Slip on three-dimensional surfactant-contaminated superhydrophobic gratings

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Trace amounts of surfactants have been shown to critically prevent the drag reduction of superhydrophobic surfaces (SHSs), yet predictive models including their effects in realistic geometries are still lacking. We derive theoretical predictions for the velocity and resulting slip of a laminar fluid flow over three-dimensional SHS gratings contaminated with surfactant, which allow for the first direct comparison with experiments. The results are in good agreement with our numerical simulations and with measurements of the slip in microfluidic channels lined with SHSs, which we obtain via confocal microscopy and micro-particle image velocimetry. Our model enables the estimation of a priori unknown parameters of surfactants naturally present in applications, highlighting its relevance for microfluidic technologies.

Superhydrophobic surfaces (SHSs) have the potential to yield enormous technological benefits in fields such as maritime transportation or pipeline hydraulics, primarily due to their ability to reduce fluid drag [1]. Through a combination of hydrophobic chemistry and microscopic surface patterning, these substrates are able to retain a superficial layer of air, thereby producing an apparent slip when in contact with a liquid flow [2]. Early theoretical work [3–5] modeled the air pockets trapped within these textures as flat boundaries with no shear, predicting large drag reductions in the laminar regime. Although initial studies reported promising levels of drag reduction [6–9], subsequent experiments found a reduced or even non-existent slip [10–12], pointing at the interfacial stresses induced by surface-active contaminants as one possible cause of this discrepancy.

Recently, independent experimental studies have reported time-dependent and nonlinear dynamics that unequivocally demonstrate the importance of surfactant-induced stresses on SHSs [13–15]. Theoretical and computational works have then confirmed the extent to which trace amounts of these surfactant contaminants can influence liquid slip [15–17]. Indeed, ambient levels of surfactants, often extremely difficult to avoid or control in common experimental settings, are known to play a central role altering the behavior of numerous small-scale multiphase flows [18].

Even though the underlying physical mechanism behind the increase of drag induced by surfactant is clear, modelling it in the case of realistic SHSs textures is challenging. In addition to the four partial differential equations governing the coupled physics and the six associated dimensionless numbers [19], there is a major difficulty stemming from the geometry of the problem and the alternating boundary conditions at the SHS boundaries. The concentration gradients that induce interfacial Marangoni stresses appear in the streamwise direction, owing to stagnation points at the downstream ends of the interfaces where surfactants advected by the flow can accumulate. Initial theoretical studies only considered two-dimensional flows over transverse SHS gratings, since this is the simplest geometry to capture the negative effect of streamwise surfactant-induced Marangoni stresses [16, 17]. However, these models cannot capture any three-dimensional effect. Here, we consider three-dimensional parallel gratings oriented in a longitudinal fashion, since this geometry yields higher slip [5, 20]. In contrast with most studies which assume infinitely long gratings without stagnation points, we consider long but finite gratings, such that surfactant can accumulate at the downstream end of each grating, as it occurs in reality. This realistic geometry necessarily involves a three-dimensional flow field coupled with the surfactant transport in the bulk and at the interface. Such complex nonlinear coupled problem constitutes a formidable challenge for analytical progress, explaining why previous theoretical studies only considered two-dimensional geometries.

In this paper, we introduce an asymptotic theory that accounts for the three-dimensional nature of the flow in the case of finite longitudinal gratings. We consider the general case of an interfacial stress varying in the streamwise direction along each plastron. Then, assuming a surfactant-induced shear along the plastron, we model the interfacial stress by a Marangoni shear stress obtained from scaling analysis. We compare our theoretical predictions for the slip velocity and slip length with experimental measurements of the flow in microchannels lined with SHSs in which no surfactants are artificially added. This constitutes the first direct realistic comparison between a three-dimensional theory inclusive of surfactant, experiments and simulations. The comparison shows a good agreement across several orders of magnitude of the slip velocity. Our theory provides an essential and simple theoretical tool for the estimation or the prediction of slip in realistic microfluidic applications with SHSs. It also enables to estimate some a priori unknown physicochemical parameters of the surfactant, which are naturally present in our microfluidic devices. Given the inevitability of surfactants both in nature and artificial settings [18] and the growing evidence of
surface-active molecules being naturally leached by polymers widely used in microfabrication [21–24], we expect these results to have a broad impact not only in specific applications like drag reduction or micro-cooling, but also throughout lab-on-a-chip technologies.

The derivation of our theory starts by considering steady, laminar flow driven by a mean pressure gradient $\hat{G}$ across a channel of half-height $\hat{h}$ [19]. The bottom of the channel is lined with a pattern of slender, parallel rectangular gratings. Each of these gratings supports a gas-liquid interface that we assume remains flat and flush with the channel floor. Due to the periodicity of the array in the streamwise and spanwise directions, we focus on a unit cell consisting of one grating and its surrounding ridges, as depicted in Figure 1a. The streamwise, wall-normal, and spanwise directions are denoted by $\hat{x}$, $\hat{y}$ and $\hat{z}$, respectively, with the coordinate origin at the center of the unit cell. Note that throughout the analysis we use hats to designate dimensional quantities, while dimensionless ones are without hats.

We leverage the disparity of scales between the length $\hat{L}$ and the half-height $\hat{h}$ of the unit cell (see Figure 1a), and define a small parameter $\varepsilon = \hat{h}/\hat{L} \ll 1$. Unlike in the typical Héle-Shaw flow approximation [25], here we do not assume that the spanwise length scale (the pitch $\hat{P}$) is also much larger than $\hat{h}$, since in microfluidic applications with longitudinal gratings the values of both $\hat{h}$ and $\hat{P}$ lie in the order of tens of micrometers, with $\hat{L}$ typically ranging in the millimeter or centimeter scale [6, 7, 11, 26]. Consequently, we define the nondimensional coordinates $x = \hat{x}/\hat{L}$, $y = \hat{y}/(\varepsilon \hat{L})$ and $z = \hat{z}/(\varepsilon \hat{L})$. It then follows from the incompressibility condition $\nabla \cdot \hat{u} = 0$ that the flow is approximately unidirectional, with the dominant streamwise velocity component scaling as $\hat{u} \sim \hat{U}$, whereas the wall-normal and spanwise components scale as $\hat{v} \sim \varepsilon \hat{U}$ and $\hat{w} \sim \varepsilon \hat{U}$, respectively. The velocity scale $\hat{U}$ of the flow is defined from the imposed mean pressure gradient as $\hat{U} = \hat{h}^2 \hat{G}/\mu$, with $\mu$ the dynamic viscosity of the fluid. At leading order in $\varepsilon$, the Stokes equations describing the flow simplify to $\partial_y u + \partial_z u = \partial_x p$ and $\partial_y p = \partial_z p = 0$, where $u(x, y, z) = \hat{u}/\hat{U}$ and $p(x) = \hat{p}/(\hat{G} \hat{L})$ are the dimensionless streamwise velocity and pressure [19]. The unidirectional nature of this leading-order flow is only a good approximation far from the downstream and upstream edges of the plastron, specifically, in regions where $|x \pm \phi_s/2| \gg \varepsilon$, with $\phi_s$ the streamwise gas fraction as shown in Fig. 1a. Therefore, the asymptotic expansion in $\varepsilon$ is singular, as is typically found in the thin-gap approximation [27]. Since we consider slender gratings with $\varepsilon \ll 1$, the regions of validity represent most of the domain and useful approximations of both local and integrated flow quantities can be obtained.

We then impose boundary conditions, with first no-slip boundary conditions $u = 0$ at solid walls and ridges. Additionally, the surfactant-laden interface imposes a tangential Marangoni shear stress $\hat{\gamma}_{Ma}$ on the fluid that is determined by the local gradient of surfactant, which is in turn coupled to the flow through a transport equation. It can be shown from the full boundary condition that, under mild assumptions [19], this stress is only dependent on $x$ at leading order in $\varepsilon$, and thus we take the remaining nondimensional boundary condition at the air–water interface as $\partial_z u|_I = \gamma_{Ma}(x)$, with $\gamma_{Ma}(x) = \hat{\gamma}_{Ma}/(\hat{U}/\varepsilon \hat{L})$ and where the subindex $I$ denotes a field evaluated at the air-water interface.

