Mathematical Modeling of Water Uptake Through Diffusion in 3D Inhomogeneous Swelling Substrates

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Diffusion-driven water uptake in a substrate (imbibition) is a subject of great interest in the field of food technology. This is a particular challenge for rice grains that are preprocessed to accelerate the water uptake, i.e., to reduce the cooking time. Rice preprocessing disrupts the mesostructural order of starch and induces a microporous structure in the grains. The meso- and microstructural length scales have not been considered in joint approach until now. The (re)hydration of rice grains can be modeled by free (concentration-driven) diffusion or by water demand-driven diffusion. The latter is driven by the ceiling moisture content related to the extent of gelatinization of the rice substrate network. This network can be regarded as a fractal structure. As the spatial resolution of our models is limited, we choose to model the apparent water transport by a set of coupled partial differential equations (PDEs). Current models of water uptake are often limited to a single dimension, and the swelling of the substrate is not taken into account. In this article, we derive a set of PDEs to model water uptake in a three-dimensional (3D) inhomogeneous substrate for different types of water diffusion as well as the swelling of the substrate during water uptake. We will present simulation results for different 3D (macroscopic) structures and diffusion models and compare these results, qualitatively, with the experimental results acquired from magnetic resonance imaging. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 1834–1848, 2009

Keywords: diffusion, swelling, water demand, hydration, imbibition

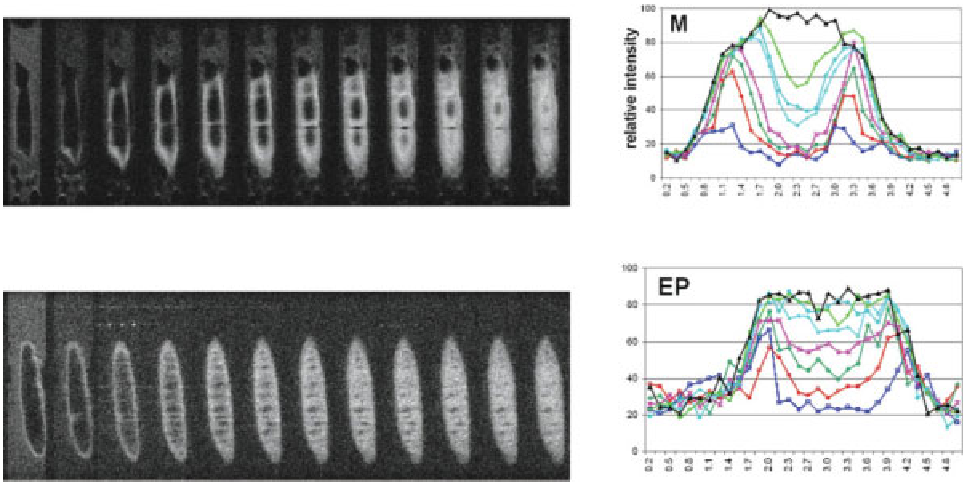

Figure 1. Time series of images of two different single kernels rice acquired during the process of cooking.

The top series corresponds to a massive rice grain with a relatively steep diffusion front. The bottom series corresponds to an open porous rice grain with a more uniformly distributed water uptake. The graphs on the right show the relative moisture profile across the centre of the kernel during cooking. The images are acquired at a rate of approximately one three-dimensional image per minute with a 0.7 T Bruker Avance MRI system using a 5-mm inner diameter microimaging detection coil. The image size is 128 × 32 × 16 voxels with a resolution on the order of 150 × 150 × 300 μm^3. The rice grains were fixated in a narrow tube filled with hot water. During the image acquisition process, the water was kept at a temperature of 90°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Introduction

Rice provides a major part of the global nutritional need for carbohydrates. In rice, carbohydrates predominantly appear as starch in the form of linear amylose and highly branched amylopectin. In native rice kernels, starch is organized in semicrystalline granules. Rice needs considerable processing in the form of cooking to melt these granules and obtain a masticable product. This process is called gelatinization. Gelatinization requires, besides heat, water, but the transport of water is slow because of the compact nature of the native rice grains, even during cooking. Consequently, the high degree of structural order within the rice kernels makes the cooking of rice an energy- and time-consuming process. A range of technologies have been developed to shorten the cooking time of rice, typically by disrupting the mesoscopic semicrystalline order of starch within the rice kernel and by inducing a microporous structure that enhances the uptake of water. The challenge is to develop preprocessing techniques for rice that reduce the actual cooking time to a few minutes without any loss of taste, mouth feel, and nutritional value. The significant impact of preprocessing on the rehydration during cooking is depicted in two magnetic resonance imaging (MRI) time series for different types of rice in Figure 1. The top series clearly shows a relatively steep diffusion front penetrating the rice grain, whereas the bottom series shows a more uniformly distributed water uptake. MRI allows for obtaining quantitative water ingress profiles during cooking of single rice grains with adequate spatial and temporal resolution.[1]

These profiles are shown in the graphs in Figure 1. The rice grain in the top series is a massive rice grain, even at the resolution of a micro X-ray CT imager (≈1 μm). The rice grain in the bottom series is a preprocessed rice grain. After preprocessing, this rice grain consists of a network of thin interconnected walls of substrate and many pores. These walls and pores are present at scales between 1 μm and 1 mm; the pores can be very large. Figure 2 shows a cross-section of the massive rice grain and the porous rice grain acquired with an X-ray CT imager [SkyScan 1072 desktop X-ray micro-tomography system (SkyScan, Belgium)].

In this article, we will model the water uptake and swelling in a rice grain during cooking to study the joint effect of meso- and microstructure on cooking time. The MRI images shown in Figure 1 are used to classify the water

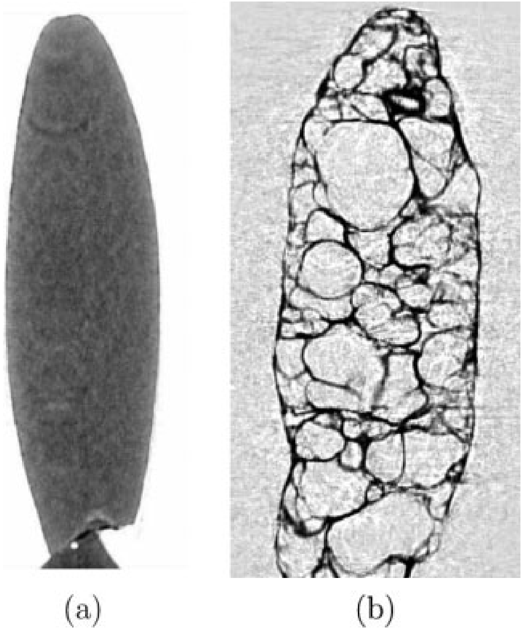

Figure 2. (a) Micro X-ray CT image of massive rice grain; (b) preprocessed rice grain.

uptake in a qualitative manner. This classification is not only based on MRI images but also on other techniques, such as differential scanning calorimetry (DSC) and X-ray diffraction (XRD). This research is described in detail elsewhere.[2] Several approaches have already been described for modeling water uptake in rice. In current models, moisture gradients are considered to be the driving force of Fickian diffusion.[3–7] Furthermore, models have been presented that account for events at the mesoscopic scale such as starch gelatinization at the water ingress front.[8] Noninvasive MRI experiments prove that these approaches fail to describe adequately water transport in starch-based systems during cooking.[9,10] Recently, the concept of water demand (WD) was introduced, which assumes that the driving force of diffusion is a gradient in the water storage capacity.[9,10] A simple one-dimensional (1D) model based on this concept was in agreement with MRI measurements of a simple 1D model system.[9,10] This 1D approach, however, is not applicable to complex three-dimensional (3D) microstructures of real food systems. Furthermore, the impact of swelling, because of starch gelatinization, is not properly accounted for in the 1D model. Cylindrical and elliptical models incorporating nonlinear diffusion and swelling in homogeneous substrates have been presented.[11,12] These models use a parameterized geometry to describe the rice grain, which can be incorporated in the partial differential equations (PDEs). In this article, we will focus on the development of a 3D model that jointly considers the mesoscopic organization of starch, i.e., the gelatinization degree, as well as the (porous) microstructure of the grain. Our model considers the gelatinization degree of starch by using an appropriate WD function, it takes into account the swelling of the starch matrix during water uptake, and it enables describing water transport in a complex 3D porous microstructure. Because our starch matrix cannot be parameterized, we cannot use the approach of McGuiness et al.[11] and Davey et al.[12] In this article, we will derive a discrete (local) model that is applicable to anisotropic rice grains, i.e., arbitrary initial conditions which reflect the structure of a rice grain, whereas their models are continuous (global) models applicable to isotropic rice grains.

Methods

Models that incorporate swelling often represent the substrate by a set of grid elements of fixed mass.[13] Swelling will cause a net transport of mass elements, causing a local deformation of the grid. For a fixed volume, grid swelling of the substrate (as a result of water uptake) implies transport of mixture mass, i.e., substrate mass having taken up water, from one grid element to neighboring grid elements. In this article, we have chosen a fixed volume grid for the simple reason that our simulation results then have the same representation as the MRI images, which enables a comparison. Furthermore, this approach allows for direct conversion from the sampled rice grain to an initial structure that can be used as input for our simulations. The consequence of representing a complex structured substrate by a regular grid of volume elements is that the volume occupied by the mixture mass (substrate and water) can vary from (practically) zero, at the positions of the pores, to the maximum volume of a voxel in the case of presence of substrate and water.

Consider an isolated rectangular container that is filled with free water and a single rice grain in the center of the container that is not in contact with the walls of the container. This implies that free water is surrounding the rice grain. The rice grain is regarded as a substrate that can take up water. The complete content of the container and the walls of the container are kept at a fixed temperature T, i.e., there is thermal equilibrium. Furthermore, the walls of the container imply that there is no inward- or outward-directed mass transfer, i.e., there is conservation of mass inside the container. Furthermore, we will assume that when free water is taken up by the starch molecules (substrate) in the rice grain, the densities of the compounds will not change, i.e., the density of dry substrate and free water equals the density of moistured substrate having taken up water. Dry substrate is substrate that has not yet taken up any water. In other words, we are considering incompressible compounds, i.e., there is also conservation of volume inside the container. The cooking of rice, the uptake of water by rice will be modeled as a process during which free water is converted to immobilized water bound to the substrate; in gelatinized starch immobilized water still has a considerable self-diffusion constant.

The rice grains that we will consider in our simulations are either solid, i.e., they do not contain any pores, or have a porous structure such that any pore inside the rice grain is in contact with the outside of the rice grain. We assume that when the porous rice grain is immersed from air into (boiling) water, the air present in the pores of the rice grain does not get trapped in the pores, but escapes from the rice grain instantly and the pores are immediately filled with free water. This assumption allows us to discard air in our model. Now, we only need to consider three compounds: substrate, free water, and immobilized water. The fact that there is conservation of volume and mass in our model implies that we only need to monitor two of these three quantities, i.e., there are only two independent quantities. The substrate can be either

- dry: the moisture content $m_{\mathrm{ls}}(\vec{x})$ (defined as the immobilized water mass per unit substrate mass) is zero and free water can be taken up,
- moistured: the moisture content is less than the maximum moisture content and free water can still be taken up, or
- water saturated: the moisture content equals the maximum moisture content, free water cannot be taken up anymore.

