Mass transport in wavy falling films: reduced modeling and experiment

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Abstract

In many industrial units such as packing columns, falling film reactors, etc., the liquid phase is designed as a falling film. It is well known that the mass and heat transfer in laminar wavy film flows is significantly enhanced compared to flat films. The kinetic phenomena underlying the increase in mass and heat transfer are, however, still not fully understood. For an efficient design of falling film units, computational models that account for these enhanced transport mechanisms are of key importance. In this paper, we present a reduced modeling approach based on a long-wave approximation to the fluid dynamics of the film. For the numerical simulation of the mass transport of absorbed gas in the moving film in the reduced model we use an arbitrary Lagrangian-Eulerian method. The proposed method can be used to simulate liquid-side controlled mass transfer for different liquid-gas pairs. As a representative example we study the physical absorption of oxygen into a water film. Results of a series of forward simulations for Reynolds numbers ranging from 5 to 200 are presented. Furthermore, we introduce a new 2D high-resolution laser-induced luminescence measurement technique. The results obtained from the experiments are used for validation of the reduced model. Both in the numerical simulation results and in the high-resolution 2D-concentration measurements obtained in the experiments we observe similar patterns of high concentrations locally, especially in the areas close to the wave hump. Finally, Sherwood correlations, based on the integral information of our model calculations and experimental data, are presented to

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perform a quantitative comparison with literature values.

 $Keywords:\;$ Wavy falling film, mass transfer, reduced model, PLIL measurements, ALE approach

Nomenclature

Notation	Description
x	position in flow direction
y	position in direction of the wave height
t	time
$\mathbf{u} = (u, v)$	velocity field given by the Navier-Stokes equations
Γ	gas-liquid interface
$C_H = 0.0334$	dimensionless Henry coefficient
h(x,t)	local film height
q(x,t)	local volume flux of the liquid film
λ	wave length
δ	average film thickness
Re	Reynolds number
We	Weber number
Ka	Kapitza number
\mathbf{Sc}	Schmidt number
\mathbf{Sh}	Sherwood number
σ	surface tension coefficient
η	dynamic viscosity
ρ	density of the liquid film
$\nu = \frac{\eta}{\rho}$	kinematic viscosity of the liquid
$u_{Nu} = g\delta^2 \rho/3\eta$	average Nusselt velocity
$u_{max} = g\rho\delta^2/2\eta$	maximum Nusselt velocity
D	diffusion constant
$D_{ m mol}$	molecular diffusion coefficient
$D_{\mathrm{eff}}(x,y,t)$	effective diffusion coefficient
Ω_t	time-dependent domain
$\hat{\Omega}$	fixed reference domain
h_{Ω}	mesh size used in the spatial discretization
С	oxygen concentration
c_h	half value oxygen concentration, at which $\tau/\tau_0 = 1/2$
c_w	oxygen concentration at the wall
c_i	oxygen concentration at the interface
c_s	saturated concentration of oxygen
c_{in}	integrated inlet oxygen concentration
c_{out}	integrated dissolved oxygen concentration
k_L	overall liquid-side mass-transfer coefficient
$k_L^*(x)$	local mass transfer coefficient

Notation	Description
$k_{Nu}^*(x)$	local transfer coefficient for the case of a laminar $flat$ film
au	phosphorescence lifetime of the indicator
I(t)	phosphorescence intensity
L	measure for the local excitation energy of the laser
P	integrated light intensity
U	inner circumference of the tubular reactor
A	effective mass transfer area

1. Introduction

In industrial applications such as CO_2 scrubbers, falling film evaporators, absorption heat pumps as well as many others, falling films are widely used. In these devices the liquid phase occurs as a gravity driven thin film. It is well-known, that the heat and mass transfer properties in these films are significantly intensified by the waviness of the film¹. Most previous works provide only integral information, besides the 1D data presented in^{2,3,4}. To our knowledge, currently no 2D high-resolution local measurement data are available. Thus, this transport enhancement mechanism is still not fully understood.

Due to the strong convective transport in falling films, mass transfer modeling in falling films is based on fluid dynamics modeling. The calculation of the fluid dynamics in a falling film is typically done either by a two-phase model, i.e., by solving the Navier-Stokes equations (NSE) simultaneously in the liquid and gas phases, or by a simplified one-phase approach considering the NSE only in the liquid phase with a free boundary at the gas-liquid interface.

In^{5,6} a simplified 2D Navier-Stokes model and a standard finite difference method are used to simulate fluid dynamics of moving waves, applying a periodic disturbance at the inflow boundary. It is found that the recirculation at the solitary wave enhances the transport process and that the periodic disturbance leads to an enhancement of the gas absorption. Other results with simplified models can be found in the literature, e.g., ^{7,8,9}.

Compared to the simplified approach, only few direct numerical simulations (DNS) of the two-phase model have been reported in the literature. One of the recent DNS¹⁰ employs a sharp interface model in the two-phase NSE and the mass transfer is described by non-stationary convection-diffusion equations in both phases. For spatial discretization, a finite-volume approach is used, and the interface is captured by the volume-of-fluid (VOF) method. In the simulations, mass transfer enhancement mechanisms have been identified in specific wave regimes, especially waves with a vortex. Note that, compared to the real system, an artificially increased diffusion coefficient had to be used for stability reasons. Nevertheless, the detailed simulations give insight into interesting transport phenomena inside the film, including a "finger" of high concentration which starts at the downstream critical point of the wave hump.

However, the DNS of the film fluid dynamics requires huge computational effort and sophisticated numerical tools which limit their use in practice, e.g., to perform comprehensive model identification 11,12,13 . Therefore, there is a need

for a reduced modeling approach, which is capable of representing the most important properties of the transport phenomena in falling films at a modest computational cost.

