# Physicochemical Basis for Water-Actuated Movement and Stress Generation in Nonliving Plant Tissues

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Generating stresses and strains through water uptake from atmospheric humidity is a common process in nature, e.g., in seed dispersal. Actuation depends on a balance between chemical interactions and the elastic energy required to accomplish the volume change. In order to study the poorly understood chemical interactions, we combine mechanosorption experiments with theoretical calculations of the swelling behavior to estimate the mechanical energy and extract the contribution of the chemical energy per absorbed water molecule. The latter is highest in the completely dry state and stays almost constant at about 1.2 kT for higher hydrations. This suggests that water bound to the macromolecular components of the wood tissues acquires one additional hydrogen bond per eight water molecules, thus providing energy for actuation.

Nature shows many examples of nanocomposite tissues comprising soft materials reinforced by complex architectures of stiff components. Their hierarchical structure is tailored to bear and distribute loads [1,2]. Generally, water is an important component of these materials, which are carefully designed to optimize the interactions of their molecular or macromolecular components with water to obtain the desired properties. In many tissues, the chemistry of the constituents drives water absorption that, thanks to the peculiar arrangement of the macromolecular components or to their structure, results in anisotropic volume changes (swelling). This swelling and deswelling has been shown to generate complex (ametabolic) movements that are exploited in nature for different aims as, for example, the opening of pine and spruce cones [3] or other plants' seeds dispersal units [4–6], swimming of wheat awns [7], and self-planting of *Erodium Cicutarium* [8,9]. In a similar way, swelling is responsible for the growth of stresses in trees to compensate for the load of branches or of side winds [10]. In the aforementioned examples actuation is a structure mediated, chemomechanical energy conversion process of recognized efficiency, where the molecular forces are exploited at the nanometric level to generate mechanical energy [11]. For this reason, many of these systems have been recently taken as a source of inspiration for the realization of actuators [12,13]. Typically, the "fuel" for these processes are H-Bond formation or breaking or entropic forces associated with the dilution of the molecular or macromolecular components. As no intramolecular bonds are broken, these swelling processes are easily reversible and can be controlled by changes in the environmental relative humidity (RH) or, in general, by changes of the chemical potential of the swelling agent. Nevertheless, the partial free energy density associated with water sorption is relatively high (around 400 MPa for the first molecules absorbed), so that, potentially, significant mechanical work can be accomplished. However, the extent of the actuation is largely dominated by the cell structure, that has to be stiff enough to transform the sorption free energy differences in directional stresses and soft enough not to hinder water sorption.

Water sorption by wood tissues has been thoroughly investigated although many aspects remain elusive (see [14] for an overview and [15] for a review of the critical aspects). Also, since the seminal work of Barkas [16], the dependence of the moisture content from the applied stress (hygroelastic effect) has been the object of several papers, but a model describing the free energy changes of the wood cells under swelling has not been developed so far.

In this Letter, starting from a simple mechanical model [17] and using the thermodynamics of open system, elastic, bodies, we define a constitutive equation for solvent sorption in a composite material constituted by a stiff, inert component and a swelling matrix. The model is suitable to describe wood cells. We give explicit solutions for the problem in the free swelling case and when the cell is not allowed to swell in the axial direction. Finally, using a simple tensile testing setup, we test the validity of the model and assess the chemical potential of water in a wood cell undergoing swelling in the specific case of a high microfibrillar angle tissue (compression wood).

*General equilibrium.*—The solvent uptake of a composite material can be described considering the sorption

equilibrium between a solid phase (the absorbent, i.e., the swelling matrix) and a mobile phase (the absorbate, water in this case) that can be exchanged between the absorbent and the gas phase. The total energy change of the wood-water system by absorption of a small amount of water $dN$ has to be 0:

$$dG^c + dG^e - v_m \Pi dN = 0. \tag{1}$$

The first term is the chemical energy change in the tissue resulting from the interaction between the solvent and the macromolecular constituents of the wood tissue (i.e., hemicelluloses and lignin); the second is the elastic energy change due to the distortion of the tissue, and the last term is the chemical energy change in the surrounding medium at osmotic pressure $\Pi$ (or chemical potential $v_m \Pi$). $N$ is just the number of mols of water (with molar volume $v_m$) inside the tissue that are in equilibrium with the osmotic pressure $\Pi$. As a consequence, all quantities at equilibrium will be functions of $\Pi$ and Eq. (1) defines an implicit relation between $N$ and $\Pi$, i.e., the sorption isotherm. The function $N(\Pi)$ can be determined experimentally by gravimetry. Here we try to extract $dG^c/dN$ and $N(\Pi)$ from mechanical experiments. To do so we need to express $dG^e/dN$ in terms of quantities experimentally measurable. The type of experiment we perform is a uniaxial testing along the macroscopic wood fiber direction which we call $x$. The fiber is placed in air at controlled humidity, so that, for temperatures close to room temperature, $v_m \Pi = RT \ln(\text{RH})$ in Eq. (1), where RH is the relative humidity of the air, $R$ is the universal gas constant and $T$ is the temperature.

*Mechanical equilibrium.*—If the volume of the $N$ water molecules in the wood tissue ($v_m N$) is small with respect to the total volume $V$, its volume fraction $\phi$ is related to the total eigenstrain of the tissue $\eta$ as follows:

$$\eta = \frac{v_m N}{3V} = \frac{\phi}{3}. \tag{2}$$

We consider wood cells subjected to external stresses and strains along the $x$ direction (as defined in Fig. 1) only and swelling due to changing environmental air humidity. Following the treatment in [17], the elastic behavior is described as follows, with the assumption of plane stress ($\sigma_3 = 0$):

$$\frac{1 - \nu^2}{E} \sigma_1 - f\epsilon_1 = (\epsilon_1 - \eta) + \nu(\epsilon_2 - \eta),$$

$$\frac{1 - \nu^2}{E} \sigma_2 = \nu(\epsilon_1 - \eta) + (\epsilon_2 - \eta), \tag{3}$$

$$\frac{2(1 + \nu)}{E} \tau_{12} = \gamma_{12},$$

we denote $\sigma_1$, $\sigma_2$, $\tau_{12}$ as tensile stresses in direction 1 and 2 and the shear stress, respectively, while $\epsilon_1$, $\epsilon_2$, $\gamma_{12}$ are the corresponding strains. $E$ and $\nu$ are Young's modulus and Poisson's coefficient of the (isotropic) matrix surrounding
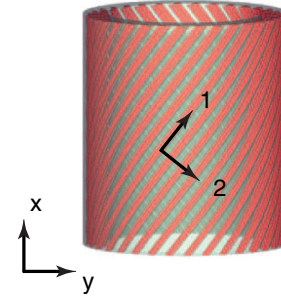


FIG. 1 (color online).   Schematic view of a wood cell and its reference systems. The microfibrillar angle $\mu$ corresponds to the pitch angle of the helix. The direction $x$ coincides with the longitudinal direction of the wood tissue.

the cellulose fibrils, respectively. The parameter $f$ corresponds to the stiffening of the composite in direction 1 (see Fig. 1) due to the cellulose fibrils. With $f = 0$, Eq. (3) would correspond to an isotropic material.

It is important to note that the right side depends on the difference between total strain and eigenstrain, while the term due to fibril stretching on the left side is proportional to the total strain. In this model, the fibers act as an external constraint with respect to the swelling matrix. Without any constraints, the matrix would swell by $\eta$ in each direction and no elastic energy would be stored at all. The fibers, however, counteract this swelling and introduce elastic strains.

With the standard equations for tensor rotation, we obtain a stress-strain curve in the $x$ direction (if no torsion of the cell is allowed, i.e., $\gamma_{xy} = 0$):

$$\sigma_x = Y_e(\epsilon_x - \bar{\alpha}\eta), \tag{4}$$

where $Y_e$ is the effective Youngs modulus

$$Y_e = \frac{E}{1 - \nu^2} \frac{1 - \nu^2 + f[1 - 2(1 + \nu)m^2 n^2]}{1 + f n^4} \tag{5}$$

and $\bar{\alpha}$ is

$$\bar{\alpha} = (1 + \nu) \frac{1 - \nu - f(m^2 - n^2)n^2}{1 - \nu^2 + f[1 - 2(1 + \nu)m^2 n^2]}, \tag{6}$$