The rectangular container consists of a grid of rectangular volume elements; micro-CT images of rice grains can then be taken as input for our simulations. Any volume element V is in one of the following seven states depending on its content:

1. only free water ($\Omega_{\mathrm{f}} = 1$; $\Omega_{\mathrm{m}} = 0$),
2. only dry substrate ($\Phi_{\mathrm{w}} = 0$; $\Omega_{\mathrm{m}} = 1$; $\Omega_{\mathrm{f}} = 0$, free water from neighboring volume elements can be taken up),
3. dry substrate and free water ($\Phi_{\mathrm{w}} = 0$; $0 < \Omega_{\mathrm{m}}, \Omega_{\mathrm{f}} < 1$; $\Omega_{\mathrm{m}} + \Omega_{\mathrm{f}} = 1$),
4. only moistured substrate ($0 < \Phi_{\mathrm{w}} < \Phi_{\mathrm{w}}^{\max}$; $\Omega_{\mathrm{m}} = 1$; $\Omega_{\mathrm{f}} = 0$, free water from neighboring volume elements can still be taken up),

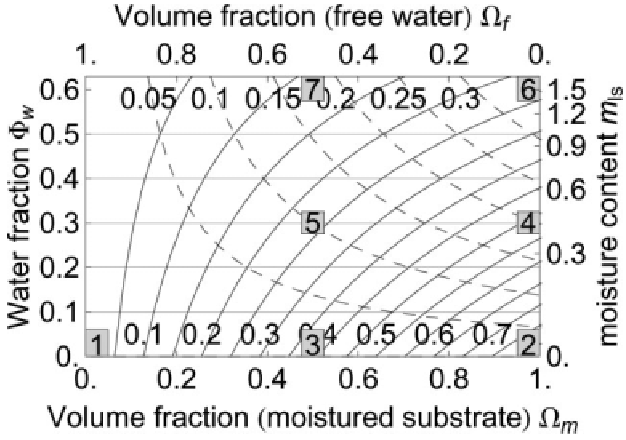

Figure 3. This graph shows the water fraction Φ_w vs. the moistured substrate volume fraction Ω_m.

The right vertical axis defines the corresponding moisture content m_{ls} and the top horizontal axis defines the corresponding free water volume fraction Ω_f. The solid lines with positive slope are lines of constant substrate mass: m_s = constant ranging from 0.05 to 0.75 kg. The dashed lines with negative slope are lines of constant immobilized water mass: m_w = constant ranging from 0.05 to 0.35 kg. The numbers inside the gray boxes indicate the seven different states of a volume element as explained in the text.

5. nonsaturated substrate and free water ($0 < \Phi_w < \Phi_w^{max}$; $0 < \Omega_m, \Omega_f < 1$; $\Omega_m + \Omega_f = 1$),
6. only water-saturated substrate ($\Phi_w = \Phi_w^{max}$; $\Omega_m = 1$; $\Omega_f = 0$), or
7. water-saturated substrate and free water ($\Phi_w = \Phi_w^{max}$; $0 < \Omega_m, \Omega_f < 1$; $\Omega_m + \Omega_f = 1$),

with Φ_w the water fraction of moistured substrate ranging from 0 for dry substrate (no water taken up) to Φ_w^{max} for water-saturated substrate, $\Omega_m = \Omega_m(\vec{x})$ the volume fraction $\frac{V_m(\vec{x})}{V}$ occupied by the substrate with (or without) immobilized water, and $\Omega_f = \Omega_f(\vec{x})$ the volume fraction $\frac{V_f(\vec{x})}{V}$ occupied by the free water such that $\Omega_m(\vec{x}) + \Omega_f(\vec{x}) = 1$. States 2, 4, and 6 represent the interior of the rice grain and states 3, 5, and 7 represent the edge of the rice grain; the interface between the rice grain and the free water from volume elements in state 1. The gray-boxed numbers in Figure 3 showing a graph of the water fraction Φ_w vs. the volume fraction Ω_m indicate these states; states 1, 2, and 6 are located in the lower left, lower right, and upper right corner of the graph, respectively. State 3 is always located between the states 1 and 2; state 4 is always located between the states 2 and 6. State 7 is located along the top horizontal boundary of the graph in Figure 3 and state 5 is anywhere in the interior of the graph. The volumes $V_m(\vec{x}) < V$ and $V_f(\vec{x}) < V$ are the absolute volumes occupied by the substrate with immobilized water and the free water, respectively. The equation $V_m(\vec{x}) + V_f(\vec{x}) = V$ makes the conservation of volume explicit.

The driving force of water uptake by the substrate is the WD, a quantity we will describe in more detail in section "water uptake." The WD is a function of the moisture content m_{ls} cq. water fraction Φ_w. This is the main reason why the process of water uptake will be expressed in terms of Φ_w. In short, if the temperature is sufficiently high, the drier the substrate, the larger the WD, the faster the uptake of water; dry substrate has a maximum WD, water-saturated substrate has no WD anymore. In a solid dry rice grain, water uptake will initially only take place at the edge of the rice grain; water will be immobilized in the starch network. When the edge is getting moistured, a gradient in WD pointing from the edge of the rice grain inward will initiate transport of immobilized water toward the inner part of the rice grain. Water uptake stops when the WD becomes zero.

Definitions

In this section, we will introduce the physical quantities of interest and the important relations between them.

1. The volume fraction $\Omega_m(\vec{x})$ is the fraction of V occupied by the dry substrate or by the moistured substrate after water uptake, and $\Omega_f(\vec{x})$ is the fraction of V occupied by the free water:

$$0 \leq \Omega_m(\vec{x}) = \frac{V_m(\vec{x})}{V} \leq 1, \quad 0 \leq \Omega_f(\vec{x}) = \frac{V_f(\vec{x})}{V} \leq 1, \tag{1}$$

with

$$\Omega_m(\vec{x}) + \Omega_f(\vec{x}) = 1, \quad V_m(\vec{x}) + V_f(\vec{x}) = V, \tag{2}$$

and $(\vec{x}) = [m, n, k]$ a discrete grid position. We will distinguish between volume elements containing free water $\Omega_m(\vec{x}) < 1$, and volume elements without free water $\Omega_m(\vec{x}) = 1$.

2. The mass $m_m(\vec{x})$ represents the mass of moistured substrate and immobilized water and equals the sum of the mass of dry substrate $m_s(\vec{x})$ and the mass of immobilized water $m_w(\vec{x})$: $m_m(\vec{x}) = m_s(\vec{x}) + m_w(\vec{x})$. If $m_w(\vec{x}) = 0$, then the substrate is dry and $m_m(\vec{x}) = m_s(\vec{x})$ represents the dry substrate mass. The volume fraction $V_m(\vec{x})$ occupied by the moistured substrate and the immobilized water equals the sum of the volume of the dry substrate and the volume of immobilized water:

$$V_m(\vec{x}) = \frac{m_s(\vec{x})}{\rho_s} + \frac{m_w(\vec{x})}{\rho_w}, \tag{3}$$

with ρ_s and ρ_w the densities of the dry substrate and water, respectively. This relation makes the incompressibility of the compounds explicit. The free water mass $m_f(\vec{x})$ follows from $V_f(\vec{x}) = \frac{m_f(\vec{x})}{\rho_w}$, such that the total mass of a volume element equals $m_s(\vec{x}) + m_w(\vec{x}) + m_f(\vec{x})$.

3. The water fraction $\Phi_w(\vec{x})$ and the substrate fraction $\Phi_s(\vec{x})$ of the moistured substrate are defined as follows:

$$\Phi_w(\vec{x}) = \frac{m_w(\vec{x})}{m_m(\vec{x})}, \quad \Phi_s = \frac{m_s(\vec{x})}{m_m(\vec{x})}, \quad \Phi_s(\vec{x}) + \Phi_w(\vec{x}) = 1, \tag{4}$$

where $\Phi_w(\vec{x}) = 0$ corresponds to dry substrate, $0 < \Phi_w(\vec{x}) < \Phi_w^{max}$ to moistured substrate and $\Phi_w(\vec{x}) = \Phi_w^{max}$ to water-saturated substrate.

4. The moisture fraction or moisture content $m_{ls}(\vec{x})$ is defined as the immobilized water mass per unit dry substrate mass:

$$m_{ls}(\vec{x}) = \frac{m_w(\vec{x})}{m_s(\vec{x})}. \tag{5}$$

The moisture fraction is related to the water fraction as follows:

$$\Phi_{\mathrm{w}}(\vec{x}) = \frac{m_{\mathrm{w}}(\vec{x})}{m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})} = \frac{m_{\mathrm{ls}}(\vec{x})}{1 + m_{\mathrm{ls}}(\vec{x})}. \tag{6}$$

Rewriting this result yields

$$m_{\mathrm{ls}}(\vec{x}) = \frac{\Phi_{\mathrm{w}}(\vec{x})}{1 - \Phi_{\mathrm{w}}(\vec{x})}. \tag{7}$$

5. The density $\rho_{\mathrm{m}}(\vec{x})$ of the moistured substrate with immobilized water in the volume $V_{\mathrm{m}}(\vec{x})$ depends on the water fraction. The exact relation is given by:

$$\frac{1}{\rho_{\mathrm{m}}(\vec{x})} = \left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{1}{\rho_{\mathrm{s}}}. \tag{8}$$

This relation is derived in Appendix A. Given $0 \leq \Phi_{\mathrm{w}} \leq \Phi_{\mathrm{w}}^{\max}$, this relation implies $\rho_{\mathrm{w}} \leq \rho_{\mathrm{m}} \leq \rho_{\mathrm{s}}$.

Based on these definitions and the conservation of volume and mass, the content of a volume element V is completely determined by $\Omega_{\mathrm{m}}(\vec{x})$, and $\Phi_{\mathrm{w}}(\vec{x})$ given ρ_{s} and ρ_{w}. Figure 3 shows a graph of the water fraction $\Phi_{\mathrm{w}}(\vec{x})$ vs. the volume fraction $\Omega_{\mathrm{m}}(\vec{x})$. The lower left corner ($\Omega_{\mathrm{m}} = 0$, $\Phi_{\mathrm{w}} = 0$) represents a volume element completely occupied with free water (state 1). The lower right corner ($\Omega_{\mathrm{m}} = 1$, $\Phi_{\mathrm{w}} = 0$) corresponds to a volume element completely filled with dry substrate (state 2). The upper right corner corresponds to a volume element containing water-saturated substrate (state 6). Curves with a negative slope (dashed lines) in this graph are curves with $m_{\mathrm{w}} = $ const., and curves with a positive slope (solid lines) are curves with $m_{\mathrm{s}} = $ const.

Consider now a volume element at the edge of the rice grain that is partially filled, $\Omega_{\mathrm{m}} < 1$, with moistured substrate, $\Phi_{\mathrm{w}} < \Phi_{\mathrm{w}}^{\max}$, and partially with free water (state 5). The substrate can still take up free water without any consequence, except for a change $\frac{\partial \Omega_{\mathrm{m}}}{\partial \mathrm{t}}$ of partial volume occupied by the moistured substrate and a change $\frac{\partial \Omega_{\mathrm{w}}}{\partial t}$ in water fraction of the moistured substrate, as long as two conditions are met. The first condition is that the partial volume V_{m} remains smaller than a volume element V, or $\Omega_{\mathrm{m}} < 1$. The second condition is that the substrate remains unsaturated, i.e., $\Phi_{\mathrm{w}} < \Phi_{\mathrm{w}}^{\max}$. In terms of the graph in Figure 3, the water fraction Φ_{w} should stay below the top horizontal boundary and the volume fraction Ω_{m} should stay to the left of the right vertical boundary. In the graph, water uptake in a volume element with this composition means moving along a curve with a positive slope (curve of constant substrate mass).