In this paper three related topics are treated which lead to a validated reduced model of mass transport in wavy falling films. Firstly, a *new reduced transport model* for liquid falling films is presented. It is based on a long-wave approximation to the fluid dynamics of the film introduced by Balakotaiah and his coauthors^{14,15}. This spatially one-dimensional model yields a height function and a flow field which approximate the fluid dynamics in a realistic (essentially) 2D falling film. This information is used as input for a mass transport equation, which is discretized on the moving wavy domain by a stabilized arbitrary Lagrangian-Eulerian (ALE) finite-element method^{16,17}. The numerical simulations (presented in Section 5) show that the long-wave approximation is able to represent the major hydrodynamic properties of the film such as roll cells in the solitary wave hump and a back flow in the capillary wave region. Furthermore, mass transfer enhancement is observed in these regions when using the reduced transport model. Due to the (relative) simplicity of the reduced model, the simulations can be realized at low computational costs.

A second important contribution of this paper is a new 2D high-resolution measurement technique. The characteristic properties of a falling film, such as the small thickness and the transient as well as highly dynamic behavior, ask for fast and non-invasive measurement techniques. This way it is assured, that no mechanical disturbances of the film occur during the measurements. A suitable 1D measurement technique to investigate the mass and heat transfer into a falling film is the laser induced luminescence (LIL) method, which was successfully applied to measure the concentration and temperature distributions within solitary waves flowing down an inclined plate 2,3,4 . However, the influence of complex phenomena on the mass transfer, such as vortices or roll cells, cannot be investigated with LIL. Rather a 2D measurement method is necessary, which is capable to measure concentration fields. A suitable technique include, for instance, the planar laser induced fluorescence (PLIF)^{18,19,20,21,22} or the molecular tagging thermometry $(MTT)^{23,24}$. Nevertheless, neither PLIF nor MTT were used so far to measure the mass transfer within a falling film. In this paper, the planar laser induced luminescence (PLIL) measurement method is used. PLIL, like MTT, is an intensity-ratio-based measurement technique. It enables the simultaneous 2D-measurement of the film thickness and the absorption of oxygen into a wavy, aqueous falling film.

The third topic treated in the paper is a validation of the reduced model based on the new PLIL measurement data. From a comparison of numerical simulation results for the reduced model with results from the PLIL experiment it follows that for several important physical quantities (e.g., film profile, mass distribution) there is a good qualitative agreement between model prediction and physical data.

The rest of the paper is organized as follows: In Section 2, the modeling ap-

proach is described, focusing on the derivation of the reduced model. This is followed by an explanation of the numerical methods, in particular the ALE approach, in Section 3. The PLIL measurement method as well as the experimental setup is introduced in Section 4. In Section 5, the results of our simulations and experiments are presented and discussed.

2. Mass transfer modeling in falling films

As a case study for the investigation of mass transfer in falling films, we consider in this paper the physical absorption of oxygen into a water film. This two-phase mass transfer problem can be modeled by a coupled system of momentum and mass balances describing the fluid dynamics in both phases (aqueous film, ambient gas) and the conservation of the transferred species (oxygen). Due to its huge computational complexity, this detailed model, which is outlined in Section 2.1, is not suitable as a design model. We therefore propose a reduced model (Section 2.2), which requires much less computational effort but still exhibits the most important fluid dynamics and mass transfer features of the falling film.

2.1. Detailed model

In the model for the falling film that we consider, we assume isothermal conditions, i.e., the energy balance can be omitted. We also assume that the mass transfer of oxygen does not influence the fluid dynamics, and thus the momentum and mass balances in the bulk (fluid dynamics) are decoupled from oxygen transfer. Both assumptions are realistic for the falling film experiment described in Section 4. Based on these assumptions, we obtain the two-phase incompressible Navier-Stokes equations for the fluid dynamics and a transient convection-diffusion equation for the mass transfer. We specify this convectiondiffusion equation, because we will also need it in the reduced model considered below:

$$\frac{\partial c_i}{\partial t} + \mathbf{u} \cdot \nabla c_i - \nabla \cdot (D_i \nabla c_i) = 0, \quad \text{in } \Omega_i(t), \ i = 1, 2, \ t \in [0, T], \quad (1)$$

where **u** denotes the velocity field given by the Navier-Stokes equations, c_i denotes the concentration of oxygen and D_i is the molecular diffusion coefficient in the respective phase Ω_i , i = 1, 2. At the gas-liquid interface Γ , the local chemical equilibrium is imposed by applying Henry's law,

$$c_1 = C_H c_2, \qquad \text{on } \Gamma(t), \ t \in [0, T], \tag{2}$$

where $C_H = 0.0334$ is the dimensionless Henry coefficient. The value for the dimensional Henry coefficient $(C_{Hcp} = 1.389 \times 10^{-3} \frac{\text{mol}}{\text{L atm}})$ is taken from²⁵.

The numerical simulation of the two-phase Navier-Stokes and mass transfer equations is an active research area ^{10,26,27}. The direct numerical simulation of mass transfer in falling films, in particular in three-dimensional flows, is numerically very challenging and requires massive computational effort. This

is mainly due to the large, dynamic, wavy interface, the large jumps in density and viscosity across the liquid-gas interface, and the very thin concentration boundary layers. As a consequence, the detailed modeling approach is currently not suitable for process equipment design. A simplified approach is introduced in the next section.