Note that, while these leading-order equations and boundary conditions also describe the infinite-grating problem, in the case of finite gratings the pressure gradient is not constant throughout the domain, and the functional form of $p(x)$ must be determined from two integral constraints [19]. First, the volumetric flow rate $\dot{Q} = \int_{-\phi_s/2}^{\phi_s/2} \int_0^{1/2} u(x, y, z) \, dy \, dz$ must be constant through every cross-section of the domain, in order to satisfy mass conservation. Second, the pressure drop across the whole unit cell must be compatible with the imposed mean pressure gradient, such that $\int_{-1/2}^{1/2} \partial_z p(x) \, dx = -1$. These two conditions lead to a final expression for the flow field given by

FIG. 1. (a) Unit cell of the SHS, periodic in $\hat{x}$ and $\hat{z}$, illustrating the downstream accumulation of surfactant. (b) Longitudinal cross section at mid-grating ($\hat{z} = 0$), showing the typical distribution of bulk surfactant, with adsorption/desorption regions at the upstream/downstream ends, respectively. (c) Interface concentration (blue) and shear stress (red), for the same $\hat{z} = 0$ cross section.
\[ u(x, y, z) = \begin{cases} 
\left(\frac{2P+3Q}{2P+3Q^\infty} + \frac{3Q^\infty d}{2P+3Q^\infty} \langle \gamma_M a \rangle \right) u_p(y) 
\left(\frac{2P+3Q}{2P+3Q^\infty} - \frac{3Q^\infty d}{2P+3Q^\infty} \langle \gamma_M a \rangle \right) u_p(y) 
\end{cases} \]

where \( u_p(y) = (1 - y^2)/2 \) is the nondimensional plane Poiseuille profile and \( u_d^\infty(y, z) \) is the deviation from \( u_p(y) \) in the infinite-grating case. In other words, \( u(x, y, z) = u_p(y) + u_d^\infty(y, z) \) in the case of \( \phi_x = 1 \) and \( \gamma_M a(x) = 0 \), where \( u_d^\infty(y, z) \) is known from previous studies [3, 28]. In Equation (1), \( P = \hat{P}/\hat{h} \) denotes the normalized pitch (see Fig. 1a) and \( Q^\infty \) the contribution of \( u_d^\infty \) to the flow rate [i.e. \( Q_d^\infty = \int_{\phi_x P/2}^{\phi_x P/2} \int_{-1}^{1} u_d^\infty(y, z) dy dz \)], which is itself dependent on \( P \) and \( \phi_c \). The quantity \( \langle \gamma_M a \rangle \) is the average Marangoni shear across the plastron \( \gamma_M a(x) = \frac{1}{\phi_x \int_{\phi_x P/2}^{\phi_x P/2} \gamma_M a(x) dx} \), and ranges between 0, in the case of a clean slip-free interface, and \( 1 \) for a fully immobilized no-slip interface. All terms in Eq. (1) are now either prescribed or known from the well-studied infinite-grating problem, and thus we have arrived to an approximation of the three-dimensional flow as a linear combination of two known, simpler flow fields. The expression still holds for an arbitrary shear stress profile at the interface, and not necessarily one induced by surfactants, as long as \( \gamma_M a(x) \) remains a function of \( x \) only. Eq. (1) could also be applied as a leading-order flow field for other configurations in which the infinite-grating problem is known, provided \( \epsilon \ll 1 \), like channels with SHS on both sides [28] or more complicated SHS patterns [29].

The final step is to find an expression for \( \gamma_M a(x) \) as a function of the surfactant dynamics. With our choice of nondimensionalization, the (linearized) governing equations describing the transport of soluble surfactant [19] are given by

\[ \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} = \frac{1}{\epsilon Pe} \left( \epsilon^2 \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right), \quad (2a) \]

\[ \frac{\partial (u T)}{\partial x} + \frac{\partial (w \Gamma)}{\partial z} = \frac{1}{\epsilon Pe_t} \left( \epsilon^2 \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) + \frac{\partial (\Gamma u)}{\partial z} = \frac{Bi}{\epsilon} (c_1 - \Gamma), \quad (2b) \]

\[ \frac{\partial u}{\partial y} = Da (c_1 - \Gamma), \quad (2c) \]

\[ \frac{\partial u}{\partial y} = \gamma_M a(x) = \epsilon k_M a (\partial \Gamma / \partial x), \quad (2d) \]

Equations (2a) and (2b) describe the advection and diffusion of the bulk surfactant concentration \( c \) and of the interface surfactant concentration \( \Gamma \), respectively. The adsorption and desorption kinetics governing the exchange between the two species is modeled through the flux boundary condition (2c), whereas the Marangoni boundary condition (2d) relates the fluid shear stress at the interface with the gradient of surfactant concentration. Note also that Eqs. (2b) to (2d) are defined only at the air-water interface.

In addition, Eqs. (2) introduce six nondimensional numbers. The bulk and interface Péclet numbers are defined as \( Pe = \hat{h} \hat{U}/D \) and \( Pe_t = \hat{h} \hat{U}/\hat{D}_t \), respectively, where \( D \) and \( \hat{D}_t \) are the diffusivities of the two species. The Marangoni number \( Ma = n_i \hat{R} \hat{\Gamma}_m / (\hat{\mu} \hat{U}) \) depends on the maximum packing concentration at the interface \( \hat{\Gamma}_m \), the ideal gas constant \( \hat{R} \), the temperature \( \hat{T} \) and a parameter \( n_i \) quantifying the effects of salinity. Moreover, the Biot \( Bi = \hat{h}_t \hat{U}/D \) and Damköhler \( Da = \hat{h}_a \hat{\Gamma}_m / D \) numbers parametrize the effect of kinetics [30], with \( k_a \) and \( k_d \) the adsorption and desorption rate constants. Finally, the normalized concentration \( k = \hat{\Gamma}_0 / \hat{\Gamma}_m = \hat{k}_a \hat{\gamma}_0 / \hat{k}_d \) is a measure of the degree of saturation of the interface, since \( \hat{\Gamma}_0 = \hat{\Gamma}_m \) is a scale for the typical interface concentration and \( \hat{\gamma}_0 \) is the background bulk concentration present in the liquid. These six dimensionless groups, in addition to four geometrical parameters that we choose as \( \phi_x, \phi_c, P \) and \( g = \hat{g}/\hat{h} = \phi_x/\epsilon \), fully describe the problem.

A scaling analysis of Eqs. (2), similar to the one performed in [16] for the case of transverse gratings, leads to a semi-empirical expression for \( \gamma_M a(x) \) that can then be combined with the flow field (1) to obtain a closed theory [19]. These scaling arguments are based on the assumption that the normalized concentration is sufficiently low (i.e. \( k \ll 1 \)), which justifies the choice of linearized equations in (2) and is typically the case in situations in which surfactants are not artificially added. Furthermore, the stress at the interface (and thus the gradient of surfactant as well) is assumed to remain approximately constant (i.e. \( \gamma_M a(x) \approx \langle \gamma_M a \rangle \)), a condition that usually holds in small-scale applications in which the flow is not fast enough to reach the so-called stagnant-cap regime [16].

To test our theory, we select the centerline slip velocity \( u_{ic} = u(x, y = -1, z = 0) \) [31] as a way to quantify the degree of slip and drag reduction of a given SHS. The main reason for this choice is that, as opposed to the local slip length \( \lambda(x, z) = u_{ic}/\partial_z u_{ic} \), the experimental measurement of \( u_{ic} \) does not require the estimation of velocity gradients at the interface [12], ensuring a higher accuracy in the already challenging measurement of the flow field at the air–water interface. The expression that our model provides for \( u_{ic} \) is

\[ u_{ic} = \begin{cases} 
\left( \frac{1}{Pe_t} + \frac{Bi g^2}{(1 + \delta Da)} \right) u_{ic}^{clean}, & \text{if } |x| < \frac{\phi_x}{2}, \\
\left( \frac{1}{Pe_t} + \frac{1}{a_1 k Ma} u_{ic}^{clean} + \frac{Bi g^2}{(1 + \delta Da)} \right) u_{ic}^{clean}, & \text{if } \frac{\phi_x}{2} < |x| \leq 1/2, 
\end{cases} \]

where the parameter \( \delta = \hat{\delta}/\hat{h} \) denotes the diffusive boundary layer thickness of the bulk concentration close to the interface (Fig. 1b), which we model as \( \delta(g, Pe) = a_3(1 + a_4 Pe/g)^{-1/3} \) following further scaling analysis of Eq. (2a). The quantity \( u_{ic}^{clean} \) is the centerline slip velocity of the \emph{clean} problem involving a finite-length grating, which we find by setting \( \gamma_M a(x) = \langle \gamma_M a \rangle = 0 \) in (1). This leads to \( u_{ic}^{clean} = \)
with $u_\infty^c$, the centerline slip velocity of the infinite-grating problem, which is known from previous work [3, 28]. It is worth noting that other local and global quantities such as the effective slip length $\lambda_c$ can also be readily obtained from our model [19].

The parameters $a_1$, $a_2$, $a_3$ and $a_4$ in (3) are empirical coefficients that arise in the scaling analysis of Eqs. (2). In order to estimate them, we performed 155 finite-element simulations of the full, three-dimensional governing equations, spanning a wide range of values in the dimensionless groups to ensure proper coverage of the parameter space. Fitting (3) to the results for $u_t$, obtained from these simulations yielded $a_1 \approx 0.345$, $a_2 \approx 0.275$, $a_3 \approx 5.581$ and $a_4 \approx 3.922$, which are values of order one as expected for scaling coefficients.

Additionally, the computation of the full governing equations allowed to corroborate the validity of our modeling assumptions [19].

Equipped with a three-dimensional theory, we can compare the values of $u_t$, obtained from (3) with experimental measurements. To this end, we employed micro-particle image velocimetry ($\mu$-PIV) in microfluidic channels, using a confocal microscope (Leica SP8 Resonant Scanning) in a setup similar to the one in [13]. The devices were fabricated with polydimethylsiloxane (PDMS) using photolithography and soft lithography techniques [19], and their design is shown in Fig. 2a and 2b. The SHS consists of longitudinal gratings of pitch $\hat{P} = 60 \mu m$ and spanwise gas fraction of $\phi_z = 2/3$. A good approximation of a periodic array is achieved with a chamber of width $\hat{W} = 2 \mathrm{mm}$ that results in 33 parallel gratings across the spanwise direction. The nominal half-height of the channel is $\hat{h} = 60 \mu m$, although due to the PDMS casting process this value varies slightly between experiments, and thus we incorporate its deviation into the uncertainty analysis.

