Poroelastic model for adsorption-induced deformation of biopolymers obtained from molecular simulations

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Molecular simulation of adsorption of water molecules in nanoporous amorphous biopolymers, e.g., cellulose, reveals nonlinear swelling and nonlinear mechanical response with the increase in fluid content. These nonlinearities result from hydrogen bond breakage by water molecules. Classical poroelastic models, employing porosity and pore pressure as basic variables for describing the “pore fluid,” are not adequate for the description of these systems. There is neither a static geometric structure to which porosity can sensibly be assigned nor arrangements of water molecules that are adequately described by giving them a pressure. We employ molar concentration of water and chemical potential to describe the state of the “pore fluid” and stress-strain as mechanical variables. A thermodynamic description is developed using a model energy function having mechanical, fluid, and fluid-mechanical coupling contributions. The parameters in this model energy are fixed by the output of the initial simulation and validated with the results of further simulation. The poroelastic properties, e.g., swelling and mechanical response, are found to be functions both of the molar concentration of water and the stress. The basic fluid-mechanical coupling coefficient, the swelling coefficient, depends on the molar concentration of water and stress and is interpreted in terms of porosity change and solid matrix deformation. The difference between drained and undrained bulk stiffness is explained as is the dependence of these moduli on concentration and stress.

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I. INTRODUCTION

Adsorption originates at the molecular scale from the interactions between the atoms of the solid matrix and the molecules of the fluid. When the size of the pores in a material is on the order of the range of molecular interactions, a mechanical pressure arises due to fluid-solid interactions, leading to adsorption-induced deformation (swelling). Such materials are commonly referred to as microporous according to IUPAC classification of materials (pores less than 2 nm). For clarity, we will refer to these materials as nanoporous materials, when the size of the interacting fluid molecules is on the order of size of the nanopores (≈ 1 nm). Nanoporous media showing adsorption-induced deformations are important for a huge variety of engineering applications: for instance, for sequestration of carbon dioxide in coal (e.g., [1]), storage of hydrogen in metal-organic frameworks, or purification of water [2], etc. Adsorption-induced deformation in nanoporous materials may induce undesired internal effects such as a decrease in permeability due to crack closure or cracking due to a restraining of the deformations, processes that lead to operational or durability problems.

Poromechanics has proven to be a consistent theory to model the mechanical coupling between fluids and solids and also fluid-induced deformations of a porous material. Poromechanics [3] was developed initially for the case of fluids saturating the porous medium, introducing as state variables pore pressure and porosity excess ϕ , the latter defined as the difference between the current porosity ϕ and the porosity in a reference state ϕ_0 .

For unsaturated media, interfacial stresses between the fluid and gas phases start to play a dominant mechanical role.

At higher fluid content, menisci develop due to capillary condensation which introduce capillary forces, also acting on the solid matrix. Coussy [4] developed adequate poroelastic theories to take into account interfacial and capillary forces. These concepts are applicable to meso- and macroporous materials, since the fluid is in its bulk state.

In nanoporous materials the fluid, due to high fluid-solid interaction forces (e.g., van der Waals forces), is no longer in its bulk state, showing a higher density in the adsorbed layers close to the solid. Ravikovitch and Neimark [5] introduced the adsorption stress concept which, for nanopores of simple geometry like slit-shaped pores, reduces to the classical disjoining or solvation pressure. The disjoining pressure is the difference between the mechanical pressure acting on a thin film of fluid in a slit-like pore and the bulk pressure of the fluid. A disjoining pressure appears when the thickness of the film is on the order of the range of the molecular interactions. In the case of nanoporous materials, with the exception of materials with specific ideal pore geometries such as slit pores (e.g., Refs. [6,7]) the determination of the fluid pressure is not unambiguous. Brochard *et al.* [8] derived poroelastic constitutive equations which are valid for a generic porous medium, i.e., even for a disordered porous medium with pores of nanometer size. They show that in order to determine the poroelastic properties, the dependence of the amount of fluid adsorbed on both the fluid bulk pressure and the strain of the medium needs to be known.

In nanoporous solids, adsorption is not described by surface covering, but rather by a pore filling. The concept of excess porosity is then difficult to use, since it cannot be unambiguously defined. However, the state of the adsorbent

is fully characterized by the number of molecules adsorbed and its chemical potential. In this paper we use the chemical potential and molar concentration of water molecules as fluid state variables to describe the state of the adsorbed fluid.

In Carmeliet *et al.* [9], a poroelastic theory for the derivation of the constitutive equations for unsaturated porous materials was formulated at the macroscale. The theory employed a free energy that included mechanical and fluid contributions and the coupling between fluid and mechanics. In this paper we use a poromechanical theory of the same style as that of Carmeliet *et al.* [9] to study water molecules' interactions in a nanoporous biopolymer: amorphous cellulose. In place of fluid content and fluid pressure we use molar concentration of water and chemical potential.