2.2. Reduced model

Since the species transport is dominated by the liquid side, the key idea towards a reduced model is to reduce the detailed two-phase model to a one-phase model of the liquid film phase only, which is still able to account for the wavy enhancement mechanisms. To this end, the two-phase NSE are replaced by the one-phase NSE in the liquid phase only. A number of such type of models have been developed ^{14,28,29,30}. In this paper, the 2D long-wave expansion presented in ¹⁴ is used to model the film. We outline the main ingredients of this model. One restricts to a spatially 2D flow with velocity profile denoted by $\mathbf{u} = (u, v)$. x, y and t denote the flow direction, the direction of the wave height and time, respectively. Note that unit dimensions of all model quantities correspond to a 2D flow. The long wave equations (LWE) are formulated in terms of two states, namely the local film height h(x, t) and the volume flux q(x, t) defined as

$$q(x,t) = \int_0^{h(x,t)} u(x,y,t) \, dy.$$
(3)

The velocity profile $\mathbf{u} = (u, v)$ inside the film is then computed by assuming a parabolic Nusselt velocity profile

$$u(x,y,t) = \frac{q}{h^3} \left(yh - \frac{y^2}{2} \right),\tag{4}$$

according to the analytical solution in the flat film model by Nusselt³¹, and a corresponding v(x, y, t) such that $\nabla \cdot \mathbf{u} = 0$ holds. The nonlinear LWE in dimensionless form¹⁴ are given by

$$\frac{8}{5}\operatorname{Re}\frac{\partial q}{\partial t} = 4h - \frac{4q}{h^2} + 4\operatorname{Re}\left(\frac{18q^2}{35h^2}\frac{\partial h}{\partial x} - \frac{34q}{35h}\frac{\partial q}{\partial x}\right) - \frac{339}{70h}\frac{\partial h}{\partial x}\frac{\partial q}{\partial x} + \left(\frac{373q}{70h^2} - \frac{9h}{7}\right)\left(\frac{\partial h}{\partial x}\right)^2 - \left(\frac{41h^2}{84} + \frac{2837q}{420h}\right)\frac{\partial^2 h}{\partial x^2} + \frac{449}{70}\frac{\partial^2 q}{\partial x^2} + 4\operatorname{ReWe}\frac{h}{3}\frac{\partial^3 h}{\partial x^3},$$
$$\frac{\partial h}{\partial t} = -\frac{\partial q}{\partial x}.$$

In this work, we choose periodic boundary conditions, implicitly enforcing a wave length of $\lambda = 300 \,\delta$ (as in³²), with δ being the average film thickness. Physical properties are described by fixing the dimensionless parameters

$$\operatorname{Re} = \frac{\rho u_{Nu} \delta}{\eta}, \qquad \operatorname{We} = \frac{\sigma}{\rho u_{Nu}^2 \delta}, \qquad \operatorname{Ka} = \frac{\sigma \rho^{1/3}}{g^{1/3} \eta^{4/3}}, \tag{5}$$

which are the Reynolds, Weber and Kapitza numbers, respectively. Here σ is the surface tension coefficient, η and ρ the dynamic viscosity and density of the liquid film, respectively, g the gravitational acceleration and $u_{Nu} = g\delta^2 \rho/3\eta$ the average Nusselt velocity. Note that compared to ¹⁴ we rescaled the Reynolds number by a factor of 4 to make the definition in (5) consistent with the definition of Re in (17) for annular flow used to characterize the experimental conditions. For a given liquid, the Kapitza number Ka is independent of the flow conditions and can be pre-computed. An explicit relation between the three parameters Re, We, Ka was suggested in^{14,15}. The numerical solution of the LWE yields only approximations to the film shape and velocity field, but also requires much less computational effort than solving the two-phase NSE of the detailed model. The quality of the flow approximations obtained by the LWE is assessed in Section 5.1.1.

The species balance is reduced to a one-phase convection-diffusion equation for the liquid phase only. The time-dependent film height h(x,t) defines a time-varying domain $\Omega_t = \{(x,y) : 0 \le x \le \lambda, 0 \le y \le h(x,t)\}, t \in [0,T]$, representing the liquid phase. The transient convection-diffusion equation

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c - \nabla \cdot (D\nabla c) = 0, \qquad x \in \Omega_t, t \in [0, T], \tag{6}$$

holds on the domain Ω_t . The boundary concentration at the free interface is assumed to be equal to the equilibrium concentration according to Henry's law (2). The numerical discretization of this mass transfer equation on a moving domain is described in Section 3.

For the diffusion constant D in (6) we use the most simple choice, i.e., a constant molecular diffusion coefficient $D \equiv D_{\text{mol}}$.

Summarizing, the reduced model that we consider consists of the LWE and the convection-diffusion equation (6). The former is spatially one-dimensional and yields the time dependent two-dimensional domains Ω_t and the velocity field $\mathbf{u}(x, y, t)$ needed for the latter. Results of simulations based on this reduced model and a comparison with experimental results are given in Section 5.

Since the considered reduced model makes some assumptions (2D geometry, domain and velocity from LWE) to reduce the computational time, the results will be of course different from a DNS simulation or real measurements. To compensate for modeling errors and improve the model in future works, we may apply the incremental identification methodology, that has been already introduced in previous papers^{11,12,13}. The main idea is to replace the molecular diffusion coefficient D in eq. (6) by a function that we call effective diffusion coefficient, which depends on space and time, i.e. $D = D_{\text{eff}}(x, y, t)$. Since using PLIL, the concentration may be measured as a function $c_m(x, y, t)$ of space and time. From that measurement data we could estimate $D_{\text{eff}}(x, y, t)$, e.g. by minimizing the prediction error $||c(D_{\text{eff}}) - c_m||_2$. In a next step, we could assume a model for D_{eff} as a function of concentration c and free parameters p, i.e. $D_{\text{eff}}(c, p)$. Using the estimates D_{eff} and the measured concentrations c_m , we could estimate the parameters p and get hence a more reliable model, which is still efficient from a computational point of view.

3. Numerical simulation methods

In this section we discuss the numerical simulation methods used for the reduced model. The computational complexity of the reduced model is rather low (compared to the full Navier-Stokes model) and the numerical methods that we use are fairly straightforward. We only give a short explanation of the numerical methods used.

We apply different numerical techniques to simulate the fluid dynamics and the mass transfer in the reduced model. For numerical simulation of the fluid dynamics based on the LWE, we developed a software in which an external Mathematica code provided by Balakotaiah^{14,15} is embedded. This code uses high order finite differences for the discretization of the spatially one-dimensional nonlinear LWE. For more explanation on the numerical simulation of the LWE we refer to^{14,15}.