The depth of the gratings is chosen as $\hat{d} = 25 \mu m$, enough to ensure a stable plastron for the duration of each experiment. Since our theory highlighted the grating length as the most relevant geometric parameter that could be adjusted to maximize slip, we tested gratings of $\hat{g} = 15 \mu m$, $\hat{g} = 25 \mu m$, $\hat{g} = 35 \mu m$ and $\hat{g} = 45 \mu m$. The length of the solid ridges remains constant with a value of $(1 - \phi_z)\hat{g}/\phi_z = 20 \mu m$.

Motivated by previous observations [13] of strong Marangoni stresses in the absence of any added surfactant, we used clean de-ionized water without any additives in our experiments. We thoroughly washed the $\mu$-PIV beads (ThermoFisher FluoSpheres carboxylate 0.5-µm diameter) in order to avoid contamination from the surfactant included in their solution [15], and we followed a cleaning protocol [19] for the syringes (Hamilton Gastight) and tubing (Tygon S3) used to drive the flow through the device. Our goal was to quantify the effects on SHSs of natural contaminants present in typical experimental settings, and also to evaluate the accuracy of our model predictions. This is especially relevant in microfluidics, where PDMS is an extremely popular substrate despite having a role in the release of surface-active molecules [22, 23].

The flow was driven using a syringe pump (KD Legato 111) with a net constant flow rate of $\dot{Q}_{\text{TOT}} = 1.152 \mu L \text{ min}^{-1}$, ensuring a fixed cross-sectional mean velocity $\langle \hat{u} \rangle_{yz} = \dot{Q}_{\text{TOT}}/(2\hat{h}\hat{W})$ within the chamber. The value of $\langle \hat{u} \rangle_{yz}$ provides a coarse estimate of $\hat{U} \approx 3(\hat{h})_{yz}$, which is exactly valid only if $\langle \gamma_{Ma} \rangle = 1$ yet useful to estimate the dimensionless groups of the problem [13]. Under these conditions, we measured velocity profiles over two consecutive gratings [31, 32] at different distances $\Delta y$ (see Fig. 2b) from the interface; an example is displayed in Figs. 2d and 2e, for a grating length of $\hat{g} = 45 \mu m$. A noticeable increase in the fluid velocity can be observed over the gratings, with the flow over the solid ridges appearing to gradually converge towards the expected no-slip condition at the wall. From these vertically spaced profiles, the local velocity at the centerline was extrapolated to the interface using a least-squares linear fit, thereby obtaining $\hat{u}_{tc}$.

Comparing these experimental measurements to the predictions from our model requires assumptions on the type and amount of surfactant present in the channel. While some parameter values are known and others can be accurately esti-
mated, the normalized surfactant concentration $k$ and the kinetic rate constants $\hat{k}_a$ and $\hat{k}_d$ can vary across a broad range. Nevertheless, it is possible to combine our model for the slip velocity (3) with previous experimental results [13] to obtain an estimate, as described in detail in the Supplementary Material [19]. We find approximate ranges for the normalized concentration $7.3 \cdot 10^{-3} \leq k \leq 10^{-1}$ and for the ratio of constants $7.1 \cdot 10^3 \text{m}^2\text{mol}^{-1} \leq \hat{k}_a/\hat{k}_d \leq 1.8 \cdot 10^3 \text{m}^2\text{mol}^{-1}$. Obtaining merely the ratio of constants $\hat{k}_a/\hat{k}_d$ is enough for a complete estimation of the surfactant type, since we expect the values of $\hat{k}_a$ and $\hat{k}_d$ to have a weak effect on the model separately. This is due to the fact that most surfactants have high enough values of $\hat{k}_a$ to guarantee the condition $Da \gg 1$ [19, 33], which ensures that the surfactant governing equations (2) are only dependent on the ratio $\hat{k}_a/\hat{k}_d$ at leading order.

Choosing the specific middle-range values $k = 3.58 \cdot 10^{-2}$ and $\hat{k}_a/\hat{k}_d = 1.19 \cdot 10^2 \text{m}^2\text{mol}^{-1}$, our theoretical predictions of the slip velocity show good agreement with experimental data, as illustrated in Figure 3. Results from our finite-element simulations [19] are also plotted, but are restricted to values of $g < 60$ due to constraints in our computational capacity. The results show a good agreement of (3), with both the simulations and the experiments showing a trend compatible with the theoretical prediction. Furthermore, all our experimental measurements fall within the estimate of concentration and kinetic constants (the grey band in Fig. 3) that was obtained exclusively from previous experimental results performed in a similar setting, albeit in a completely different laboratory. It is worth noting that $\hat{k}_d$ is set as $\hat{k}_d = 0.75 \text{s}^{-1}$, although both the theory and simulations are very weakly dependent on its specific value as long as the ratio $\hat{k}_a/\hat{k}_d$ remains constant and $Da \gg 1$ as expected in practice. Indeed, the limits of the band in Fig. 3, which represents the $Da \to \infty$ case, move only marginally when the value of $Da$ takes finite values as low as $Da = 1$.

Regarding the possible source of contamination, one of the main candidates is the PDMS substrate of the microfluidic channels, which is known to leach surface-active uncrosslinked oligomer chains [22, 23]. However, PDMS is usually regarded as a purely insoluble surfactant [34, 35]. In this limit case, our theory yields $\nu_{Ic} = \nu_{Ic}^{\text{clean}}/(1 + a Ma_{\text{ins}} \nu_{Ic}^{\text{clean}})$ [19], where $a$ is another scaling coefficient of order one and $Ma_{\text{ins}} = n R T_0 \hat{h}/(\mu D)$, with $\hat{T}_0$ an independent parameter unrelated to $\hat{c}_0$ in this insoluble case. It is worth noting that this expression for $\nu_{Ic}$ does not depend on $g$, directly contradicting the experimental results in Fig. 3 and highlighting the importance of at least some solubility of the contaminant to replicate the observed behavior.

With the results described here, we provide important insights about the slip and drag of superhydrophobic surfaces. The novel theory accounting for laminar flows over long finite longitudinal gratings enables, for the first time, the direct comparison between theory and experiments for practically relevant 3D SHS patterns in the realistic conditions in which surfactants need to be taken into account. It also provides a powerful tool for the quantification of SHS performance with general sources of shear stress at the air-water interface, circumventing the need for computationally expensive simulations of the full problem. We thus expect this theory to be useful in the design of SHSs in which surfactant effects can be mitigated, as well as a stepping stone towards theories for other texture types (e.g. posts or unstructured SHSs) and even for the turbulent flow regime. Furthermore, our model has proven essential to obtain estimates of the properties of the surfactants naturally present in PDMS channels, which is crucially important due to the widespread use of PDMS in microfluidic applications.

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[31] Note that the assumption of a roughly constant shear stress \( \gamma_{Ma}(x) \approx \langle \gamma_{Ma} \rangle \), when introduced in Eq. (1), implies that our model considers \( u_c \) to be also constant along \( x \). In the simulations and experiments, however, it is necessary to choose a specific value of \( x \) to evaluate \( u_c \).
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S1. FULL SET OF GOVERNING EQUATIONS

We consider a steady fluid flow at low Reynolds number, within the unit cell depicted in Figure 1a. The three-dimensional velocity field is denoted by \( \vec{u} = \hat{u} \hat{e}_x + \hat{v} \hat{e}_y + \hat{w} \hat{e}_z \), where \( \hat{e}_x, \hat{e}_y, \) and \( \hat{e}_z \) are unit vectors in the streamwise, wall-normal and spanwise directions (see Fig. 1a). The scalar fields \( \hat{p} \) and \( \hat{c} \) represent the pressure and the bulk surfactant concentration, respectively. The governing equations describing the conservation of mass, momentum, and surfactant in the bulk fluid are, in dimensional form,

\[
\begin{align*}
\frac{\partial \hat{u}}{\partial x} + \frac{\partial \hat{v}}{\partial y} + \frac{\partial \hat{w}}{\partial z} &= 0, \\
\mu \left( \frac{\partial^2 \hat{u}}{\partial x^2} + \frac{\partial^2 \hat{u}}{\partial y^2} + \frac{\partial^2 \hat{u}}{\partial z^2} \right) &= \frac{\partial \hat{p}}{\partial x}, \\
\mu \left( \frac{\partial^2 \hat{v}}{\partial x^2} + \frac{\partial^2 \hat{v}}{\partial y^2} + \frac{\partial^2 \hat{v}}{\partial z^2} \right) &= \frac{\partial \hat{p}}{\partial y}, \\
\mu \left( \frac{\partial^2 \hat{w}}{\partial x^2} + \frac{\partial^2 \hat{w}}{\partial y^2} + \frac{\partial^2 \hat{w}}{\partial z^2} \right) &= \frac{\partial \hat{p}}{\partial z}, \\
\hat{u} \frac{\partial \hat{c}}{\partial x} + \hat{v} \frac{\partial \hat{c}}{\partial y} + \hat{w} \frac{\partial \hat{c}}{\partial z} &= D \left( \frac{\partial^2 \hat{c}}{\partial x^2} + \frac{\partial^2 \hat{c}}{\partial y^2} + \frac{\partial^2 \hat{c}}{\partial z^2} \right),
\end{align*}
\]

(S1a) (S1b) (S1c) (S1d) (S1e)

