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Modelling drop dynamics at the interface between free and porous-medium flow using the mortar method

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Abstract The objective of this work is the development and testing of an REV(Darcy)-scale coupling concept that accounts for drop dynamics at the interface between free and porous-medium flow.

We develop an interface concept that describes drop formation, growth and detachment on a hydrophobic interface. The concept is based on the assumption of thermodynamic equilibrium. The interface stores the mass and energy of the drops without resolving them. The direct exchange between free-flow and porous-medium region next to the drop is also part of the coupling concept. The fraction of the interface which is covered by drops is used to obtain an area-weighted average of the coupling conditions with and without drop so that coupling conditions for the whole interface are obtained. The temporal evolution of the drop volume is an outcome of the model, whereas the number of drops that can form on the interface is defined a priory.

The coupled model is implemented in the C++ simulator DuMu^x using the mortar method and is applied to simulate drop formation in the cathode of polymer-electrolyte-membrane fuel cells.

The numerical two-dimensional results show that it is possible to include drop dynamics in the REV-scale coupling conditions between free and porous-medium flow. Drop formation, growth and detachment are represented correctly, if the evaporation from the drop surface is neglected. The interfacecoverage ratio, which is an indicator for the quality of the water management, can be predicted. The simulations for a higher number of drops suggest that the interface conditions dominate the system. A parameter study shows that interface wettability and free-flow velocity have a significant influence on the drop growth and detachment.

Keywords model coupling, free flow, porous media, drop dynamics, mortar method, interface

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partial pressure of component κ in phase

Nomenclature

A_{Γ}	area of the interface
ACA	drop contact area
Δ^{o}	drop surface area
A drop	total energy spatian of all pares of a contain
$A_{\rm pore}$	total cross-section of an poles of a certain
4	class of the pore-size distribution
$A_{\rm proj}$	projected area
A_g	drop-free area of the interface
D_g^{κ}	diffusion coefficient of component κ in the
	gas phase
D_{α}	binary diffusion coefficient
$D^{\kappa,\mathrm{pm}}_{\alpha}$	porous-medium diffusion coefficient of
u	component κ in phase α
F_{drag}	drag force
F_{π}	shear force
F.	pressure force
F^{p}	maximum retention force
Γ_{γ}	dynamia prossure force
Г р v ² Па	User a soff signt
Π_{gl}	Henry coefficient
M^n	molar mass of component κ
$\stackrel{R}{\sim}$	ideal gas constant
S_{lpha}	saturation of phase α
T	temperature
$T_{\rm drop}$	drop temperature
T_c	critical temperature
$V_{\rm cap}$	volume of a spherical cap
$V_{\rm drop}$	drop volume
X^{κ}_{α}	mass fraction of component κ in phase α
v_{lpha}	velocity of phase α
g	gravity vector
X	distance from the drop
b	domain depth in 2D
f^{κ} $(r_{d}$	(rep) evaporation from the drop surface
h	height
\sqrt{K}	component of the permeability matrix
$\nabla \Pi_{i}$	unit matrix
I V	intringio norma ability tongon
N	intrinsic permeability tensor
$u_{ m drop}$	ratio of the interface and drop-surface
	area
$a_{\rm drop}$	ratio of the drop contact area and the in-
	terface area
a_g	ratio of the area without drop and the
	interface area
c_s	heat capacity of the solid phase
c_w	drag coefficient
$d_{\rm drop}$	drop diameter
$f_{\bar{r}_{\text{pore}}}$	percentage per class of the pore-size dis-
* pore	tribution
h^{κ}	specific enthalpy of component κ
h_{α}	specific enthalpy of phase α
$h_{\rm FF}$	height of the free-flow region
k	relative permeability of phase α
$n_{r\alpha}$	number of pores per class of the pore size
$r_{\rm pore}$	distribution
m	program of phase of
p_{α}	pressure or phase α

- $p_{\rm drop}$ drop pressure capillary pressure p_c $p_{\rm sat}^w$ water vapour pressure q_T heat source source term of phase α q_{α} source term of component κ in phase α q_{α}^{κ} $r, r_{\rm drop}$ radius, drop radius $r_{\rm drop}^{\rm CA}$ radius at the drop c radius at the drop contact area ttime u_{α} specific internal energy of phase α specific internal energy of the liquid phase $u_{l,drop}$ inside the drop mole fraction of water inside the drop $x_{l,\mathrm{drop}}^{\kappa}$ $x_{g, \inf}^{\dot{w}}$ mole fraction of water in the gas phase far away from the drop $x_{g,\text{drop}}^w$ mole fraction of water in the gas phase above the drop x^{κ}_{α} mole-fraction of component κ in phase α average pore radius $\bar{r}_{\rm pore}$ $\mathbf{f}^{\hat{\kappa}}$ component flux heat flux \mathbf{f}_T total mass flux \mathbf{f}_m basis of the tangent plane of the interface \mathbf{t}_i Reynolds number Re $\Delta \theta^{\max}$ maximally sustained contact-angle hysteresis the interface Г $\varOmega^{\mathrm{ff}}, \varOmega^{\mathrm{pm}}$ free-flow and porous-medium domain $\Omega_{\rm drop}$ drop REV $\alpha \in \{l, g, s\}$ phase index: liquid, gas and solid Beavers-Joseph coefficient $\alpha_{\rm BJ}$ shear-stress tensor auδ thickness of the bundle-of-tube model surface tension γ_{lg} $\kappa \in \{w, a\}$ component index: water and air $\lambda, \lambda_x, \lambda_T, \lambda_p, \lambda_{v_x}, \lambda_{v_y}$ Lagrange multiplier heat conductivity of phase α λ_{lpha} Lagrange multiplier for the storage of the $\lambda_{V_{ ext{drop}}}$ water component inside the drop effective heat conductivity of the porous $\lambda_{\rm pm}$ medium viscosity of phase α μ_{α} test function ω, ψ porosity ϕ tortuosity τ
- $\theta^* \qquad \text{contact angle} \qquad$

 p_{α}^{κ}

- θ_a, θ_r advancing and receding contact angle
- ϱ^{κ} molar density of component κ
- $\varrho_{\alpha} \qquad \text{molar density of phase } \alpha$
- ϱ_{α}^{m} mass density of phase α
- $\varrho_{l,drop}$ liquid phase density inside the drop

1 Introduction

The interaction of free and porous-medium flow is dominated by interface processes. The quantification of transfer fluxes of mass, momentum and energy is crucial for applications like evaporation from soil, heat and mass transfer through textiles or transport of therapeutic agents in the human body. Moreover, the water management in polymer-electrolyte-membrane (PEM) fuel cells is dominated by the heat and mass exchange at the interface between the free-flow gas channel (GC) and the porous gas-diffusion layer (GDL). In any case, the challenge is the correct and efficient description of the governing forces, conditions and exchange processes at the interface which are influenced by the non-isothermal, compositional, multi-phase nature of the surrounding systems. This can be particularly demanding due the thin heterogeneous porous structures or due to complex processes like film flow, pooling and drop formation at the interface. In fuel cells, for example, the water distribution is significantly influenced by drops which form at the hydrophobic gas-diffusion-layer–surface [Cho et al., 2012a, Gurau and Mann, 2009].

The focus of this work is on the extension of existing REV(Darcy)-scale coupling concepts [Baber et al., 2012, Mosthaf et al., 2011] to account for drop formation, growth and detachment at the interface between free-flow and porous-medium region. The derivation of this complex interface description is based on phenomenological considerations. The developed model concept is motivated by processes occurring in PEM fuel cells, but can be applied to any application where drops form on porous surfaces influenced by a flow field.

1.1 Modelling drop dynamics

When a two-phase porous medium is in contact with free gas flow, it may happen that water flowing towards the free-flow region does not fully evaporate at the interface. Driven by capillary forces, the water emerges from the pores as liquid phase and forms drops or puddles on the porous-medium surface. These drops will grow and merge until they detach eventually due to the drag force exerted by the gas flow. Decreasing the cross-section available for the free gas flow, the drops have a significant influence on the flow conditions within the free-flow region. The emergence and growth of drops and their influence and interaction with the free gas flow is a complex interplay of different processes and forces. Sinha and Wang [2008] point out that the interface wettability and the corresponding water behaviour influence the saturation within the porous medium. Water removal from the surface by gas drag is significantly influenced by the wettability.

In the following, a review of literature dealing with drop dynamics in PEM fuel cells is presented. First we summarise investigations of drops influenced by a flow field. Then, pore- and REV-scale approaches for the coupled system of free-flow, porous-medium and drop dynamics are reviewed.

Drop behaviour Theodorakakos et al. [2006] perform a numerical and experimental analysis of the detachment behaviour of drops subjected to a flow field and give a comprehensive literature review of fuel-cell and drop models. They determine values for the static, advancing and receding contact angle experimentally and model the dynamic deformation and detachment process using the Navier-Stokes equations and the volume-of-fluid (VOF) method. Chen et al. [2005] and Kumbur et al. [2006] develop analytical models for the instability of spherical drops influenced by flow at low Reynolds numbers based on a force-balance approach. Cho et al. [2012a,b] conclude that viscous drag dominates the detachment of small drops whereas the pressure force becomes more dominant for larger drops.

These studies neglect the influence of the gas-channel geometry, assuming that the drop does not touch the gas-channel walls. Zhang et al. [2006] observe the water distribution in the gas-diffusion layer and drop formation as well as drop detachment due to shear forces or due to wicking into the gas-channel corners in transparent fuel cells. They find a relation between gas-flow velocity, detachment mechanism and radius. Gopalan and Kandlikar [2014] perform ex-situ experiments, investigating the detachment time and the required pressure drop in trapezoidal gas channels for different gas-channel corner angles and gas velocities. They find that at low velocities (gas-phase velocity $v_g \leq 4 \text{ m/s}$) drops interact with the hydrophilic channel walls, but that the drops are detached before interaction with the wall happens for larger velocities. Qin et al. [2012c] use the VOF method to describe drop and film dynamics in the gas channel. They observe a significant elongation of the contact line and a significant

influence of the wettability of the gas-channel walls on the drop behaviour and film-flow development. Carton et al. [2012] analyse the coalescence of drops and slug movement comparing VOF simulations and experiments.

Pore-scale approaches Sinha and Wang [2008] explain the behaviour of water on a mixed-wet GDL-GC interface theoretically. Water emerging from the GDL at the interface will form a film on the hydrophilic surface. When it reaches hydrophobic parts, pinning of the contact line occurs and drops form. The drops grow with increasing contact angle until a threshold contact angle is reached and the contact line unpins to let the drop grow further. They analyse the effect of mixed wettability on the water distribution inside the GDL using a pore-network model with cubic pore-bodies and pore-throats with a square cross-section. They reveal the role of capillary fingering with respect to the water-distribution process (supported by Kuttanikkad et al. [2011]) and discuss the applicability of the two-phase Darcy law. Suresh and Jayanti [2010] perform pore-scale VOF simulations in a two-dimensional (2D) segment of GDL and GC, investigating the influence of the GC-flow conditions on the water transport in the GDL and on the drop formation. They observe fingering and channelling within the hydrophobic fibre structure and drop formation, growth and detachment on the interface.

