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## **Sorption hysteresis in wood and its coupling to swelling: a new modelling approach**

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### **ABSTRACT**

Sorption hysteresis of amorphous cellulose is studied. Cellulose, as a renewable organic biopolymer, is an essential component of various natural composites such as wood. A coupling process between sorption and deformation leads to the hysteresis as observed in sorption and swelling, both experimental and simulated for cellulose and wood in general.

### **KEYWORDS**

Sorption, hysteresis, swelling, cellulose, modelling.

### **INTRODUCTION**

An appealing, but not fully understood characteristic of many porous building materials is the appearance of sorption hysteresis: i.e. the moisture content differs at same relative humidity (RH) depending on the loading history, ad -or desorption. Hysteresis has been commonly attributed to capillary condensation hysteresis and pore ink-bottle effects, where for the latter the pore body can only empty when the smaller neck pore is emptied. Such behavior can appropriately be described using models based on the independent domain theory, where hysteresis originates from hysteretic bottle elements, which do not interact necessarily with each other (see e.g. Coasne et al. 2005, Derluyn et al. 2012, Patera et al. 2016). The assumption of non-interaction and pore independence is for most materials however most likely not valid, and invasion percolation, where a pore can only empty when at least one neighboring pore is empty, has been adopted to model hysteresis. For an assembly of connected pores, invasion percolation effects appear where pores can only be emptied when a percolating path is present (see e.g. Carmeliet et al. 1999).

In the above mentioned approaches, the materials are assumed not to deform, remaining at constant volume and do not incorporate the influence of sorption induced swelling. However, many materials such as soft nano-porous materials as wood show an important sorption induced swelling. Soft nanoporous matter encompasses anthropic materials such as compliant porous solids, foams, intrinsically porous polymers, organic membranes, as well as natural materials such as wood, bamboo, plants, linen, kerogen in gas shale. Owing to their large internal surface area and compliant solid matrix, strong fluid-solid interactions lead to sorption-induced deformation or swelling. For example, cellulose, wood most redundant component, on adsorption of water may swell as much as 30% volumetrically (Mihranyan et al. 2004). An important feature of nanoporous polymers is the hysteresis in sorption isotherms extending to very low RH, a different type of hysteresis to the one associated with capillary condensation, where the hysteresis disappears below a certain RH.

The coupling between sorption and swelling in porous materials has been investigated experimentally and with atomistic simulations (Derome et al. 2011). In parallel, much theoretical effort has been devoted to unify mechanical constitutive equations and surface thermodynamics relationships into the same framework known as poromechanics (Kulasinski et al. 2015). In spite of being successful at describing the coupling between sorption and

swelling, the physical microscopic mechanism behind this coupling is often ignored in studying the hygroscopic behavior of materials like wood. The question arises whether the swelling of the material and the accompanying pore structure changes play an important role in the sorption behavior and are at the origin of the observed sorption hysteresis. In this paper, we will show that this coupling effect is essential in explaining the observed sorption hysteresis effect.

### SORPTION AND SWELLING HYSTERESIS OF SOFT MICRO-POROUS MATERIAL

In this paper, we study sorption hysteresis of amorphous cellulose considering its wide presence in nature. Cellulose, as a renewable organic biopolymer, is an essential component of various natural composites such as wood. Because of its abundance, cellulose is also a popular raw material to design innovative products for science, medicine and technology. Cellulose shows an important hygroscopic behavior because of the exposed hydroxyl sites in the nanoporous polymer. Understanding the hygroscopic hysteretic behavior of cellulose may lead to a better understanding of the origin of sorption hysteresis in wood. We use atomistic simulations to study the hysteresis behavior. Part of the atomistic model of cellulose used in this work is shown in Figure 1. The figure shows the material structure at RH=1 while the blue dashed line shows the non-swollen state of the system before adsorption.