At the interface, the interfacial surfactant concentration \( \Gamma \) follows a conservation law. An adsorption–desorption flux couples \( \Gamma \) to the bulk concentration. Marangoni boundary conditions link the interfacial shear stress to the concentration gradient. The corresponding equations, defined only at the air–water interface, read

\[
\frac{\partial (\hat{u} \Gamma)}{\partial x} + \frac{\partial (\hat{w} \Gamma)}{\partial z} = D \left( \frac{\partial^2 \hat{c} \Gamma}{\partial x^2} + \frac{\partial^2 \hat{c} \Gamma}{\partial z^2} \right) + \dot{S}(\hat{c}, \hat{\Gamma}),
\]

(S1f)

\[
D \frac{\partial \hat{c}}{\partial y} \bigg|_{\Gamma} = \dot{S}(\hat{c}, \hat{\Gamma}),
\]

(S1g)

\[
\dot{\mu} \frac{\partial \hat{c}}{\partial y} \bigg|_{\Gamma} = \dot{N}(\hat{\Gamma}) \frac{\partial \hat{\Gamma}}{\partial y},
\]

(S1h)

\[
\dot{\mu} \frac{\partial \hat{w}}{\partial y} \bigg|_{\Gamma} = \dot{N}(\hat{\Gamma}) \frac{\partial \hat{\Gamma}}{\partial y},
\]

(S1i)

where \( \dot{N}(\hat{\Gamma}) \) is a possibly nonlinear term quantifying the dependence of the surface tension with \( \hat{\Gamma} \), and depends on the specific model of equilibrium isotherm chosen [1]. The term \( \dot{S}(\hat{c}, \hat{\Gamma}) \) represents the adsorption–desorption kinetics, and must be compatible with the choice of isotherm. Here, we use a model derived from the Frumkin isotherm [2, 3], which leads to

\[
\dot{S}(\hat{c}, \hat{\Gamma}) = k_a \hat{c} (\hat{\Gamma}_m - \hat{\Gamma}) - k_d \hat{c} \hat{\Gamma} e^{(\hat{\gamma} / \hat{c})},
\]

(S1j)

\[
\dot{N}(\hat{\Gamma}) = n_\Gamma \hat{\Gamma} \left( \frac{\hat{\Gamma}_m}{\hat{\Gamma}_m - \hat{\Gamma}} + A \frac{\hat{\gamma}}{\hat{\Gamma}_m} \right).
\]

(S1k)

The above equations are complemented with the imposition of a mean background level of bulk concentration

\[
\frac{1}{2 \hat{h} \hat{P} \hat{L}} \int_{-\hat{h} / 2}^{\hat{h} / 2} \int_{-\hat{L} / 2}^{\hat{L} / 2} \hat{c} \, d\hat{x} \, d\hat{y} \, d\hat{z} = \hat{c}_0,
\]

(S1l)
as well as with streamwise and spanwise periodicity conditions for variables defined in the bulk fluid,
\[ \hat{u}(\hat{x}) = \hat{u}(\hat{x} + \alpha \hat{L} + \beta \hat{P} \hat{e}_z) \] for any integers \( \alpha, \beta, \) (S1m)
\[ \hat{c}(\hat{x}) = \hat{c}(\hat{x} + \alpha \hat{L} + \beta \hat{P} \hat{e}_z) \] for any integers \( \alpha, \beta, \) (S1n)

which in the case of the pressure also includes a mean pressure drop such that
\[ \hat{p}(\hat{x}) = \hat{p}(\hat{x} + \alpha \hat{L} + \beta \hat{P} \hat{e}_z) + a GL \] for any integers \( \alpha, \beta, \) (S1o)

and where \( \hat{x} = \hat{x} \hat{e}_x + \hat{y} \hat{e}_y + \hat{z} \hat{e}_z \) is the position vector. The remaining equations are the boundary conditions
\[ \hat{u} = 0 \] on all solid surfaces (no slip and no penetration), (S1p)
\[ \hat{v} = 0 \] on the air–water interface (no penetration), (S1q)
\[ \frac{\partial \hat{c}}{\partial \hat{y}} = 0 \] on all solid surfaces (no flux), (S1r)
\[ \frac{\partial \hat{c}}{\partial \hat{x}} = 0 \] at \( \hat{x} = \pm \phi_x \hat{L} \) when \( |\hat{x}| \leq \phi_x \hat{L} \) (no flux), (S1s)
\[ \frac{\partial \hat{c}}{\partial \hat{z}} = 0 \] at \( \hat{z} = \pm \phi_z \hat{L} \) when \( |\hat{z}| \leq \phi_z \hat{L} \) (no flux). (S1t)

We normalize Equations (S1a)-(S1t) following
\[ x = \hat{x}/\hat{L}, \ y = \hat{y}/(\epsilon \hat{L}), \ z = \hat{z}/(\epsilon \hat{L}) \]
\[ u = \hat{u}/\hat{U}, \ v = \hat{v}/(\epsilon \hat{U}), \ w = \hat{w}/(\epsilon \hat{U}), \ p = \hat{p}/(G \hat{L}) \]
\[ c = \epsilon \hat{c}, \ \Gamma = \Gamma \hat{L}/\Gamma_0, \] (S2)

where \( \hat{U} = h^2 \hat{G}/\hat{h} \) and \( \hat{\Gamma}_0 = \hat{k}_a \hat{c}_0 \hat{f}_m / k_d \) are the natural scales for the velocity and the interfacial surfactant. Applying this normalization to Equations (S1a)-(S1k) results in
\[ \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \] (S3a)
\[ \epsilon^2 \left( \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) = \frac{\partial p}{\partial x}, \] (S3b)
\[ \epsilon^2 \left( \frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} + \frac{\partial^2 v}{\partial z^2} \right) = \frac{\partial p}{\partial y}, \] (S3c)
\[ \epsilon^2 \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial y^2} + \frac{\partial^2 w}{\partial z^2} \right) = \frac{\partial p}{\partial z}, \] (S3d)
\[ \frac{\partial c}{\partial x} + \frac{\partial c}{\partial y} + \frac{\partial w}{\partial z} = \frac{1}{\epsilon Pe} \left( \epsilon^2 \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right), \] (S3e)
\[ \frac{\partial (u \Gamma)}{\partial x} + \frac{\partial (w \Gamma)}{\partial z} = \frac{1}{\epsilon Pe_1} \left( \epsilon^2 \frac{\partial^2 \Gamma}{\partial x^2} + \frac{\partial^2 \Gamma}{\partial y^2} + \frac{\partial^2 \Gamma}{\partial z^2} \right) + \frac{Bi}{\epsilon} S(c_1, \Gamma), \] (S3f)
\[ \frac{\partial c}{\partial y} \bigg|_{\Gamma} = Da S(c_1, \Gamma), \] (S3g)
\[ \frac{\partial u}{\partial y} \bigg|_{\Gamma} = ekMa N(\Gamma) \frac{\partial \Gamma}{\partial x}, \] (S3h)
\[ \epsilon^2 \frac{\partial w}{\partial y} \bigg|_{\Gamma} = ekMa N(\Gamma) \frac{\partial \Gamma}{\partial z}, \] (S3i)
\[ S(c_1, \Gamma) = c_1 (1 - k \Gamma) - \Gamma e^{k \Delta \Gamma}, \] (S3j)
\[ N(\Gamma) = \left( \frac{1}{1 - \Delta \Gamma} + k \Delta \Gamma \right). \] (S3k)

The parameters appearing in Equations (S1a)-(S3k) are detailed in Tables SI and SII, as well as the values that they take in our experiments. Since, as explained in the main text, the surfactant type and concentration in the liquid are unknown, only an estimate can be obtained in some cases (see Section S6 for details). We choose \( g = \hat{g}/\hat{h}, \ P = \hat{P}/\hat{h}, \phi_x \) and \( \phi_z \) as the four independent geometric parameters of the problem, noting that \( \epsilon \) can then be obtained as \( \epsilon = \phi_x / g. \)
TABLE SI. Parameters appearing in the dimensional equations (S1a)-(S2) and in the geometry of the domain (Fig. 1a), alongside with their values in the simulations and experiments. The symbol $\dagger$ indicates that the quantity is estimated as the value for the well-characterized SDS, since its order of magnitude does not change appreciably for other substances. The symbol $\ddagger$ denotes values that have been coarsely estimated combining our theory and the experimental results in [4] (see Section S6 for details).

| Dimensionless group | Definition | Range in simulations | Value (or best estimate) in experiments |
|---------------------|------------|----------------------|----------------------------------------|
| Normalized concentration | $k = \hat{k}_a\overline{c}_0/\hat{k}_d = \hat{\Gamma}_0/\hat{\Gamma}_m$ | $2.7 \cdot 10^{-5} - 5.4 \cdot 10^{-2}$ | $4 \cdot 10^{-2}$ |
| Marangoni number | $Ma = n_0\hat{\Gamma}\hat{\Gamma}_m/(\mu\hat{U})$ | $3.1 \cdot 10^{-3} - 2.3 \cdot 10^{2}$ | $9 \cdot 10^{4}$ |
| Pécel number | $Pe = \hat{h}\hat{U}/\hat{D}$ | $1.5 \cdot 10^{-2} - 1.2 \cdot 10^{2}$ | $2 \cdot 10^{1}$ |
| Interface Pécel number | $Pe_\theta = \hat{h}\hat{U}/\hat{D}_\theta$ | $1.7 \cdot 10^{-1} - 6 \cdot 10^{2}$ | $2 \cdot 10^{3}$ |
| Biot number | $Bi = \hat{h}\hat{k}_d/\hat{U}$ | $8.6 \cdot 10^{-3} - 2.5 \cdot 10^{2}$ | $2 \cdot 10^{-1}$ |
| Damköhler number | $Da = \hat{h}\hat{k}_d/\hat{D}$ | $2.5 \cdot 10^{1} - 6.4 \cdot 10^{3}$ | $3 \cdot 10^{1}$ |
| Normalized grating length | $g = \hat{g}/\hat{h}$ | $1.54 - 58.33$ | $2.5 \cdot 10^{-2} - 7.5 \cdot 10^{2}$ |
| Normalized pitch | $P = \hat{\rho}/\hat{\nu}$ | $0.92 - 2$ | $1$ |
| Streamwise gas fraction | $\phi_s$ | $0.833 - 0.994$ | $0.9986 - 0.9995$ |
| Spanwise gas fraction | $\phi_c$ | $0.667 - 0.980$ | $2/3$ |

TABLE II. Characteristic dimensionless numbers governing the full problem.

