# Impact of hydrophobic surfaces on capillary wetting

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ABSTRACT

The dynamic wetting behavior as first step in reconstitution of heterogeneous model food powders was investigated in the present work. Therefore, we studied the capillary rise of water into single pores and pore systems containing hydrophilic and hydrophobic walls. A two-wall setup was developed to realize the capillary rise in a single gap containing walls with two different contact angles but a constant pore size. The equilibrium penetration height was measured and compared to calculated heights using advancing contact angles inserted in a model equation. Wetting experiments in a Washburn setup were performed with respect to the investigation of water penetration into a heterogeneous pore network which leads to a variable pore size during the rise. In order to determine the effect of contact angle, three different glass materials at varied levels of hydrophobicity were prepared. Furthermore, a focus was put on understanding the impact of the pore network on the wetting kinetics by mixing two size fractions of glass beads. The equilibrium heights determined in heterogeneous single gaps fit well with the calculated heights by inserting advancing contact angles into the model equation. The results of the powder systems show a significant impact on the wetting with an increasing hydrophobic fraction, while an increased hydrophobic contact angle further increased the wetting time only at higher quantities of the hydrophobic component in the sample. Furthermore, our findings emphasize the complexity of wetting into a system with heterogeneity in pore size and contact angle.

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## 1. Introduction

The dry state of food products provides an enhancement of stability, storage, transport, weighing and processing [1]. However for consumption very often a rehydration process is necessary in order to convert a dry powder back into a liquid [2]. During rehydration of a food powder generally four steps can be distinguished: the wetting of the powder surface, the sinking, the dispersing and finally the dissolving in case of soluble material [3,4]. These steps take place consecutively but with overlap. Mitchell et al. [5] studied the whole reconstitution process of amorphous maltodextrin as model food powder and developed a mapping strategy in order to identify the limiting rate constants. Dupas et al. [6] investigated the reconstitution of carbohydrate powders comparing crystalline and amorphous materials and the effect of particle size, initial water content and temperature. According to their results, different mechanisms can be rate-limiting depending on the state of the material.

As the first step, the wetting has a major role within rehydration, often being the time limiting factor [3]. Thus, many authors have focused on studying the wetting step during food powder reconstitution in terms of different impact factors and using different methods [3,7–10]. Dupas et al. [7] used a static wetting test to characterize the

wettability of food powders and proposed a model to predict the wetting time. Kim et al. [10] studied the wetting behaviour of four different milk powders before and after fat extraction in order to understand the impact of surface coverage with a hydrophobic component on wetting time. In both studies, the powder was poured on a static liquid surface and the time until the powder sinks was determined. Another method to investigate the wettability of powders was applied by Forny et al. [8]. They measured penetration rates of liquid into single agglomerates and powder beds by Washburn technique with the aim to model an entire rehydration process. The static and dynamic water wetting of cocoa powder which represents a highly hydrophobic food powder was investigated by Galet et al. [9]. The data was used to estimate a surface energy of cocoa powder of 30 mJ/m² which confirms the very poor wettability in water.

The wetting of a powder bed with a certain liquid is generally a highly dynamic process and is mainly driven by capillary forces since liquid enters the pore space within the particle bulk due to compensation of capillary pressure. While high contact angles generally lead to an insufficient or slow wetting, small contact angles support a fast wetting process. In general, we have to distinguish between apparent contact angles which can be determined on a microscopic level and intrinsic contact angles on a molecular level which are based on a force balance and described by Young [11]. Furthermore, there is a difference between static and dynamic contact angles. When a liquid

moves along a solid surface the static contact angle does not provide the proper information about the moving behaviour of the interface. In a dynamic process, the advancing (maximum) and receding (minimum) contact angles describe the interaction between the solid and the liquid material [12,13]. The advancing contact angle occurs when the liquid front is expanding [12], and is therefore of interest in wetting processes of powders due to capillary forces. In the case of soluble components, dynamic wetting is even more complex with a contact angle that varies with contact line speed due to water condensation and diffusion and due to material dissolution [14]. Additionally, the pore size which is mostly determined by the particle size distribution, has a major impact on the rate of capillary rise [15]. Eq. (1) represents the capillary pressure equation where $P_C$ is the capillary pressure, $\sigma_{lv}$ the surface tension, $\theta$ the contact angle and $r_P$ is the pore radius:

$$P_C = \frac{2 \cdot \sigma_{lv} \cdot \cos\theta}{r_P}. \tag{1}$$

A liquid penetrates into a pore until the equilibrium with the hydrostatic pressure is reached. Using this equilibrium state the equilibrium height $h_{eq}$ which presents the maximum level of a liquid in a single pore can be determined with $\rho$ as liquid density and $g$ as gravity:

$$h_{eq} = \frac{2 \cdot \sigma_{lv} \cdot \cos\theta}{\rho \cdot g \cdot r_P}. \tag{2}$$