We developed an efficient finite element solver for the non-stationary convection-diffusion equation (6). The solver is implemented in the finite-element (FEM) package DROPS³³. For spatial discretization, piecewise linear finite elements on a tetrahedral grid are employed, using SUPG^{34,35,36} for stabilization of the convection-dominated problem. A standard backward Euler method is used for time discretization. The resulting linear systems are solved by a preconditioned GMRES method³⁷.

To handle the time-dependent domain Ω_t , we use the Arbitrary Lagrangian-Eulerian (ALE) approach 16,17,38,39 . The key idea is to map a fixed reference domain $\hat{\Omega}$ to the time-dependent domain Ω_t by means of a mapping $\Phi^t : \hat{\Omega} \to \Omega_t$. Since the height of the free surface is an a-priori known function h(x,t), it is natural to use a mapping of the form $\Phi^t(\hat{x}, \hat{y}) = (\hat{x}, h_t(\hat{x}, t) \frac{\hat{y}}{\hat{y}_{\max}})$, which simply scales the y-coordinate such that the free boundary of Ω_t matches the film height (Fig. 1).



Figure 1: ALE approach: The reference domain $\hat{\Omega}$ is mapped to the physical domains Ω_{t_1} and Ω_{t_2} by Φ^{t_1} and Φ^{t_2} , respectively.

The partial differential equation (6) can be reformulated in ALE form as

$$\frac{\partial c}{\partial t}|_{\hat{\Omega}} + (\mathbf{u} - \mathbf{u}_{\Omega_t}) \cdot \nabla c - \nabla \cdot (D_{mol} \nabla c) = 0 \quad \text{in } \Omega_t, \quad t \in [0, T], \quad (7)$$



Figure 2: Relationship between phosphorescence intensity curve and the resulting image intensity. The colored areas resemble the light collected on the CCD-sensor for the first image (P_1) and the second image (P_2) .

where $\frac{\partial c}{\partial t}|_{\hat{\Omega}}$ is the time derivative w.r.t. the fixed reference domain $\hat{\Omega}$ and \mathbf{u}_{Ω_t} is the mesh velocity induced by the mesh transformation Φ^t . We refer to ¹⁶ for more details.

4. Measurement of oxygen concentration in the liquid film by a phosphorescence-based technique

In this section, we introduce a phosphorescence-based measurement technique as a special case of the planar laser-induced luminescence. This technique can be used for obtaining 2D measurement data on film thickness and concentration distributions. In this paper we use it for measuring film thickness and local oxygen concentration in the liquid film to validate the reduced model described in Section 2.2.

4.1. Measurement principle

The PLIL method uses tris(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) dichloride (abbreviated as Ru(dpp)) as an optical indicator, which upon excitation with UV-light emits solely phosphorescence. In an aqueous solution, this emission is quenched by dissolved oxygen and thus reduces the phosphorescence lifetime τ of the indicator according to the Stern-Volmer relation⁴⁰,

$$\frac{\tau}{\tau_0} = \frac{1}{1 + c/c_h} ,$$
 (8)

where τ_0 is the phosphorescence lifetime in an oxygen-free environment, c is the oxygen concentration and c_h denotes the half value concentration, at which $\tau/\tau_0 = 1/2$. At 20 °C the according values are $\tau_0 = 3.57 \ \mu s$ and $c_h = 0.105 \ mol m^{-3}$. If there is a concentration distribution within the falling film, each excited volume element will emit a phosphorescence signal dependent on the local oxygen concentration. This phosphorescence signal is characterized by its lifetime according to equation (8). Recording these emissions with an intensified CCD-camera yields a grayscale image, in which the graytone of each pixel correlates to the local lifetime of the phosphorescence signal, and thus also to the local oxygen concentration. Figure 2 shows the relationship between the phosphorescence and resulting integrated intensity for each pixel of the image.

As the laser is turned on at t = 0, the phosphorescence intensity increases according to the equation

$$I(t) = KL\tau(1 - e^{-\frac{t}{\tau}}) \qquad \text{for } t \in [0, t_L].$$
(9)

Here, I(t) denotes the phosphorescence intensity, K is a device constant and L is a measure for the local excitation energy of the laser. As the laser is turned off at $t = t_L$, the phosphorescence decays exponentially according to the equation

$$I(t) = KL\tau e^{-\frac{t}{\tau}} \left(e^{\frac{t_L}{\tau}} - 1 \right) \quad \text{for } t \in (t_L, \infty).$$

$$\tag{10}$$

The light intensity P, which is integrated on each pixel of the camera sensor during the exposure times $\Delta t_1 = t_2 - t_1$ and $\Delta t_2 = t_4 - t_3$, corresponds to the area under the phosphorescence curve (colored areas in Figure 2). For an image recorded during the laser excitation,

$$P_1 = \int_{t_1}^{t_1 + \Delta t_1} KL\tau (1 - e^{-\frac{t}{\tau}}) dt = KL\tau (\Delta t_1 + \tau e^{-\frac{t_1}{\tau}} (e^{-\frac{\Delta t_1}{\tau}} - 1)).$$
(11)

Similarly, for images captured during the phosphorescence decay,

$$P_2 = \int_{t_3}^{t_3 + \Delta t_2} KL\tau (e^{\frac{t_L}{\tau}} - 1)e^{-\frac{t}{\tau}} dt = KL\tau^2 (e^{\frac{t_L}{\tau}} - 1)e^{-\frac{t_3}{\tau}} (1 - e^{-\frac{\Delta t_2}{\tau}}).$$
(12)