Due to their abundance and often unusual properties, biopolymers are intensely studied by researchers and engineers [10]. Among biopolymers, cellulose is the most common polymer on earth [11] and of particular interest. Recently Kulasinski *et al.* [12] showed, using molecular simulation of water adsorption in amorphous cellulose [13], that the particular mechanical weakening and swelling phenomenon with increasing fluid content can be attributed to the breaking of hydrogen bonds of cellulose chains. These bonds are replaced by water-cellulose bonds. In this paper, we want to see if the poroelastic theory is able to model the observed complexity of solid-fluid interaction forces in a nanoporous amorphous polymeric material. More specifically, can the poroelastic theory capture the consequences of the complex phenomenon of hydrogen bond breaking occurring at molecular scale, as well as its influence on the mechanical and adsorption behavior? We want also to see whether we can model the mechanosorptive behavior, i.e., the stress dependence of the adsorption isotherms.

We highlight that the strength of this paper lies in (1) demonstrating that a poroelastic approach is not only applicable at the macroscale, but can also be used at the molecular scale, when adequate variables are chosen to represent the state of the fluid in the porous medium, i.e., chemical potential and water concentration; (2) the formulation of proper constitutive equations at molecular scale based on an energy formulation, where the poroelastic material properties depend nonlinearly

both on water concentration and stress; and (3) giving a physical interpretation of the nonlinear dependencies with respect to porosity changes and material weakening.

We first report results from molecular dynamics simulations of water in amorphous cellulose, in which adsorption-induced effects such as swelling and mechanical weakening have been observed. Then the poroelastic model is formulated including adsorption-induced effects in a thermodynamically consistent way. The model is validated and used to study the mechanosorptive effect. Finally, physical interpretations of the coupling coefficient with respect to pore filling-induced swelling and of the dependence of the drained bulk modulus on stress and fluid concentration are given.

II. MOLECULAR DYNAMICS MODEL

Amorphous cellulose is a strongly hydrophilic biopolymer due to its open porous structure and the presence of exposed hydroxyl (O2 and O3) and hydroxymethyl (O6) groups [see Fig. 1(a)] [14,15]. Water molecules can easily form hydrogen bonds with the mentioned oxygen atoms [13], as labeled in Fig. 1(b). The adsorption of water is known to induce a swelling of the material and weakening of the mechanical properties of wood polymers [16,17]. As the adsorption process is an atomic-scale process, molecular dynamics (MD) simulations are an appropriate tool for its investigation. Contrary to mesoscale methods, such as coarse grain, MD can capture hydrogen bond formation or dipole interaction and, unlike better-resolution methods (e.g., density functional theory), MD enables simulation of larger structures and at larger time scales. Although crystalline cellulose has been extensively investigated with MD simulations [18–25], amorphous cellulose is less commonly studied with MD [18,26–28].

The molecular dynamics simulations are carried out using GROMACS 4.6 software [29] with leapfrog algorithm for integration of Newton's equations of motion and the GROMOS 53a6 united-atom force field where aliphatic carbons together with their hydrogens are considered one bead [30,31]. The initial configuration of $I\beta$ cellulose was constructed using the "CELLULOSE-BUILDER" tool [32] that uses the structural data obtained with x-ray diffraction [15]. The procedure of

FIG. 1. (Color online) (a) Representation of the repetitive chain fragment of amorphous cellulose. The oxygen atoms forming hydrogen bonds with water, O2, O3, and O6, are labeled next to their positions. (b) Illustration of hydrogen bonds in disordered structure. Adsorbed water molecules break hydrogen bonds and push the chains apart, increasing pore space.

amorphization, described previously [33], has two stages. First, the polymer is raised to a temperature of 700 K and equilibrated there in stress-free conditions until the chains lose their ordered structure, typically after 1 ns. Then the amorphized chains are quenched to a temperature of 300 K and equilibrated there for 10 ns. The model of dry amorphous cellulose consists of three chains of degree of polymerization = 60 each, that gives the total of 2520 atoms in 180 cellulose residues. Its dry volume is 36.6 nm^3 and the corresponding density is 1.33 g cm^3 . The resulting dry polymers are characterized by 2.37 hydrogen bonds per residue, on average.

In order to study the response of the polymers to water, simple point-charge (SPC) water molecules [34] are introduced to the system using the algorithm described in [13]. Starting from a dry system, water molecules are inserted one by one into the void space between the polymer chains. Successful insertion of a water molecule is followed by a relaxation run of 10 ps at stress-free conditions. Once the desired number of water molecules has been inserted, relaxation runs of 1 ns and production runs of 2 ns are carried out. The water molecules interact with the polymer through van der Waals (implemented as Lennard-Jones potential) and long-range Coulomb forces. The hydrogen bonds in the employed force field are not explicitly defined; the determination of the existence of a hydrogen bond is based on a donor-acceptor distance and the angle donor-hydrogen-acceptor [12].