REV-scale approaches In Qin et al. [2012a,b], a macroscopic one-dimensional model for water flooding in the gas-channel is proposed. It includes the description of film flow in the gas-channel corners and of drops on the GDL surface. The drop radius is assumed to be directly dependent on a given local water flux from the GDL, gas flow velocity, GC geometry and an empirical parameter. Qin et al. [2012b] find that the pressure drop increases significantly in the presence of droplets. Qin et al. [2012a] stress the importance of a more comprehensive droplet model.

If a coupled system of GC and GDL is considered, the occurrence of sessile drops makes it hard to find realistic boundary conditions at the GDL-surface. Often, a value for the saturation or capillary pressure is specified at the interface [Berning and Djilali, 2003, Natarajan and Nguyen, 2001]. Gurau et al. [2008] and Gurau and Mann [2010] include drop formation and detachment into a three-dimensional (3D) model of the cathode side. They employ a multi-phase multi-fluid REV-scale model in both the porous GDL and the free-flow GC domain. At the interface, they assume a saturation equilibrium based on the description of sessile drops. The water pressure $p_l^{\rm pm}$ is set equal to the internal drop pressure $p_{\rm drop}$ which in turn depends on the drop radius. This leads to a jump in saturation and a discontinuity in the capillary-pressure gradient at the interface. Drop formation depends on the pore-size distribution at the interface and the porous-medium water pressure. Drops grow until they are detached due to gravity and shear forces. Gurau et al. [2008] and Gurau and Mann [2010] find cyclic variations of the water saturation in areas feeding the drops. The main limitations of this approach are that one drop per pore is assumed and that drops do not merge.

Berning et al. [2009] also focus on the interface treatment using a stationary 3D multi-fluid model of the PEM fuel-cell cathode. They derive an interface condition for the capillary pressure based on the water flux inside the porous medium and the number of drops at the interface which is assumed to be constant during the simulations. The interaction of drops and gas flow is not included in the model. They find that the interface condition has only limited influence on the water saturation within the GDL. In Berning et al. [2010] the multi-fluid model is extended by a kinetic phase-change approach. It is used to analyse the effect of an interdigitated flow field in the gas channel. A more effective water transport is observed. In Berning et al. [2011], the model is extended to account for the polymerelectrolyte membrane and the anode side. The focus is on a better understanding of the transfer mechanisms of water through the membrane which are found to depend strongly on the surface area of the electrolyte in the catalyst layer.

Wang et al. [2011] see the combination of drop dynamics at the GC-GDL interface, transport processes in all fuel-cell compartments and chemical reactions as a current research request.

1.2 Objective and structure

The literature review reveals the need for a model that can predict the number and size of drops in dependence of the conditions in the free-flow and porous-medium region. The goal of this work is to integrate the occurrence of droplets into the REV-scale interface concept presented in Mosthaf et al.



Fig. 1 Schematic depiction of the two-domain coupling concept [Mosthaf et al., 2011].

[2011] and Baber et al. [2012]. The formation, growth and detachment of drops is described in an averaged manner without resolving the drops. The influence of the drops on the free flow and the fate of the drops after detachment is not included in our model until now.

In the following, the basic coupled model describing evaporation and condensation but not considering droplets is reviewed briefly (Section 2.1). Then, the interface concept for drop formation, growth and detachment is explained in detail (Section 2.2). The total coupling conditions resulting from a combination of Sections 2.1 and 2.2 are given in Section 2.2.5. In Section 2.3, we describe the implementation in the C++ simulator DuMu^x [Flemisch et al., 2011] which is based on the mortar method. A parameter study is presented in Section 3 investigating the influence of flow conditions, material properties and model assumptions. Finally, we conclude with a summary and outlook.

2 Model concept

In Section 2.1, the coupled model for flow and mass/energy transport in the porous medium and free flow, which is based on the two-domain approach, is explained briefly. The information follows the publications of Mosthaf et al. [2011] and Baber et al. [2012] which are summarised for the sake of completeness. Then, the new model concept for drop formation, growth and detachment is presented (Section 2.2).

2.1 General coupled model

Figure 1 illustrates the problem setting: two domains Ω^{ff} and Ω^{pm} are separated by the interface $\Gamma = \partial \Omega^{\text{ff}} \cap \partial \Omega^{\text{pm}}$ with the outward unit normal vectors \mathbf{n}^{ff} and \mathbf{n}^{pm} . For simplicity of notation, the superscripts (ff) and (pm) are only applied for the quantities at the interface, where (ff) refers to the values in the free-flow sub-domain and (pm) stands for the porous-medium side [Baber et al., 2012]. Both porous medium and free flow are described by REV-scale models solving mass-, momentum- and energy-balance equations.

The processes in the porous-medium are described with a non-isothermal, two-phase, two-component Darcy model. Under the assumption of local thermal equilibrium $(T_l = T_g = T_s = T)$, justified by slow flow conditions, one single energy-balance is employed. The system of equations in the porous medium is given in Table 1. It is based on the following assumptions [Mosthaf et al., 2011]:

- local thermodynamic (mechanical, thermal and chemical) equilibrium,
- a purely hydrophobic, rigid solid phase (subscript s),
- two-phase flow consisting of a liquid phase (subscript l) and a gas phase (subscript g),

Balance equations	Primary variable
Mass balance for component $\kappa \in \{w, a\}$:	
$\sum_{\alpha \in \{l,g\}} \phi \frac{\partial \left(\varrho_{\alpha} x_{\alpha}^{\kappa} S_{\alpha} \right)}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{f}^{\kappa} - \sum_{\alpha \in \{l,g\}} q_{\alpha}^{\kappa} = 0 \qquad (1)$	S_l or x^{κ}_{α}
$\mathbf{f}^{\kappa} = \sum_{lpha \in \{l,g\}} \left(\varrho_{lpha} \boldsymbol{v}_{lpha} x^{\kappa}_{lpha} - D^{\kappa, \mathrm{pm}}_{lpha} \; \varrho_{lpha} \boldsymbol{ abla} x^{\kappa}_{lpha} ight)$	
Total mass balance:	
$\sum_{\alpha \in \{l,g\}} \phi \frac{\partial(\varrho_{\alpha} S_{\alpha})}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{f}_m - \sum_{\alpha \in \{l,g\}} q_{\alpha} = 0 \qquad (2)$	p_{g}
$\mathbf{f}_m = \sum\limits_{lpha \in \{l,g\}} \left(arrho_lpha oldsymbol{v}_lpha ight)$	
Darcy's law:	
$oldsymbol{v}_lpha = -rac{k_{rlpha}}{\mu_lpha} {f K} \left(oldsymbol{ abla} p_lpha - arrho_lpha {f g} ight), \qquad lpha \in \{l,g\}$	
Energy balance:	
$\sum_{\alpha \in \{l,g\}} \phi \frac{\partial(\varrho_{\alpha} u_{\alpha} S_{\alpha})}{\partial t} + (1 - \phi) \frac{\partial(\varrho_{s} c_{s} T)}{\partial t} + \nabla \cdot \mathbf{f}_{T} - q_{T} = 0 $ (3)	T
$\mathbf{f}_T = \sum_{lpha \in \{l,g\}} (arrho_lpha h_lpha oldsymbol{v}_lpha - \lambda_{ m pm} oldsymbol{ abla} T)$	

Table 1 Porous-medium equations and according primary variables.

- two components being present in each phase: water (superscript w) and air (superscript a),
- the gas phase is considered to be an ideal gas, the liquid phase a Newtonian fluid,
- slow flow velocities (Re \ll 1) allow the application of the multi-phase Darcy law for the phase velocities,
- binary diffusion,
- negligible influence of dispersion due to slow flow velocities and comparatively high diffusion coefficients in the gas phase.

The complete porous-medium model, which is explained in more detail in Class et al. [2002], accounts for the transfer of components from one phase to another and for vaporisation and condensation as well as dissolution and degassing.

Depending on the local phase state, primary variables have to be chosen and the secondary variables have to be expressed as functions of the primary variables. Here, the gas-phase pressure p_g , the saturation of the liquid phase S_l and the temperature T are chosen as primary variables for the two-phase two-component system. If one phase disappears locally, the system of equations is significantly simplified by a primary-variable switch [Class et al., 2002]. The secondary variables can be calculated using the relations in Table 2.

In the free-flow region, a non-isothermal, one-phase, two-component Navier-Stokes model is applied (see Table 3), based on the following assumptions:

- laminar, fully developed flow field,
- binary diffusion,
- single-phase flow of a Newtonian fluid (here a gas phase is considered: $\alpha = q$),
- two components in the gas phase: water (superscript w) and air (superscript a).

The equations of state shown in Table 2 are used to calculate enthalpy and internal energy.

As primary variables, the pressure of the gas phase p_g , the mole fraction of water in the gas phase x_q^{κ} , the velocity of the gas phase v_g and the temperature T are chosen.

Suitable coupling conditions for the two systems of equations have to be found that account for the physics at the interface and the transfer processes of mass, momentum and energy. The coupling conditions are valid on the REV scale, but should still account for the pore-scale processes. By making sensible assumptions based on phenomenological explanations, coupling conditions were deduced in Mosthaf et al. [2011] that are motivated by thermodynamic equilibrium and get as close as possible -

	Equations of state	References
Parameters:		
Density ρ_{α}	$\varrho_{\alpha} = f(\varrho^{\kappa}, x_{\alpha}^{\kappa}, p_{\alpha}, T)$	IAPWS [2009]
Component density ϱ^κ	incompressible fluid and ideal gas	Reid et al. [1987]
Viscosity μ_{α}	$\mu_l = \mu^w, \mu_g $ (Wilke method)	Poling et al. [2001]
Surface tension γ_{lg}	$\gamma_{lg} = 0.2358 \left(1 - \frac{T}{T_c}\right)^{1.256}$	
	$\left(1 - 0.625\left(1 - \frac{T}{T_c}\right)\right)$	IAPWS [1994]
Diffusion coefficient $D_{\alpha}^{\kappa,\mathrm{pm}}$	$D_{\alpha}^{\kappa,\mathrm{pm}} = \tau \phi S_{\alpha} D_{\alpha}$	Millington and Quirk [1960]
		Acosta et al. [2006]
Tortuosity τ	$\tau = \frac{(\phi S_\alpha)^{7/3}}{\phi^2}$	Millington and Quirk [1960]
Capillary pressure p_c	$p_c = f(S_l)$	van Genuchten [1980]
		Acosta et al. [2006]
Relative permeability $k_{r\alpha}$	$k_{r\alpha} = f(S_l)$	van Genuchten [1980]
		Acosta et al. $[2006]$
Eff. heat conductivity $\lambda_{\rm pm}$	$\lambda_{\mathrm{pm}} = f(\phi, S_l, \lambda_g, \lambda_l, \lambda_s)$	
Internal energy u_{α}	$u_{\alpha}(p_{\alpha},T) = h_{\alpha} - p_{\alpha}/\varrho_{\alpha}(p_{\alpha},T)$	
Enthalpy h		
- gas phase	$h_g = \sum_{\kappa} X_g^{\kappa} h^{\kappa}$	
- water phase	$h_l = h^w$	
- component air	$h^a(T)$	Kays et al. [2005]
- component water	$h^w(p_l,T)$	IAPWS [2009]
a 1 · · 11		
Secondary variables:		
Saturation S_g	$S_g = 1 - S_l$	

Table 2 Material laws and equations of state dependent on primary variables.