It is, of course, possible that a volume element with moistured substrate occupies the complete volume element, i.e., $\Omega_{\mathrm{m}} = 1$ (state 4). This might happen for all trajectories along curves of constant substrate mass that reach the right vertical boundary of the graph in Figure 3. Continuation of water uptake will result in a change of water fraction $\frac{\partial \Phi_{\mathrm{w}}}{\partial t}$ and, moreover, it will force some of the moistured substrate with immobilized water out of that volume element into neighboring volume elements, while keeping the volume fraction $\Omega_{\mathrm{m}} = 1$. The moistured substrate with immobilized water that is forced out of the voxel will have the same water fraction, cq. density as the moistured substrate that remains in the volume element. This implies that the total volume occupied by the moistured substrate is increasing; it is larger now than a single volume element V, i.e., the rice grain is swelling. Consequently, we must distinguish between volume elements that have reached $\Omega_{\mathrm{m}} = 1$ and volume elements that still contain free water: $\Omega_{\mathrm{m}} < 1$ ($\Omega_{\mathrm{f}} = 1 - \Omega_{\mathrm{m}} > 0$), because their behavior is described by different PDEs.

A particular volume element may go from state (1) via (5) to state (4), state (6) or state (7); from state (2) via state (4) to state (6); or from state (3) via state (5) to state (4), state (6) or state (7).

From the discussion so far, it is clear that we need to derive PDEs for the rate of change of the volume fraction of the moistured substrate $\frac{\partial \Omega_{\mathrm{m}}}{\partial t}$ and the rate of change of the water fraction $\frac{\partial \Phi_{\mathrm{w}}}{\partial t}$ in the case $\Omega_{\mathrm{m}} < 1$ (edge of rice grain; states 3, 5, and 7). In the case $\Omega_{\mathrm{m}} = 1$ (interior of rice grain; states 2, 4, and 6), we only need to derive one PDE for the rate of change of the water fraction $\frac{\partial \Phi_{\mathrm{m}}}{\partial t}$. These PDEs will not describe the transport of moistured substrate with immobilized water from volume elements with $\Omega_{\mathrm{m}} = 1$ to neighboring volume elements with $\Omega_{\mathrm{m}} < 1$, i.e., they do not describe the swelling of the substrate during water uptake. This issue will be addressed in section "swelling: substrate transport derived from micro-balances between connected volume elements."

Water uptake: modeling the water flux ($-\vec{\nabla} \cdot \vec{J}''_{\mathbf{w}}$)

The starting point for our derivations is the continuity equation for immobilized water:

$$\frac{1}{V}\frac{\partial}{\partial t} m_{\mathrm{w}}(\vec{x}) = (-\vec{\nabla} \cdot \vec{J}''_{\mathrm{w}}), \tag{9}$$

where $\vec{J}''_{\mathrm{w}}$ is the water flux due to diffusion. In the case of free diffusion, the water flux follows from Fick's first law[14]:

$$\vec{J}''_{\mathrm{w}} = -D\vec{\nabla}\frac{m_{\mathrm{w}(}\vec{x})}{V} = -D\vec{\nabla}\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x}), \tag{10}$$

with D the diffusion constant. This equation says that the flux of water in the substrate is driven by a negative gradient in the water concentration, i.e., water is transported from a high water concentration to a low water concentration. In this article, we will use a non-Fickian diffusion model based on the WD.[9,10] The WD is defined as the amount of water that can still be taken up by the substrate. The driving force in the case of WD-driven diffusion is a positive gradient of the WD. The water flux is then defined as follows:

$$\vec{J}''_{\mathrm{w}} = D\vec{\nabla}\rho_{\mathrm{s}}\mathrm{WD}(m_{\mathrm{ls}}(\vec{x})) \tag{11}$$

The following is a summary from Ref. 9. If we consider starch as the substrate, then the WD depends on the terminal extent of gelatinization (TEG). The TEG itself is a function of the temperature θ in °C and the water fraction $\Phi_{\mathrm{w}}(\vec{x})$[15]:

$$\mathrm{TEG}(\Phi_{\mathrm{w}}(\vec{x})) = \frac{3.15\Phi_{\mathrm{w}}(\vec{x}) - 0.946}{1 + \exp(-0.1792(\theta - 69.1))}. \tag{12}$$

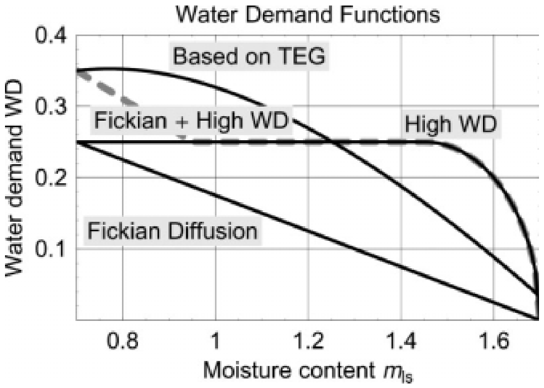

Figure 4. Four different water demand functions.

One is based on the terminal extent of gelatinization. The other three curves represent a water demand function related to ordinary diffusion, a high water demand function and the last curve is a combination of ordinary diffusion and a high water demand.

This equation shows that there is a linear relation between the TEG and the water fraction at a fixed temperature. Given a certain level of TEG, the ceiling moisture fraction $m_{\rm ls}^{\rm ceil}(\vec{x})$ is given by:

$$m_{\rm ls}^{\rm ceil}(\vec{x}) = [1 - {\rm TEG}(\Phi_{\rm w}(\vec{x}))]m_{\rm ls,i} + {\rm TEG}(\Phi_{\rm w}(\vec{x}))m_{\rm ls,f}, \quad (13)$$

where $m_{\rm ls,i}$ and $m_{\rm ls,f}$ are the initial and final moisture fractions of the mixture, respectively. The WD follows then as

$${\rm WD}(\vec{x}) = m_{\rm ls}^{\rm ceil}(\vec{x}) - m_{\rm ls}(\vec{x}). \quad (14)$$

Figure 4 shows the WD based on the TEG as a function of the moisture fraction. In this figure, three other WD functions are shown; one is related to ordinary diffusion, one is a constantly high WD function, and the last one is a combination of ordinary diffusion and a high WD. The main point here is that these WD functions only depend on the current moisture fraction $m_{\rm ls}(\vec{x})$, which is directly related to the current-immobilized water fraction $\Phi_{\rm w}(\vec{x})$.

WD-driven diffusion is related to so-called Case 2 diffusion; a Fickian diffusion model in which a reaction is taking place at the diffusion front.[8]

WD-driven diffusion describes ordinary diffusion, if the WD is defined as follows:

$${\rm WD}(m_{\rm ls}(\vec{x})) = \begin{cases} {\rm WD}_0 - m_{\rm ls}(\vec{x}), & \Omega_{\rm m}(\vec{x})<1 \\ {\rm WD}_0 - \frac{\rho_{\rm w}\ln\rho_{\rm w}}{4\rho_{\rm s}-2\rho_{\rm w}} - m_{\rm ls}(\vec{x}) + \mathcal{O}(m_{\rm ls}(\vec{x}))^2, & \Omega_{\rm m}(\vec{x}) = 1 \end{cases} \quad (15)$$

where ${\rm WD}_0$ is the initial water demand. This WD function is the straight line with a negative slope in Figure 4. Proof of Eq. 15 is given in Appendix B: modeling ordinary diffusion using water demand.

These WD functions allow for computation of the divergence of the water flux $(-\vec{\nabla}\cdot\vec{J}''_{\rm w})$.

Diffusion of immobilized water, Case 1: $\Omega_m = 1$

First, we will treat the case of diffusion of immobilized water in volume elements with $\Omega_{\rm m} = 1$ or $\Omega_{\rm f} = 0$. These volume elements are located in the interior of the rice grain. We assume that once a voxel has reached $\Omega_{\rm m} = 1$, it will remain at $\Omega_{\rm m} = 1$. In other words, immobilization of water is an irreversible process. Hence, we have

$$\frac{\partial}{\partial t}\Omega_{\rm m}(\vec{x}) = 0. \quad (16)$$

Given that the substrate is not saturated, water uptake by the substrate implies forcing moistured substrate (with immobilized water) out of the volume element. Consequently, the increase of immobilized water volume equals the decrease in volume of moistured substrate:

$$\frac{1}{\rho_{\rm w}}\frac{\partial}{\partial t}m_{\rm w}(\vec{x}) = -\frac{1}{\rho_{\rm m}}\frac{\partial}{\partial t}m_{\rm m}(\vec{x}). \quad (17)$$

Only a single mass balance is needed to model diffusion of immobilized water for this case:

$$\frac{1}{V}\frac{\partial}{\partial t}m_{\rm w}(\vec{x}) = \frac{\partial}{\partial t}\rho_{\rm m}(\vec{x})\Phi_{\rm w}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right), \quad (18)$$

Expanding this differential equation yields:

$$\rho_{\rm m}(\vec{x})\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) + \Phi_{\rm w}(\vec{x})\frac{\partial}{\partial t}\rho_{\rm m}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right). \quad (19)$$

Inserting Eq. A5 in Eq. 19 amounts to:

$$\rho_{\rm m}(\vec{x})\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) - \rho_{\rm m}^2(\vec{x})\Phi_{\rm w}(\vec{x})\left(\frac{1}{\rho_{\rm w}} - \frac{1}{\rho_{\rm s}}\right)\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right). \quad (20)$$

Using the Eqs. A1 or 8, this can be rewritten as:

$$\rho_{\rm m}(\vec{x})\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) - \rho_{\rm m}^2(\vec{x})\left(\frac{1}{\rho_{\rm m}(\vec{x})} - \frac{1}{\rho_{\rm s}}\right)\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right). \quad (21)$$

This result simplifies to

$$\frac{\rho_{\rm m}^2(\vec{x})}{\rho_{\rm s}}\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = \left(-\vec{\nabla}.\vec{J}''_{\rm w}\right). \quad (22)$$

Multiplying the mixture density $\rho_{\rm m}(\vec{x})$ and the substrate density $\rho_{\rm s}$ by the voxel volume V yields:

$$\frac{\rho_{\rm m}(\vec{x})}{\Phi_{\rm s}(\vec{x})}\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right). \quad (23)$$

Finally, we obtain

$$\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = \frac{\Phi_{\rm s}(\vec{x})}{\rho_{\rm m}(\vec{x})}\left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right) = \frac{1-\Phi_{\rm w}(\vec{x})}{\rho_{\rm m}(\vec{x})}(-\vec{\nabla}\cdot\vec{J}''_{\rm w}) \quad (24)$$

This result can be rewritten in terms of the immobilized water fraction $\Phi_{\rm w}(\vec{x})$ by inserting Eq. 8:

$$\frac{\partial}{\partial t}\Phi_{\rm w}(\vec{x}) = (1-\Phi_{\rm w}(\vec{x}))\left[\left(\frac{1}{\rho_{\rm w}} - \frac{1}{\rho_{\rm s}}\right)\Phi_{\rm w}(\vec{x}) + \frac{1}{\rho_{\rm s}}\right]\left(-\vec{\nabla}\cdot\vec{J}''_{\rm w}\right). \quad (25)$$

This equation describes the rate of change of the immobilized water fraction, given the current-immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$, and the water flux $\vec{J}''_{\mathrm{w}}$. In the next section, we present an iterative procedure for solving Eq. 25 numerically.