All MD measurements are carried out at a constant temperature of 300 K and at constant pressure. Further details on the MD model can be found in [13]. The thermodynamic units used are MPa (stress), nm^3/nm^3 (strain), mol dm^{-3} (concentration), and Kj mol^{-1} (chemical potential).

The simulated model has been validated against experimental measurements. This includes adsorption isotherm, density, and chemical structure of the amorphous cellulose [35]. Qualitatively, the swelling curve with swelling coefficient and the weakening versus moisture content have been compared with the corresponding experiments done on softwood samples [36]. It is reasonable to validate qualitatively the MD results of amorphous cellulose against wood properties, as wood cell wall crystallinity (amorphous to crystalline ratio) ranges 40%–60%.

III. RESULTS

A. Molecular dynamics simulations

The adsorption behavior of cellulose is characterized by the relation between the molar chemical potential μ and the molar concentration of water molecules $n = N/V_0$. N is the number of molecules and V_0 the volume at zero stress and zero concentration, also called Lagrangian molar concentration. The molar chemical potential μ equals the average free energy of a water molecule insertion under constant volume and temperature conditions. Among numerous methods to estimate the free energy, the one-step perturbation method is used, as it meets the criteria of the simulated system and it is less time consuming [37]. Using the Zwanzig formula (1a) [38], we obtain the relation between change in chemical potential $\Delta\mu$ and concentration n at different mechanical stress σ , or $\Delta\mu(n, \sigma) = \mu(n, \sigma) - \mu(n = n_{\text{sat}}, \sigma = 0)$, where the

reference chemical potential is taken at zero stress and full saturation. The relative humidity RH is determined using Kelvin's formula (1b):

$$\mu = \Delta F = -k_B T \ln \left\langle \exp \left(-\frac{\Delta E}{k_B T} \right) \right\rangle, \quad (1a)$$

$$\text{RH} = e^{-\Delta\mu/k_B T}, \quad (1b)$$

where T is the temperature, k_B the Boltzmann constant, ΔE is the energy difference between the states containing n and $n-1$ molecules, and angle brackets denote averaging over trajectory. The limitation of this approach is that for the sake of accuracy, the number of molecules has to be large and the trajectory must be long enough so that, on average, the water molecules ideally sample the whole phase space.

Figure 2(a) shows the MD results of chemical potential difference (note the negative sign, $-\Delta\mu$) versus concentration. With increasing concentration, $-\Delta\mu$ decreases, meaning the chemical potential or the energy state of a water molecule increases with the number of molecules in the material. Figure 2(b) shows the adsorption isotherm or concentration versus RH. The adsorption isotherm obtained by MD was validated with measurements on amorphous cellulose by Beever and Valentine [39] and good agreement was found [13]. We also note that the molecular simulations show that adsorption is governed by a pore filling process instead of a surface covering or capillary condensation process [12].

During the adsorption process, the volumetric strain ε_V is determined as a function of the concentration n using

$$\varepsilon_V(n, \sigma) = \frac{V(n, \sigma) - V(0, 0)}{V(0, 0)}, \quad (2)$$

where $V(n, \sigma)$ is the volume at concentration n and volumetric stress σ . As a reference state, the volume at zero stress and zero concentration is taken and the strain is therefore referred to as the Lagrangian strain [4]. Figure 2(c) shows the volumetric strain in function of the concentration. We observe a nonlinear swelling. Although in the literature a linear swelling is mostly reported for cellulosic materials like wood, Siau [40] reports sigmoid swelling curves with less swelling at low moisture content. This observation at low concentration is explained by the fact that water molecules at these concentrations first fill the initial pore space resulting in a smaller than linear swelling of the material. At higher concentration, the adsorption of water molecules results in a linear swelling due to the creation of new pore space also facilitated by the hydrogen bond breakage process.

The bulk stiffness is measured for a sequence of concentrations. During the mechanical measurement, the number of inserted water molecules is unchanged so the reported moduli are for undrained conditions. The polymer system is found to behave isotropically. A uniform volumetric stress of 100 MPa is applied. The stress value is chosen in such a way that the material remains in the linear elastic regime. The system is allowed to evolve to equilibrium, the concentration being held at n and the change in volume V is measured. Then the bulk modulus is determined as

$$K(n) = \frac{\sigma}{\frac{V(n, \sigma) - V(n, 0)}{V(n, 0)}}, \quad (3)$$

FIG. 2. (Color online) MD results (dots) and poroelastic model results (blue line). (a) Chemical potential difference $|\Delta\mu|$ as a function of the concentration at zero stress condition with reference experiment represented as empty squares [35]. (b) Adsorption isotherm: water concentration versus relative humidity. (c) Volumetric strain versus concentration during free swelling. (d) Undrained bulk modulus as a function of concentration. (e) Hydrogen bonds within the polymer per unit volume as a function of concentration. Breaking of the hydrogen bonds is the main mechanism of the material mechanical weakening. (f) Validation of the poroelastic model. Comparison of the poroelastic prediction of the swelling at a volumetric tensile stress of 100 MPa with the MD results.