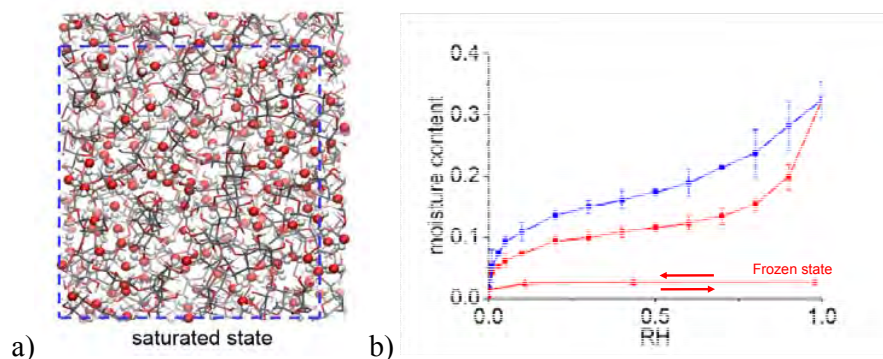


Figure 1 a). Atomistic model of cellulose in saturated state. The sticks are the bonds between the C, O and H atoms in cellulose, red and white spheres the O and H atoms of water. Box size  $3.1 \times 3.3 \text{ nm}^2$ . Blue dashed line shows the system size of dry material before adsorption. b) MD simulation of sorption hysteresis with swelling and adsorption in frozen state.

Water sorption and deformation are simulated with a hybrid Grand Canonical ensemble (GCMC)/ Molecular Dynamics (MD) method. Monte Carlo simulations in GCMC allow studying the sorption process by inserting or deleting a number of water molecules in order to reach the target RH (chemical potential). However, since the system is at constant volume, this method does not allow to study swelling and its effect on sorption. Therefore, MD simulations are consecutively used to obtain the deformation state. As the deformation changes the RH, we iterate between GCMC and MD until the target RH at equilibrium is reached. By using this hybrid strategy combining GCMC and MD, the atom-scale simulations probe adsorption phenomena while allowing for swelling of the host porous polymer.

Figure 2a shows the ad- and desorption isotherms, i.e. the moisture content (kg/kg) versus RH. Figure 2b shows the swelling isotherms, i.e. the swelling strain (m/m) versus RH. Figure 2a shows that the moisture content increases rapidly with RH in the low RH region and then increases less rapidly as initial pores in cellulose get filled. Upon further increasing RH, an inflection point in the adsorption isotherm is observed as pores open up upon swelling and significant subsequent adsorption occurs. The pore sizes in this nanoporous material, even upon swelling (0.2 – 0.4 nm), are too small to allow for capillary condensation (Coasne et al 2005). The sorption curves also exhibit significant hysteresis. The simulation results agree qualitatively well with experimental data (Mihranyan et al. 2004). We note a systematic offset

of the experimental data (around 0.5 moisture content) with our simulations. This offset is attributed to the presence of residual water not being removed in the experimentally dried sample (presence of non-desorbable water).

Figure 2b shows the swelling isotherms. The volumetric strain shows significant swelling strains reaching as high as 36% close to  $RH = 1$ . Large hysteresis in sorption-induced swelling is observed reflecting the hysteretic sorption isotherm. Significant hysteresis in sorption and sorption induced deformation is observed. When we plot the swelling strain versus moisture content (Figure 2c), hysteresis disappears and the data collapse in a single almost linear curve. This is in agreement with experimental observations in wood (Patera et al. 2013). This shows that swelling is a direct consequence of filling of the deforming material with a number water molecules and therefore a linear relation between swelling and moisture content is observed.

The impact of swelling on the sorption isotherms was probed by simulating water adsorption keeping the material non-deformable (frozen material). We found that in this case, much less adsorption occurs (almost 10 times lower) and the hysteresis effect disappears. This indirectly shows that swelling of the material essentially contributes to the total sorption amount, and that hysteretic sorption depends on the swelling