Implementation scheme, Case 1: $\Omega_m = 1$

Given the current-immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$ at instant *t*, then the new immobilized water fraction at instant $t + \Delta t$ can be computed using the recipe outlined later:

1. Compute the water flux $\vec{J}''_{\mathrm{w}}$ given the current-immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$. The water flux depends on the choice of the diffusion model.
2. Compute the change of the immobilized water fraction $\Delta\Phi_{\mathrm{w}}(\vec{x})$ given the following discretization of the PDE in Eq. 25:

$$\Delta\Phi_{\mathrm{w}}(\vec{x}) = (1 - \Phi_{\mathrm{w}}(\vec{x}))\left[\left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{1}{\rho_{\mathrm{s}}}\right]\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right)\Delta t. \tag{26}$$

3. Update the immobilized water fraction: $\Phi_{\mathrm{w}}(\vec{x}; t + \Delta t) = \Phi_{\mathrm{w}}(\vec{x}; t) + \Delta\Phi_{\mathrm{w}}(\vec{x}; t)$.
4. Update the mixture mass, the immobilized water mass, and the substrate mass using the new water fraction $\Phi_{\mathrm{w}}(\vec{x})$ and Eq. 8:

$$\begin{cases} m_{\mathrm{m}}(\vec{x}) = \rho_{\mathrm{m}}(\vec{x})V, \\ m_{\mathrm{w}}(\vec{x}) = \Phi_{\mathrm{w}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})V, \\ m_{\mathrm{s}}(\vec{x}) = (1 - \Phi_{\mathrm{w}}(\vec{x}))\rho_{\mathrm{m}}(\vec{x})V. \end{cases} \tag{27}$$

5. Redistribute moistured substrate mass from volume elements with $\Omega_{\mathrm{m}} = 1$ (no free water present) over neighboring elements with $\Omega_{\mathrm{m}} < 1$ (free water present).
6. Go to step (1).

Water uptake and diffusion of immobilized water, Case 2: $\Omega_m < 1$

This section treats the case of volume elements containing free water: $\Omega_{\mathrm{m}}(\vec{x}) < 1$; these voxels are located at the edge of the rice grain. In these voxels, free water is taken up and immobilized in the substrate network. The immobilized water will diffuse from the edge of the rice grain toward the interior of the rice grain. This diffusion process is governed by the WD. Our approach is to set the rate of change of the substrate $m_{\mathrm{s}}(\vec{x})$ to zero as long as the voxel contains free water $\Omega_{\mathrm{f}}(\vec{x}) > 0$; if the WD is not zero, free water from the voxel can be taken up by the substrate. Thus, we have the following condition:

$$\Omega_{\mathrm{m}}(\vec{x}) < 1(\Leftrightarrow \Omega_{\mathrm{f}}(\vec{x}) > 0) \Rightarrow \frac{\partial}{\partial t}m_{\mathrm{s}}(\vec{x}) = 0. \tag{28}$$

We start again with a water balance for a single voxel:

$$\frac{1}{V}\frac{\partial}{\partial t}m_{\mathrm{w}}(\vec{x}) = \frac{\partial}{\partial t}\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})\Omega_{\mathrm{m}}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \tag{29}$$

Expanding this differential equation yields:

$$\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})\frac{\partial}{\partial t}\Omega_{\mathrm{m}}(\vec{x}) + \Phi_{\mathrm{w}}(\vec{x})\Omega_{\mathrm{m}}(\vec{x})\frac{\partial}{\partial t}\rho_{\mathrm{m}}(\vec{x}) + \Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \tag{30}$$

Comparing this equation to the water balance of Eq. 19, we have one more term describing the rate of change of the moistured substrate volume fraction. We will again insert Eq. A5 in this water balance. Next, we have to derive an expression for the rate of change of the moistured substrate volume fraction $\frac{\partial}{\partial t}\Omega_{\mathrm{m}}(\vec{x})$. Inserting the definition of the moistured substrate volume (Eq. 3) in the definition of the moistured substrate volume fraction (Eq. 1) gives:

$$\Omega_{\mathrm{m}}(\vec{x}) = \frac{1}{V}\left(\frac{m_{\mathrm{s}}(\vec{x})}{\rho_{\mathrm{s}}} + \frac{m_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}}\right). \tag{31}$$

Taking derivatives with respect to time of both sides of the equation and recalling that $\frac{\partial}{\partial t}m_{\mathrm{s}}(\vec{x}) = 0$ in this case yields:

$$\frac{\partial}{\partial t}\Omega_{\mathrm{m}}(\vec{x}) = \frac{1}{\rho_{\mathrm{w}}}\left(\frac{1}{V}\frac{\partial}{\partial t}m_{\mathrm{w}}(\vec{x})\right). \tag{32}$$

The term between brackets at the right-hand side of this equation is the left-hand side of the water balance, thus:

$$\frac{\partial}{\partial t}\Omega_{\mathrm{m}}(\vec{x}) = \frac{1}{\rho_{\mathrm{w}}}\left(-\vec{\nabla}.\vec{J}''_{\mathrm{w}}\right). \tag{33}$$

Inserting Eqs. 33 and A5 in the water balance (Eq. 30) yields an expression in terms of the rate of change of the immobilized water fraction and the water flux:

$$\left[\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{m}}(\vec{x}) - \Phi_{\mathrm{w}}(\vec{x})\Omega_{\mathrm{m}}(\vec{x})\rho^2_{\mathrm{m}}(\vec{x})\left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\right]\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \left(1 - \frac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}\Phi_{\mathrm{w}}(\vec{x})\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right) \tag{34}$$

Using again Eq. 8, this can be rewritten and simplified into:

$$\frac{\Omega_{\mathrm{m}}(\vec{x})\rho^2_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}}}\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \left(1 - \frac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}\Phi_{\mathrm{w}}(\vec{x})\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \tag{35}$$

Multiplying the dry substrate density and the moistured mixture density by the moistured substrate volume fraction $V_{\mathrm{m}}(\vec{x})$ yields:

$$\frac{\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})}{\Phi_{\mathrm{s}}(\vec{x})}\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \left(1 - \frac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}\Phi_{\mathrm{w}}(\vec{x})\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \tag{36}$$

Finally, we obtain the following equation for the rate of change of the water fraction $\Phi_{\mathrm{w}}(\vec{x})$ for the case $\Omega_{\mathrm{m}}(\vec{x}) < 1$:

$$\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \frac{1 - \Phi_{\mathrm{w}}(\vec{x})}{\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})}\left(1 - \frac{\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}}\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \tag{37}$$

Comparing this equation to Eq. 24, we see an extra term, because the rate of change of the moistured substrate volume fraction is not zero in this case. Setting this rate of change equal to zero in Eq. 37 yields Eq. 24. The second factor on the right-hand side in Eq. 37 can be simplified using Eq. A3:

$$\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \frac{1-\Phi_{\mathrm{w}}(\vec{x})}{\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})}\left(\frac{\rho_{\mathrm{m}}(\vec{x})-\rho_{\mathrm{w}}}{\rho_{\mathrm{s}}-\rho_{\mathrm{w}}}\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \quad (38)$$

Because the mixture density $\rho_{\mathrm{m}}(\vec{x})$ is smaller than the dry substrate density ρ_{s}, the second factor of Eq. 38 is always smaller than unity. The ratio between this factor and the moistured substrate volume fraction $\Omega_{\mathrm{m}}(\vec{x})$ determines if the water uptake is faster or slower compared with the uptake in volume elements with $\Omega_{\mathrm{m}}(\vec{x}) = 1$. Equation 38 can be further simplified by eliminating $\rho_{\mathrm{m}}(\vec{x})$. Rewrite Eq. 38 as follows:

$$\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \frac{1-\Phi_{\mathrm{w}}(\vec{x})}{\Omega_{\mathrm{m}}(\vec{x})}\left(\frac{1-\frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})}}{\rho_{\mathrm{s}}-\rho_{\mathrm{w}}}\right)\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right), \quad (39)$$

and insert Eq. A4:

$$\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) = \frac{(1-\Phi_{\mathrm{w}}(\vec{x}))^2}{\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{s}}}\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right). \quad (40)$$

This final result describes the rate of change of the water fraction given the current water fraction and moistured substrate volume fraction. In the next section, we will discretize the PDEs of Eqs. 33 and 40 and present an iterative scheme for solving them numerically.

Implementation scheme, Case 2: $\Omega_m < 1$

Given the current-immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$, and the moistured substrate volume fraction $\Omega_{\mathrm{m}}(\vec{x}) < 1$ at instant *t,* then the water fraction and the moistured substrate volume fraction at instant $t + \Delta t$ can be computed by taking the following steps:

1. Compute the water flux $\vec{J}''_{\mathrm{w}}$ given the current-immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$. The water flux depends on the choice of the diffusion model.

2. Compute the change of the immobilized water fraction $\Delta\Phi_{\mathrm{w}}(\vec{x})$ given the following discretization of the PDE in Eq. 40:

$$\Delta\Phi_{\mathrm{w}}(\vec{x}) = \frac{(1-\Phi_{\mathrm{w}}(\vec{x}))^2}{\Omega_{\mathrm{m}}(\vec{x})\rho_{\mathrm{s}}}\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right)\Delta t. \quad (41)$$

3. Compute the change of the moistured substrate volume fraction $\Delta\Omega_{\mathrm{m}}(\vec{x})$ given the following discretization of Eq. 33:

$$\Delta\Omega_{\mathrm{m}}(\vec{x}) = \frac{1}{\rho_{\mathrm{w}}}\left(-\vec{\nabla}\cdot\vec{J}''_{\mathrm{w}}\right)\Delta t. \quad (42)$$

4. Update the immobilized water fraction: $\Phi_{\mathrm{w}}(\vec{x}; t+\Delta t) = \Phi_{\mathrm{w}}(\vec{x}; t) + \Delta\Phi_{\mathrm{w}}(\vec{x}; t)$.

5. Update the moistured substrate volume fraction: $\Omega_{\mathrm{m}}(\vec{x}; t+\Delta t) = \Omega_{\mathrm{m}}(\vec{x}; t) + \Delta\Omega_{\mathrm{m}}(\vec{x}; t)$.

6. Update the moistured mixture density $\rho_{\mathrm{m}}(\vec{x})$ according to Eq. 8 using the new immobilized water fraction $\Phi_{\mathrm{w}}(\vec{x})$.

7. Update the moistured substrate volume $V_{\mathrm{m}}(\vec{x})$ according to Eq. 1 using the new moistured substrate volume fraction $\Omega_{\mathrm{m}}(\vec{x})$.

8. Update the moistured mixture mass, and the immobilized water mass using the results from steps (4) to (6):

$$\begin{cases} m_{\mathrm{m}}(\vec{x}) = \rho_{\mathrm{m}}(\vec{x})\Omega_{\mathrm{m}}(\vec{x})V, \\ m_{\mathrm{w}}(\vec{x}) = \Phi_{\mathrm{w}}(\vec{x})\rho_{\mathrm{m}}(\vec{x})\Omega_{\mathrm{m}}(\vec{x})V \end{cases} \quad (43)$$

9. Go to step (1).

Note that there is no need for substrate redistribution, because $\frac{\partial}{\partial t}m_{\mathrm{s}}(\vec{x}) = 0$.