where σ is the applied volumetric tensile stress and $V(n, \sigma)$ is the volume at fluid concentration n and stress σ . Figure 2(d) shows the undrained bulk modulus as a function of the concentration. We observe a mechanical weakening with a drop in bulk modulus from 8000 to 2000 MPa. Figure 2(e) shows the number of hydrogen bonds within the polymer per unit volume as a function of concentration. Kulasinski [12] found a one-to-one relation between the scaled bulk modulus and the scaled number of hydrogen bonds, meaning that mechanical weakening can be explained by the process of breaking polymer hydrogen bonds.

B. Poroelastic constitutive equations

In the MD simulations, molar concentration of water and mechanical stress are externally controlled, called external state variables, while the strain and chemical potential μ are measured, called internal state variables. So we use molar concentration of water and chemical potential as fluid external and internal state variable, respectively. For isotropic behavior, the stress tensor and the strain tensor can then be decomposed into their volumetric and deviatoric parts. When the porous material behaves isotropically, it has been shown that adsorption does not depend on the deviatoric strain [41].

As the aim of this paper is to study the coupling between adsorption and mechanical effects for isotropic materials, we therefore limit the poroelastic derivations to the volumetric parts, i.e., volumetric stress σ and volumetric strain ε .

Energy can be provided to the system either by mechanically deforming it or by adding fluid molecules to it. We note that during the MD testing, the porous medium was kept at constant temperature, or $dT = 0$. We begin with the Helmholtz free energy, F (with $dT = 0$):

$$dF = -\sigma d\varepsilon + \mu dn. \quad (4)$$

In this equation, all variables are expressed per unit undeformed volume of the porous medium V_0 at $n = 0$ and $\sigma = 0$. Further elaboration of Eq. (4) leads to constitutive equations where the molecular concentration n and the strain ε are the external (control) variables, while the stress σ and chemical potential μ are the internal variables. In the MD simulations n and σ are controlled, while μ and strain ε are measured. Thus we introduce W via Legendre transformation:

$$W = F + \sigma\varepsilon, \quad (5)$$

which leads to

$$dW = \varepsilon d\sigma - \mu dn. \quad (6)$$

From the above equation we can see that Eqs. (7a) and (7b) for strain and chemical potential are

$$\varepsilon = \frac{\partial W}{\partial \sigma}; \quad \mu = -\frac{\partial W}{\partial n}. \quad (7)$$

As ε and μ are functions of σ and n we have

$$d\varepsilon = \frac{\partial \varepsilon}{\partial \sigma} d\sigma + \frac{\partial \varepsilon}{\partial n} dn; \quad d\varepsilon = \frac{\partial^2 W}{\partial \sigma^2} d\sigma + \frac{\partial^2 W}{\partial \sigma \partial n} dn, \quad (8a)$$

$$d\mu = \frac{\partial \mu}{\partial \sigma} d\sigma + \frac{\partial \mu}{\partial n} dn; \quad d\mu = -\frac{\partial^2 W}{\partial \sigma \partial n} d\sigma - \frac{\partial^2 W}{\partial n^2} dn. \quad (8b)$$

From these equations we define the poroelastic properties as

$$C = \frac{\partial \varepsilon}{\partial \sigma} = \frac{\partial^2 W}{\partial \sigma^2}; \quad B = \frac{\partial \varepsilon}{\partial n} = -\frac{\partial \mu}{\partial \sigma} = \frac{\partial^2 W}{\partial \sigma \partial n};$$

$$\frac{1}{M} = \frac{\partial \mu}{\partial n} = -\frac{\partial^2 W}{\partial n^2}, \quad (9)$$

with C the bulk compliance, equal to the inverse of the bulk stiffness K ; B a coupling coefficient, that will be discussed below; and M the moisture capacity (note that the minus sign is introduced to have a positive capacity M). We note that, for isotropic materials, C , B , and M are scalars. Using Eq. (9) in Eq. (8), the incremental constitutive equations can be written as

$$d\varepsilon = C d\sigma + B dn, \quad (10a)$$

$$d\mu = -B d\sigma + \frac{1}{M} dn. \quad (10b)$$

The coupling coefficient B satisfies the Maxwell relation:

$$B = \left. \frac{\partial \varepsilon}{\partial n} \right|_{\sigma} = - \left. \frac{\partial \mu}{\partial \sigma} \right|_n. \quad (11)$$

Integration of the Maxwell relation with respect to n leads to the constitutive equation for the strain (adding the elastic strain due to mechanical stress):

$$\varepsilon = C\sigma - \frac{\partial}{\partial \sigma} \left[\int_0^n \mu(\sigma, n) dn' \right]. \quad (12)$$