S2. DERIVATION OF THE THEORY FOR THE FLOW FIELD

S2.1. Assumption of a spanwise constant interface shear stress

Note that, although $\varepsilon \ll 1$ and $k \ll 1$ in the conditions considered in our study (see Section S3), the product $ekMa$ appearing in Eqs. (S3h) and (S3) is typically not small, since the Marangoni number is expected to be large $Ma \gg 1$ (see estimates in Table SII) and the term $N(\Gamma) \approx 1$ as long as $k$ and $|kA|$ remain small. In fact, Equation (S3h) implies that only when $ekMa \gg 1$ the Marangoni stresses at the interface are non-negligible, as it is observed experimentally [4–7]. Since $\varepsilon \ll 1$, it is possible to assume that $ekMa \gg 1 \gg \varepsilon^2$, and in that case it follows from (S3i) that $\partial_{\Gamma} \approx 0$ at leading order in $\varepsilon$. As detailed in the main text, the asymptotic expansion leading to Eqs. (S3h) and (S3i) is singular, and thus the approximation $\partial_{\Gamma} \approx 0$ is valid only in regions far from the upstream and downstream stagnation points, i.e. for $|x - \phi_s/2| \gg \varepsilon$. Indeed, our finite-element simulations of the full problem confirm that this approximation remains valid in all the cases that were considered (see Fig. S1b). The Marangoni shear $\gamma_{\nu_s}(x) = \partial_{nu_s}$ is thus also assumed to be constant in the spanwise direction and only dependent on $x$, following Eq. (S3h).
S2.2. Velocity field

At leading order in the small parameter \( \epsilon \), the equations (S3b)-(S3d) for the flow field lead to

\[
\begin{align*}
\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} &= \frac{\partial p}{\partial x}, \quad (S4a) \\
\frac{\partial p}{\partial y} &= 0. \quad (S4b)
\end{align*}
\]

It is clear from Eq. (S4b) that \( p \), and thus also \( \partial_p p \), will only depend on \( x \). Since the solution \( u \) only depends on \( x \) through the right-hand-side of Eq. (S4a), we pose a piecewise solution

\[
u(x, y, z) = \begin{cases} \nu_1(x, y, z) & \text{if } |x| < \phi_z/2, \\ \nu_2(x, y, z) & \text{if } \phi_z/2 \leq |x| \leq 1/2. \end{cases} \quad (S5)
\]

Taking into account the boundary conditions, the function \( \nu_1 \) satisfies the mixed boundary-value problem given by Eq. (S4a) and the boundary conditions

\[
\begin{align*}
u_1 &= 0 & \text{if } y = 1 \text{ or } y = -1 \text{ and } |z| \geq \phi_z P, \\
\frac{\partial \nu_1}{\partial y} &= \gamma_{Ma}(x) & \text{if } y = -1 \text{ and } |z| < \phi_z P. \quad (S6)
\end{align*}
\]

We then introduce the Poiseuille profile \( \nu_p(y) = (1 - y^2)/2 \) and, by virtue of the linearity of the problem, decompose the solution following \( \nu_1 = -[\partial_p p(x)] \nu_p(y) - [\gamma_{Ma}(x) + \partial_p p(x)] \nu_d^\infty \). The resulting problem for \( \nu_d^\infty \) is homogeneous, yielding

\[
\begin{align*}
\frac{\partial^2 \nu_d^\infty}{\partial y^2} + \frac{\partial^2 \nu_d^\infty}{\partial z^2} &= 0, \\
\nu_d^\infty &= 0 & \text{if } y = 1 \text{ or } y = -1 \text{ and } |z| \geq \phi_z P, \\
\frac{\partial \nu_d^\infty}{\partial y} &= -1 & \text{if } y = -1 \text{ and } |z| < \phi_z P. \quad (S7)
\end{align*}
\]

The problem given by Eqs. (S7) has been solved in closed form [8, 9], and highlights that \( \nu_d^\infty(y, z) \) is simply the deviation from the Poiseuille profile in the infinite-grating problem.

The function \( \nu_2 \) satisfies Eq. (S4a) with the no-slip boundary conditions \( \nu_2 = 0 \) at \( y = \pm 1 \), and the solution is given by \( \nu_2 = -[\partial_p p(x)] \nu_p(y) \). Consequently, the following linear combination of \( \nu_p(y) \) and \( \nu_d^\infty(y, z) \) solves Eqs. (S4):

\[
u(x, y, z) = \begin{cases} \left[ -\frac{\partial p}{\partial x} \right] \nu_p(y) - \left[ \gamma_{Ma}(x) + \frac{\partial p}{\partial x} \right] \nu_d^\infty(y, z) & \text{if } |x| < \phi_z/2, \\ \left[ -\frac{\partial p}{\partial x} \right] \nu_p(y) & \text{if } \phi_z/2 \leq |x| \leq 1/2. \end{cases} \quad (S8)
\]

In order to determine the pressure gradient term in Eq. (S8), we first pose a piecewise pressure field

\[
p(x) = \begin{cases} p_1(x) & \text{if } |x| < \phi_z/2, \\ p_2(x) & \text{if } \phi_z/2 \leq |x| \leq 1/2. \end{cases} \quad (S9)
\]

Integrating the continuity equation (S3a) across any cross section of the domain evidences that the volumetric flow rate \( Q = \int_{\phi_p/2}^{1/2} \int_{-1}^{1} u(x, y, z) \ dy \ dz \) remains constant in \( x \). Further integrating the piecewise solution (S8) and invoking Eq. (S9), we obtain two expressions for the flow rates

\[
\begin{align*}
Q_1 &= \int_{-\phi_p/2}^{\phi_p/2} \int_{-1}^{1} u_1(x, y, z) \ dy \ dz = \left[ -\frac{\partial p_1}{\partial x} \right] \frac{2P}{3} - \left[ \gamma_{Ma}(x) + \frac{\partial p_1}{\partial x} \right] Q_d^\infty, \\
Q_2 &= \int_{-\phi_p/2}^{\phi_p/2} \int_{-1}^{1} u_2(x, y, z) \ dy \ dz = \left[ -\frac{\partial p_2}{\partial x} \right] \frac{2P}{3},
\end{align*}
\]
where $2P/3$ and $Q^\infty_d(\phi, P)$ are the flow rates given by $u_P(y)$ and $u^\infty_d(y, z)$, respectively. Note that, since $Q_2$ must be constant in $x$, the term $\partial_x p_2$ is necessarily independent of $x$ as well. Equating $Q_1 = Q_2$ yields a relationship between the two pressure gradients,

$$\frac{\partial p_1}{\partial x}(x) = \left[\frac{2P}{2P + 3Q^\infty_d}\right] \frac{\partial p_2}{\partial x} - \left[\frac{3Q^\infty_d}{2P + 3Q^\infty_d}\right] \gamma_{Ma}(x).$$

(S11)

The last condition that must be satisfied by the solution is the fixed pressure drop across the domain given by Eq. (S10). The nondimensional version of this equation, taking $\alpha = 1$ and $\beta = 0$ in (S10), leads to $p(x) = p(x + 1) + 1$. This equation can be made specific to $x = -1/2$ and recast into an integral equation for the gradient

$$\int_{-1/2}^{1/2} \frac{\partial p}{\partial x}(x) \, dx = -1$$

which, after applying the decomposition (S9), leads to

$$\int_{-\phi/2}^{\phi/2} \frac{\partial p_2}{\partial x} \, dx + \int_{-\phi/2}^{\phi/2} \frac{\partial p_1}{\partial x} \, dx + \int_{-1/2}^{1/2} \frac{\partial p_2}{\partial x} \, dx = -1. \quad (S12)$$

Substituting (S11) into (S12), we arrive at

$$\frac{\partial p_1}{\partial x}(x) = \frac{2P + 3Q^\infty_d(1 - \phi_x)\gamma_{Ma}}{2P + 3Q^\infty_d(1 - \phi_x)} + \frac{3Q^\infty_d}{2P + 3Q^\infty_d}((\gamma_{Ma}) - \gamma_{Ma}(x)), \quad \frac{\partial p_2}{\partial x} = \frac{-2P + 3Q^\infty_d(1 - \phi_x)\gamma_{Ma}}{2P + 3Q^\infty_d(1 - \phi_x)},$$

(S13)

which can finally be introduced in (S8) to produce the closed form solution for the flow field Equation (1) in the main text. The term $\gamma_{Ma}(x)$ in (S13) represents the average value of $\gamma_{Ma}(x)$ at the interface, i.e. $\left\langle \gamma_{Ma} \right\rangle = \frac{1}{\theta_e} \int_{-\phi/2}^{\phi/2} \gamma_{Ma}(x) \, dx$.