Swelling: substrate transport derived from microbalances between connected volume elements

In the previous sections, PDEs for the rate of change of the water fraction and the rate of change of the volume fraction of the moistured substrate have been derived. Water uptake in volume elements with $\Omega_{\mathrm{m}} = 1$ will result in a redistribution of moistured substrate, and consequently, swelling will take place. This is not incorporated in the PDEs. In this section, we will introduce microbalances between connected volume elements to describe the redistribution of the moistured substrate mass.

We will first discuss the 1D case; a cross-section through the symmetry axis of the rice grain is described by a sequence of *N* volume elements. At the start and at the end, the volume elements are in state 1 ($\Omega_{\mathrm{f}} = 1$; $\Omega_{\mathrm{m}} = 0$) and contain only free water. In the center, there are a number of volume elements in state 2 ($\Phi_{\mathrm{w}} = 0$; $\Omega_{\mathrm{m}} = 1$; $\Omega_{\mathrm{f}} = 0$) or 4 ($0 < \Phi_{\mathrm{w}} < \Phi_{\mathrm{w}}^{\max}$; $\Omega_{\mathrm{m}} = 1$; $\Omega_{\mathrm{f}} = 0$). Furthermore, there are two volume elements representing the edge of the rice grain; these two volume elements are in state 5 ($0 < \Phi_{\mathrm{w}} < \Phi_{\mathrm{w}}^{\max}$; $0 < \Omega_{\mathrm{m}}, \Omega_{\mathrm{f}} < 1$; $\Omega_{\mathrm{m}} + \Omega_{\mathrm{f}} = 1$). Let $\Delta m_{\mathrm{m}}[n]$ be the net surplus of moistured substrate in the volume elements in state 4 after a certain iteration. This quantity follows as

$$\Delta m_{\mathrm{m}}[n] = \frac{1}{2}\mu_{\mathrm{m}}[n-1] - \mu_{\mathrm{m}}[n] + \frac{1}{2}\mu_{\mathrm{m}}[n+1], \quad (44)$$

where $\frac{1}{2}\mu_{\mathrm{m}}[n-1]$ and $\frac{1}{2}\mu_{\mathrm{m}}[n+1]$ represent half of the moistured mass transferred from volume elements $n-1$ and $n+1$, respectively, into the volume element *n,* and $\mu_{\mathrm{m}}[n]$ represents the moistured mass transferred from volume element *n* into volume elements $n-1$ and $n+1$. Similarly, the other half of the moistured mass from volume element $n-1$ is transferred into volume element $n-2$. Same reasoning holds for volume element $n+1$. For the other volume elements, we can write down similar microbalances in terms of the transferred mass $\mu_{\mathrm{m}}[n]$, $1 \le n \le N$. This leads to a set of equations, which can be written in matrix form. The inverse of the matrix represents the substrate transport $\mu[n]$. We will illustrate this idea with the following three examples.

Example 1. Consider the 1D situation as illustrated in Table 1, where $\Delta m_{\mathrm{m}}[n]$ refers to the surplus of moistured substrate that must be redistributed as a result of water uptake and $\mu_{\mathrm{m}}[n]$ to the transported moistured substrate. If $\Omega_{\mathrm{m}}[n] < 1$, then $\Delta m_{\mathrm{m}}[n] = 0$ as discussed earlier. The equations for $n = 3, 4, 5$ can be written as follows:

$$\begin{pmatrix} \Delta m_{\mathrm{m}}[3] \\ \Delta m_{\mathrm{m}}[4] \\ \Delta m_{\mathrm{m}}[5] \end{pmatrix} = \begin{pmatrix} -1 & \frac{1}{2} & 0 \\ \frac{1}{2} & -1 & \frac{1}{2} \\ 0 & \frac{1}{2} & -1 \end{pmatrix} \begin{pmatrix} \mu_{\mathrm{m}}[3] \\ \mu_{\mathrm{m}}[4] \\ \mu_{\mathrm{m}}[5] \end{pmatrix}. \quad (45)$$

Table 1. One-Dimensional Example of Moistured Substrate Transport in Volume Elements with $\Omega_m = 1$

n	$\Omega_m\ [n]$	$\Delta m_m\ [n]$	$\mu_m\ [n]$
1	0	0	0
2	<1	0	$\frac{1}{2}\mu_m[3]$
3	1	$\Delta m_m[3] = -\mu_m[3] + \frac{1}{2}\mu_m[4]$	
4	1	$\Delta m_m[4] = \frac{1}{2}\mu_m[3] - \mu_m[4] + \frac{1}{2}\mu_m[5]$	
5	1	$\Delta m_m[5] = \frac{1}{2}\mu_m[4] - \mu_m[5]$	
6	<1	0	$\frac{1}{2}\mu_m[5]$
7	0	0	0

Columns represent index n, $\Omega_m\ [n]$, the measure for surplus of moistured substrate mass $\Delta m_m\ [n]$ to be redistributed, and moistured mixture mass to be transported $\mu_m[n]$. If last two columns are merged, then these two quantities are equal, otherwise moistured substrate mass is added to volume element. For all volume elements $\Phi_w[n] < \Phi_w^{max}$.

The inverse relation follows as

$$\begin{pmatrix} \mu_m[3] \\ \mu_m[4] \\ \mu_m[5] \end{pmatrix} = \begin{pmatrix} -\frac{3}{2} & -1 & -\frac{1}{2} \\ -1 & -2 & -1 \\ -\frac{1}{2} & -1 & -\frac{3}{2} \end{pmatrix} \begin{pmatrix} \Delta m_m[3] \\ \Delta m_m[4] \\ \Delta m_m[5] \end{pmatrix}. \tag{46}$$

This result implies that the moistured mass to be transferred from volume element with $n = 3$ to the volume element with $n = 2$, which is $\frac{1}{2}\mu_m[3]$ (the volume element with $n = 4$ receives the other half of $\mu_m[3]$), is given by

$$\mu_m[3] = \left(-\frac{3}{2}\Delta m_m[3] - \Delta m_m[4] - \frac{1}{2}\Delta m_m[5]\right) \tag{47}$$

and has contributions of all moistured mass surpluses in the rice grain; the further away from the volume element under consideration, the smaller the contribution. This is in agreement with the intuitive notion that swelling is local.

Example 2. We will analyze the situation where there is a pore in the 1D rice grain; for simplicity, this pore is represented by a single volume element in state 5 ($0 < \Phi_w < \Phi_w^{max}$; $0 < \Omega_m, \Omega_f < 1$; $\Omega_m + \Omega_f = 1$) in the center of the rice grain. This situation is illustrated in Table 2. This situation is readily evaluated: $\mu_m[3] = -\Delta m_m[3]$, $\mu_m[5] = -\Delta m_m[5]$, such that the rice grain is not only swelling at the outer edge but also the pore in the rice grain is shrinking.

Table 2. One-Dimensional Example of Moistured Substrate Transport in Volume Elements with $\Omega_m = 1$

n	$\Omega_m[n]$	$\Delta m_m[n]$	$\mu_m[n]$
1	0	0	0
2	<1	0	$\frac{1}{2}\mu_m[3]$
3	1	$\Delta m_m[3] = -\mu_m[3]$	
4	<1	0	$\frac{1}{2}\mu_m[3] + \frac{1}{2}\mu_m[5]$
5	1	$\Delta m_m[5] = -\mu_m[5]$	
6	<1	0	$\frac{1}{2}\mu_m[5]$
7	0	0	0

In the center, a pore is represented by $\Omega_m < 1$. See caption Table 1. For all volume elements $\Phi_w[n] < \Phi_w^{max}$.

Example 3. We will treat the case that some volume elements inside the rice grain with $\Omega_m = 1$ have reached the maximum water fraction ($\Phi_w = \Phi_w^{max}$). At the maximum water fraction no water can be taken up anymore by the wet substrate, and no substrate can be forced out. This situation is shown in Table 3. This example is the same as the first example with $\Delta m_m[4] = \Delta m_m[5] = 0$, such that $\mu_m[3] = -\frac{3}{2}\Delta m_m[3]$, $\mu_m[4] = -\Delta m_m[3]$, and $\mu_m[5] = -\frac{1}{2}\Delta m_m[3]$. This example shows that $\Delta m_m[3] > \Delta m_m[5]$ or that swelling is local and has little influence on volume elements further away.

This approach can easily be extended to two or three dimensions. In the 2D case, the four side-connected neighbors have weight $\frac{1}{4}$, whereas the four point-connected neighbors have weight 0. In the 3D case, the six face-connected neighbors have weight $\frac{1}{6}$, whereas the 12 side-connected neighbors and the eight point-connected neighbors have weight 0. This suggests that moistured substrate transport only occurs in the directions of the axes of the reference frame and not diagonally. This approximation is valid, as long as the volume corresponding to the moistured substrate mass to be transported is much smaller than the volume of a volume element.

The computation of the substrate transport in a 2D or 3D substrate becomes computationally intensive with a growing number of volume elements with $\Omega_m(\vec{x}) = 1$. The limiting factors are the computation of all nonzero elements of the matrix and the computation of the resulting mass transport in the substrate given all $\mu_m(\vec{x})$. We will present two methods to speed up the computation of the resulting mass transport.

Method 1. A zero-order approximation is obtained as follows. Let $R = \{(\vec{x}) = [m, n, k] | \Omega_m(\vec{x}) = 1\}$. Compute the total moistured substrate mass M_m that needs to be redistributed:

$$M_m = \sum_R \Delta m_m(\vec{x}). \tag{48}$$

A dilation[16] of the set R identifies the set R' of grid elements $\vec{x}'$ that will receive the moistured substrate mass to be redistributed. The zero-order approximation is that the total

Table 3. One-Dimensional Example of Moistured Substrate Transport in Volume elements with $\Omega_m = 1$

n	$\Omega_m[n]$	Φ_w	$\Delta m_m[n]$	$\mu_m[n]$
1	0	0	0	0
2	<1	$<\Phi_w^{max}$	0	$\frac{1}{2}\mu_m[3]$
3	1	$<\Phi_w^{max}$	$\Delta m_m[3] = -\mu_m[3] + \frac{1}{2}\mu_m[4]$	
4	1	$=_w^{max}$	$0 = \frac{1}{2}\mu_m[3] - \mu_m[4] + \frac{1}{2}\mu_m[5]$	
5	1	$=_w^{max}$	$0 = \frac{1}{2}\mu_m[4] - \mu_m[5]$	
6	<1	$<_w^{max}$	0	$\frac{1}{2}\mu_m[5]$
7	0	0	0	0

Columns represent index n, $\Omega_m[n]$, $\Phi_w[n]$ measure for surplus of moistured substrate mass $\Delta m_m[n]$ to be redistributed, and moistured mixture mass to be transported $\mu_m[n]$. If last two columns are merged, then these two quantities are equal, otherwise moistured substrate mass is added to volume element.

surplus of the moistured substrate is redistributed equally over all grid elements at the edge of the set R, i.e., R':

$$\mu_\mathrm{m}(\vec{x}) = \frac{1}{N'} M_\mathrm{m}, \tag{49}$$

with N' the number of elements in R'. This approximation does not take into account that grid elements further away from elements with a large change of substrate mass receive less substrate mass than grid elements closer to these grid elements.