This equation shows that, to determine the coupling between mechanics and fluid, we have to know the chemical potential as a function of stress and fluid concentration. It also shows that the strain depends both on stress and concentration. Thus we need a nonlinear poroelastic theory, where the poroelastic properties depend both on stress and concentration. In the stress range considered in the MD experiments, the material was found to remain linear elastic in the undrained experiment, meaning that the undrained bulk compliance (or stiffness) does not depend on the stress. We will show later that, in contrast, the drained modulus is dependent both on stress and concentration. We also note that, in order to determine the nonlinear poroelastic properties, we have to know, according to Eq. (12), the chemical potential as a function of stress and concentration. Since the determination of the chemical potential in MD is delicate and sensitive to fluctuations, we follow an alternative route and formulate an analytical expression for the energy W , the form of which is inspired by the MD results. The coefficients in the energy function W are determined from the MD experiments presented above. This energy approach is described below.

C. Energy formulation

We define the energy W which allows us to derive the poroelastic constitutive equations and poroelastic coefficients using Eqs. (9) and (10). Owing to the additive character of the energy W , we write $W = W_{\sigma} + W_n + W_{\sigma,n}$ where the first term describes the mechanical energy contribution of the polymer material, and the second term the energy contribution due to the insertion of water molecules at zero stress, while the third term describes the coupling energy contribution due to the interaction between the porous polymer and water molecules. In Kulasinski *et al.* [13] it was found that a part of the latter energy change can be attributed to the breakage of hydrogen bonds and consequently is related to the change of the mechanical properties dependent on concentration. In classical poroelastic theory, the energy terms are of quadratic form. For the polymer under consideration, based on the MD observations, we found that we have to use a more complex energy formulation, especially for the mechanical-water molecules coupling.

For the elastic mechanical energy W_{σ} , we can use the classical second-order formulation. A second-order formulation is sufficient since the material was found to react in a linear elastic manner in the given stress range or, in other words, the undrained bulk compliance is found to be independent of stress:

$$W_{\sigma}(\sigma, n) = \frac{1}{2} a_2 \sigma^2. \quad (13)$$

Note that we use superscript “2” referring to the second-order term parameter. For the energy related to the inserted water molecules at zero stress, we use an integral formulation

TABLE I. Poroelastic parameters.

α	β	γ	a_2	a_3	a_4	a_5	a_6
18.0	0.23	0.96	1.02×10^{-4}	8.8×10^{-3}	1.19×10^{-5}	7.97×10^{-4}	-1.62×10^{-5}

as already proposed in [Ref. 9]:

$$W_n(\sigma, n) = -n \int_0^n \mu_{\sigma=0}(n') dn'. \quad (14)$$

The chemical potential at zero stress equals $\mu_0 = \mu_{\sigma=0}(n)$. Inverting this relation gives the concentration versus chemical potential, or using Eq. (1) for RH, we get the adsorption isotherm at zero stress $n_0(\text{RH})$. The adsorption isotherm is commonly determined in experiments. This adsorption isotherm is given in Fig. 2(b). Common adsorption models are the Langmuir and Brunauer-Emmett-Teller theory models, which are valid for adsorption in macro- or mesoporous solids, where the pore size is large compared to the range of molecular interactions which lies $\sim 1\text{--}2$ nm. However, these models are not appropriate to describe adsorption in nanoporous solids, where the pore size is smaller than the range of intermolecular interactions. In such nanoporous solids, as mentioned above, adsorption cannot be explained by surface covering, but rather by a pore filling mechanism. Models describing such behavior are, e.g., the Dubinin-Radushkevich model [42], where the concentration n depends on the energy of adsorption and chemical potential. Following this approach, but simplifying $\mu_{\sigma=0}(n)$ to an exponential function, we use the following relation:

$$\mu_0 = \alpha e^{-\beta n^\gamma}, \quad (15)$$

where α , β , and γ are parameters to be determined.

In classical linear poroelastic theory [3], the coupling energy is written as a linear combination of the external variables, or proportional to the term $n\sigma$ in our case, resulting in constant poroelastic properties. The MD results showed that the polymer cellulose shows nonlinear coupling behavior, which, following Carmeliet *et al.* [9], can be taken into account by introducing higher-order coupling terms in the energy formulation. Such a formulation may include the following terms:

$$W_{\sigma,n}(\sigma, n) = a_3 n \sigma + \frac{1}{2} a_4 n \sigma^2 + \frac{1}{2} a_5 \sigma n^2 + \frac{1}{3} a_6 \sigma n^3, \quad (16)$$

where the term in a_3 is the classical linear coupling term. Using the definition of the compliance in Eq. (9a) (C equals the second partial derivative of W to the stress), we find that the term in a_4 describes the dependence of C on the concentration n . Using the definition of the volumetric strain in Eq. (7a) (the strain equals the partial derivative of W to the stress), we find that the terms in a_5 and a_6 describe the nonlinearity in the free swelling ($\sigma = 0$) versus concentration as observed in Fig. 2(c).