The contributions of K and L to the recorded signal are difficult to determine experimentally, but can be eliminated by calculating pixel-wise the ratio R of the two images P_1 and P_2^{24} , according to

$$R = \frac{P_1}{P_2} = \frac{\Delta t_1 + \tau \ e^{-\frac{t_1}{\tau}} \left(e^{-\frac{\Delta t_1}{\tau}} - 1\right)}{\tau \ \left(e^{\frac{t_L}{\tau}} - 1\right)e^{-\frac{t_3}{\tau}} \left(1 - e^{-\frac{\Delta t_2}{\tau}}\right)}.$$
(13)

This yields an expression, which only depends on the phosphorescence lifetime τ and the experimental settings Δt_1 , Δt_2 , t_1 , t_3 and t_L . For fixed experimental settings, this correlation gives unique identifiable values of τ . Therefore, the oxygen concentration can be determined, since R is known. Note that equation (13) only describes the fundamental principle of the developed PLIL method. For a quantitative evaluation of the obtained images, additional contributions to the measurement signal (e.g. image intensifier, noise) must be taken into consideration. This is omitted here for clarity.



Figure 3: Scheme of the experimental setup of a falling film absorber.

4.2. Film thickness

The film thickness can be determined since only the excited liquid emits phosphorescence, whereas the glass wall and the gas phase appear black in the resulting gray scale image. The film thickness can be quantified by counting the illuminated pixels. In order to convert the number of pixels into the dimension of length, e.g. μ m, the conversion factor f of the camera system needs to be known. This conversion factor is determined by a calibration experiment, for which a test target, on which a grid with known dimensions is etched, is photographed. The resulting conversion factor is $f = 7.12 \ \mu$ m per pixel. Nevertheless, due to optical distortions, the achievable spatial resolution is $\pm 14.24 \ \mu$ m pixel⁻¹.

4.3. Experimental setup and settings

Figure 3 shows the experimental setup of the falling film absorber, which has been designed and implemented to validate the PLIL technique and gather data for mass transfer model identification. A main reservoir contains demineralized water which is degassed with purified nitrogen. The concentration of Ru(dpp) in water is set to 100 mg l^{-1} . To produce forced waves, the liquid is pumped to the falling film absorber using a peristaltic pump. The absorber consists of a glass tube of 1 m length with an inner diameter of 50 mm and a wall thickness of 5.5 mm. An annular film flow is created on the inside wall by a film producing element, which also facilitates the simultaneous addition of a gas stream. The

Table 2: Settings used during the experiments.			
Parameter / Unit	Value		
Temperature / °C	20		
Liquid side Reynolds number $Re_l/$ -	43.8		
Liquid flow rate \dot{V}_l / L h ⁻¹	25		
Gas side Reynolds number $Re_g/$ -	55.4		
Gas flow rate \dot{V}_q / L h ⁻¹	120		
Gas stream composition N_2 / O_2 / $\%$	79.5/20.5		
Initial concentration of liquid $c_0/ \text{ mol m}^{-3}$	< 0.0256		
Interfacial concentration of liquid $c_i/$ mol m ⁻³	0.285		
Forcing frequency $/$ Hz	5.6		
Spatial accuracy $/\mu m$	± 14.24		
Water density $ ho/~{ m kg}~{ m m}^{-3}$	995		
Water viscosity η / Pa s	0.001		
Water surface tension σ / N m ⁻¹	0.073		

gas phase flows co-currently in the core of the glass tube and is set by a mass flow controller (ANALYT-MTC).

A diode laser (Omicron) is used as a light source, which is connected through light conductors to the sheet generating optics. The resulting light sheet has a full width half maximum (FWHW) of 229 μ m and is 10 mm high. The laser sheet optics and the camera system (LaVision) are positioned perpendicular to each other on a vertically adjustable platform. The camera system consists of an image intensifier and a CCD camera. A long distance microscope (Infinity, Distamax) is mounted to the image intensifier. In order to eliminate any scattered laser light, an edge filter (GG 495) is used. The observed image area is $4.8 \times 3.6 \text{ mm}^2$ and can only portray a part of the observed wave. In addition, the frame rate of the camera is too low to grab several images of the same wave. Nevertheless, since 500 images at each measurement position were taken, it was possible to stitch several images together to create an entire wave. The experimental parameters are listed in table 2.

The accuracy of the PLIL method is limited by the optical boundary conditions of the experimental setup (thickness of laser sheet, optical distortions and overlaps). Theoretical calculations for a worst case scenario yield a maximum deviation of the oxygen concentration of < 9% with respect to the saturation concentration. In the present case this is 0.0256 mol m⁻³. The solubility of oxygen in water is low. Therefore the overall resistance of the transport resides in the liquid phase. As a consequence the gas-liquid interface can be assumed to be saturated. Due to optical limitations, no direct proof of this assumption can be provided.



Figure 4: Fluid dynamics simulation of a fully developed wave based on the LWE for Re = 41.

5. Results and discussions

In this section, numerical simulation results and experimental results for a vertically oxygen-absorbing wavy falling water film are presented and compared. In Section 5.1 numerical simulation results of the reduced model introduced in Section 2.2 are given. Experimental data from the PLIL measurements described in Section 4 and a comparison of these results with numerical simulation results for the reduced model and with results from the literature are given in Section 5.2.

5.1. Numerical simulation results for the reduced model

5.1.1. Fluid dynamics

The understanding of the complex fluid dynamics under the wavy surface is crucial to further investigate the mass transfer enhancement mechanisms in falling films. As a starting point for the simulation of the single-phase masstransfer on the time-varying spatial domain, an approximation of the transient film thickness and flow field is obtained by LWE. Depending on the length of the film (e.g. 25 cm, 50 cm or 100 cm, etc.), a certain number of periodic waves are consecutively simulated. As an example, Fig. 4 shows the velocity magnitude distribution within one wave period for Re = 41, which adequately reflects the experimental conditions. The wave pattern results from the periodic solution of the LWE. A large solitary wave followed by several small capillary waves is clearly revealed by the wave structure. More details of the flow field near the large solitary wave are shown in Fig. 5(a). A zoomed view of the region between the big wave hump and the first capillary wave (see Fig. 5(b)) shows a back flow. Similar results were also reported in ^{41,42}. However, much less computational effort is required here to obtain this characteristic flow phenomenon. Furthermore, in a reference frame moving with the phase velocity, a pronounced vortex is observed under the large wave hump (see Fig. 6). This fluid dynamics is combined with mass transfer as explained in Section 2.2.