Method 2. A first-order approximation is the following. Let R' represent the edge of R obtained by dilation of R. All elements of the set R' will receive some moistured substrate mass. Let $\vec{x} \in R$ and $\vec{x}\,' \in R'$, such that $D\vec{x}, \vec{x}$ denotes the distance between these two elements, then

$$w(\vec{x}', \vec{x}) = \sum_R \frac{\Delta m_\mathrm{m}(\vec{x})}{D(\vec{x}', \vec{x})^2} \tag{50}$$

defines a weight between these two elements that is proportional to the moistured substrate mass to be redistributed and inversely proportional to the squared distance $D\vec{x}, \vec{x}$. We have taken the squared distance, because in a 3D volume the mass must be redistributed over a surface. The amount of moistured substrate mass that the volume element at $\vec{x}$ receives follows as

$$\mu_\mathrm{m}(\vec{x}) = \frac{w(\vec{x}', \vec{x})}{\sum_{R'} w(\vec{x}', \vec{x})} M_\mathrm{m}. \tag{51}$$

Results

In this section, we will show various simulation results; the simulations in one dimension are limited to a solid "rice grain", i.e., a 1D substrate without any pores. The main goal of these simulation results is to show the influence of the various WD functions from Figure 4 on the water uptake and the swelling of the substrate. Furthermore, we applied the full 3D simulation to a 3D porous rice grain as acquired by micro-CT. These simulations will show that the pores will shrink as a consequence of the swelling of the substrate. These simulations in three dimensions will also confirm our statement that our model is applicable to any random 3D geometry.

Simulation results in one dimension

We used the following quantities for the 1D simulations:

- substrate density: $\rho_\mathrm{s} = 1564$ kg/m^3,[10]
- water density: $\rho_\mathrm{w} = 1000$ kg/m^3,
- initial and final moisture content: $m_\mathrm{ls,init} = 0.7$ kg water/kg substrate, $m_\mathrm{ls,final} = 1.7$ kg water/kg substrate,
- the grid contained 100 elements with a width $h = 80$ μm; the initial substrate was 40 elements long ($\Omega_\mathrm{m} = 1$) covering a length of 3.2 mm,
- the diffusion constant $D = 2.32 \times 10^{-6} \exp\left(\frac{2070}{\theta+273}\right)$, with the temperature $\theta = 100°\mathrm{C}$,[10]
- The timestep $\Delta t = 50$ ms, the simulations run over ~30,000 iterations covering a total time interval of 25 min.

The most important quantities of interest are the water fraction $\Phi_\mathrm{w}(\vec{x})$ and the volume fraction occupied by the moistured substrate $\Omega_\mathrm{m}(\vec{x})$. These two quantities allow for calculation of, e.g., $m_\mathrm{m}(\vec{x})$, $m_\mathrm{s}(\vec{x})$, $m_\mathrm{w}(\vec{x})$, $m_\mathrm{ls}(\vec{x})$, and $\mathrm{WD}(\vec{x})$. Figure 5 shows the various quantities of interest. Every column in this graph corresponds to a different WD function; the first column shows the spatiotemporal behavior of the various quantities for a WD function based on Fickian diffusion. The second column shows the results for a WD function based on the TEG, the third column is related to a high WD function, and the last column to a WD function that is initially based on Fickian diffusion and continues with a high WD.

- Fickian diffusion: WD function can be considered as a linearized version of TEG WD function. The distributions of $m_\mathrm{s}(\vec{x})$ and $m_\mathrm{w}(\vec{x})$ are smooth; there is not a distinct diffusion front. Distribution of $m_\mathrm{s}(\vec{x})$ has a Gaussian-like profile, which corresponds to the solution of the linear diffusion equation. Swelling is the fastest in the initial stage of the simulation. The WD function is a smooth function with a maximum in the center, which rapidly goes down.
- TEG WD function: This WD function has a smooth character and is comparable to the WD function for Fickian diffusion; again, there is no distinct diffusion front. The swelling of the rice grain is the fastest in the early stage of the simulation.
- High WD: This WD function remains constantly high for a large range of moisture contents. A gradient in WD occurs only at high moisture content. This induces the sharp diffusion front as can be seen in the distributions of $m_\mathrm{s}(\vec{x})$, $m_\mathrm{w}(\vec{x})$, and $\Phi_\mathrm{w}(\vec{x})$. Swelling is the fastest in the beginning of the simulation. WD in the center of the rice grain is constantly high for a long time, until the diffusion front reaches this area.
- Initially Fickian diffusion, later high WD: This WD function implies initially Fickian diffusion, albeit at a faster rate. This explains the Gaussian-like part of the profile of the diffusion front, which is followed by the steep diffusion front of the second part of the WD function. As a consequence, the WD function follows first the WD function of Fickian diffusion; later it follows the high WD function.

The shape of the WD function clearly determines the shape of the diffusion fronts. In the case of the high WD function, see Figure 4, the WD remains constant over a large range of moisture content levels. This implies that there is no gradient in the WD, even if the moisture content at one position is high, let us say $m_\mathrm{ls} = 1.4$ and at the next position it is low, let us say $m_\mathrm{ls} = 0.7$. The absence of a gradient in WD prevents a water flux to positions with a lower moisture content. Consequently, it takes a long time before the immobilized water in the substrate reaches the center of the rice grain and the moisture content level in the center starts to rise. In the case of Fickian diffusion, a difference in moisture content always implies a gradient in WD, resulting in a water flux from low WD or high moisture content to high WD or low moisture content.

Simulation results in three dimensions

For our simulations in three dimensions, we used a very high resolution reconstructed 3D X-ray CT image of a particular rice grain consisting of a network of thin walls and pores of different sizes as shown in Figure 2b. This image was binned to an image with dimensions 67 × 67 × 108 voxels. Each voxel was given a volume $V = h^3$ with $h = 80$

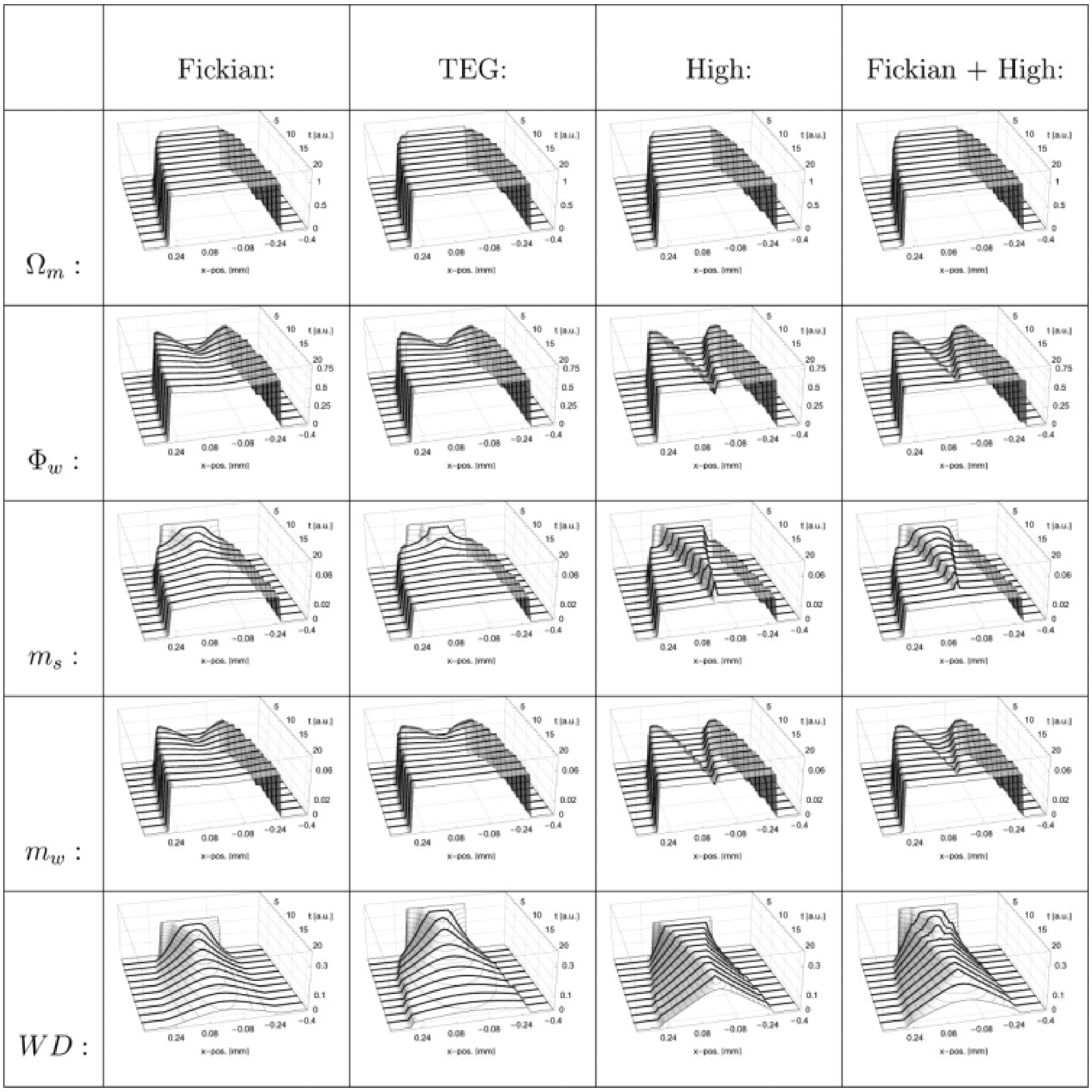

Figure 5. This table of figures shows the water uptake in a one-dimensional substrate under influence of the various water demand functions.

First column is based on Fickian diffusion, second column is based on the terminal extent of gelatinization, third column on a high water demand, and fourth column on water demand function that is based initially on Fickian diffusion and later becomes high water demand. The first row shows the spatiotemporal behavior of Ω_m, the second row of Φ_w, the third and fourth row of m_s and m_w, respectively, the last row the water demand.

μm. A simple threshold on the dry substrate mass was used to separate the image into two initial phases, i.e., pure dry substrate ($\Omega_m = 1$) and pure free water ($\Omega_m = 0$). This assumes that the porosity of the rice grain is so large that every pore can be reached and be filled with free water, when immersing this rice grain in boiling water. This assumption seems to be valid for the open porous rice grain such as depicted in Figure 2b. We used the same values for the physical quantities of interest as for the 1D simulations. Figure 6 shows two series of seven longitudinal cross-sections through the porous rice grain; the gray levels are a measure for the substrate's moisture content; black refers to a moisture content of zero, i.e., in these voxels, there is only free water present. White refers to the maximum moisture content $m_{ls,final} = 1.7$ kg water/kg substrate. The initial moisture content in the bottom series is $m_{ls,init} = 0.7$ kg water/kg substrate. The WD function used in this simulation is the high WD function, which explains the sharp gray–white transitions. As can be seen, water is taken up along the entire edge of the rice grain. The swelling of the rice grain is not so clearly visible in this simulation; the swelling of the rice grain is the fastest in the initial stage of the simulation. The