Saturation S_g	$S_g = 1 - S_l$	
Liquid-phase pressure p_l	$p_c = p_l - p_g$	
Gas component in water phase x_l^a	Henry's law: $x_l^a = p_g^a / H_{gl}^a$	
Vapour in gas phase x_g^w	$x_g^w = p_{ m sat,Kelvin}^w/p_g$	
Kelvin equation	where $p_{\text{sat,Kelvin}}^w = p_{\text{sat}}^w \exp\left(-\frac{p_c}{\varrho_l RT}\right)$	Galvin $[2005]$
		Butt et al. [2007]
Mass fractions	$\sum_{\kappa} X_{\alpha}^{\kappa} = \sum_{\kappa} x_{\alpha}^{\kappa} = 1$	
	$X^{\kappa}_{\alpha} = x^{\kappa}_{\alpha} \mathbf{M}^{\kappa} / (x^{w}_{\alpha} \mathbf{M}^{w} + x^{a}_{\alpha} \mathbf{M}^{a})$	

to a description for a so-called simple interface that has no thickness and is devoid of thermodynamic properties [Hassanizadeh and Gray, 1989]. The reasoning behind the coupling conditions is explained in detail in Mosthaf et al. [2011]. For brevity, we only list them here. The mechanical equilibrium (equilibrium of forces) is given by

- the continuity of the normal stresses resulting in a possible jump in the gas-phase pressure

$$\mathbf{n} \cdot \left[\left(\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g + p_g \mathbf{I} - \underbrace{\mu_g \left(\boldsymbol{\nabla} \boldsymbol{v}_g + \boldsymbol{\nabla} \boldsymbol{v}_g^T \right)}_{\boldsymbol{\tau}} \right) \mathbf{n} \right]^{\mathrm{ff}} = [p_g]^{\mathrm{pm}}, \qquad (8)$$

Balance equation	Primary variable
Mass balance for component κ	
$\frac{\partial(\varrho_g x_g^{\kappa})}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{f}^{\kappa} - q_g^{\kappa} = 0, \ \mathbf{f}^{\kappa} = \left(\varrho_g \boldsymbol{v}_g x_g^{\kappa} - D_g^{\kappa} \varrho_g \boldsymbol{\nabla} x_g^{\kappa}\right) $ (4)	x_g^κ
Total mass balance:	
$\frac{\partial \varrho_g}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{f}_m - q_g = 0, \ \mathbf{f}_m = (\varrho_g \boldsymbol{v}_g) \tag{5}$	p_g
Momentum balance (Navier-Stokes equations):	
$\frac{\partial \left(\varrho_g^m \boldsymbol{v}_g\right)}{\partial t} + \boldsymbol{\nabla} \cdot \left(\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g\right) + \boldsymbol{\nabla} \cdot \mathbf{f}_{\boldsymbol{v}} - \varrho_g^m \mathbf{g} = 0 \qquad (6)$	$oldsymbol{v}_g$
$\mathbf{f}_{oldsymbol{v}} = p_{g}\mathbf{I} - \mu_{g}\left(oldsymbol{ abla} oldsymbol{v}_{g} + oldsymbol{ abla} oldsymbol{v}_{g}^{T} ight)$	
Energy balance:	
$\frac{\partial(\varrho_g u_g)}{\partial t} + \boldsymbol{\nabla} \cdot \mathbf{f}_T - q_T = 0 , \ \mathbf{f}_T = (\varrho_g h_g \boldsymbol{v}_g - \lambda_g \boldsymbol{\nabla} T) $ (7)	T

Table 3 Free-flow equations and according primary variables.

- the continuity of the mass fluxes

$$\left[\varrho_g \boldsymbol{v}_g \cdot \mathbf{n}\right]^{\mathrm{ff}} = -\left[\left(\varrho_g \boldsymbol{v}_g + \varrho_l \boldsymbol{v}_l\right) \cdot \mathbf{n}\right]^{\mathrm{pm}},\tag{9}$$

 the Beavers-Joseph-Saffman condition for the tangential component of the free-flow velocity [Beavers and Joseph, 1967, Saffman, 1971]

$$\left[\left(\boldsymbol{v}_g + \frac{\sqrt{K_i}}{\alpha_{\rm BJ}\,\mu_g}\boldsymbol{\tau}\,\mathbf{n}\right)\cdot\mathbf{t}_i\right]^{\rm ff} = 0, \quad i \in \{1,\ldots,d-1\}.$$
(10)

The thermal equilibrium is given by [Alazmi and Vafai, 2001]

- the continuity of the temperature

$$[T]^{\rm ff} = [T]^{\rm pm},$$
 (11)

- the continuity of the heat fluxes

$$\left[\left(\varrho_g h_g \boldsymbol{v}_g - \lambda_g \boldsymbol{\nabla} T\right) \cdot \mathbf{n}\right]^{\mathrm{ff}} = -\left[\left(\varrho_g h_g \boldsymbol{v}_g + \varrho_l h_l \boldsymbol{v}_l - \lambda_{\mathrm{pm}} \boldsymbol{\nabla} T\right) \cdot \mathbf{n}\right]^{\mathrm{pm}}.$$
(12)

The chemical equilibrium is represented by

- the continuity of mole fractions

$$[x_g^{\kappa}]^{\rm ff} = [x_g^{\kappa}]^{\rm pm},\tag{13}$$

- the continuity of the component fluxes across the interface

$$\begin{bmatrix} \left(\varrho_g \boldsymbol{v}_g \boldsymbol{x}_g^{\kappa} - D_g^{\kappa} \varrho_g \boldsymbol{\nabla} \boldsymbol{x}_g^{\kappa}\right) \cdot \mathbf{n} \end{bmatrix}^{\text{ff}} = \\ - \begin{bmatrix} \left(\varrho_g \boldsymbol{v}_g \boldsymbol{x}_g^{\kappa} - D_g^{\kappa, \text{pm}} \varrho_g \boldsymbol{\nabla} \boldsymbol{x}_g^{\kappa} + \varrho_l \boldsymbol{v}_l \boldsymbol{x}_l^{\kappa} - D_l^{\kappa, \text{pm}} \varrho_l \boldsymbol{\nabla} \boldsymbol{x}_l^{\kappa} \right) \cdot \mathbf{n} \end{bmatrix}^{\text{pm}}.$$
(14)

2.2 Coupling concept for drop formation, growth and detachment

The coupling concept of the simple interface is extended to account for drop dynamics on the free-flow side of the interface. The resulting complex interface includes the mass and energy of drops that form on the interface.

First, the required assumptions and simplifications are listed in Section 2.2.1. Then, the strategy employed to account for the drops in the REV-scale coupling concept without resolving them is presented in Section 2.2.2. Drop formation and detachment are discussed in Sections 2.2.3 and 2.2.6. The coupling conditions for a drop covered interface are derived in Section 2.2.4. The combination with the coupling conditions for a drop-free interface from the previous section yields the coupling concept for the complete interface in Section 2.2.5.

2.2.1 Assumptions and simplifications

The interplay between sessile droplets, free gas flow and hydrophobic porous surfaces leads to deformation of the drop and to different detachment and drop transport mechanisms. A detached drop can either slide on the porous-medium surface, lift and float or wick into the film flow in the corners of the gas channel. Such processes are not yet resolved by the current model since the focus is on the interface description and drop formation. The model describes drop formation, growth and detachment. Merging of drops cannot be resolved by the model since the drop surfaces and distances are not tracked by the averaged continuum approach. To account for the drop as part of the coupling conditions, simplifications have to be made:

- local thermodynamic (mechanical, thermal and chemical) equilibrium,
- equilibrium conditions,
- symmetrical, non-deformed drop, except for calculating the retention force F_{γ}^{\max} (Equation (39)). With the drop height h, the curvature radius r and the radius of the contact area c, the drop volume, surface and contact area of a spherical cap are:

$$V_{\rm drop} = \frac{\pi}{3} h^2 (3r - h) \quad \text{with} \quad r = \frac{h}{1 - \cos \theta^*}, \tag{15}$$

$$\mathbf{A}_{\mathrm{drop}}^{o} = 2\pi r \mathbf{h},\tag{16}$$

$$A_{\rm drop}^{\rm CA} = \pi (r_{\rm drop}^{\rm CA})^2 \quad \text{with} \quad r_{\rm drop}^{\rm CA} = r \sin \theta^*, \tag{17}$$

- constant pressure around the drop and constant curvature of the drop surface.
- rapid mixing: constant temperature, mass fractions and pressure inside the drop,
- neglicence of gravity [Butt et al., 2007, Cho et al., 2012a],
- slow free flow: the applicability of expressions for evaporative fluxes derived for drops in still air [Erbil et al., 2002, Picknett and Bexon, 1977, Song et al., 2011] and constant-contact-angle evaporation mode [Erbil et al., 2002, Picknett and Bexon, 1977, Song et al., 2011] is assumed,
- the maximally sustained contact-angle hysteresis is taken as a material parameter (see Section 2.2.6),
- a circular contact line is assumed, neglecting elongation of the contact area [Chen et al., 2005, Kumbur et al., 2006].

2.2.2 REV-drop concept

The motivation of this work is to integrate the drop dynamics into the REV-scale interface concept, see (8)-(14). To do so, an area of influence for one drop (a drop-REV) $\Omega_{\rm drop}$ is chosen, where the total interface area A_{Γ} is an integral multiple of $|\Omega_{\rm drop}|$: $A_{\Gamma} = n \cdot |\Omega_{\rm drop}|$ $n \in \mathbb{N}$ (see Figure 2). All water-filled pores within one $\Omega_{\rm drop}$ feed one single drop. Thus, there is only one drop per drop-REV. The choice of $\Omega_{\rm drop}$ determines the possible number of drops. The numerical realisation and the resulting limitations and numerical results are discussed in Sections 2.3 and 3.2.

Figure 2 illustrates the conceptual idea. On the left-hand side, free flow and porous medium are coupled across the interface Γ . The drop can be imagined as part of the interface sitting between bottom free-flow and top porous-medium boundary. Free flow and porous medium interact directly across A_g and through the drop across the contact area $A_{\rm drop}^{\rm CA}$. To fulfil the conservation laws, mass that enters the drop across an area equivalent to $A_{\rm drop}^{\rm CA}$. Following the REV approach further, the exact location of drop-free and drop-covered interface is not needed. Only the area fractions of each interface status are required: $a_{\rm drop} = \frac{A_{\rm drop}^{\rm CA}}{|\Omega_{\rm drop}|}$ and $a_g = \frac{A_g}{|\Omega_{\rm drop}|}$. Equivalently, $a_{\rm drop}^o = \frac{A_{\rm drop}^o}{|\Omega_{\rm drop}|}$ describes the relation of drop-surface area $A_{\rm drop}^o$ and the area of influence $\Omega_{\rm drop}$. The decision for a continuum description entails that the local phenomena of drop formation and

The decision for a continuum description entails that the local phenomena of drop formation and resulting local pressure loss or resulting local changes in the water content cannot be described. It is inherent of a continuum description that local distributions cannot be resolved but average quantities like saturation or an average drop volume are defined. The averaged quantity of interest here is the

(18)



Fig. 2 Conceptual model: The interface Γ between free flow and porous medium is divided into an integral number of areas of influence Ω_{drop} . There is one drop per area of influence. The area of influence is partly covered by the drop $\Omega_{\text{drop}} = A_g + A_{\text{drop}}^{\text{CA}}$.