(a) Velocity field near the big wave hump. The circle indicates the region of back flow.



(b) Zoomed-in picture shows the back flow between wave hump and capillary wave.

Figure 5: Simulated velocity field of a fully developed wave based on the LWE for Re = 41.

5.1.2. Mass transfer: concentration distributions

Using the computed velocity profiles, the ALE-FEM discretization with stabilization of the convective terms is applied to solve the transient convectiondiffusion equation (7) as described in Section 3. Dirichlet conditions are set at the inlet and at the phase boundaries. At the inlet, a low oxygen concentration close to zero $(10^{-5} \text{ mol m}^{-3})$ is assumed, which corresponds to the degassing of the liquid in our experimental investigations. This value is also used as the initial concentration $c(t_0) = c_0$. We assume that the transport process is only limited in the liquid phase and the concentration at the interface c_i corresponds to the equilibrium concentration c_s according to Henry's law, hence, $c_i = c_s = 0.28$ mol m^{-3} (oxygen saturation concentration of air in water) is used as Dirichlet boundary condition on the film surface of the wavy film. Homogeneous Neumann conditions are used at the remaining boundary conditions. Compared to a flat film, the calculation of the wavy film is more complicated and requires a much finer discretization in order to ensure the necessary numerical accuracy. For this reason, for all calculations the length of the wavy film is limited to 0.25 m. The numerical problems are solved on a sufficiently fine discretized domain. Taking Re = 100 as an example, we employed a time step of $\Delta t = 1.5 \times 10^{-4}$ s and mesh sizes $\Delta x = 1.57 \times 10^{-4}$ m and $\Delta y = 9.76 \times 10^{-5}$ m for spatial discretization in the direction of flow and film thickness, respectively. The adequacy of the grid resolution was checked by performing a grid convergence study.

As a representative example, the simulated concentration distributions of dissolved oxygen in water for Re = 41 at a position close to the inlet is shown in



(c) Concentration (mol/m^3) at t =0.03 s with the vortex plot at the wave hump.

Figure 6: Simulated concentration distributions of oxygen in water for Re = 41 shows the mixing effects by rolling cells in the wave hump. Top and middle: Concentration distributions at two different instants in time. The bottom plot adds additional streamlines to the middle plot.

Fig. 6. The concentration distributions at two selected time instants are shown in Fig. 6(a) and Fig. 6(b). The emerging vortex at t = 0.03 s is plotted in Fig. 6(c). We observe that during this short time period the circulation under the wave hump transported a large amount of oxygen into the wave.

The simulation results for the wavy-film model show that the mass transfer increases significantly compared to a flat-film model. All simulations reach the stationary states much faster, and the average oxygen concentration at the outlet is relatively high even for short film lengths.

5.1.3. Mass transfer: integral concentration at the outlet

Figure 7 shows the simulated integral oxygen concentration at the outlet of the film at x = 0.25 m for Re = 25, including the time-oscillating integral concentration and a smoothed curve averaged over one wave period.

Figure 8 shows the respective results for all conducted simulations. The dots indicate that the steady state has been reached, i.e., that the relative change of the smoothed concentrations over time are below a certain tolerance limit, e.g. 1%. The results show that the time required to reach the steady state is continuously decreasing as the Reynolds number increases. The steady-state values of the smoothed concentrations are used in Section 5.2.2 below for the calculation of the overall mass transfer coefficient (19).

5.1.4. Mass transfer: local mass transfer coefficient

The experiment and the simulation provide two-dimensional concentration field data. Based on these data, the following local mass transfer coefficient can be calculated as a function of the position x in flow direction,

$$k_L^*(x) = -\frac{D_{mol} \partial c(x, y) / \partial y|_{y=d_f}}{c_i - c_w(x)},$$
(14)

where $\partial c/\partial y|_{y=d_f}$ is the concentration gradient at the interface and c_w, c_i are the oxygen concentration at the wall and the interface, respectively ². Since c_i is constant and c_w is under the current boundary conditions virtually zero, it becomes clear, that the magnitude of k_L^* is mainly influenced by the concentration gradient at the interface. Therefore the coefficient k_L^* indicates the magnitude of the local interfacial molar flux transporting oxygen across the interface from the gas phase to the liquid phase.

Note that the gradient is calculated in y-direction and not in the direction normal to the wavy film surface which might be more natural but also more complicated (e.g., accurate evaluation of the normal, correct wall position to evaluate c_w). This simplification may lead to inaccurate results at locations where the surface is nearly perpendicular to the flow direction (front of the wave), where the determined gradient still can be low even if the mass transfer across the interface is large. However, at the back of the wave where the surface is flat this simplified approach is suitable to predict the local rate of mass transfer.



Figure 7: Simulated oxygen concentration over time for Re = 25: average concentrations at the end of the film at 0.25 m (solid line), average concentrations smoothed over one wave period (dashed line).



Figure 8: Simulated oxygen concentrations over time for nine different Reynolds numbers: average concentrations at the end of the film at 0.25 m (solid line), average concentrations smoothed over one wave period (dashed line). Circles correspond to values at steady state conditions that are used for the evaluation of the mass transfer function.



Figure 9: Film profile (solid line) and local transfer coefficient (dashed line) obtained from the simulation for Re = 41. For comparison, the local transfer coefficient k_{Nu}^* for the corresponding flat film is plotted as well (dotted line).