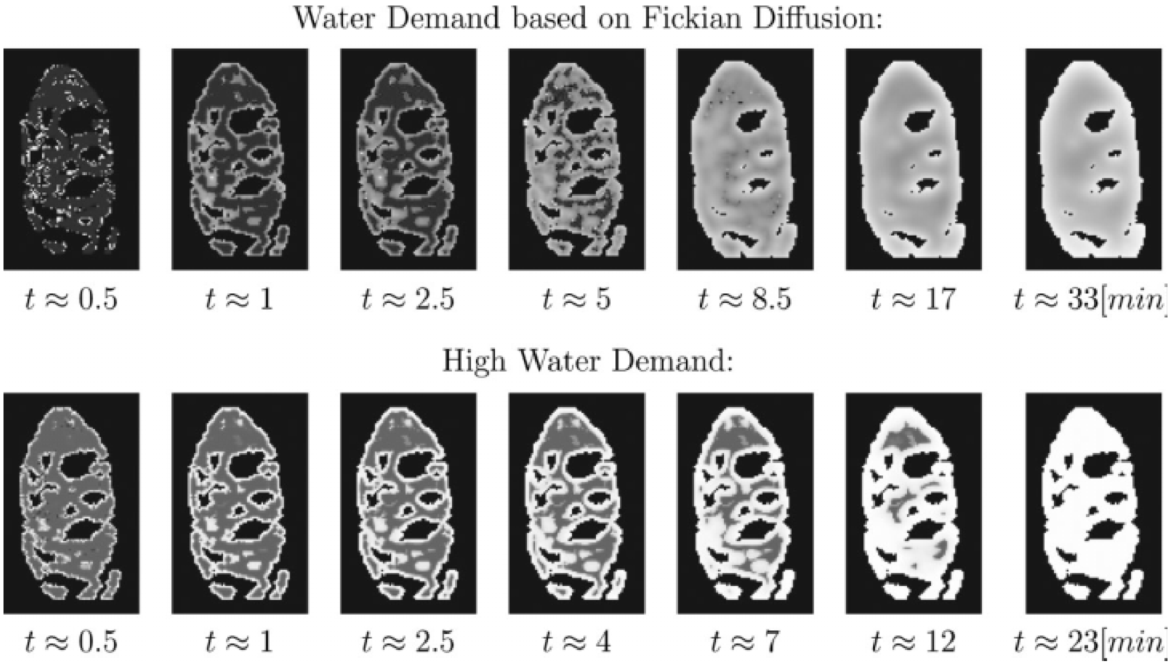

Figure 6. Longitudinal cross-sections through the porous rice grain showing the moisture content at seven different instants in time.

Black refers to free water. In top series, simulation is based on high water demand function, leading to steep diffusion fronts; white refers to $m_{\mathrm{ls}}^{\max}$; $m_{\mathrm{ls}}^{\min} = 0.3$. In bottom series, simulation is based on Fickian diffusion; white refers to $m_{\mathrm{ls}}^{\max}$; $m_{\mathrm{ls}}^{\min} = 0.7$.

initial moisture content in the top series was set to $m_{\mathrm{ls,init}} = 0.3$ kg water/kg substrate (the first cross-section in the top series has the same structure as the first cross-section in the bottom series, but the gray level, i.e., moisture content is much lower). This implies that much more substrate is present, which can take up more water. This leads to a more significant swelling of the rice grain; at the end of the simulation, practically all pores have disappeared and the rice grain has become a solid rice grain, except for some very large pores. The WD function used in this simulation is the one related to Fickian diffusion; this explains the smooth diffusion fronts. Inserting the definition of the moisture content (Eq. 5) in the definition of the volume occupied by the moistured substrate (Eq. 3) yields $V = (\frac{1}{\rho_{\mathrm{s}}} + \frac{m_{\mathrm{ls}}}{\rho_{\mathrm{w}}})\, M_{\mathrm{s}}$, with V the total volume of the moistured substrate and M_{s} the total dry substrate mass. The relative increase in volume as a result of water uptake follows then as

$$\frac{V_{\mathrm{final}}}{V_{\mathrm{init}}} = \frac{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls,final}}}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls,init}}}. \tag{52}$$

For $m_{\mathrm{ls,init}} = 0.7$ and $m_{\mathrm{ls,final}} = 1.7$ this ratio is $\sim$1.7 and for $m_{\mathrm{ls,init}} = 0.3$ and $m_{\mathrm{ls,final}} = 1.7$ this ratio is $\sim$2.5; the initial volume of the rice grain was on the order of 60×10^3 voxels, the final volumes were on the order of 106×10^3 and 133×10^3 voxels, respectively.

Conclusions and Discussion

This article presents a mathematical model for water uptake in rice grains. The model considers incompressible compounds, such that mass and volume are conserved. The driving force of water uptake is the WD; a WD function that is linearly decreasing as a function of moisture content leads to Fickian diffusion of the immobilized water in the starch network; the smooth diffusion front corresponds to the solution of the linear diffusion equation, i.e., Gaussian blurring. A constantly high WD function leads to a steep diffusion front. The model is based on a constant volume grid, such that swelling of the substrate as a result of water uptake implies transport of moistured substrate from one voxel to its neighboring voxels. The most important quantities in this model are the volume occupied by the moistured substrate $\Omega_{\mathrm{m}}(\vec{x})$ and the water fraction $\Phi_{\mathrm{w}}(\vec{x})$, because they allow for computation of all quantities of interest. The model discriminates between voxels at the edge ($\Omega_{\mathrm{m}} < 1$) of the rice grain and voxels in the interior of the rice grain ($\Omega_{\mathrm{m}} = 1$). For voxels at the edge of the rice grain, two PDEs were derived for the rate of change of the occupied moistured substrate volume $\frac{\partial \Omega_{\mathrm{m}}(\vec{x})}{\partial t}$ and for the rate of change of the water fraction $\frac{\partial \Phi_{\mathrm{w}}(\vec{x})}{\partial t}$. For voxels in the interior of the rice grain, $\frac{\partial \Omega_m(\vec{x})}{\partial x} = 0$ and only a PDE for the rate of change of the water fraction was derived. These PDEs do not describe the swelling of the substrate as a result of water uptake. The swelling, i.e., the transfer of moistured substrate from one voxel to its neighboring voxels is described by mass-balances between the neighboring voxels. The model is implemented using discretizations of the PDEs; the implementation schemes take the redistribution of moistured substrate into account as well. An important advantage of this model over models where the rice grain is parameterized is that our model allows for simulations of water uptake in any possible geometry; we have taken binned X-ray micro-CT images as input for our simulations.

Our model contains a number of free parameters, e.g., the initial and final moisture content, the type of diffusion, and the geometry of the substrate. As a result, there are many parameters to tune in this relatively simple diffusion model. Our model is simple in a sense that it assumes that (1) the rate of water uptake is governed by a static WD function, (2) the driving force of water uptake is a gradient in the water concentration, (3) water uptake, i.e., gelatinization is instantaneous, (4) substrate properties related to water uptake do not change, (5) the network of interconnected substrate walls is not fractal, and (6) the imbibition of the kernels via connected pores is instantaneous.

From the experimentally acquired image sequences of cooking rice kernels, quantitative water ingress profiles are derived[1] as shown in the graphs of Figure 1. These ingress profiles can be used to classify water uptake in a qualitative manner. This classification will be described elsewhere.[2] The following is a comparison between our qualitative classification and our simulation model.

- Some types of rice reveal a relatively slow increase of water content and steep diffusion fronts moving inward as shown in the top series of images in Figure 1. This could imply that the diffusion process is governed initially by Fickian diffusion and later by high WD-driven diffusion. Our 1D simulation based on this WD function is in agreement with this observation.
- Other preprocessing techniques amount to anisotropic diffusion fronts, which can be attributed to pores too small to generate an open structure. These types of rice grains cannot be described in a realistic manner by our model; the pores will not be filled with free water when immersed into boiling water, but air will remain present.
- Other types of rice kernels show Gaussian-like diffusion fronts, indicative for Fickian diffusion. Our 1D simulation shows these Gaussian-like diffusion fronts as well.
- Rice grains with a very open porous structure facilitate penetration of water in the kernel, before actually being taken up by the starch. This amounts to a uniform increase of water content throughout the entire rice grain as shown in the bottom series of images in Figure 1. Water uptake in these types of rice grains is completely determined by the porous structure of the rice grain. Our 3D simulations show this as well; water is taken up along the entire edge of the rice grain. Integrating the water uptake over all polar angles amounts to an approximately uniform water uptake as a function of the radial position in an axial cross-section. The walls in the network of interconnected walls are much thinner than as suggested in our 3D simulations. Furthermore, the scale at which this network of interconnected walls is present is also below the scale of our simulations.
- The underlying WD function can be estimated from methods that assess the mesostructural order of starch, i.e., crystallinity and gelatinization degree, such as DSC and XRD. The acquired MRI data, however, can be compared with our 3D simulations of water uptake under the influence of Fickian diffusion and a high WD function.

We conclude that our simulations are in agreement with MRI observations made during cooking, DSC measurements, and XRD experiments. We expect that this modeling approach can be used to understand the cooking behavior of rice kernels that underwent a broad range of other preprocessing alternatives as well.

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Appendix A: Relations Between Mixture Density and Water Fraction

- The reciprocal of the mixture density $\frac{1}{\rho_m(\vec{x})}$ is related to the water fraction $(\vec{x})$ as follows:

$$\frac{1}{\rho_m(\vec{x})} = \left(\frac{1}{\rho_w} - \frac{1}{\rho_s}\right)\Phi_w(\vec{x}) + \frac{1}{\rho_s}. \tag{A1}$$

Proof:

$$\begin{aligned}\frac{1}{\rho_{\mathrm{m}}(\vec{x})} &= \frac{V_{\mathrm{m}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})} = \frac{v_{\mathrm{s}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})} + \frac{v_{\mathrm{w}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})}\\ &= \frac{v_{\mathrm{s}}(\vec{x})}{m_{\mathrm{s}}(\vec{x})}\frac{m_{\mathrm{s}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})} + \frac{v_{\mathrm{w}}(\vec{x})}{m_{\mathrm{w}}(\vec{x})}\frac{m_{\mathrm{w}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})}\\ &= \frac{\Phi_{\mathrm{s}}(\vec{x})}{\rho_{\mathrm{s}}} + \frac{\Phi_{w}(\vec{x})}{\rho_{\mathrm{w}}} = \frac{1-\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{s}}} + \frac{\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}}\\ &= \left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{1}{\rho_{\mathrm{s}}}\end{aligned}$$

- **Corollary**.

$$\frac{\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}} = \frac{\rho_{\mathrm{s}} - \rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}} \tag{A2}$$

Proof:

$$\begin{aligned}\frac{1}{\rho_{\mathrm{m}}(\vec{x})} &= \left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{1}{\rho_{\mathrm{s}}}\\ \rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})\left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right) &= \frac{\rho_{\mathrm{s}} - \rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}}}\\ \rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x}) &= \frac{\rho_{\mathrm{s}} - \rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}}}\left(\frac{\rho_{\mathrm{s}}\rho_{\mathrm{w}}}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}}\right)\\ \rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x}) &= \rho_{\mathrm{w}}\frac{\rho_{\mathrm{s}} - \rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}}\\ \frac{\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}} &= \frac{\rho_{\mathrm{s}} - \rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}}\end{aligned}$$

From this corollary follows:

$$1 - \frac{\rho_{\mathrm{m}}(\vec{x})\Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{w}}} = 1 - \frac{\rho_{\mathrm{s}}\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}} = \frac{\rho_{\mathrm{m}}(\vec{x}) - \rho_{\mathrm{w}}}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}} \tag{A3}$$

- **Corollary**.

$$\frac{1 - \dfrac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})}}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}} = \frac{1 - \Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{s}}}. \tag{A4}$$