Fig. 3 A bundle-of-tubes model describes the interface region between porous medium and free flow representing pores ending in the free-flow region. Possible pore constitutions are: a) gas flux through pore, b) water meniscus in pores with direct evaporation, c) spherical caps with diameter equal to pore diameter, d) drop fed by porous medium, evaporating into the free-flow region.

fraction of the interface which is covered by drops $a_{\rm drop}$. This area fraction is used to form an area-weighted average of the coupling conditions with and without drop.

2.2.3 Drop formation

To describe the drop formation, the top layer of the porous medium is considered to be a bundle of tubes (see Figure 3). The bundle-of-tubes approximation describes the top layer of thickness δ where the pores of the porous medium do not intersect any more and enter the free-flow region. This description is based on the pore-size distribution at the interface which is sorted into classes of tubes with mean radius \bar{r}_{pore} with $f_{\bar{r}_{pore}}$ percent of pores and $n_{\bar{r}_{pore}} = \frac{\phi A_{\Gamma}}{f_{\bar{r}_{pore}}} A_{pore}$ pores per class [Gurau et al., 2008]. We assume that the porosity at the interface and inside the porous medium are the same [Gurau and Mann, 2010]. Note that this pore-scale model is not explicitly included as a pore-network model. Only its concept and physics are used to derive the condition for the averaged drop formation.

Assuming circular pores that do not have corner flow, three conditions are possible for pores at the interface (see Figure 3). Pores can allow gas flow (see Figure 3 a.)). Other pores can have a water meniscus at the bottom where direct evaporation happens (see Figure 3 b.)). Equation (9) already

accounts for cases a) and b) of the possible pore conditions. Finally, pores can be covered by drops (see Figure 3 d)). In the following, the smallest entity that is considered a drop is a spherical cap with the diameter of a pore (see Figure 3c)).

The bundle-of-tubes concept is employed to determine which classes of tubes will be invaded by water based on the conditions in the porous-medium and the free-flow region. Water accumulates in the porous medium until a threshold pressure is reached. Caps form on water-filled pores. Once the cap radius equals the pore radius, it is considered a drop (see Figure 3c)). This is the limit case where the drop has the minimum radius $r_{\rm drop} = \bar{r}_{\rm pore}$, meaning that the pressure which has to be overcome by the pressure of the water phase in the porous medium to let the drop grow is at a maximum [Gurau and Mann, 2009, 2010]. Hence, drops form on all pores where the porous-medium water pressure $p_l^{\rm pm}$ is larger than the sum of the free-flow forces and the capillary pressure of the curved drop surface:

$$p_g^{\rm ff} + \frac{2\gamma_{lg}}{\bar{r}_{\rm pore}} \le p_l^{\rm pm}.$$
(19)

The two-phase porous-medium model does not resolve the water distribution locally, but only provides averaged quantities. For the vertical movement of the meniscus inside the pores, the influence of shear stress of the surrounding phases is negligible [Hassanizadeh and Gray, 1993]. Hence, the gas pressure in the free-flow region $p_g^{\rm ff}$ is employed directly. We assume that spherical caps with $r = \bar{r}_{\rm pore}$ form on all pore classes for which condition (19) is fulfilled. Knowing the pore-size distribution, it is now possible to determine the initial drop volume by adding up all cap volumes $V_{\rm cap} = \frac{2}{3}\pi(\bar{r}_{\rm pore})^3$ within an area of influence $\Omega_{\rm drop}$:

$$V_{\rm drop} = \sum_{\bar{r}_{\rm pore} \in \Omega_{\rm drop}} V_{\rm cap}(\bar{r}_{\rm pore}) \cdot n_{\bar{r}_{\rm pore}}.$$
 (20)

After checking whether the porous-medium flow conditions can provide the estimated water volume, the drop radius $r_{\rm drop}$ can be calculated assuming the drop to have the form of a spherical cap:

$$r_{\rm drop} = \sqrt[3]{\frac{\frac{3}{\pi} V_{\rm drop}}{(1 - \cos \theta^*)^2 (2 - \cos \theta^*)}}.$$
 (21)

With the drop radius, the drop surface A^o_{drop} and drop contact area A^{CA}_{drop} can be calculated (see Figure 2). The area fractions of drop-covered $a_{drop} = \frac{A^{CA}_{drop}}{|\Omega_{drop}|}$ and drop-free $a_g = \frac{A_g}{|\Omega_{drop}|}$ interface are calculated and used to obtain the complete coupling conditions for the interface (see Section 2.2.5).

2.2.4 Coupling conditions for the drop-covered interface

Since the drops are not resolved, all conditions have to be valid at the interface, meaning at the drop contact area $A_{\rm drop}^{\rm CA}$ to fit into the interface coupling concept.

Flux balance Balancing the total mass fluxes across the interface yields:

$$\underbrace{\frac{\partial}{\partial t} \int_{V_{\rm drop}} \varrho_{l,\rm drop} \, dV}_{\frac{d(\varrho_l,\rm drop \, V_{\rm drop})}{dt}} + \int_{A_{\rm drop}^{\rm CA}} [\varrho_l \boldsymbol{v}_l \cdot \mathbf{n}]^{\rm pm} d\mathbf{x} = \int_{A_{\rm drop}^{\rm CA}} - [\varrho_g \boldsymbol{v}_g \cdot \mathbf{n}]^{\rm ff} d\mathbf{x}.$$
(22)

Where the interface is covered by drops, the gas phase cannot flow from the porous medium into the free-flow region and all water leaving the porous-medium increases the drop volume $V_{\rm drop}$ (see the first term in (22)). To estimate the mass of water stored inside the drop volume $V_{\rm drop}$, the density of water inside the drop is assumed to be equal to the water density in the porous medium.

The balance of the component and energy fluxes is given accordingly for $\kappa \in w, a$:

$$\frac{\partial}{\partial t} \underbrace{\int_{V_{\rm drop}} \varrho_{l,\rm drop} x_{l,\rm drop}^{\kappa} dV}_{\lambda_{V_{\rm drop}}} + \int_{A_{\rm drop}^{\rm CA}} [(\varrho_l \boldsymbol{v}_l x_l^{\kappa} - \varrho_l D_l^{\kappa,\rm pm} \boldsymbol{\nabla} x_l^{\kappa}) \cdot \mathbf{n}]^{\rm pm} dx$$
$$= -\int_{A_{\rm drop}^{\rm CA}} [(\varrho_g \boldsymbol{v}_g x_g^{\kappa} - \varrho_g D_g^{\kappa} \boldsymbol{\nabla} x_g^{\kappa}) \cdot \mathbf{n}]^{\rm ff} dx = -\int_{A_{\rm drop}^{\rm co}} \mathbf{f}_{\rm evap}^{\kappa}(r_{\rm drop}) dx, \quad (23)$$

$$\frac{\partial}{\partial t} \int_{V_{\rm drop}} \varrho_{l,\rm drop} \ u_{l,\rm drop} \ dV + \int_{A_{\rm drop}^{\rm CA}} \left[(\varrho_l \boldsymbol{v}_l h_l - \lambda_{\rm pm} \boldsymbol{\nabla} T) \cdot \mathbf{n} \right]^{\rm pm} \ d\mathbf{x} \\ = -\int_{A_{\rm drop}^{\rm CA}} \left[(\varrho_g \boldsymbol{v}_g h_g - \lambda_g \boldsymbol{\nabla} T) \cdot \mathbf{n} \right]^{\rm ff} \ d\mathbf{x}.$$
(24)

The major difference compared to the flux-continuity conditions on a drop-free interface is that mass and heat can be stored inside the drops. Hence, the interface can now store mass and energy, and is not a simple interface devoid of thermodynamic properties any more.

In (23), $\lambda_{V_{\text{drop}}}$ is a Lagrange multiplier introduced as a new unknown on the interface, which will be explained in more detail in Section 2.3. The evaporation from the droplet surface f_{evap}^{κ} has to be equal to the flux into the free-flow region, see (23). Figure 2 illustrates that the conceptual drop model sees the drop as part of the interface. Hence, everything that evaporates across the drop surface has to enter the free-flow region across an area equivalent to $A_{\text{drop}}^{\text{CA}}$. According to Erbil et al. [2002] and Song et al. [2011] the evaporative flux can be estimated depending on the drop radius r_{drop} and the static contact angle θ^* :

$$\int_{A_{\rm drop}^o} f_{\rm evap}^\kappa \, d\mathbf{x} = 4\pi r_{\rm drop} D_g^w \varrho_g (x_{g,\rm drop}^w - x_{g,\rm inf}^w) f(\theta^*),\tag{25}$$

with the geometric factor for 3D problems:

$$f(\theta^*) = 0.5 \cdot \left(0.00008957 + 0.6333\theta^* + 0.116\theta^{*2} - 0.08878\theta^{*3} + 0.01033\theta^{*4} \right).$$

We derived the following expression for a two-dimensional problem accounting for advection and diffusion:

$$\int_{A_{\rm drop}^{o}} f_{\rm evap}^{\kappa} d\mathbf{x} = -2\theta^{*} \varrho_{g} D_{g}^{w} \frac{180}{\pi} \left(x_{g,\rm inf}^{w} - x_{g,\rm drop}^{w} \right) \frac{1}{\ln\left(\frac{\mathbf{X}}{r_{\rm drop}}\right)}$$
(26)

Mechanical equilibrium The equilibrium of normal forces is known at the drop surface A^o_{drop} . The inside pressure has to balance the outside pressure and the capillary pressure caused by the curvature:

$$\int_{A_{\rm drop}^{o}} \left[\mathbf{n} \cdot \left(\left(\varrho_{g}^{m} \boldsymbol{v}_{g} \otimes \boldsymbol{v}_{g} + p_{g} \mathbf{I} - \boldsymbol{\tau} \right) \mathbf{n} \right) \right]^{\rm ff} + \frac{2\gamma_{lg}}{r_{\rm drop}} \, d\mathbf{x} = \int_{A_{\rm drop}^{o}} p_{\rm drop} \, d\mathbf{x}.$$
(27)

This condition physically acts on the drop surface A^o_{drop} and not on the contact area of the drop A^{CA}_{drop} . Since the drops are not resolved, (27) has to be transformed into a condition at the interface, thus at the drop contact area A^{CA}_{drop} . Figure 4 illustrates the internal pressure acting normal to the drop surface. Only the forces on

Figure 4 illustrates the internal pressure acting normal to the drop surface. Only the forces on the drop's cap $A_{drop}^{o^*}$ have to be considered since forces acting on the grey shaded areas cancel out. Considering normal forces, the projected surface is relevant for the calculation of the pressure force. The projected surface of the drop's cap $A_{drop}^{o^*}$ is equal to the contact area A_{drop}^{CA} . Hence, the integral of the inside pressure p_{drop} over the drop surface A_{drop}^{o} is equal to the integral over the contact area A_{drop}^{CA} .

$$\int_{A_{\rm drop}^o} p_{\rm drop} \, d\mathbf{x} = \int_{A_{\rm drop}^{\rm CA}} p_{\rm drop} \, d\mathbf{x} = \int_{A_{\rm drop}^{\rm CA}} p_l^{\rm pm} \, d\mathbf{x}.$$
(28)



Fig. 4 Internal force balance on drop.