Once the leading-order velocity field (S8) is fully determined from known parameters, the relevant quantities characterizing the performance of the SHS can be readily obtained. The local centerline slip velocity $u_{lc} = u(x, y = -1, z = 0)$ is

$$u_{lc}(x) = 2P \left[\frac{1}{2P + 3Q^\infty_d(1 - \phi_x)} + \frac{((\gamma_{Ma}) - \gamma_{Ma}(x))}{2P + 3Q^\infty_d}\right] u^\infty_{lc}.$$  \ (S14)

with $u^\infty_{lc}(\phi, P) = u^\infty_d(y = -1, z = 0)$. With the additional assumption of a uniform shear stress $\gamma_{Ma}(x) = \left\langle \gamma_{Ma} \right\rangle$, justified in Section S3, Eq. (S14) further simplifies to

$$u_{lc} = \left[\frac{2P \gamma_{lc}}{2P + 3Q^\infty_d(1 - \phi_x)}\right] (1 - \left\langle \gamma_{Ma} \right\rangle) := u_{lc}^\text{clean} (1 - \left\langle \gamma_{Ma} \right\rangle),$$  \ (S15)

where we define $u_{lc}^\text{clean}(\phi, \phi, P)$ as the centerline slip velocity for the finite-grating clean case (i.e. $\gamma_{Ma}(x) = \left\langle \gamma_{Ma} \right\rangle = 0$). Equation (S15) leads directly to Equation (3) of the main text after the introduction of a model for $\gamma_{Ma}$. Another common, global measure of SHS performance is the increase in flow rate with respect to that of a Poiseuille flow. Our theory predicts

$$Q_d = \int_{-\phi/2}^{\phi/2} \int_{-1}^{1} \left[u(x, y, z) - u_P(y)\right] \, dy \, dz = \left[\frac{2P \gamma_{lc}}{2P + 3Q^\infty_d(1 - \phi_x)}\right] (1 - \left\langle \gamma_{Ma} \right\rangle) := Q_d^\text{clean} (1 - \left\langle \gamma_{Ma} \right\rangle).$$

(S16)

where we again introduce $Q_d^\text{clean}(\phi, \phi, P)$ by definition as the increase in flow rate for the finite-grating, clean problem. Perhaps the most common global quantity sought in theoretical SHS studies is the effective slip length, i.e. the quantity $\lambda_e$ such that a unit cell (Fig. 1a), in which the mixed boundary conditions on $y = -1$ are substituted by $u = \lambda_e \partial_t u$, yields the same increase $Q_d$ in flow rate. Such a flow yields a solution $u(x, y) = u_P(y) + \lambda_e(1 - y)/(2 + \lambda_e)$ and thus an increase in flow rate of $2P \lambda_e/(2 + \lambda_e)$ which, when equated to $Q_d$, yields an expression for the slip length

$$\lambda_e = \frac{Q_d}{2P - Q_d} = \frac{2\phi_x Q^\infty_d(1 - \left\langle \gamma_{Ma} \right\rangle)}{2P + [3 - \phi_x(4 - \left\langle \gamma_{Ma} \right\rangle)] Q^\infty_d}.$$  \ (S17)

S3. SCALING THEORY FOR THE SURFACTANT TRANSPORT

S3.1. Full problem

The analysis of the surfactant transport equations is similar to that in [10], but we fully describe it here in order to achieve an exhaustive characterization of the differences between the two-dimensional and three-dimensional cases. The first key assumption of our model for the surfactant transport problem given by Equations (S3e)-(S3k) is that the concentration of surfactant is
low enough to ensure a *dilute regime* in which \( k \ll 1 \). We expect this assumption to be the case for most situations in which surfactants are not artificially added, for instance, when unwanted contaminants are naturally present in water [10]. Additionally, since the interaction parameter \( A \) is typically not large in absolute value, with \(|A| \leq 20\) [2], it is possible to assume that \( k|A| \ll 1 \) as well. The nonlinear terms [Eqs. (S3j) and (S3k)] in the governing equations can then be linearized, leading to
\[
S(c_I, \Gamma) = c_I - \Gamma + O(k) + O(k|A|) \quad \text{and} \quad N(\Gamma) = 1 + O(k) + O(k|A|).
\]
Consequently, at leading order in \( k \) and \( k|A| \), Equations (S3f)-(S3k) can be simplified, yielding Equations (2) in the main text.

Applying an integral average to Eq. (2b) along the spanwise direction, we obtain
\[
\frac{\partial \langle u_I \Gamma \rangle_z}{\partial x} = \frac{e}{Pe} \frac{\partial^2 \langle \Gamma \rangle_z}{\partial x^2} + \frac{Bi}{e} \langle (c_I)_z - \langle \Gamma \rangle_z \rangle,
\]
where the spanwise average across the plastron of an arbitrary integrable function \( f(z) \) is defined as \( \langle f \rangle_z = \frac{1}{\phi_x} \int_{-\phi_x/2}^{\phi_x/2} f(z) \, dz \), and where the terms in (2b) associated with derivatives in \( z \) vanish due to the no-slip (\( w = 0 \)) and no-flux (\( \partial_z \Gamma = 0 \)) boundary conditions at the edges \( z = \pm \phi_x/2 \) of the plastron. If Equation (S18) is further integrated from \( x = -\phi_x/2 \) to \( x = \phi_x/2 \) and equivalent boundary conditions \( u = 0 \) and \( \partial_x \Gamma = 0 \) are applied at \( x = \pm \phi_x/2 \), we have that
\[
\int_{-\phi_x/2}^{\phi_x/2} \langle (c_I)_z - \langle \Gamma \rangle_z \rangle \, dz = 0,
\]
and thus by virtue of the mean value theorem an equilibrium condition \( \langle c_I \rangle_z = \langle \Gamma \rangle_z \) must occur at some coordinate along the interface, which we call \( x_0 \). Downstream from \( x_0 \), the flow advection promotes the accumulation of interfacial surfactant, which in turn triggers a net desorption flux and an increase in bulk surfactant with respect to the background level. Upstream from \( x_0 \), the situation is the opposite, with a deficit of \( \Gamma \) and \( c_I \) with respect to the equilibrium values and a net adsorption flux. Figures 1b and 1c depict this physical scenario with the two distinct regions along the interface.

The second main assumption is to consider the interfacial concentration \( \Gamma \) as *approximately linear*. In this case, Eq. (S19) implies that the equilibrium point must be approximately at the center of the interface (i.e., \( x_0 \approx 0 \)), and thus the bulk concentration at \( x_0 \) is approximately the background concentration and we have \( \langle c_I \rangle_{x_0} = \langle \Gamma \rangle_{x_0} \approx 1 \). Consequently, this assumption allows to scale the concentrations at both ends of the interface \( x = \pm \phi_x/2 \) as
\[
c(x = \pm \phi_x/2) \sim 1 \pm \Delta c,
\]
\[
\Gamma(x = \pm \phi_x/2) \sim 1 \pm \Delta \Gamma,
\]
with \( \Delta c \) and \( \Delta \Gamma \) the characteristic variation of the concentrations (see Figures 1b and 1c). Additionally, note that an approximately linear \( \Gamma \) also implies [Eq. (S3h)] that the Marangoni shear at the interface is taken as *approximately constant* (i.e. \( \gamma_{Ma}(x) \approx \gamma_{Ma} \)). This assumption is expected to hold as long as the flow is not in the so-called stagnant cap regime [10], characterized by a strongly nonuniform interfacial concentration. Such a regime is reached when advection at the interface overcomes both diffusion and kinetic effects [11], that is, when \( ePe_{\Gamma} \ll 1 \) and either \( Bi/e \ll 1 \) or \( Da \gg 1 \) [see Eq. (S1f)]. Given the typical parameter values in small-scale flows like the ones considered in this study (see Section S6 and Table SII), we conclude that for long gratings \( ePe_{\Gamma} \ll 1 \), justifying this assumption. Furthermore, we perform an analysis a posteriori using the results of the numerical simulations (see Section S4), confirming the approximately linear profile of \( \Gamma \) in all cases considered.

