] Lucassen Reynders E and Lucassen J 1969 *Adv. in Colloid and Interface Sci.* **2** 347–395
- [17] Lucassen J 1982 *J. Colloid Interface. Sci.* **85** 52–58
- [18] Georgantaki A, Vatteville J, Vlachogiannis M and Bontozoglou V 2011 *Phys. Rev. E* **84** 026325
- [19] Chang H and Demekhin E A 2002 (Elsevier, Amsterdam)
- [20] Vlachogiannis M and Bontozoglou V 2001 *J. Fluid Mech.* **435** 191
- [21] Chang H C 1994 *Annu. Rev. Fluid Mech.* **26** 103–136
- [22] Dusngprasert T, Sirivat A, Siemanond K and Wiles J O 2007 *Exp. Therm. and Fluid Sci.* **32** 808–817