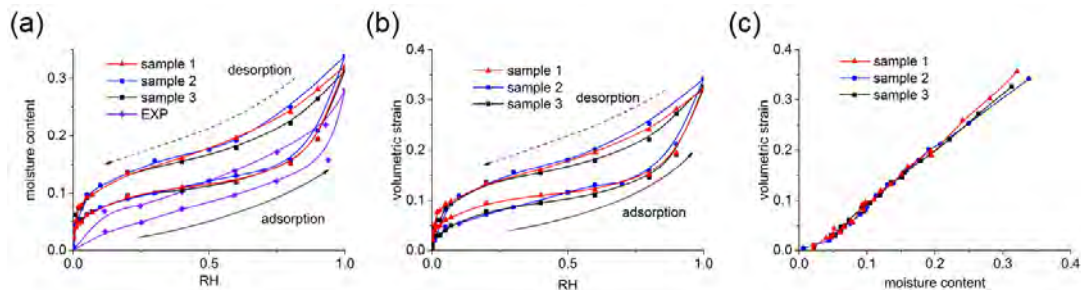


Figure 2. (a) Significant hysteresis in simulated and experimental sorption isotherms. (b) Hysteresis in simulated volumetric swelling strain isotherms. (c) Hysteresis disappears when plotting volumetric swelling strain in function of moisture content.

To better understand the coupling between sorption and swelling and more especially the origin of hysteresis, we further interrogate the systems looking at hydrogen bonding. Amorphous cellulose is a non-cross-linked polymer, where hydrogen bonds are a metric to monitor the interactions inside the polymer system, revealing different configurations of material and water molecules during adsorption and desorption. We study the number and nature of the hydrogen bonds in the material. Three types of hydrogen bonds (HB) are distinguished. In the dry material, polymer chains are interconnected with cellulose-cellulose hydrogen bonds ( $HB^{CC}$ ). Upon adsorption of water molecules, swelling occurs and CC hydrogen bonds between the polymer chains are broken. Upon breaking the CC hydrogen bonds, new hydroxyl adsorption sites become available. Increasing RH, these new sites become occupied with new water molecules forming cellulose-water hydrogen bonds ( $HB^{CW}$ ). Figure 4a-b show the normalized decrease of  $HB^{CC}$  and increase of  $HB^{CW}$  with moisture content. Increasing further the moisture content, water molecules start to form more and more water-water hydrogen bonds ( $HB^{WW}$ ), since only a limited number of free hydroxyl sites is still available. In desorption, first water molecules in water-water hydrogen bonds will leave the system, while the remaining water molecules are attached to cellulose chains. As cellulose-water HBs are stronger than cellulose-cellulose HBs, hydroxyl sites will preferentially remain occupied by the water molecules at lower relative humidity. Cellulose-cellulose HBs between the polymer chains will only reform at lower RH. This process explains the lower number of cellulose-cellulose HBs during desorption.

In conclusion, at a given moisture content, the polymer system accommodates to receive the

same number of water molecules but distributes them differently as observed by different hydrogen bonding configurations during ab- and desorption. During adsorption process, new sites are created by breaking cellulose-to-cellulose hydrogen bonds between polymer chains due to material swelling. These sites become receptors for new water molecules changing cellulose-to-cellulose into cellulose-to-water hydrogen bonds. However, the recovery of these new adsorption sites back to cellulose-to-cellulose hydrogen bonds during desorption is less likely since the sites more likely remain occupied by water molecules. This coupling process between sorption and deformation leads to the hysteresis as observed in sorption and swelling, both experimental and simulated for cellulose and wood in general. The mechanism documented by observing configurations of hydrogen bonds gives a clear understanding of the coupling between sorption and swelling in soft porous matter that goes well beyond cellulose, wood and other soft polymer materials. While such mechanism was merely hypothesized in the literature, no experimental or theoretical evidence has been reported so far. With our atomistic approach, a clear understanding of hysteresis due to coupling between sorption and swelling in soft polymer materials is shown.