At the contact area the internal drop pressure has to be equal to the porous-medium pressure of the liquid phase p_l^{pm} since a continuous fluid phase exists and the microscopic pressure is assumed to be equal to the REV-scale pressure [Gurau and Mann, 2009, Gurau et al., 2008].

The same reasoning is applied to the outside pressure but cannot be applied to the capillary pressure which is still integrated over the drop surface, yielding

$$\int_{A_{\rm drop}^{\rm CA}} \left[\mathbf{n} \cdot \left(\left(\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g + p_g \mathbf{I} - \boldsymbol{\tau} \right) \mathbf{n} \right) \right]^{\rm ff} \, d\mathbf{x} + \int_{A_{\rm drop}^o} \frac{2\gamma_{lg}}{r_{\rm drop}} \, d\mathbf{x} = \int_{A_{\rm drop}^{\rm CA}} p_l^{\rm pm} \, d\mathbf{x}, \tag{29}$$

as a definition of mechanical equilibrium. It is an assumption that the integral of the normal forces $[\mathbf{n} \cdot ((\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g + p_g \mathbf{I} - \boldsymbol{\tau})\mathbf{n})]^{\text{ff}}$ over the drop surface and the drop contact area are equal. Even if the pressure is constant around the drop, the contribution of the normal shear stresses might be different. However, we assume a fully developed flow field on top of the drop and slow changes due to slowly growing drops. Furthermore, the normal shear forces on the side of the drop are neglected.

Chemical equilibrium The water-saturated gas directly above the drop in the free-flow region is in chemical equilibrium with the water phase of the drop:

$$[x_g^w]^{\rm ff} = \frac{p_{\rm sat,Kelvin}^w}{p_q^{\rm ff}} [x_l^w]^{\rm pm}.$$
(30)

The saturated vapour pressure is calculated using the Kelvin equation (see Table 2), since the curvature of the drop leads to higher evaporation rates [Butt et al., 2007]. The mole fraction of water in the liquid phase in the drop x_l^w corresponds to the respective mole fraction in the porous medium.

Thermal equilibrium Assuming local thermal equilibrium, the temperature T^{pm} of the porous medium at the drop contact area is equal to the temperature T_{drop} inside the drop. Assuming a constant drop temperature and again local thermal equilibrium, drop and free-flow gas temperature have to be equal, too,

$$T^{\rm pm} = T_{\rm drop} = T_a^{\rm ff}.$$
(31)

2.2.5 Combined coupling conditions for the drop-covered and drop-free interface

The partition of the interface in drop-covered A_{drop}^{CA} and drop-free A_g area is an idealisation and only area fractions a_{drop} and a_g are known being an outcome of the continuum description (see Sections 2.2.2 and 2.2.3). We assume that the integrals given in the previous Section are valid for every arbitrary control-volume size. Without a fixed and defined control volume (or control area), the integral formulation of equations (22)-(29) can be transformed directly to a differential formulation. The set of differential coupling conditions for drop-covered surfaces is combined with those given in Section 2.1 to obtain the total coupling framework. The area weighted average of the coupling conditions with and without drop yields the complete set of coupling conditions for the whole interface A_{Γ} .

=1

Flux balance Combining conditions (9) and (22) yields the overall condition for the total mass flux:

$$\frac{\frac{\partial \left(\varrho_{l,\mathrm{drop}} V_{\mathrm{drop}}\right)}{\partial t}}{\frac{\partial t}{\partial t}} + \left[\varrho_{g} \boldsymbol{v}_{g} \cdot \mathbf{n} + \varrho_{l} \boldsymbol{v}_{l} \cdot \mathbf{n}\right]^{\mathrm{pm}} a_{g} \ \Omega_{\mathrm{drop}} + \left[\varrho_{l} \boldsymbol{v}_{l} \cdot \mathbf{n}\right]^{\mathrm{pm}} a_{\mathrm{drop}} \ \Omega_{\mathrm{drop}}$$
$$= \left[\rho_{g} \boldsymbol{v}_{g} \cdot \mathbf{n}\right]^{\mathrm{ff}} \cdot \left(a_{\mathrm{drop}} + a_{g}\right) \ \Omega_{\mathrm{drop}}. \tag{32}$$

The total component balance across the interface is obtained by averaging (14) and (23):

$$\underbrace{\frac{\partial \left(\varrho_{l} \cdot \operatorname{drop} x_{l,\operatorname{drop}}^{\kappa} V_{\operatorname{drop}}\right)}{\partial t}}_{\frac{\partial \lambda_{V_{\operatorname{drop}}}}{\partial t}} + \sum_{\alpha \in \{l,g\}} \left[(\varrho_{\alpha} \boldsymbol{v}_{\alpha} x_{\alpha}^{\kappa} - D_{\alpha}^{\kappa,\operatorname{pm}} \varrho_{\alpha} \boldsymbol{\nabla} x_{\alpha}^{\kappa}) \cdot \mathbf{n} \right]^{\operatorname{pm}} a_{g} \Omega_{\operatorname{drop}} + \left[(\varrho_{l} \boldsymbol{v}_{l} x_{l}^{\kappa} - D_{l}^{\kappa,\operatorname{pm}} \varrho_{l} \boldsymbol{\nabla} x_{l}^{\kappa}) \cdot \mathbf{n} \right]^{\operatorname{pm}} a_{\operatorname{drop}} \Omega_{\operatorname{drop}} = -\left[\left(\varrho_{g} \boldsymbol{v}_{g} x_{g}^{\kappa} - D_{g}^{\kappa} \varrho_{g} \boldsymbol{\nabla} x_{g}^{\kappa} \right) \cdot \mathbf{n} \right]^{\operatorname{ff}} \underbrace{(a_{\operatorname{drop}} + a_{g})}_{=1} \Omega_{\operatorname{drop}}. \quad (33)$$

The total energy balance results from (12) and (24):

$$\frac{\partial \left(\varrho_{l,\mathrm{drop}} u_{l,\mathrm{drop}} V_{\mathrm{drop}}\right)}{\partial t} + \left[\left(\varrho_{g} h_{g} \boldsymbol{v}_{g} + \varrho_{l} h_{l} \boldsymbol{v}_{l} - \lambda_{\mathrm{pm}} \boldsymbol{\nabla} T\right) \cdot \mathbf{n}\right]^{\mathrm{pm}} a_{g} \Omega_{\mathrm{drop}} + \left[\left(\varrho_{l} h_{l} \boldsymbol{v}_{l} - \lambda_{\mathrm{pm}} \boldsymbol{\nabla} T\right) \cdot \mathbf{n}\right]^{\mathrm{pm}} a_{\mathrm{drop}} \Omega_{\mathrm{drop}} \\
= -\left[\left(\varrho_{g} h_{g} \boldsymbol{v}_{g} - \lambda_{g} \boldsymbol{\nabla} T\right) \cdot \mathbf{n}\right]^{\mathrm{ff}} \underbrace{\left(a_{\mathrm{drop}} + a_{g}\right)}_{-1} \Omega_{\mathrm{drop}}.$$
(34)

The drop volume V_{drop} is an outcome of the model. From the drop volume, the drop radius, which is needed for the force balance (35), can be calculated (see equation (21)). Furthermore, a new partition of the interface in drop-covered and drop-free area is calculated yielding the area fractions a_g and a_{drop} .

Mechanical equilibrium The continuity of normal force across drop-free and drop-covered interface is given by combining (8) and (29):

$$\begin{bmatrix} \mathbf{n} \cdot \left(\left(\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g + p_g \mathbf{I} - \mu_g \left(\boldsymbol{\nabla} \boldsymbol{v}_g + \boldsymbol{\nabla} \boldsymbol{v}_g^T \right) \right) \mathbf{n} \right) \end{bmatrix}^{\text{ff}} \underbrace{(a_{\text{drop}} + a_g)}_{=1} = p_g^{\text{pm}} a_g + \left(p_l^{\text{pm}} - \frac{2\gamma_{lg}}{r} \frac{a_{\text{drop}}^o}{a_{\text{drop}}} \right) a_{\text{drop}}.$$
(35)

An area-weighted average is questionable in case of the mechanical equilibrium. A combination of equation (8) and (29) means averaging pore and REV-scale pressure definitions. The water and gas pressure inside the porous medium are connected by the macroscopic capillary pressure which is of different order than the capillary pressure exerted by the curved drop surface. Consequently, a combined condition leads to a non-physical jump in the gas pressure across the interface (see Section 3).

The Beavers-Joseph-Saffman condition (10) can be employed as condition for the tangential freeflow velocity at the interface. The Beavers-Joseph coefficient α_{BJ} needs to be determined as a function of the fraction of the interface covered by drops a_{drop} , the drop height and diameter, and the saturation at the interface. This is beyond the scope of this work.



Fig. 5 Deformed drop due to drag force exerted by the flow field. The different drag-force contributions as well as the retention force are illustrated.

Chemical equilibrium By averaging (13) and (30), the definition of the total local chemical equilibrium boils down to

$$[x_g^w]^{\rm ff} = [x_g^w]^{\rm pm} \ a_g + \frac{p_{\rm sat,Kelvin}^w}{p_q^{\rm ff}} \ [x_l^w]^{\rm pm} \ a_{\rm drop}.$$
(36)

Thermal equilibrium Local thermal equilibrium is still given by the continuity of temperature, see (11) and (31).

2.2.6 Drop detachment

Drops formed based on the conditions explained in Section 2.2.3 can grow due to the framework presented in 2.2.4 until they detach. Figure 5 shows that a sessile drop deforms subjected to pressure F_p and shear F_{τ} forces and the dynamic-pressure force F_{pv^2} exerted by the external flow field. Altogether these forces form the drag force F_{drag} acting on the drop:

$$F_{\rm drag} = F_{\tau} + F_p + F_{pv^2} = \frac{1}{2} \varrho_g v_g^2 c_w(Re) A_{\rm proj}.$$
 (37)

The drag force can either be calculated with a control-volume force-balance approach or estimated based on the drag coefficient c_w [Chen et al., 2005, Cho et al., 2012a,b]. The drag coefficient c_w depends on the form of the drop and on the Reynolds number. Different expressions can be found in the literature [Cho et al., 2012a, Zhang et al., 2006], e.g. $c_w = \frac{24}{Re}(1+0.1925Re^{0.63})$ or $c_w = \frac{30}{\sqrt{Re}}$. Cho et al. [2012a,b] suggest the empirical expression (38), stating that it might be impossible to describe the drag force for all possible channel dimensions and flow conditions with only one formula,

$$c_w = (46.247 \frac{d_{\rm drop}}{h_{\rm FF}}^{0.1757}) \cdot Re^{(0.2158 \frac{d_{\rm drop}}{h_{\rm FF}} - 0.6384)} \quad \text{with} \quad Re = \frac{\varrho_g |\boldsymbol{v}_g| h_{\rm FF}}{\mu_g}.$$
 (38)

A retention force F_{γ}^{max} works against the drag force F_{drag} . The retention force is caused by contactangle hysteresis and elongation of the contact area due to the deformation of the drop [Chen et al., 2005, Extrand and Gent, 1990, Kumbur et al., 2006, Qin et al., 2012c]. The adhesion force has a horizontal and a vertical component. Horizontal drag and vertical lift forces are hence responsible for detachment. According to Cho et al. [2012a], the vertical retention force can be neglected.