D. Parameter determination

In total we introduced eight parameters in the energy formulation, which we arrange in three sets (α, β, γ) , (a_2, a_4) , and (a_3, a_5, a_6) . The first set of parameters (α, β, γ) is directly obtained from the MD adsorption isotherm at zero stress described by Eq. (15). Figures 2(a) and 2(b) compare the MD

data and the poroelastic modeling results. A good poroelastic description of the MD data is found.

The second parameter set (a_2, a_4) is identified from the undrained bulk modulus as function of the concentration as determined by MD. Based on the definition of the undrained bulk compliance C_u [Eq. (9a)] we get

$$C_u = a_2 + a_4 n, \quad (17a)$$

$$K_u = (a_2 + a_4 n)^{-1}, \quad (17b)$$

where the undrained bulk modulus K_u is given by the inverse of the compliance C_u . At zero concentration, the bulk compliance equals a_2 and the bulk modulus equals $1/a_2$. Figure 2(d) compares the MD data. A good poroelastic description of the MD data is found.

The third set of parameters (a_3, a_5, a_6) is determined from the nonlinear free swelling MD results. Based on the definition of the volumetric strain [Eq. (7a)], we find

$$\varepsilon = a_2 \sigma + a_3 n + a_4 n \sigma + \frac{1}{2} a_5 n^2 + \frac{1}{3} a_6 n^3. \quad (18)$$

At $\sigma = 0$, we find the free swelling strain as function of the concentration, which is a cubic function of n :

$$\varepsilon|_{\sigma=0} = a_3 n + \frac{1}{2} a_5 n^2 + \frac{1}{3} a_6 n^3. \quad (19)$$

The parameter set (a_3, a_5, a_6) can be directly determined from the free swelling curve versus concentration. Figure 2(c) compares the MD data and the poroelastic modeling. A good poroelastic description of the MD data is found.

The poroelastic parameters as obtained from the identification procedure are summarized in Table I.

E. Validation

Having determined the parameters describing the energy function W , we can now validate the poroelastic model. The validation is based on a coupling experiment, where the specimen is first loaded with a volumetric tensile stress, followed by an insertion of water molecules at constant stress, in order to determine the swelling strain versus concentration. We note that the loading protocol of this swelling experiment at constant stress is different from the protocol for determining the undrained bulk modulus. In the latter, we first insert water molecules until a certain concentration and then a volumetric tensile stress is incrementally applied keeping the concentration constant. Since the loading protocol is different for the two experiments, we can consider the swelling experiment under constant stress as a proper validation experiment of the proposed model. According to Eq. (18), the swelling strain equals, after regrouping,

$$\varepsilon|_{\sigma \neq 0} = a_2 \sigma + \left(a_3 n + \frac{1}{2} a_5 n^2 + \frac{1}{3} a_6 n^3 \right) + a_4 \sigma n. \quad (20)$$

The first term on the right-hand side describes the elastic deformation due to the mechanical stress. The second term describes the nonlinear swelling due to the adsorption

of molecules at zero stress. The third term describes the combined effect of stress and concentration: It describes how adsorption depends on the mechanical stress and in turn how increased adsorption influences the swelling. This last term was also identified as the term responsible for the mechanical weakening due to the breakage of hydrogen bonds. We performed an additional MD swelling experiment at 50 and 100 MPa and compared the MD results with the poroelastic predictions [Fig. 2(f)]. We determined the difference between the MD results for swelling at a given stress $\sigma \neq 0$ and the free swelling, or we determined $\varepsilon|_{\sigma \neq 0} - \varepsilon|_{\sigma=0}$, and compared these data with the poroelastic model prediction. The spread in the MD results is due to the subtraction of two MD results, which show substantial scatter. The poroelastic model predicts a linear relation for a given stress value σ . $\varepsilon|_{\sigma \neq 0} - \varepsilon|_{\sigma=0} = (a_2 + a_4 n)\sigma$. Good agreement is observed showing that the poroelastic model captures adequately the coupling phenomena as observed in the MD simulations.

F. Mechanosorptive effect

After parameter determination and validation of the poroelastic model, we use the model to analyze whether the model predicts a mechanosorptive behavior; i.e., does the adsorption isotherm depend on mechanical stress? Based on the definition of the chemical potential [Eq. (7b)], we find, after regrouping,

$$\mu(\sigma, n) = \mu_0(n) - (a_3\sigma + \frac{1}{2}a_4\sigma^2) - (a_5n + a_6n^2)\sigma. \quad (21)$$