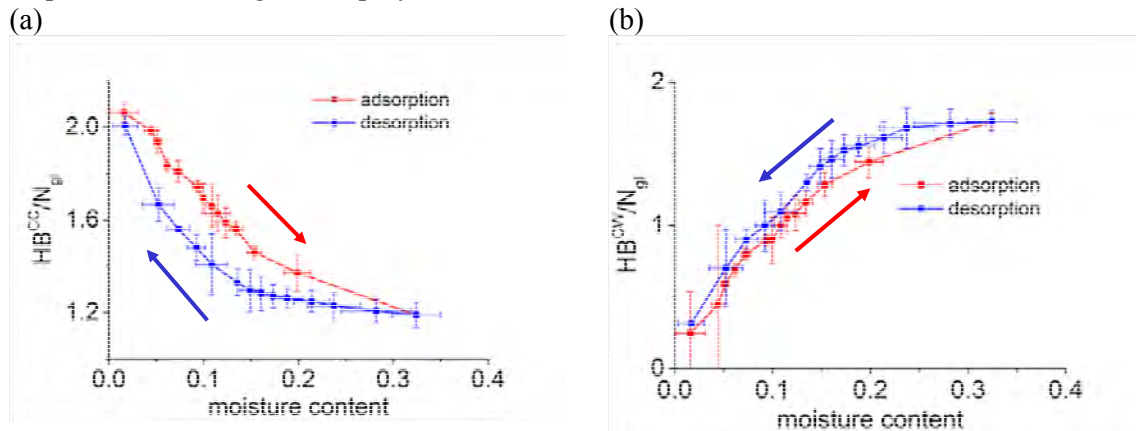


Figure 3. (a) Evolution of number of cellulose-to-cellulose hydrogen bonds with moisture content. (b) number of cellulose-to-water hydrogen bonds with moisture content.

### DISCUSSION ON MODELLING HYSTERESIS USING INDEPENDENT/DEPENDENT DOMAIN THEORY

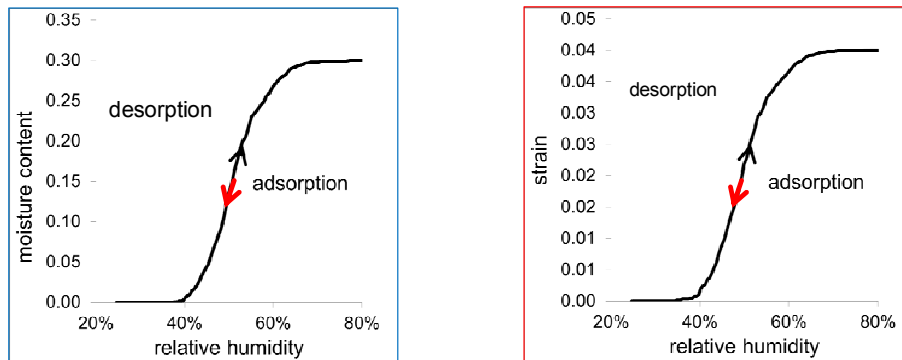
A common approach to describe sorption hysteresis in a phenomenological way is the independent domain theory, where hysteresis originates from local hysteretic elements, that do not interact with each other. In this approach, sorption hysteresis is explained by hysteretic pore scale phenomena like capillary condensation, contact angle or ink-bottle effects caused by smaller size entry pores. Based on these physical explanations, sorption hysteresis is considered to be merely a local pore phenomenon, i.e. sorption at the pore level itself is hysteretic. Thus, in the independent domain theory, pores are assumed not to interact with each other, and changes in moisture content are the outcome of the behavior of an assemblage of independent sorption sites. Different independent domain models have been proposed for different types of materials, where the main difference results from the way the distribution of hysteretic elements is derived from experimental data. These phenomenological models have appeared in different forms and fitted to experimental data. Although these phenomenological models seem to adequately simulate the observed behavior following the experimental data, no direct proof for their physical correctness has been yet given. Our recent atomistic modelling results show that independent theories, which do not include sorption induced swelling in nanoporous soft polymeric materials do not capture the correct physics.

Our atomistic analysis reveals that water molecules first adsorb at free sorption sites leading to a swelling of the material. The swelling is followed by an unravelling of the polymer

chains favoring the creation of new sorption sites. In desorption however, these extra-created sorption sites remain favorably occupied by water molecules and the material remains longer in a swollen state at higher moisture content. The question now remains how to model such a behavior in an elegant engineering way.