To calculate the horizontal retention force a geometric description for the contact area and the volume is needed. Often, a circular contact line is assumed, neglecting deformation of the contact line and assuming contact-angle hysteresis to be the only cause for the retention force.

We use an expression for the retention force given in Kumbur et al. [2006] based on a linear variation of the contact angle along the contact line,

$$F_{\gamma}^{\max} = \gamma_{lg} r_{drop}^{CA} \pi \left[\frac{\sin(\Delta\theta^{\max} - \theta^*) - \sin\theta^*}{\Delta\theta^{\max} - \pi} + \frac{\sin(\Delta\theta^{\max} - \theta^*) - \sin\theta^*}{\Delta\theta^{\max} + \pi} \right].$$
(39)

This shows that the surface-tension force is proportional to the radius of the contact area r_{CA} and related to the difference in advancing and receding contact angle $\Delta\theta$. The maximum retention force is given for the maximally sustained difference in contact angles which can be determined experimentally. Schillberg and Kandlikar [2007] summarise and compare existing approaches to estimate drag and retention forces and to describe drop detachment. They conclude that increased hydrophobicity of the porous surface, a large static contact angle and high gas-flow velocities lead to earlier detachment and that the interface roughness has a minor influence only.

Detachment can be due to sliding, rolling or lifting of the drop. Note that sliding and rolling still leads to coverage of the porous medium. However, we do not distinguish between these detachment mechanisms and assume that the drop leaves the porous-medium surface once $F_{\rm drag} > F_{\gamma}^{\rm max}(V_{\rm drop})$ and is then transported by the flow field. These transport processes are not described in the scope of this work.

2.3 Implementation based on the mortar method

The implementation of the presented model is based on the modelling toolbox DuMu^x. "DuMu^x is a free and open-source simulator for flow and transport processes in porous media, based on the Distributed and Unified Numerics Environment (DUNE) [Bastian et al., 2008]. Its main intention is to provide a sustainable and consistent framework for the implementation and application of model concepts, constitutive relations, discretisations and solvers" [Flemisch et al., 2011]. The spatial discretisation of the geometric domain and the designation of sub-domains are based on the software package DUNE-Multidomaingrid [Müthing and Bastian, 2010], which allows us to represent arbitrarily complex subdomain shapes with conforming interfaces. For the management of the different sub-domains and their associated function spaces, we employ PDELab [Bastian et al., 2010], and its extension DUNE-Multidomain. DUNE-Multidomain allows a transparent definition of local operators and variables on the individual sub-domains and supports the assembly of a global system matrix. The global matrix contains the sub-matrices for the two sub-domains and the coupling matrices. The ability to do a full system assembly enables us to solve the strongly coupled highly non-linear system in a fully implicit fashion without any sub-domain iteration scheme. The numerical model for the implementation of the coupling concept without drop is described in detail in Baber et al. [2012].

The mortar method, a numerical domain-decomposition technique [Ewing et al., 2000, Helmig et al., 2009, Wohlmuth, 2000], is employed for the implementation of the coupled system of equations (Tables 1, 3, Equations (32) - (36)). Mostly, this technique is used in case of non-conforming meshes. Here, its use is motivated by the fact that an additional degree of freedom is specified on the interface. The storage of water within the drop $\lambda_{V_{drop}} = \varrho_l x_l^w V_{drop}$ (see (33)) is introduced as an unknown so that the drop volume is an inherent result of the model.

2.3.1 Discretisation

For the discretisation of the coupled model, the implicit Euler time-integration and a vertex-centred control-volume finite-element method (also called box method, Huber and Helmig [2000]) in space is used. The computational domain is covered by a structured finite-element grid (primal mesh). The values of all primary variables are computed at the vertices of the elements. The dual mesh which describes the control volumes is obtained by connecting the centres of gravity of each element with the associated edge midpoints. Thus, each control volume is associated with a vertex. We consider a quadrilateral grid and approximate all primary variables using piecewise bilinear functions (equal order method), which are mapped from the standard-reference-element basis functions. The application of the box method includes constant weighting functions ($\omega = 1.0$ within a control volume and $\omega = 0$ everywhere else). Consequently, the term including the derivative of the weighting function in (42) below vanishes. In the free-flow domain, a stabilisation technique similar to Franca et al. [1993] is generalised and implemented for the Navier-Stokes equations [Baber et al., 2012]. The arising non-linear system is solved fully implicitly by applying a Newton solver.

2.3.2 The mortar method

The mortar method is explained on the basis of the general form of the balance equation:

$$\frac{\partial M(u)}{\partial t} + \boldsymbol{\nabla} \cdot (\mathbf{f}(u)) - q = 0 \tag{40}$$

where $u \in \{ \boldsymbol{v}_g^{\mathrm{ff}}, p_g^{\mathrm{ff}}, x_g^{\mathrm{wff}}, T^{\mathrm{ff}}, S_l^{\mathrm{pm}} \text{ or } x_g^{\mathrm{wpm}}, T^{\mathrm{pm}} \}$ is an entry of the solution vector, M(u) is the storage, $\mathbf{f}(u)$ the flux and q the source/sink term. Equation (40) is integrated over the domain $\Omega^i, i \in \{\mathrm{FF}, \mathrm{PM}\}$, and multiplied by a test function ω :

$$\int_{\Omega^i} \frac{\partial M(u)}{\partial t} \,\omega \, d\Omega^i + \int_{\Omega^i} \nabla \cdot (\mathbf{f}(u)) \,\omega \, d\Omega^i - \int_{\Omega^i} q \,\omega \, d\Omega^i = 0.$$
⁽⁴¹⁾

Integration by parts yields:

$$\int_{\Omega^{i}} \frac{\partial M(u)}{\partial t} \,\omega \, d\Omega^{i} + \int_{\Omega^{i}} \nabla \mathbf{f}(u) \cdot \nabla \omega \, d\Omega^{i} - \int_{\partial \Omega^{i} \setminus \Gamma} \mathbf{f}(u) \cdot \mathbf{n} \,\omega \, d\Omega^{i} \\ - \int_{\Gamma} \underbrace{\mathbf{f}(u) \cdot \mathbf{n}}_{\lambda} \,\omega \, d\Gamma - \int_{\Omega^{i}} q \,\omega \, d\Omega^{i} = 0.$$
(42)

On the outer boundaries $\partial \Omega^i \setminus \Gamma$ either Dirichlet or Neumann conditions are imposed.

The normal flux across the interface Γ is represented by the Lagrange multiplier λ such that flux continuity is ensured across the interface. Additionally, the continuity condition at the interface is enforced in a weak sense as

$$\int_{\Gamma} (u^i - u^j) \ \psi \ d\mathbf{x} = 0 \tag{43}$$

where ψ is a Lagrange-multiplier test function and u_i and u_j are unknowns of the neighbouring subdomains.

The application of the mortar method to the coupling of the component and energy balance equations (see Tables 2 and 3) is straight forward. The Lagrange multipliers are defined as

$$\lambda_{x} := \mathbf{f}^{\kappa} \cdot \mathbf{n} = \left(\varrho_{g} \boldsymbol{v}_{g} x_{g}^{\kappa} - D_{g}^{\kappa} \varrho_{g} \boldsymbol{\nabla} x_{g}^{\kappa}\right)^{\mathrm{ff}} \cdot \mathbf{n}^{\mathrm{ff}}$$
$$= -\sum_{\alpha \in \{l,g\}} \left(\varrho_{\alpha} \boldsymbol{v}_{\alpha} x_{\alpha}^{\kappa} - D_{\alpha}^{\kappa,\mathrm{pm}} \varrho_{\alpha} \boldsymbol{\nabla} x_{\alpha}^{\kappa}\right) \cdot \mathbf{n}^{\mathrm{pm}}, \tag{44}$$

$$\lambda_T := \mathbf{f}_T \cdot \mathbf{n} = (\varrho_g h_g \boldsymbol{v}_g - \lambda_g \boldsymbol{\nabla} T)^{\mathrm{ff}} \cdot \mathbf{n}^{\mathrm{ff}}$$
$$= -(\varrho_g h_g \boldsymbol{v}_g + \varrho_l h_l \boldsymbol{v}_l - \lambda_{\mathrm{pm}} \boldsymbol{\nabla} T)^{\mathrm{pm}} \cdot \mathbf{n}^{\mathrm{pm}}.$$
(45)

The corresponding continuity conditions are:

$$\int_{\Gamma} \left(\left[x_g^w \right]^{\mathrm{ff}} - \left[x_g^w \right]^{\mathrm{pm}} a_g - \frac{p_{\mathrm{sat,Kelvin}}^w}{p_g^{\mathrm{ff}}} \left[x_l^w \right]^{\mathrm{pm}} a_{\mathrm{drop}} \right) \psi \ d\mathbf{x} = 0, \tag{46}$$

$$\int_{\Gamma} (T^{\rm ff} - T^{\rm pm})\psi \ d\mathbf{x} = 0.$$
(47)

For the momentum transfer, the mortar method has to be applied in a different way. This is due to the fact that in the porous medium, the pressure is a primal variable and the mass flux a dual variable, while the opposite holds in the free-flow domain. We choose the Lagrange multipliers and continuity conditions as

$$\lambda_p := (\mathbf{f}_{\boldsymbol{v}} \mathbf{n}) \cdot \mathbf{n} = [((\varrho_g^m \boldsymbol{v}_g \otimes \boldsymbol{v}_g + p_g \mathbf{I} - \boldsymbol{\tau})\mathbf{n}) \cdot \mathbf{n}]^{\text{ff}},$$
(48)

$$\lambda_{v_x} := [\boldsymbol{v}_q \cdot \mathbf{t}]^{\mathrm{ff}},\tag{49}$$

$$\lambda_{v_y} := \mathbf{f}_m \cdot \mathbf{n} = \left[\left(\varrho_g \boldsymbol{v}_g + \varrho_l \boldsymbol{v}_l \right) \cdot \mathbf{n} \right]^{\mathrm{pm}},\tag{50}$$



Fig. 6 Visualisation of the REV drop concept: instead of one small drop per grid cell, these volumes are assembled to form one large drop per drop REV Ω_{drop} . Drop radius and the area weighting a_g and a_{drop} are calculated from the large drop and are valid for all contributing cells.

$$\int_{\Gamma} \left(\left[p_g^{\rm pm} a_g + \left(p_l^{\rm pm} - \frac{2\gamma_{lg}}{r_{\rm drop}} \frac{a_{\rm drop}^0}{a_{\rm drop}} \right) a_{\rm drop} \right] - \lambda_p \right) \psi \ d\mathbf{x} = 0, \tag{51}$$

$$\int_{\Gamma} \left(\left[\left(\frac{\sqrt{K_i}}{\alpha_{\rm BJ} \, \mu_g} \boldsymbol{\tau} \, \mathbf{n} \right) \cdot \mathbf{t} \right] - \lambda_{v_x} \right) \psi \, d\mathbf{x} = 0, \tag{52}$$

$$\int_{\Gamma} \left(\left[\boldsymbol{v}_g^{\mathrm{ff}} \cdot \mathbf{n} \right] - \lambda_{v_y} \right) \psi \, d\mathbf{x} = 0.$$
(53)

The duality of flux and continuity conditions characteristic for the mortar method is given by the coupling conditions since fluxes are substituted by primary variables. The choice of Lagrange multipliers is not imperative. In the future, a combination of direct coupling (see Baber et al. [2012]) and mortar coupling is envisaged introducing Lagrange multipliers only where appropriate and necessary.