Using these two key assumptions, it is possible to use scaling arguments on Equations (2) to obtain an expression for \( \langle \gamma_{Ma} \rangle \) as a function of the nondimensional groups of the problem. We start by scaling the terms in Eq. (2d) as \( \partial_x u_I \sim \langle \gamma_{Ma} \rangle \) and \( \partial_x \Gamma \sim \Delta \Gamma/\phi_x \), leading to
\[
\Delta \Gamma = \frac{\phi_x\langle \gamma_{Ma} \rangle}{e k \Gamma_M}.
\]
Next, we evaluate the terms in Eq. (S3j) at the interface ends \( x = \pm \phi_x/2 \). We take \( \partial_x c_I \sim [1 - (1 \pm \Delta c_I)]/\delta \sim \mp \Delta c_I/\delta \) and \( (c_I - \Gamma) \sim [1 \pm \Delta c_I - (1 \pm \Delta \Gamma)] \sim \pm \Delta c_I - \Delta \Gamma \), where \( \delta = \hat{h}/\hat{h} \) is the characteristic boundary layer thickness of the bulk concentration (Fig. 1b). We arrive at
\[
\Delta c_I \sim \frac{\delta Da}{(1 \pm \delta Da)} \frac{\phi_x\langle \gamma_{Ma} \rangle}{e k \Gamma_M}.
\]
Finally, Equation (S18) is integrated from \( x = -\phi_x/2 \) to \( x = x_0 \), leading to
\[
\langle u_I \Gamma \rangle_z(x_0) = \frac{e}{Pe} \frac{\partial \langle \Gamma \rangle_z}{\partial x}(x_0) + \frac{Bi}{e} \int_{-\phi_x/2}^{x_0} \langle (c_I)_z - \langle \Gamma \rangle_z \rangle \, dx,
\]
whose terms we scale as $\langle uI\Gamma \rangle(x_0) \sim u_{tc}, \partial_x \langle \Gamma \rangle(x_0) \sim \Delta \Gamma/\phi_x$, and $\int_{-\phi_x/2}^{\phi_x/2} (\langle cI \rangle - \langle \Gamma \rangle) dx \sim \phi_x(\Delta cI - \Delta \Gamma)$. Making use of Equations S21 and S22 and introducing $g = \hat{g}/h = \phi_x/e$, we arrive at

$$u_{tc} \sim \frac{\langle \gamma_{Ma} \rangle}{kMa} \left( \frac{1}{Pe_1} + \frac{Bi g^2}{(1 + \delta Da)} \right),$$

which, after introducing empirical coefficients for each term, yields

$$u_{tc} = \frac{\langle \gamma_{Ma} \rangle}{a_1 kMa} \left( \frac{1}{Pe_1} + a_2 \frac{Bi g^2}{(1 + \delta Da)} \right). \quad (S24)$$

Making use of the theory for the flow field [Eq. (S15)], we substitute $u_{tc} = (1 - \langle \gamma_{Ma} \rangle)u_{tc}^{clean}$ into (S24) and obtain the final expression for $\langle \gamma_{Ma} \rangle$ as a function of the parameters of the problem,

$$\langle \gamma_{Ma} \rangle = \frac{a_1 k Ma u_{tc}^{clean}}{1 + a_1 k Ma u_{tc}^{clean} + a_2 \frac{Bi g^2}{(1 + \delta Da)}}. \quad (S25)$$

Equation (S25) can now be introduced in (S15) to obtain the formula for the slip velocity (3) from the main text. Similarly, combining Eq. (S25) with (S16) and (S17), expressions for the increase in flow rate and effective slip length can be reached.

The only yet undetermined part of the model is an expression for the boundary layer thickness $\delta$, which we seek through scaling of the conservation law for the bulk surfactant (2a). In situations with $\varepsilon Pe \gg 1$, streamwise advection must balance wall-normal diffusion $u\partial_\gamma c \sim \frac{1}{\nu_p} \partial_x c$, which is only possible if $c$ varies over a small length scale $\delta \ll 1$ [11]. We take $\partial_x c \sim \Delta cI/\phi_x, \partial_x c \sim \Delta cI/\delta^2$ and the velocity inside the boundary layer as $u \sim u_{tc} + \langle \gamma_{Ma} \rangle \delta$. In the case of an interface close to immobilization, i.e. $u_{tc} \sim 0$ and $\langle \gamma_{Ma} \rangle \sim 1$, these scalings indicate that $\delta \sim (Pe/g)^{1/3}$ when $\varepsilon Pe \gg 1$. In the opposite case of $\varepsilon Pe \ll 1$, Equation (2a) is dominated by diffusion, and thus the characteristic length scale of variation of $c$ in the wall-normal direction is the whole half height of the domain, implying $\delta \sim 1$. We choose

$$\delta = a_3(1 + a_4 Pe/g)^{-1/3} \quad (S26)$$

to satisfy these two extremes, with $a_3$ and $a_4$ empirical parameters. It is also possible to obtain a similar expression with an exponent of $-1/2$ instead, by assuming that the boundary layer is essentially shear-free (i.e. $u_{tc} \sim 1$ and $\langle \gamma_{Ma} \rangle \sim 0$). In practice, the overall value of quantities like $u_{tc}$ are only weakly dependent on the specific functional form of $\delta$, so we only consider the expression (S26). Additionally, in the case of interest of long gratings $\varepsilon \ll 1$ in small-scale flows we typically have $Pe/g \leq 1$ (Section S6) and thus the boundary layer thickness is approximately independent of $Pe$ or $g$.

### S3.2. Insoluble surfactant

All previous theoretical expressions can also be obtained in the case of an insoluble surfactant, i.e. taking $S(cI, \Gamma) = 0$ in (S3g) and neglecting Equations (S3e) and (S3f). In this case, $\Gamma_0$ is an independent parameter that can not be linked to $\hat{c}_0$, since the latter is undefined. The value of $k$ is now simply $k = \Gamma_0/\Gamma_{\infty}$, although we assume $k \ll 1$ still holds and leads to $N(\Gamma) \approx 1$. Furthermore, since $\varepsilon Pe_1 \ll 1$ remains valid we can still assume a regime away from the stagnant cap and thus an approximately linear profile for $\Gamma$. The same steps taken for the scaling of Eqs. (2d) and (S18) can be followed to arrive at

$$\langle \gamma_{Ma} \rangle = \frac{a Ma_{ins} u_{tc}^{clean}}{1 + a Ma_{ins} u_{tc}^{clean}},$$

$$u_{tc} = \frac{u_{tc}^{clean}}{1 + a Ma_{ins} u_{tc}^{clean}},$$

with $Ma_{ins} = k Ma Pe_1 = n_s \hat{K}_0 \hat{h}/(\hat{\mu} \hat{D}_1)$, and $a$ another empirical parameter.

### S4. FINITE-ELEMENT SIMULATIONS

We solve numerically the full governing equations (S1a)-(S1t) of the problem in dimensional form, performing a total of 155 simulations. The objectives of such a computational study are to (i) determine the values of the empirical parameters $a_1, a_2,$
and $a_4$ present in our model [Section S3], (ii) confirm the modeling assumptions of an (approximately) spanwise constant [Section S2 S2.1] and streamwise linear profile [Section S3 S3.1] for the interfacial concentration $\Gamma$, and (iii) test the performance of the theory against simulations of realistic microchannels in conditions representative of our experiments [Section S5].

We implemented the three-dimensional simulations using the finite-element software COMSOL Multiphysics 5.5®. The simulation domain is one half of the SHS unit cell depicted in Fig.1a, with $\hat{z}$ spanning only between $\hat{z} = 0$ and $\hat{z} = \hat{P}/2$ due to the spanwise symmetry of the solution. The volume is meshed with tetrahedral elements, concentrating the finest regions around the upstream and downstream edges of the interface $\hat{x} = \pm \hat{\varphi}_L/2$ since it is in those areas where the most abrupt variations of the solution occur (see Fig. S1). Across all the simulations, the minimum element size (understood as the diameter of a sphere circumscribing the smallest element) is set to $1.5 \cdot 10^{-9}$ m.

The solution of the governing equations is achieved with a combination of the Creeping Flow module for the flow equations [Eqs.(S1a)-(S1d)] and the Dilute Species Transport module for the transport of bulk surfactant [Eq.(S1e)]. The conservation law for the interfacial surfactant [Eq.(S1f)] is implemented through a General Form Boundary PDE, using (S1j) as source term. The Marangoni boundary conditions (S1b) and (S3i) are enforced through a Weak Contribution constraint, as is the condition that fixes the mean bulk concentration (S11).

The system of nonlinear equations is solved through a Newton-type iterative method using the PARDISO direct solver for the linear system at each iteration. We set a relative tolerance of $10^{-3}$ as a convergence criterion for the solution, which is satisfied by all of our simulations. The pressure, bulk concentration and interfacial concentration are discretized using linear elements, and the velocity field uses either quadratic or linear elements, depending on the computational demands of each specific simulation.

Although we do not pursue an exhaustive investigation of the parameter space as in [10], we vary the problem parameters to ensure that each of the distinct terms that are pre-multiplied by an empirical factor in (S25) varies its value over a few orders of magnitude. The ranges of variation of each dimensional quantity in the simulations, as well as of the corresponding nondimensional numbers, is indicated in Tables S1 and SII. A small number of simulations were chosen with the same parameters as those estimated in the experiments, in order to achieve a direct comparison (see Fig. 3 in the main text). However, due to constraints in computational power, the value of the grating length $\hat{g}$ could not be matched with that of the microfluidic devices.

The parameters $a_1$, $a_2$, $a_3$ and $a_4$ are obtained through least-squares fitting using the MATLAB function lsqnonlin. We use the absolute error between the centerline slip velocities computed in the simulations and those predicted by the theory (3) to define the error, i.e. \( \text{ERR} = \sum (u_{\text{sim}}^{\text{theory}} - u_{\text{sim}}^{\text{num}})^2 \). Using this approach, we find $a_1 = 0.345$, $a_2 = 0.275$, $a_3 = 5.581$, and $a_4 = 3.922$. As illustrated in Fig. S2, the agreement between simulations and theory, using this set of empirical coefficients, is excellent over more than four orders of magnitude.