For comparison we also introduce the corresponding local transfer coefficient for the case of a laminar flat film,

$$k_{Nu}^{*}(x) = \sqrt{\frac{D_{mol} \ u_{max}}{\pi x}},$$
 (15)

where $u_{max} = g\rho \delta^2/2\eta$ is the maximum Nusselt velocity. Assuming $c_w = 0$, this local transfer coefficient can be derived from the analytical mass transport solution ⁴³.

A numerical simulation result for both coefficients k_L^* , k_{Nu}^* is given in Figure 9, which will be compared to experimental results in Section 5.2.3 below. At the back of the wave we observe $k_L^* > k_{Nu}^*$ indicating that the interfacial transport is enhanced compared to a flat film. This is caused by a steeper concentration gradient at the interface resulting in a higher molar flux. We assume that this thinner boundary layer results from the recirculating flow in the wave hump, which flows over a residual layer and transports liquid with low oxygen concentration from this residual layer to the back of the wave. In contrast to that, the boundary layer is broader in the region of the wave hump due to mixing effects of the vortex which transports oxygen from the gas-liquid interface to the interior of the wave (Figure 6). This leads to a flattening of the concentration gradient at the interface and, thus, to $k_L^* < k_{Nu}^*$. In the capillary wave region the local transfer coefficient increases again, oscillating towards a ratio $k_L^*/k_{Nu}^* > 1$. This is a result of the local film thinning effect increasing the conductive transport. Similar observations were made by ⁴⁴ investigating the heat transfer in a wavy film.



Figure 10: Measured film thickness and local oxygen concentration. Measurement position starts at x = 50 mm after the inlet, Re = 43.8.

5.2. Experimental data

In this section we present several experimental results and compare these with those from the literature and from numerical simulation results of the reduced model.

5.2.1. Film profile and concentration distribution

The measured concentration distribution within a wave period of a falling film at Re = 43.8 close to the inlet (Section 4.3) is shown in Figure 10. We observe a good qualitative agreement with the simulation results in Figure 6. Both the concentration distributions in the simulation and those measured in the experiment show that a thin residual layer exists below the surface waves, where the oxygen concentration remains comparatively low. Furthermore, the measurement result shows that on top of this residual layer there is an area of high oxygen concentration inside the wave hump. Due to velocity differences between the residual layer and the wave hump, a roll cell emerges inside the wave hump, which transports the oxygen from the surface into the wave. In the numerical simulations the impact of this vortex on mass transfer inside the wave hump is also observed (Fig. 6). Furthermore, in both simulation and experiment, we observe a high concentration at the tip of the capillary waves. These results are also in qualitative agreement with other numerical studies ^{6,7,10,45}.

Comparing the film profiles in simulation and experiment (Figures 6 and 10), we observe the same structure with a large wave hump and smaller capillary waves in front of that. However, the height of the waves is larger in the simulation which can be explained by the fact that here the waves are fully developed whereas in the experiments this state was not reached as the waves interacted and partially collapsed due to external disturbances.

5.2.2. Integral concentrations: Sherwood correlation

In this section scaled Sherwood numbers are evaluated from simulated and measured concentrations, to illustrate the efficiency of the mass transfer with respect to different Reynolds numbers. They are compared to literature values



Figure 11: Comparison of simulation and experimental data with the empirical Sherwood correlation developed by Bakopoulos⁴⁶. The error bars indicate a 13 % deviation from the correlation, which corresponds to the reported error in ⁴⁶.

from 1,46,47 . Simulation results using a flat-film model are also presented for the sake of completeness.

Figure 11 shows the computed mass transfer function $Sh/Sc^{0.5}$ as a function of the Reynolds number for both, a flat-film model and the wavy-film model proposed in this work. The Schmidt number is defined as

$$Sc = \frac{\nu}{D_{\rm mol}},\tag{16}$$

where $\nu = \frac{\eta}{\rho}$ is the kinematic viscosity of the liquid. The Reynolds number Re is defined by

$$Re = \frac{Q}{\nu U},\tag{17}$$

where Q denotes the volumetric flow rate of the liquid film and U is the inner circumference of the tubular reactor. The Sherwood number Sh is evaluated as

$$Sh = \frac{k_L \delta}{D_{\text{mol}}},\tag{18}$$

where δ denotes the mean film thickness. Here, the values $\nu = 1.004 \times 10^{-6} m^2 s^{-1}$ and $D_{\rm mol} = 1.97 \times 10^{-9} m^2 s^{-1}$ (corresponding to a temperature of 20 °C taken from⁴⁸) are used. k_L denotes the overall liquid-side mass-transfer coefficient,

$$k_L = \frac{Q}{A} \cdot \log \frac{(c_s - c_{in})}{(c_s - c_{out})},\tag{19}$$

describing the integral behavior of the absorber^{1,47}, where A and c_s are the effective mass transfer area and the saturated concentration of oxygen, respectively. c_{in} and c_{out} correspond to the inlet concentration and the dissolved

oxygen concentrations integrated over input and output boundaries and observation time. The calculated overall mass transfer coefficient for the wavy-film and flat-film models are compared to two empirical correlations from Brauer¹ and Bakopoulos⁴⁶ (Figure 11). Experimental values from the experiments performed in this work are also shown, for c_{out} evaluated at 25 cm after the inlet. The experimental data are in quantitative accordance with the correlation of ⁴⁶, which demonstrates the validity of the obtained new measurement methodology. Furthermore, the values calculated by means of the flat-film model show good agreement with the correlation in literature¹.

The simulation results for the reduced wavy film model show the strong intensification of mass transfer that is well-known from experiments. However, the calculated values for the reduced model are significantly higher than the correlation of Bakopoulos⁴⁶. This may be due to the fact that an idealized and hydro-dynamically fully developed film is assumed in the reduced model, which results in ideal conditions for a more intensive mass transfer. In reality, the film flow starts at the inlet as a flat film, which gradually becomes wavier, until fully developed waves have formed. Corresponding to this hydrodynamic evolution the mass transfer increases, since it is augmented by the convective transport within the waves. The reduced model that we consider does not take this process of hydrodynamic development into account. We consider this as the main reason for the calculated mass transfer being much higher than the one observed in the experiments.