Additionally, the Lagrange multiplier for the storage within the drop needs to be defined. The presented coupling concept provides three conditions for the component flux: the component flux across the drop-free interface (14), the component flux feeding the drop (23), and the condition for the whole interface (33). Equation (33) is used as coupling condition for the free-flow and porous-medium component-balance equations implemented via Lagrange multipliers, see (44),). The component balance for the drop (23),

$$\frac{\partial \lambda_{V_{\rm drop}}}{\partial t} + \left[\varrho_l \boldsymbol{v}_l x_l^{\kappa} - D_l^{\kappa, \rm pm} \varrho_l \boldsymbol{\nabla} x_l^{\kappa}\right]^{\rm pm} \cdot \mathbf{n} \ a_{\rm drop} \Omega_{\rm drop} = -f_{\rm evap}^{\kappa}(r_{\rm drop}) \ \Omega_{\rm drop}, \tag{54}$$

defines the Lagrange multiplier $\lambda_{V_{\text{drop}}}$ which is used henceforth in (32) and (33). Here, the evaporative flux from the drop surface is calculated depending on the drop size and is assumed to be equal to the normal flux into the free-flow region.

In A, the implementation is visualised providing a schematic view of the global system matrix.

2.3.3 Droplet specific implementation

The drop-REV $\Omega_{\rm drop}$ introduced in Section 2.2.2 is chosen independently of and larger than the discretisation length. Consequently, one big drop per grid-cell cluster $\Omega_{\rm drop}$ is modelled instead of a non-physically small drop per single grid cell (see Figure 6).

The model is solved for the Lagrange multiplier $\lambda_{V_{\text{drop}}}$ which is essentially the volumetric contribution of each node to the whole drop. The water from all grid cells within one drop REV Ω_{drop} is then aggregated to form one big physical drop (see Figure 6),

$$V_{\rm drop} = \sum_{i \in \Omega_{\rm drop}} \frac{\lambda_{\varrho V \rm drop}^i}{\varrho_w^i x_l^{wi}}.$$

The drop radius and the areal distribution needed for the coupling conditions (32) - (36) are calculated from the total drop volume $V_{\rm drop}$ (see Figure 6). $r_{\rm drop}$. Hence, a_g and $a_{\rm drop}$ can be seen as effective quantities.

Until now, the area of influence Ω_{drop} has to be chosen as an input parameter. Consequently, the number and distribution of drops is given in advance [Berning et al., 2009] and has to be chosen wisely according to the physical problem and experimental observations. The influence of the choice of Ω_{drop} is investigated in Section 3. Moreover, the total work flow of the simulation is illustrated in B.

3 Numerical example and parameter study

The general model concept presented in the previous Section is adapted to 2D to simplify the very complex system. In 2D, the drops become cylinders [Chen et al., 2005]. This affects the geometrical relations like drop volume, drop contact area or drop surface as follows:

$$V_{\rm drop} = \frac{(r_{\rm drop})^2}{2} \left(2\theta^* - \sin\theta^*\right) \mathbf{b},\tag{55}$$

$$A^o_{\rm drop} = 2\theta^* r_{\rm drop} \mathbf{b},\tag{56}$$

$$A_{\rm drop} = 2r_{\rm drop}\sin\theta^*b,\tag{57}$$

where b is the depth of the 2D system. The calculation of the retention force does not depend on the drop radius any more which is in agreement with the expression provided in Chen et al. [2005]:

$$F_{\gamma_{lg}}^{\max} = \pi \left(r_{\text{drop}} \sin \theta_a \right) \gamma_{lg} \cos(\pi - \theta_a) + \pi \left(r_{\text{drop}} \sin \theta_a \right) \gamma_{lg} \cos \theta_r.$$
(58)

The numerical example is motivated by the processes occurring in PEM fuel cells. Table 4 lists the respective material parameters. The laminar fully developed gas flow is described by the non-isothermal multi-component model presented in Section 2.1. However, calculations accounting for the inertial term lead to oscillations caused by the spatial discretisation. As the focus of this work clearly is on the interface treatment, inertial forces are neglected until a more suitable spatial discretisation is available. The flow and transport processes in the porous medium are described by the non-isothermal two-phase multi-component model given in Section 2.1, assuming that an REV-scale approach is applicable [Gurau and Mann, 2009, Qin and Hassanizadeh, 2014].

Figure 7 illustrates the setup for the drop model. The 1.5 mm x 5.1 mm domain is discretised with a rectangular mesh with 15 x 51 cells. The Neumann-flux conditions at the bottom of the domain are constant over time $(f_N^w = \mathbf{f}^w \cdot \mathbf{n} = -7.2 \cdot 10^{-4} \text{ kg/m}^2\text{s}, \sum_{\kappa} f_N^{\kappa} = -2.8 \cdot 10^{-3} \text{ kg/m}^2\text{s})$. They represent the influence of the electro-chemical reaction which occur in the catalyst layer of PEM fuel cells. The temperature at the bottom is specified by a constant Dirichlet condition. Tables 4 and 5 list the employed material parameters and values of the initial and boundary conditions.

3.1 Reference case

As a starting point, we consider the formation of one drop inside the domain choosing the area of influence equal to the area of the interface: $\Omega_{\rm drop} = A_{\Gamma}$. For the drop-formation condition (see Section 2.2.3), the pore-size distribution of the porous medium at the interface needs to be known. Table 6 provides a pore-size distribution taken from Acosta et al. [2006].

Figure 8 (black dashed-dotted line) shows the volume of the drop over time for the coupled model from Section 2.2.5. A stagnation of the drop growth can be observed. The stagnation is due to the fact that the drop grows slowly losing some of its mass by evaporation. This affects the contact-area of the

Symbol	Meaning	Value	Unit	Source
Porous	medium properties			
ϕ	porosity	0.8	-	Gurau and Mann [2010]
К	intrinsic permeability			
	$K_{\rm xx}$	$7.5\cdot10^{-12}$	m^2	Gurau and Mann [2010]
	$K_{ m yy}$	$3.9\cdot 10^{-11}$	m^2	Gurau and Mann [2010]
S_{gr}	residual saturation	0.0	-	
S_{lr}	residual saturation	0.0	-	
θ^*	contact angle	130	0	Theodorakakos (2006)
$\Delta \theta^{\max}$	contact-angle hysteresis	20	0	Cho et al. [2012a,b]
λ_s	solid-phase heat conductivity	15.6	$^{\rm W}/_{\rm K~m}$	Acosta et al. [2006]
c_s	solid-phase heat capacity	710	$W\!\!/_{\rm kg~K}$	Acosta et al. [2006]
ϱ_s	density of the solid phase	140	kg/m^3	Acosta et al. [2006]
Fluid p	roperties			
γ_{lg}	surface tension	0.0625	N/m	Acosta et al. [2006]

 Table 4 Parameter values used in the simulations.

Tab	le	5	Initial	and	boundary	condi	tions.

Symbol	Value	Unit
Gas chann	el	
$oldsymbol{v}_g^{\mathrm{ff}}$	$(6,0)^{\mathrm{T}}$	m/s
p_g^{ff}	$2.5\cdot 10^5$	Pa
X_g^w	0.075	-
T^{ff}	343.15	Κ
Gas-diffus	ion layer	
$p_g^{ m pm}$	$2.5\cdot 10^5$	Pa
$T^{\rm pm}$	343.15	Κ
S_l	0.1 - 0.45	-

 ${\bf Table \ 6} \ {\rm Pore \ distribution \ of \ the \ gas-diffusion \ layer \ after \ Acosta \ et \ al. \ [2006].$

Class	Mean pore radius	Percentage
0-100 nm	$5\cdot 10^{-8}\mathrm{m}$	15%
$100\mathrm{nm}$ - $1\mu\mathrm{m}$	$5 \cdot 10^{-7} \mathrm{m}$	30%
$1\mu{\rm m}$ - $10\mu{\rm m}$	$5\cdot 10^{-6}\mathrm{m}$	30%
$10\mu{\rm m}$ - $100\mu{\rm m}$	$5 \cdot 10^{-5} \mathrm{m}$	25%



Fig. 7 Numerical setup: the top region corresponds to the gas channel where a parabolic velocity profile is specified with a no-slip condition on the top and bottom boundary. The gas phase flows from left to right. The bottom region corresponds to the gas-diffusion layer. Neumann no-flow conditions are specified at the left and right boundaries. At the bottom, Neumann fluxes for water and air represent the catalyst layer.



Fig. 8 Drop volume $V_{\rm drop}$ over time showing cyclical drop formation and detachment and the influence of evaporation from the drop surface. The corresponding maximal drop height is approximately 0.7 mm.



Fig. 9 Distribution of the mass fraction of water in the gas phase X_g^w in the free-flow region and of the water saturation S_l in the porous medium without drop evaporation. The arrows indicate the free-flow velocity.



Fig. 10 Distribution of the gas-phase pressure and temperature in the free-flow region and porous medium at t = 294 s. The arrows indicate the free-flow velocity.

drop and reduces the fraction of the interface a_{drop} that allows water to flow into the drop. A steady state is reached when the water flux feeding the drop balances the evaporation from the drop surface.

Neglecting the evaporation from the drop surface by setting $f_{evap}^{\kappa} = 0$ in equations (23), (32) and (33), cyclic drop formation, growth and detachment can be observed (see Figure 8, red solid line, the simulation was stopped after 300s). The duration of one cycle is roughly 2 min. This behaviour is in good, qualitative agreement with the results of Berning et al. [2010]. Theodorakakos et al. [2006] show relations between drop diameter and gas velocities obtaining diameters of 1.25 - 1.6 mm dependent on the GDL material. The maximum diameter of the drop shown in Figure 8 is roughly 1 mm. The depicted drop volume corresponds to a maximum interface-coverage ratio of $a_{drop} = 0.18$, meaning that 18% of the interface are covered by water.

Figure 9 shows the water distribution at two points in time. Water is produced at the bottom of the domain and flows towards the interface due to capillary forces. The water evaporates at the interface increasing the mass fraction of water in the free-flow region. A decrease in the water saturation can be observed over time suggesting an efficient removal of excess water by evaporation and drop detachment.

The temperature distribution (see Figure 10a) shows a decrease in temperature at the interface due to evaporative cooling. The pressure field (see Figure 10b) causes gas flow from the free-flow into the porous-medium region (see Figure 11a) and a water flux towards the interface (see Figure 11b). As the influence of the drops on the gas-flow and pressure field in the free-flow compartment is not part of the model, the parasitic pressure drop in the gas channel is underestimated being only 3 Pa compared to values of 1.5-11 kPa observed by Kandlikar et al. [2014]. Film flow in the gas-channel corners is not considered either. Hence, the parasitic pressure loss cannot be predicted correctly.