Based on the evidence that swelling plays a determining role in sorption hysteresis, a correct hysteresis model should incorporate swelling, which can only be modelled by an elastic dependent domain theory. In such model, the filling of a site depends not only on the relative humidity at the site but also on the strain state of the sorption site. In view of a dependent domain approach taking into account deformation, we assume the material to consist of a set of elastic interacting elements. A distribution of non-hysteretic pores is embedded in the elastic material. In the dry state, most of these pores are not accessible to water molecules since their size is too small to receive a water molecule. However, some smaller accessible pores become filled with water molecules, swell and will exert a swelling strain field on neighboring pores. Pores, which were not accessible before, will now become accessible due to the tensile strain exerted on the pore system. The filling and unfilling of an element is thus not only dependent on RH, but also on the strain exerted on the element. A positive strain originating from an internal strain field will lead to making pores accessible to sorption. Further, the tensile strain on an element is considered to produce extra volume for additional sorption of water molecules, which has also been observed in the atomistic simulations. The behavior of a distribution of such interacting elastic elements is studied by finite elements.

a)



b)

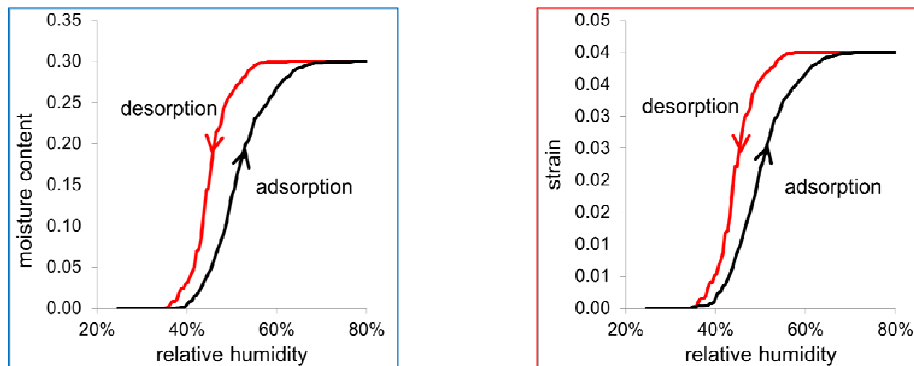


Figure 4. (a) Sorption and swelling isotherm of moisture content and strain versus RH for non-coupled dependent domain approach. No hysteresis is observed. (b) Sorption and swelling isotherm of moisture content and strain versus RH for coupled dependent domain approach, with interaction between filling and swelling process. Hysteresis both in sorption and swelling is observed (Guyer et. al 2011).

Our group in collaboration with R. Guyer from LANL (Guyer et. al 2011) developed such a dependent domain approach for an academic material. General results showing the model



performance are reported here. Figure 4a gives an example of predictions of sorption and swelling isotherms using the elastic dependent domain model of non-hysteretic elements where the coupling between sorption and swelling has been switched off. The curves show a non-hysteretic behavior. When switching on the coupling (figure 4b) meaning the filling of an element depends not only on the RH but also on the strain exerted in the element, we observe a hysteretic behavior both in sorption and in swelling. When plotting the swelling strain versus moisture content (Figure 5), we observe a quasi-linear relation between swelling strain and RH, showing no hysteresis. These results are in close qualitative agreement with our observations in experiments and atomistic simulations for wood components. This means that the elastic dependent domain approach seems to be the correct physical approach to model and predict sorption hysteresis.

In the next future, we will further develop and fine-tune this elastic dependent domain model showing its adequacy for modelling hysteresis of sorption induced swelling of nanoporous polymer materials as wood. Furthermore, we will implement this sorption model in a multiscale approach allowing modelling not only single woods components, but also layers in a wood cell wall like the S2 layer, and even wood. From there on, global macroscopic models can be improved for modelling materials behavior at macro- or structural scale. Final aim is to be able to adequately model sorption induced swelling and hysteresis. The models should be physically sound from one side, but also sufficiently simple to be used in engineering practice.

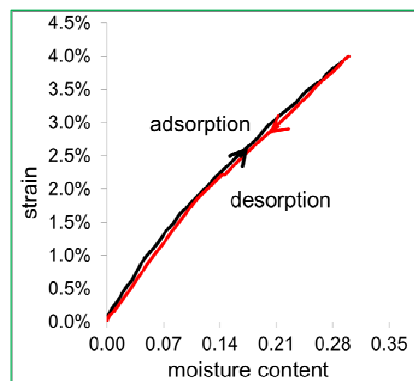


Figure 5. Swelling strain versus moisture content as determined by dependent domain. No hysteresis is observed (Guyer et. al 2011).

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