Heterogeneity makes wetting complex whereby we distinguish between geometric and chemical heterogeneity. The impact of geometric heterogeneity in terms of surface roughness was studied by Wenzel [16,17] and later by Palzer et al. [18]. They found an increasing contact angle on an increasingly rough surface if the contact angle of the smooth system was above 90° and a decreasing contact angle on an increasingly rough surface if the contact angle of the smooth system was below 90° which is also described in the Wenzel equation. The measurements of the contact angles were performed perpendicular to the orientation of the longitudinal surface roughness [18]. Besides geometric heterogeneity the chemical heterogeneity in terms of the chemical composition of the surface highly influences the wetting process and therefore the wetting time. A correlation between the composition of the powder surface and the wetting time was observed by Gaiani et al. [19] in which the wettability and the powder rehydration of three dairy powders was investigated. The higher the surface concentration of lactose and the lower the surface concentration of proteins, the faster the wetting occurs. In order to combine these different wetting behaviors within a heterogeneous system, Cassie and Baxter [20] proposed an equation where a surface consists of two area fractions $f_1$ and $f_2$ with different contact angles $\theta_1$ and $\theta_2$, respectively. An apparent contact angle $\theta_{CB}$ of the mixed system can be calculated:

$$\cos\theta_{CB} = f_1 \cdot \cos\theta_1 + f_2 \cdot \cos\theta_2. \tag{3}$$

If the two area fractions have the same size ($f_1 = f_2$) the Cassie-Baxter equation can be simplified and written as

$$\cos\theta_{CB} = 0.5 \cdot (\cos\theta_1 + \cos\theta_2). \tag{4}$$

For this special case, O'Brien et al. [21] defined a model equation which describes the equilibrium height of a capillary rise between two vertical planes where $w$ is the distance between both planes:

$$h_{eq} = \frac{\sigma_{lv} \cdot (\cos\theta_1 + \cos\theta_2)}{\rho \cdot g \cdot w}. \tag{5}$$

While several authors performed wettability studies in homogeneous systems or in real food systems which makes the distinction between single effects difficult [7–10], a detailed investigation about the impact of heterogeneity in terms of hydrophilic and hydrophobic surfaces in one system on the wettability of powders is still missing in literature. This work was carried out with regard to food powder reconstitution. But in order to identify the influence of heterogeneity, inert non-food model material was used on purpose. We studied the impact of heterogeneity in single pores on the equilibrium height of the capillary rise and the effect of increasing hydrophobic fraction and an increasing hydrophobic contact angle on the wetting kinetics in model powder mixture. Since the capillary rise into pore networks is also influenced by geometrical parameters, such as pore sizes and pore size distributions, we also focused on the impact of changing pore networks by mixing glass beads of two size fractions.

## 2. Experimental

### 2.1. Materials

Glass slides (Marienfeld superior, Germany) and two size fractions of glass spheres (Swarco, Austria) made of soda lime glass were used as model material for capillary rise experiments into a single gap and into a powder system (Washburn setup), respectively (Fig. 1). Therefore, only the wetting step could be investigated without the occurrence of dissolution or swelling. The dimensions of the slides are $76 \times 26 \times 1$ mm. The solid density of the glass is 2469 kg/m³. The procedure for the treatment of glass material was the same for slides and spheres. In order to remove organic contaminants from the glass surface, in a first step the glass material was washed in peroxymonosulfuric acid which is prepared by mixing sulfuric acid and hydrogen peroxide in a volume ratio of 3:1, respectively, for 15 min. Afterwards, the glass was rinsed in distilled water until the waste water shows a pH of 7 and finally dried at 140 °C for 2 h. This glass material is labeled as "hydrophilic". "Hydrophobic" material is obtained by modification of the clean surface with a silanization process. The glass material was treated with triethoxyoctylsilane in toluene with different concentrations and for different times in order to achieve hydrophobic glass surfaces. The silanization parameters are summarized in Table 1. The silanization process for 48 h and 72 h were performed with pre-dried toluene in order to reduce the water amount during the reaction. After silanization treatment the material was rinsed with toluene and acetone and dried under the fume hood. Sulfuric acid (96%), hydrogen peroxide (35%), triethoxyoctylsilane, toluene, ethanol and acetone were purchased from Carl Roth (Germany).

## 3. Methods

The particle size distribution of both glass bead fractions was determined by dynamic image analysis (CAMSIZER X2, Retsch Technology,
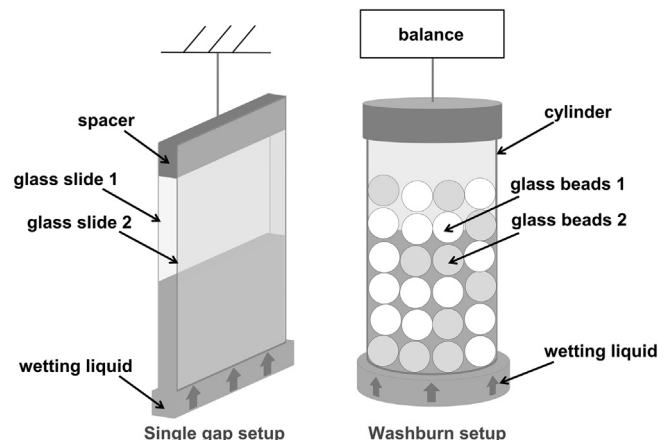


**Fig. 1.** Experimental setups of the Single gap experiment and the Washburn experiment.