### S5. EXPERIMENTAL METHODS

The experimental setup is centered around the custom-built PDMS (Sylgard 184) microfluidic device depicted in Figures 2a and 2b, which is fabricated from a master mold obtained by photolithography. The chip is bonded to a 0.1 mm-thick glass coverslip (Bellco Glass 1916-25075) through untreated adhesion, and a 40X water objective is used to image the interior of the channels through the coverslip using a confocal microscope (Leica SP8 Resonant Scanning). The device is placed inside a stage top chamber (Okolab H101-K-FRAME) that ensures a precise temperature control, which we set to $T = 296$ K throughout all experiments. The fluid is initially contained in a glass syringe (Hamilton Gastight), and driven by a syringe pump (KD Legato 111) at a constant flow rate through plastic tubing (Tygon S3) into and out of the microfluidic channel. We use the barrel of a plastic syringe (BD Luer-Lok) as an outlet reservoir open to the room, in order to establish an ambient pressure level at the end of the fluid circuit. Furthermore, the overall magnitude of the pressure inside the channel is adjusted varying the height of the outlet reservoir with an vertical translation stage (Thorlabs VAP10), in order to ensure that the air-water interface in the observed channels remains flat and thus plastron curvature effects can be safely neglected. The tolerance in the maximum deflection of the interface (at the centerline $z = 0$) with respect to its edges ($z = \pm \hat{\varphi}_L P$) is estimated to be $\pm 1 \mu m$.

Due to the extreme difficulty of removing all traces of surface-active contaminants even in controlled experimental conditions [4], we do not attempt an exhaustive cleaning protocol with that aim. Nevertheless, we follow standard cleaning procedures on all syringes and tubing, ensuring that they are rinsed with DI water with at least twice their volume before they are used. In addition, we follow a specific cleaning protocol for the $\mu$-PIV particles (ThermoFisher FluoSpheres carboxylate 0.5-µm diameter), since they typically contain surfactants to prevent particle agglomeration [12]. We use a centrifuge (Eppendorf 5418) to separate the beads from the buffer solution, which is discarded and replenished with clean 18 MΩ DI water, and we repeat the process three times. These cleaning procedures ensure that the traces of surfactants responsible for the non-negligible Marangoni stresses that we observe in the experiments are the result of contamination that would naturally occur in typical small-scale flows through microfluidic devices, and not as a byproduct of the specific experimental methods used in this study.

The $\mu$-PIV analysis is performed using the open-source MATLAB toolbox PIVlab. The acquisition window has an approximate size of $125 \mu m \times 125 \mu m$, which is sufficient to cover the span of two pitches (see Fig. 2e) at the center of the grating in the streamwise direction (i.e. $x = 0$). We image the motion of the $\mu$-PIV particles during time intervals of between 20 s and 60 s at different distances from the interface, with frame rates between 20 fps and 28 fps. Next, we compute the time average of
the obtained velocity field, as well as the average in the streamwise \( x \) direction, to obtain the final velocity profiles depicted in Figure 2d. In order to calculate the value of \( \hat{u}_{ic} \), we perform a linear least-squares fit, typically using between 3 and 5 velocity profiles to obtain an extrapolated slip velocity, from which we extract its value at \( z = 0 \). This linear fit is performed in MATLAB with a custom script that takes into account uncertainties in both the distance \( \Delta \hat{y} \) from the interface and the uncertainty in \( \hat{u} \) inherent to the measurement and the averaging in the \( x \) direction.

S6. ESTIMATE OF PLAUSIBLE SURFACTANT PARAMETERS

The main challenge in comparing the experimental measurements of \( \hat{u}_{ic} \) to the predictions from our model is the absence of information regarding the type and amount of surfactant present in the channels. Some parameters in the problem are known from the experimental conditions, and hence we fix those as \( n_s = 2 \) [3], \( \dot{R} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \), \( T = 296 \text{ K} \) and \( \mu = 8.9 \cdot 10^{-4} \text{ kg m}^{-1} \text{ s}^{-1} \) [13]. Others can be accurately estimated, since most surfactants have diffusivities (both \( D \) and \( D_I \))
bounded between $10^{-10}$ and $10^{-9}$ m² s⁻¹ and values $\Gamma_m$ between $10^{-6}$ and $5 \cdot 10^{-5}$ mol m⁻² [2]. We thus use as a reference surfactant the well-studied sodium dodecyl sulfate (SDS), setting $D = D_f = 7 \cdot 10^{-10}$ m² s⁻¹ and $\Gamma_m = 3.9 \cdot 10^{-6}$ mol m⁻² as good approximations of these two parameters. However, the typical values of the background bulk concentration $\tilde{c}_0$ and the rate constants $\tilde{k}_a$ and $\tilde{k}_d$ have a much wider range [2], making them difficult to estimate.

Despite the uncertainty, it is possible to obtain a coarse approximation of these quantities. The value of $k$ can be bounded by above, since we expect $k \ll 1$ not only because this is typically the case whenever surfactants are not artificially added, but also because values of $k \gtrsim 1$ would lead to a significant decrease of the mean surface tension and thus to a rapid plastron collapse that is not observed in experiments. We choose the bound $k < k_{\max} = 10^{-3}$, which ensures that $k$ remains at least one order of magnitude smaller than 1 and that the absolute surface tension decrease $\Delta \sigma$ is small compared to the clean surface tension value $\sigma_0 = 7.2 \cdot 10^{-2}$ N m⁻¹. Indeed, an estimation using an equation of state derived from the Langmuir isotherm [10] yields $\Delta \sigma/\sigma_0 = n \tilde{\Gamma}_m \ln(1 + k_{\max})/\sigma_0 \approx 0.025$.

The parameter $k$ can be bounded by below as well. A situation in which the plastron is highly immobilized like in the experimental study [4] necessarily requires that $ekMa/\phi_X = kMa/g \gtrsim 1$, since otherwise $\delta_u u_f^U \approx 0$ and the slip would be relatively large [see Equation (S3)]. Consequently, we choose a lower bound $k > k_{\min} = g/MA$ which, using the values $g = 600$ and $Ma \approx 8.3 \cdot 10^4$ (estimated using $\Gamma_m = 3.9 \cdot 10^{-6}$ mol m⁻² and $\dot{U} \approx 3(\tilde{u})_{\zeta} = 2.61 \cdot 10^{-4}$ m s⁻¹ from [4]), leads to

$$7.3 \cdot 10^{-3} \leq k \leq 10^{-1}.$$  \hfill (S28)

In addition, the expression (3) can be combined with the quantitative results from [4] in order to obtain an estimate of the kinetic rate constants $\tilde{k}_a$ and $\tilde{k}_d$. On one hand, note that for arbitrarily long gratings (i.e., $g \to \infty$), Eq. (3) indicates that the slip velocity converges to the clean-case value $u_{tc} \to u_{tc}^{\text{clean}}$ (see Figure 3). On the other hand, for intermediate lengths in which (3) is still converging to this plateau, the dominant balance of terms results in a simplified approximation $u_{tc} \approx a_2 Bi g^2/[a_1 kMa(1 + Da)]$. Moreover, the estimated order of magnitude of $D_f$ results in a thick boundary layer $\delta \approx a_3$, since $Pe/g = O(10^{-2}) \ll 1$ when the values $\tilde{h} = 5 \cdot 10^{-5} \text{m}$, $\dot{U} \approx 3(\tilde{u})_{\zeta} = 2.61 \cdot 10^{-4}$ m s⁻¹ and $g = 600$ from [4] are used. Similarly, the value of $\tilde{k}_a \tilde{\Gamma}_m$ is generally large enough to ensure $k_a \tilde{\Gamma}_m > 10^{-5}$ m s⁻¹ [2], which suggests that in this kind of small-scale flows we have $Da \gg 1$. This means that $(1 + Da \delta) = a_3 Da$, yielding a final estimate of

$$\frac{\tilde{k}_a}{\tilde{k}_d} \approx \frac{a_2 g^2}{a_1 a_3 Ma} \left( \frac{D_f}{\tilde{U}_{tc} \tilde{\Gamma}_m} \right).$$ \hfill (S29)

The right-hand side of (S29) is fully determined from the parameters that are already known or estimated, as well as from the result $\tilde{u}_{tc} = 12.18 \pm 3.48$ µm s⁻¹ from [4]. Combining this expression with the bounds (S28) for $k$, we obtain

$$7.1 \cdot 10^1 \leq \frac{\tilde{k}_a}{\tilde{k}_d} \leq 1.8 \cdot 10^3.$$ \hfill (S30)
As mentioned previously, the Damköhler number can be estimated to be high for most surfactants (i.e. $Da \gtrsim 1$) \cite{2}, so the individual values of $\hat{k}_a$ and $\hat{k}_d$ are expected to only have a weak effect separately, and the estimation of the ratio $\hat{k}_a/\hat{k}_d$ in (S30) is enough to effectively characterize the underlying surfactant. The grey band in Figure 3 corresponds to the limits set by (S28) and (S30) in the limit of $Da \to \infty$. The edges of the band change only slightly when values of $Da$ as low as 1 are considered. The specific choice of $\hat{c}_0 = 3 \cdot 10^{-4}$ mol m$^{-3}$, $\hat{k}_a = 89.5$ m$^3$ mol$^{-1}$ s$^{-1}$ and $\hat{k}_d = 0.75$ s$^{-1}$ (which leads to $k = 3.58 \cdot 10^{-2}$ and $\hat{k}_a/\hat{k}_d = 1.19 \cdot 10^2$ m$^3$ mol$^{-1}$) yields a good agreement with our experimental results (Figure 3).