The drop model causes discontinuities at the interface. The course of gas pressure (Figure 12) and mass fraction are parallel but show a jump directly related to the coupling conditions (35) and (36). This pressure jump can be much larger dependent on the magnitude of the water saturation and the capillary pressure in the porous medium. As defined by condition (31), the temperature is



Fig. 11 Velocity field of water and gas phase in the porous medium at t = 294 s.



Fig. 12 Pressure p at the interface at t = 294 s.

still continuous across the interface. Figure 13 shows the total mass fluxes across the interface from porous-medium (black dashed-dotted line) and the free-flow region (solid red line). The discontinuity in total mass fluxes corresponds to the storage inside the drop and reflects its cyclic variation. The total mass fluxes are continuous when the drop is detached. Even though the evaporative flux from the drop surface into the free-flow region is zero, the flux entering the free-flow region \mathbf{f}_m^{ff} is not zero in Figure 13. The mass flux \mathbf{f}_m^{ff} corresponds to the direct evaporation and the gas flux next to the drop across the drop-free fraction of the interface.

3.2 Influence of the choice of $\Omega_{\rm drop}$

As stressed in Section 2.2.2 and 2.3, the area of influence for one drop $\Omega_{\rm drop}$ has to be chosen in advance. It determines the number of drops that form on the interface a priori and has to be chosen carefully dependent on the material properties and in accordance with experimental observations. Having shown results for one drop on the 5.1 mm-long interface, we show now results for two drops (see Figure 14) and four drops (see Figure 15).

Several drops with different growth behaviour yield different capillary pressures influencing the pressure condition (35). To avoid oscillations in the free-flow region which cannot deal with locally varying pressure-boundary conditions, the pressure condition is simplified so that only the gas-phase pressures are coupled, see (8). The resulting drop volumes and the growth behaviour is different for each of the drops. The drops near the inlet grow faster than the drops further down stream. This is in accordance with the water-phase flow field shown in Figure 11b, where the water flux towards the



Fig. 13 Total mass fluxes \mathbf{f}_m across the interface plotted over time. The fluxes from the free-flow \mathbf{f}_m^{ff} and the porous-medium \mathbf{f}_m^{pm} region are discontinuous due to the storage inside the drop.



Fig. 14 Drop volume V_{drop} over time showing the first and second drop for a simulation with two drops forming at the interface $(\Omega_{\text{drop}} = 0.5A_{\Gamma})$.

Fig. 15 Drop volume V_{drop} over time showing for a simulation with forming at the interface ($\Omega_{\text{drop}} = 0.25 A_{\Gamma}$).

Table 7 Interface coverage ratio a_{drop} .

	one drop	two drops	four drops	Hussaini and Wang [2009]
$a_{ m drop}$ in %	18	32	57	20-60

interface is much larger in the left than in the right part of the domain. The growth behaviour does not appear to change significantly for more than one drop (compare Figures 8, 14 and 15). The water distribution in the porous medium decreases faster and further with an increasing number of drops. The growth rate seams not only to be determined by the water flux in the porous medium but to be dominated by the interface conditions.

Figure 16 shows the total mass fluxes across the interface from porous-medium (black dasheddotted line) to the free-flow region (solid red line). As the drops do not detach at the same time and at least one drop is present at the interface at any time, the normal fluxes at the interface differ by the mass stored inside the drops. As the evaporation from the drop surface is neglected, the flux across the drop-free part of the interface corresponds to $\mathbf{f}_m^{\rm ff}$ and is constant over time.

Kandlikar et al. [2014] stress the importance of the visualisation and quantification of the interface coverage by water to judge the efficiency of water management in fuel cells. The data found in the literature varies strongly. Sergi and Kandlikar [2011] determine the area-coverage ratio experimentally and find a low value of 4%. Hussaini and Wang [2009] determine wetted-area ratios of 20-60% experimentally. They observe that the wetted-area ratio depends on the relative humidity of the inflow gas stream. Table 7 lists the values obtained with the interface-drop approach presented in this work for one, two and four drops. Naturally, the fraction of the interface covered by water increases with the number of drops. The values are in agreement with the range provided by Hussaini and Wang [2009].

Fig. 16 Total mass fluxes \mathbf{f}_m across the interface plotted over time. The fluxes from the free-flow \mathbf{f}_m^{ff} and the porous-medium \mathbf{f}_m^{pm} region are discontinuous due to the storage inside the drop.

Fig. 17 Drop volume $V_{\rm drop}$ over time showing that drops do not form until the drop-formation condition is fulfilled. Evaporation still shows a stagnation of the growth process. The corresponding maximal drop height is approximately 0.95 mm.

Fig. 18 Drop volume $V_{\rm drop}$ over time showing the influence of a variation in contact angle.

3.3 Parameter study with a simplified model

To analyse the influence of the free-flow and porous-medium properties and of the detachment condition, an isothermal model with constant fluid properties is employed. Again, only one drop is considered. Figure 17 shows that the drops grow faster with the simplified model and that the consideration of the evaporative flux from the drop surface still leads to a stagnation of the growth process. The good convergence rate and the qualitatively correct results qualify the model to be used for the parameter study.

Figure 17 proves the applicability of the drop-formation condition. The calculations are started with a low initial water saturation of $S_l = 0.1$ causing relatively low water pressures. As long as the drop-formation condition (19) is not fulfilled, the drop volume is zero and the saturation in the porousmedium increases. Once a critical saturation level of $S_l = 0.42$ is reached, drops form, grow and detach (black dashed-dotted line in Figure 17).

3.3.1 Influence of the porous-medium properties

Increasing the contact angle means increasing the hydrophobicity of the porous matrix. Figure 18 shows that drops detach at smaller volumes for larger contact angles. A large contact angle means a smaller contact area for a given volume. This yields a smaller retention force. At the same time, the drop growth is slowed down significantly due to the decreased area available for the water flux feeding the drop.

A higher maximal value for the contact-angle hysteresis means that the drop can deform further. Naturally, this means a later detachment point (see Figure 19). Extrand and Gent [1990] analyse the retention of drops on solid surfaces and conclude that drops are better retained the larger the supported contact-angle hysteresis.

3.3.2 Influence of the free-flow conditions

As expected, higher gas velocities in the free-flow region cause faster detachment (see Figure 20). Since

Fig. 19 Drop volume $V_{\rm drop}$ over time showing the influence of the maximally sustained contact-angle hysteresis.

Fig. 20 Drop volume $V_{\rm drop}$ over time showing the influence of the variation of the maximal free-flow velocity.

Fig. 21 Drop volume $V_{\rm drop}$ over time showing the influence of the drag-force calculation.

the gas velocity influences the pressure condition and the condition for the normal fluxes, it also affects the growth rate slightly. Large velocities yield a faster growth.

3.3.3 Analysis of drop detachment

As explained in Section 2.2.6, the drag force exerted by the flow field can be calculated in different ways. Figure 21 compares the calculation of a force balance considering shear and pressure forces [Chen et al., 2005] with two expressions for the drag coefficient c_w , Equation (38) and $c_w = \frac{30}{\sqrt{Re}}$. The complex empirical expression for the drag coefficient given by Cho et al. [2012b] (see (38)) and the force-balance approach predict the same drop volume when detachment happens. The slowed growth of the red line in Figure 21 at larger volumes just before the detachment point cannot be explained.

The retention force is estimated based on (39) in all three cases. As the 2D retention force (58) does not depend on the drop size or the drop-wall interactions, it overestimates the possible drop volume.

4 Summary and outlook

We develop an interface concept at the REV(Darcy)-scale which describes drop formation, growth and detachment on a hydrophobic interface between free and porous-medium flow. The interface stores the mass and energy of the drops without resolving them. The direct exchange between free-flow and porous-medium region next to the drop is also part of the coupling concept since it preserves the exchange processes described by the simple-interface concept [Baber et al., 2012, Mosthaf et al., 2011]. The fraction of the interface which is covered by drops is used to obtain an area-weighted average of the coupling conditions with and without drop so that coupling conditions for the whole interface are obtained.

The temporal evolution of the drop volume is an outcome of the model. The number of drops that can form on the interface is defined a priori by choosing the size of the drop REV. This should be done in accordance with experimental observations.

The model describes drop formation, growth and detachment. Merging of drops cannot be resolved by the model since the drop surfaces and distances are not tracked by the averaged continuum approach. The model neither describes the fate of the drops after they are detached. A detached drop can either slide on the porous-medium surface, lift and float or wick into the film flow in the corners of the gas channel. Such processes are not yet resolved by the current model since the focus is on the interface description and drop formation.

The simulation results presented in the previous Sections prove the applicability of the interface drop model. They show that it is possible to include drop dynamics in the REV-scale coupling conditions between free and porous-medium flow. Drop formation, growth and detachment are represented correctly, if the evaporation from the drop surface is neglected. The interface-coverage ratio, which is an indicator for the quality of the water management, can be predicted. The simulations for a higher number of drops suggest that the interface conditions dominate the system. A parameter study shows that interface wettability and free-flow velocity have a significant influence on the drop growth and detachment.

Despite the promising results, the model is not predictive and cannot produce quantitative resultsAccording to Theodorakakos et al. [2006] and Kandlikar et al. [2014] two main effects limit the exchange processes at the interface between free flow and porous medium:

- 1. coverage of the interface by drops, slugs and films,
- 2. blockage of the gas channel and disruption of the fully developed flow field affecting heat and mass transfer.

The presented model captures the first point, but not the second. The free-flow model must be improved such that the influence of the drops on the flow conditions, the fate of the detached drops and film flow in the hydrophilic channel corners are included. Pressure loss is of practical interest and should be an outcome of the model. A first step in this direction is the improvement of the discretisation scheme to obtain a stable implementation of the laminar Navier-Stokes equation. Furthermore, an extension to 3D is required to represent the flow field in the free-flow region, the water distribution in the porous medium and the retention force correctly.

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A Global system matrix

Below, the implementation is visualised providing a schematic of the global system matrix (inside the braces). It contains the sub-matrices for the two sub-domains (top left, red and middle, grey), the coupling matrices between free flow and interface (top right, red) and porous medium and interface (middle right. grey) as well as the definitions of the Lagrange multipliers and continuity conditions in the bottom row (green). The first column in front of the braces contains the employed coupling conditions. Furthermore, the variables relevant in the respective conditions are indicated.

B Work flow of the simulation accounting for drop dynamics

The total work flow is illustrated in Figure 22. The system starts fully gas-saturated. It switches to a two-phase system due to a water source. As long as the pressure and flux of the water phase is not sufficient to form a drop, a non-isothermal compositional two-phase system is solved. The porous medium is coupled to the free flow in the gas distributor using the simple-interface coupling conditions without drops (see equations (8) - (14)). Between Newton steps the concept of the static pore model is used to determine the state of the interface for the next Newton step (see Figure 22 and Section 2.2.3). When the drop-formation condition is fulfilled, the initial drop properties are calculated and the drop-coupling conditions are used until the drop detaches. The drop radius and area distribution are calculated form the drop volume after each Newton step and are then valid for all contributing cells during the next Newton step. The drop-detachment condition (Section 2.2.6) is evaluated after each time step. If the drop is close to detaching or detached the time-step is reduced to capture the actual detachment point.

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Fig. 22 Visualisation of the implementation: Before each Newton step, the formation of new drops is checked and calculated. Then the drop grows and the new drop properties are calculated. At the end of a time step, the detachment condition is evaluated.

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