The first term on the right-hand side describes the chemical potential dependence on the concentration in stress-free conditions. The second, grouped term describes the dependence of the chemical potential on stress, which is a quadratic function. This term induces that the energy state of an adsorbed water molecule changes when the material is mechanically loaded. The last, grouped term describes the dependence of the energy state of a water molecule on the coupling effect of fluid and mechanics. Using Eq. (21), we determine the chemical potential difference $\Delta\mu(n, \sigma) = \mu(n, \sigma) - \mu(n_{\text{sat}}, 0)$ versus concentration for different stress levels. Figure 3(a) shows the chemical potential difference versus concentration. With increasing concentration the difference $-\Delta\mu$ decreases, meaning the chemical potential increases with concentration. With increasing volumetric tensile stress, the difference $-\Delta\mu$ increases, indicating the chemical potential decreases with

volumetric tensile stress. This means that the energy state of a water molecule increases with the number of molecules present in the material and decreases with the tensile stress. The mechanical effect can be explained as follows: A higher volumetric tensile stress results in an increase of porosity, making the pores accessible for water molecules at lower energy or chemical potential. Using Eq. (1), we transform the chemical potential curves into adsorption isotherms. We observe in Fig. 3(b) a shift of the upper part of the adsorption curves to lower RH. This indicates that the concentration of water molecules increases at a given RH when a volumetric tensile stress is applied to the material. Contrarily, a compressive stress would lead to a decrease of the concentration. This trend has also been observed in experiments using wood [43].

G. Coupling coefficient

Referring to the poroelastic equations (10a) and (10b), the coefficient B plays a prominent role in the coupling between mechanics and water adsorption. According to Eq. (10a), at stress-free conditions $d\sigma = 0$, B describes the proportionality between swelling strain and concentration, commonly referred to as the swelling coefficient. In Eq. (10b), B describes the mechanosorptive effect, i.e., the influence of stress on adsorption behavior. Following Eq. (11), B equals

$$B = a_3 + a_4\sigma + a_5n + a_6n^2. \quad (22)$$

In classical linear poroelasticity, B is a constant and equals a_3 . Here we see that B is a linear function of stress and a quadratic function of concentration. Figure 4(a) shows the coupling coefficient as a function of the concentration at different stress levels. We see that B increases nonlinearly until $n \approx 25 \text{ mol dm}^{-3}$. This increase in swelling coefficient can be explained by the fact that in the beginning the water molecules fill the existing porosity resulting in reduced swelling. When more water molecules are adsorbed, new porosity is created accompanied by a weakening of the solid matrix due to hydrogen bond breaking. In Kulasinski *et al.* [12], a method to determine porosity in MD is documented and it was found that swelling scales linearly with the porosity change φ . Next to the porosity increase, also the volume occupied by the polymer chains (or solid matrix) can change, characterized by the solid matrix strain ε_s . In MD it is difficult to determine this solid matrix strain, since it is difficult to delineate the polymer or

FIG. 3. Prediction of the mechanosorptive behavior with poroelastic model: (a) influence of the volumetric tensile stress on chemical potential difference ($-\Delta\mu$) curves. (b) Influence of volumetric tensile stress on adsorption isotherms.

FIG. 4. (Color online) (a) Swelling coefficient B as a function of the volumetric tensile stress. (b) Undrained and drained bulk modulus as function of the concentration for two volumetric tensile stresses.

solid matrix domain at molecular scale. Both porosity increase and solid matrix strain contribute to the overall swelling strain and explain the increase of the swelling coefficient B . At high concentration, the solid matrix is found not to swell further (it even shrinks again), while the porosity still increases. These two competing strain mechanisms (porosity change φ and solid matrix strain ε_s) may explain the decrease of the swelling coefficient B for $n > 25 \text{ mol dm}^{-3}$. However, more detailed MD analysis is needed to confirm this hypothesis. Figure 4(a) shows the influence of a volumetric tensile stress on the swelling coefficient. We see that B increases with the volumetric tensile stress indicating the existence of a strong coupling between mechanical loading and adsorption, or the mechanosorptive effect.

We also determined by MD the swelling of a box of water molecules, when molecules are successively added (no solid matrix). The volume change allows to determine the swelling coefficient of bulk water. The constant swelling coefficient is represented in Fig. 4(a) by the dashed line. We observe that the maximum swelling coefficient of the polymer at zero stress equals the swelling coefficient of water. At that moment the volume of every water molecule added to the material results in an equal change in volume of the material. This observation confirms the statement of Kollmann and Côté [36], indicating that, if wood swells like a gel, the volume of the colloidal structure would increase approximately with the volume of the absorbed water. However, they further point out that many wood species do not follow this trend. Our results show that cellulose almost acts as a gel at $n = 25 \text{ mol dm}^{-3}$, but that the interaction of water molecules with the solid matrix is also much more complex, involving probably as well first an increase and then a decrease of the solid matrix strain as indicated above. We finally remark that our results of nonmonotonous swelling are in line with theoretical polymers' physics models which take into account both elasticity of polymer chains and short-range interactions between monomer units including hydrogen bonding [44].