Furthermore, important properties and flow conditions relevant for the formation of waves such as the surface tension, the frequency of the waves or the type of inlet construction⁴⁶, are not considered in this diagram. This also leads to discrepancies between the simulated and experimental data from the empirical correlations.

5.2.3. Local mass transfer coefficient

We determined the local mass transfer coefficient k_L^* from the experimental data (14), and compared it to the corresponding coefficient k_{Nu}^* for a flat film (15). Figure 12 exemplary illustrates how the local mass transfer coefficients change with the shape of a wave. As mentioned above in Section 5.1.4, the local transfer coefficient k_L^* will be larger in regions where the interfacial gradient $\partial c/\partial y|_{y=d_f}$ is large.

In Figure 12(a), at the back of the wave the ratio k_L^*/k_{Nu}^* is larger than one and nearly constant. As the wave hump forms and the film thickness increases, the local mass transfer coefficient k_L^* decreases. We expect that this is due to the existence of a vortex inside the wave hump, as shown in simulations in this work and that of other researchers ^{5,6,10,45}. This vortex rolls over a residual layer and constantly transports liquid from the interface towards the interior of the wave. This increases the boundary layer and the concentration within the wave hump. The increased boundary layer then leads to a decreased interfacial concentration gradient and therefore also to smaller values of k_L^* . In the capillary wave region k_L^* gradually increases as the wave contour approaches the shape of a flat film.



(a) Measurement position starting at x = 30 mm after the inlet.



(b) Measurement position starting at x = 50 mm after the inlet.



(c) Measurement position starting at x = 70 mm after the inlet.

Figure 12: Experimentally determined concentration distributions and the corresponding local mass transfer coefficients for waves at different positions after the inlet, Re = 43.8. For comparison, the local transfer coefficients k_{Nu}^* for the corresponding flat films are plotted as well (dotted line).

As the wave develops (Figs. 12(b) and 12(c)), the concentration distribution and also the local transfer coefficient change. This is caused by the more pronounced convective transport due to the vortex within the wave hump. Especially at the back of the wave, where a region of high oxygen concentration forms (best seen in figure 12(c) at position $x \approx 77 \text{ mm}$), k_L^* locally drops below k_{Nu}^* . However, from this position on towards the top of the wave hump a short region with a very thin boundary layer forms. Accordingly, the local transfer coefficient k_L^* rises again and is almost 75% higher than compared to a Nusselt film, only to become smaller than k_{Nu}^* again at $x \approx 80 \text{ mm}$. At the front of the wave hump and the capillary waves k_L^* has small local maxima. At these locations the boundary layer is very thin and therefore the local transfer coefficient is increased. It can be concluded that these experimental results are qualitatively in agreement with local transfer coefficients reported by ^{2,3} and the works cited therein.

We compare the experimental results in Figure 12 with those of the reduced model simulation in Figure 9. First note that depending on the flow regime (measurement position) there are significant differences in the measured mass transfer coefficients, as discussed above. The reduced model assumes a fully developed flow and therefore the measurement results in Figure 12(c) are the best candidate for a comparison with the numerical simulation. The size of simulated and measured mass transfer coefficients k_L^* are in the same range, namely in the interval $[1, 8] \times 10^{-5} m s^{-1}$. The curve in Figure 9 has a much smoother behavior as the one in Figure 12(c). At least two effects may be partly responsible for this. Firstly, the reduced model clearly contains less information on the fluid dynamics. The second effect comes from the fact that measurement and simulation data are numerically differentiated to obtain the mass transfer coefficient (14). The measurement data will contain more noise than the simulation results, which may result in a more oscillatory behavior. Looking at the experimental k_L^* curve in Figure 12(c), at first the values are decreasing in the range of $x \in [70, 77]$ mm up to the front of the wave hump, followed by oscillations in the region of the capillary waves (which one also observes in Figures 12(a) and 12(b)). A similar behavior can be observed in the numerical simulation result in Figure 9. We conclude that concerning this local mass transfer coefficient the reduced model contains important properties of the underlying physics of the convective as well as the conductive mass transport.

6. Conclusions and outlook

The absorption of a gas into a falling liquid film is a complex two-phase flow problem. The flow patterns emerging within the liquid film flow cause the transport rates to be enhanced. A reduced mass transfer model was proposed, capable of representing the wave-induced transport intensification, while keeping the computational demands low. In addition to that, the PLIL measurement method was introduced to quantify two-dimensional concentration distributions within a falling film. Simulation results with the reduced model and experimental results presented in this paper are in good qualitative agreement with published concentration patterns found in previous works. The results are also compared quantitatively to literature data in the form of a mass transfer function plot. These findings form a physically sound basis to calculate the enhanced mass transfer in falling liquid films. Nevertheless, in order to gain more insight into the mechanisms underlying the augmented transfer in falling liquid films, future work will have to focus on examining the influence of different flow conditions, physical properties of the liquids and wave frequencies.

The successful application of the reduced transport model and the ability to obtain local 2D concentration measurements inside the film by the PLIL measurement technique are considered as an important step towards our future modeling goal: the development of a design model for the mass transfer in falling films by means of the incremental modeling approach^{11,12,13}. The key idea is to augment the molecular diffusion coefficient in the sense of an effective diffusion coefficient to increase the prediction quality of the model. The effective diffusion coefficient will be estimated based on local concentration data obtained by measurements, solving a hierarchy of different inverse problems. The efficient solution of the arising forward problems, which are very similar to the reduced transport model described above, as well as the development of the high-resolution PLIL measurement technique are considered as a crucial basis for the efficient solution of large-scale inverse problems arising in the incremental identification of the effective diffusion coefficient to obtain an industrial design model for falling films.

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