From Eq. A1 follows that:

$$\begin{aligned}\frac{1}{\rho_{\mathrm{m}}(\vec{x})} &= \left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{1}{\rho_{\mathrm{s}}}\\ \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})} &= \left(\frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{w}}} - \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\\ \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})} &= \left(\frac{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\\ \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})} &= \frac{\rho_{\mathrm{s}}\Phi_{\mathrm{w}}(\vec{x}) - \rho_{\mathrm{w}}\Phi_{\mathrm{w}}(\vec{x}) + \rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\\ 1 - \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})} &= \frac{\rho_{\mathrm{s}} - \rho_{\mathrm{s}}\Phi_{\mathrm{w}}(\vec{x}) + \rho_{\mathrm{w}}\Phi_{\mathrm{w}}(\vec{x}) - \rho_{\mathrm{w}}}{\rho_{\mathrm{s}}}\\ 1 - \frac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})} &= \frac{(\rho_{\mathrm{s}} - \rho_{\mathrm{w}})(1 - \Phi_{\mathrm{w}}(\vec{x}))}{\rho_{\mathrm{s}}}\\ \frac{1 - \dfrac{\rho_{\mathrm{w}}}{\rho_{\mathrm{m}}(\vec{x})}}{\rho_{\mathrm{s}} - \rho_{\mathrm{w}}} &= \frac{1 - \Phi_{\mathrm{w}}(\vec{x})}{\rho_{\mathrm{s}}}\end{aligned}$$

- Given Eq. A1, the rate of change of the of the mixture density $\frac{\partial}{\partial t}\rho_{\mathrm{m}}(\vec{x})$ is related to the rate of change of the water fraction $\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x})$ as follows:

$$\frac{\partial}{\partial t}\rho_{\mathrm{m}}(\vec{x}) = -\rho_{\mathrm{m}}^{2}(\vec{x})\left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\frac{\partial}{\partial t}\Phi_{\mathrm{w}}(\vec{x}) \tag{A5}$$

Proof:
Taking derivatives with respect to time of Eq. A1 yields:

$$-\frac{1}{\rho_{\mathrm{m}}^{2}(\vec{x})}\frac{\partial}{\partial t}\rho_{\mathrm{m}}(\vec{x}) = \left(\frac{1}{\rho_{\mathrm{w}}} - \frac{1}{\rho_{\mathrm{s}}}\right)\frac{\partial}{\partial t}\Phi_{w}(\vec{x}).$$

Multiplying this result with $-\rho_{\mathrm{m}}^{2}(\vec{x})$ amounts to the given relation.

- The mixture density $\rho_{\mathrm{m}}(\vec{x})$ is related to the moisture content as follows:

$$\rho_{\mathrm{m}}(\vec{x}) = \rho_{\mathrm{s}}\rho_{\mathrm{w}}\frac{1 + m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}}m_{\mathrm{ls}}(\vec{x})}. \tag{A6}$$

Proof:
Taking the reciprocal of Eq. A1 gives

$$\rho_{\mathrm{m}}(\vec{x}) = \frac{1}{\left(\dfrac{1}{\rho_{\mathrm{w}}} - \dfrac{1}{\rho_{\mathrm{s}}}\right)\Phi_{\mathrm{w}}(\vec{x}) + \dfrac{1}{\rho_{\mathrm{s}}}}. \tag{A7}$$

Inserting Eq. 6 and simplifying amounts to:

$$\begin{aligned}\rho_{\mathrm{m}}(\vec{x}) &= \frac{1}{\left(\dfrac{1}{\rho_{\mathrm{w}}} - \dfrac{1}{\rho_{\mathrm{s}}}\right)\left(\dfrac{m_{\mathrm{ls}}(\vec{x})}{1 + m_{\mathrm{ls}}(\vec{x})}\right) + \dfrac{1}{\rho_{\mathrm{s}}}}\\ &= \frac{1 + m_{\mathrm{ls}}(\vec{x})}{\left(\dfrac{1}{\rho_{\mathrm{w}}} - \dfrac{1}{\rho_{\mathrm{s}}}\right)m_{\mathrm{ls}}(\vec{x}) + \dfrac{1 + m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{s}}}}\\ &= \frac{1 + m_{ls}(\vec{x})}{\dfrac{m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}}} - \dfrac{m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{s}}} + \dfrac{1}{\rho_{\mathrm{s}}} + \dfrac{m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{s}}}}\\ &= \frac{1 + m_{\mathrm{ls}}(\vec{x})}{\dfrac{m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}}} + \dfrac{1}{\rho_{\mathrm{s}}}}\\ &= \frac{1 + m_{\mathrm{ls}}(\vec{x})}{\dfrac{\rho_{\mathrm{w}} + \rho_{\mathrm{s}}m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{s}}\rho_{\mathrm{w}}}}\\ \rho_{\mathrm{m}}(\vec{x}) &= \rho_{\mathrm{s}}\rho_{\mathrm{w}}\frac{1 + m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}}m_{\mathrm{ls}}(\vec{x})}\end{aligned} \tag{A8}$$

Appendix B: Modeling Ordinary Diffusion Using Water Demand

Equating Eqs. 10 and 11 yields

$$\vec{\nabla}\mathrm{W}D(m_{\mathrm{ls}}(\vec{x})) = -\frac{1}{m_{\mathrm{s}}(\vec{x})}\vec{\nabla}m_{\mathrm{w}}(\vec{x}). \tag{B1}$$

The gradient of the WD can be expressed in terms of the gradient of the immobilized water mass:

$$\vec{\nabla}\mathrm{WD}\left(m_{\mathrm{ls}}(\vec{x})\right) = \left(\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})}\right)\left(\frac{\partial m_{\mathrm{ls}}(\vec{x})}{\partial \Phi_{\mathrm{w}}(\vec{x})}\right)\left(\frac{\partial \Phi_{\mathrm{w}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})}\right)\vec{\nabla} m_{\mathrm{w}}(\vec{x}). \tag{B2}$$

From Eq. 7 follows

$$\frac{\partial m_{\mathrm{ls}}(\vec{x})}{\partial \Phi_{\mathrm{w}}(\vec{x})} = \frac{1}{\left(1-\Phi_{\mathrm{w}}(\vec{x})\right)^2}, \tag{B3}$$

and from Eq. 6 follows

$$\frac{\partial \Phi_{\mathrm{w}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})} = \frac{m_{\mathrm{s}}(\vec{x}) - m_{\mathrm{w}}(\vec{x})\dfrac{\partial m_{\mathrm{s}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})}}{\left(m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})\right)^2}. \tag{B4}$$

First, for volume elements with $\Omega_{\mathrm{m}}(\vec{x}) < 1$, $m_{\mathrm{s}}(\vec{x})$ is constant and the above equation reduces to

$$\frac{\partial \Phi_{\mathrm{w}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})} = \frac{m_{\mathrm{s}}(\vec{x})}{\left(m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})\right)^2} = \frac{1-\Phi_{\mathrm{w}}(\vec{x})}{m_{\mathrm{m}}(\vec{x})}. \tag{B5}$$

Equating Eqs. B1 and B2 and inserting the previously found relations yield

$$\left(\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})}\right)\left(\frac{1}{\left(1-\Phi_{\mathrm{w}}(\vec{x})\right)^2}\right)\left(\frac{1-\Phi_{w}(\vec{x})}{m_{\mathrm{m}}(\vec{x})}\right) = -\frac{1}{m_{\mathrm{s}}(\vec{x})}. \tag{B6}$$

Simplifying gives

$$\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})} = -1 \Rightarrow \mathrm{WD}(\vec{x}) = \mathrm{WD}_0 - m_{\mathrm{ls}}(\vec{x}). \tag{B7}$$

Second, for volume elements with $\Omega_{\mathrm{m}}(\vec{x}) = 1$, $m_{\mathrm{s}}(\vec{x})$ is not constant; its dependency on $m_{\mathrm{w}}(\vec{x})$ is embedded in Eq. 17 with $m_{\mathrm{m}}(\vec{x}) = m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})$. Rewriting this equation amounts to:

$$\frac{\partial m_{\mathrm{s}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})} = -\left(1 + \frac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}\right). \tag{B8}$$

Inserting this in Eq. B4 gives

$$\begin{aligned}\frac{\partial \Phi_{\mathrm{w}}(\vec{x})}{\partial m_{\mathrm{w}}(\vec{x})} &= \frac{m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})\left(1 + \dfrac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}\right)}{\left(m_{\mathrm{s}}(\vec{x}) + m_{\mathrm{w}}(\vec{x})\right)^2}\\ &= \ldots = \frac{1 + \Phi_{\mathrm{w}}(\vec{x})\dfrac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}}{m_{\mathrm{m}}(\vec{x})}.\end{aligned} \tag{B9}$$

Equating again Eqs. B1 and B2 and inserting the previously found relations amount to

$$\left(\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})}\right)\left(\frac{1}{\left(1-\Phi_{\mathrm{w}}(\vec{x})\right)^2}\right)\left(\frac{1 + \Phi_{w}(\vec{x})\dfrac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}}{m_{\mathrm{m}}(\vec{x})}\right) = -\frac{1}{m_{\mathrm{s}}(\vec{x})}. \tag{B10}$$

Simplifying this result gives

$$\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})} = -\frac{1-\Phi_{\mathrm{w}}(\vec{x})}{1 + \Phi_{\mathrm{w}}(\vec{x})\dfrac{\rho_{\mathrm{m}}(\vec{x})}{\rho_{\mathrm{w}}}}. \tag{B11}$$

Inserting Eqs. 6 and A8 yields

$$\begin{aligned}\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})} &= \frac{1 - \dfrac{m_{\mathrm{ls}}(\vec{x})}{1 + m_{\mathrm{ls}}(\vec{x})}}{1 + \dfrac{m_{\mathrm{ls}}(\vec{x})}{1 + m_{\mathrm{ls}}(\vec{x})} \cdot \dfrac{1}{\rho_{\mathrm{w}}} \cdot \rho_{\mathrm{s}}\rho_{\mathrm{w}}\dfrac{1 + m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}}\\ &= -\frac{\dfrac{1}{1 + m_{\mathrm{ls}}(\vec{x})}}{1 + \dfrac{\rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}} = -\frac{\dfrac{1}{1 + m_{\mathrm{ls}}(\vec{x})}}{\dfrac{\rho_{\mathrm{w}} + 2\rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}}\end{aligned} \tag{B12}$$

$$\frac{\partial \mathrm{WD}(\vec{x})}{\partial m_{\mathrm{ls}}(\vec{x})} = -\left(\frac{1}{1 + m_{\mathrm{ls}}(\vec{x})}\right)\left(\frac{\rho_{\mathrm{w}} + \rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}{\rho_{\mathrm{w}} + 2\rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x})}\right).$$

Writing this result in partial fractions and solving this differential equation using separation of variables give

$$\begin{aligned}&\mathrm{WD}(\vec{x})\\ &= \mathrm{WD}_0 - \frac{2(\rho_{\mathrm{s}} - \rho_{\mathrm{w}})\ln(1 + m_{\mathrm{ls}}(\vec{x})) + \rho_{\mathrm{w}}\ln(\rho_{\mathrm{w}} + 2\rho_{\mathrm{s}} m_{\mathrm{ls}}(\vec{x}))}{4\rho_{\mathrm{s}} - 2\rho_{\mathrm{w}}}\\ &= \mathrm{WD}_0 - \frac{\rho_{\mathrm{w}}\ln\rho_{\mathrm{w}}}{4\rho_{\mathrm{s}} - 2\rho_{\mathrm{w}}} - m_{\mathrm{ls}}(\vec{x}) + \mathcal{O}(m_{\mathrm{ls}}(\vec{x}))^2.\end{aligned} \tag{B13}$$

The first-order approximation describes again a linear relation between WD and moisture content.

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