H. Drained and undrained bulk modulus

In the MD simulations, we determine the bulk modulus in undrained conditions, meaning that first water molecules are

added until the required concentration, after which we keep the number of molecules constant and perform the mechanical test to determine the bulk modulus. During mechanical loading no water molecules can enter or leave the material.

Using the poroelastic model we can also derive the drained modulus. Here the water molecules can enter or leave the material, while keeping the chemical potential constant. Drained conditions are often assumed in experiments, where the mechanical test is performed in an environment with constant chemical potential (or RH). It is then assumed the mechanical test is performed sufficiently slowly such that the material can equilibrate with the outside environment at all times. For determining the drained modulus, we introduce $d\mu = 0$ into Eqs. (10a) and (10b), obtaining

$$K_d = C_d^{-1} = \frac{K_u}{1 + B^2 M K_u}, \quad (23)$$

where the moisture capacity M is determined using Eq. (9c):

$$M^{-1} = \frac{d\mu_0(n)}{dn} - a_5\sigma - 2a_6\sigma n. \quad (24)$$

The last equation shows that the moisture capacity M is function of both concentration and stress. In classical poroelasticity, the moisture capacity depends only on concentration. Equation (23) shows that the drained modulus K_d depends on the coupling coefficient B , moisture capacity M , and undrained K_u modulus K_u . The MD results showed that the undrained modulus depends only on concentration in the considered stress range [0, 100 MPa], while, since B and M depend both on concentration and stress, the drained modulus also depends on both the stress and concentration. This is maybe a counterintuitive result. In the drained case, additional water molecules can enter the pore system, when the pore space is enlarged due to mechanical loading. These additional molecules will break more hydrogen bonds, leading to additional mechanical weakening and as such to a reduction of the drained stiffness. This explains why the drained modulus depends both on fluid concentration and mechanical stress. Figure 4(b) compares the undrained and drained modulus as a function of the fluid concentration. We also analyzed the drained modulus at two volumetric tensile stress levels: 0 and 100 MPa. The drained modulus is lower than the undrained

modulus and the drained modulus further decreases with increasing volumetric tensile stress.

IV. CONCLUSION

In this work, we derived the poroelastic constitutive equations valid for a disordered porous medium of nanometer pore size, in which all fluid molecules are in an adsorbed state. In these porous media, the fluid molecules are not in their bulk state and the use of classical poroelasticity breaks down. The use of the classical fluid state variables, such as bulk fluid pressure and fluid content, is not unambiguous anymore since the fluid adsorbed in the pores is not in the bulk state. In this model, we use the chemical potential and molar fluid concentration as adequate fluid state variables to describe the state of the adsorbed fluid in the nanoporous material.

The material studied is a biopolymer, amorphous cellulose, for which adsorption and swelling behavior, as well as the moisture dependence of mechanical properties, are studied by performing molecular simulations. The molecular simulations show that the swelling curve is nonlinear and that adsorption is governed by a pore filling process instead of a surface covering or capillary condensation process. The molecular simulations also show a mechanical weakening process with increasing concentration, which can be attributed to the breaking of hydrogen bonds in the cellulose chains. These bonds are replaced by water-cellulose bonds, which explains the decrease of bulk stiffness. The molecular simulations allow to determine the chemical potential, or the energy state of the adsorbed molecules, which in turn allows to determine the adsorption isotherms.

The full determination of the poroelastic behavior of a porous medium requires the knowledge of how the chemical

potential depends on both the fluid concentration and stress on the medium. In this paper we propose an alternative approach using a mixed higher-order formulation of the free energy including mechanical and fluid contributions and the coupling between fluid and mechanics. The model leads to the explicit formulation of the dependence of the poroelastic properties on stress and liquid concentration. To determine the necessary coefficients in the energy formulation, the MD results of adsorption, nonlinear swelling at zero stress, and mechanical weakening of the bulk stiffness are used. The model is validated by MD testing using a different moisture-mechanical loading protocol.

We found that the model describes a mechanosorptive effect, meaning the isotherm of adsorption is dependent on stress. We found that the drained bulk modulus becomes stress dependent, even when the porous medium behaves linearly in undrained conditions. The coupling coefficient was identified as the swelling coefficient, which is dependent on fluid concentration, but also changes under mechanical loading. At low concentrations, the water molecules fill first the existing initial porosity, inducing little swelling. Interestingly, the swelling coefficient for cellulose attains values which equal the swelling of a gel-like material, where the volume of the material increases approximately with the volume of the absorbed water. The particular dependence of the nonlinear swelling coefficient on concentration has been attributed to two strain mechanisms, porosity change and solid matrix strain. Further detailed molecular studies are needed to identify these different mechanisms, which may lead to the enhancement of mechanical poroelastic models.

The poroelastic constitutive equations have been developed for a particular nanoporous material, amorphous cellulose, but this approach is generally applicable to other materials, where adsorption induces an important mechanical response.

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