where $m$ and $n$ are respectively the cosine and the sine of the microfibrillar angle (MFA) $\mu$ defined in Fig. 1. The strains in the other directions can also be calculated as a function of the strain in the $x$ direction [18]. Since the matrix is a linear elastic solid, the elastic strains are just $\tilde{\epsilon}_x = \epsilon_x - \eta$, $\tilde{\epsilon}_y = \epsilon_y - \eta$ and $\tilde{\epsilon}_z = \epsilon_z - \eta$. There are no shear terms and the elastic energy density stored in the (isotropic) matrix loaded under the plane stress condition is

$$e_m = \frac{1}{2} \sum_{i=x,y,z} \sum_{j=x,y,z} \tilde{\epsilon}_{ij} \sigma_{ij}$$

$$= \frac{1}{2} \frac{E}{1 - \nu^2} (\tilde{\epsilon}_x^2 + \tilde{\epsilon}_y^2 + 2\nu\tilde{\epsilon}_x\tilde{\epsilon}_y). \tag{7}$$

The elastic energy stored in the cellulose fibers $e_f$ can be determined using the first line in Eq. (3) where the additional stress to the fibers is $-fE\epsilon_1/(1 - \nu^2)$. Therefore,

$$e_f = \frac{1}{2}\frac{fE}{1 - \nu^2}\epsilon_1^2 = \frac{1}{2}\frac{fE}{1 - \nu^2}(m^2\epsilon_x + n^2\epsilon_y)^2. \quad (8)$$

Combining Eqs. (7) and (8), the total elastic energy stored in the composite is

$$e = e_m + e_f = \frac{1}{2}E\frac{f\eta^2 + (1 - \nu^2)(1 + fn^4)\sigma_x/E^2}{[1 - 2(1 + \nu)m^2n^2]f + 1 - \nu^2}, \quad (9)$$

where we have used Eq. (4) and the relation $\epsilon_y = [(\nu + m^2n^2f)\epsilon_x - (1 - \nu)\eta]/(1 + fn^4)$.

It is of particular interest for our scope to consider the energy changes after an amount of water was taken up under free swelling (i.e., $\sigma_x$ set to 0) or clamped ends (i.e., $\epsilon_x$ set to 0).

The elastic energy can be written as $e = kE\eta^2/2$, with the coefficient $k$ given by

$$k = \frac{f}{(1 - 2(1 + \nu)m^2n^2)f + 1 - \nu^2} \quad (10a)$$

$$k = \frac{1 - \nu + 2fn^4}{(1 - \nu)(1 + fn^4)}, \quad (10b)$$

respectively, for the free swelling (10a) and the constrained case (10b). The dependence of $k$ on the MFA is reported in Fig. 2. The elastic energy associated with a water content change of $\eta$ is in general lower for the free swelling case, as expected, the difference being small at low MFA, but becoming almost 3 times larger at high microfibrillar angles.
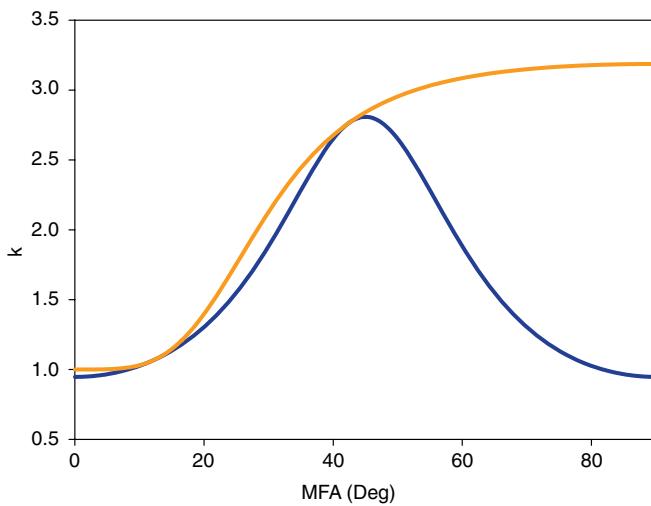


FIG. 2 (color online).   Dependence of $k$ on the MFA for the free swelling (blue curve) and constrained ends (orange curve) cases. Curves are calculated for $f = 15$ and $\nu = 0.4$.

Going back to Eq. (1) and making use of (2)

$$\frac{dG^e}{dN} = \frac{d}{dN}\left(\frac{1}{2}VkE\eta^2\right) = v_m\frac{1}{9}kE\phi. \quad (11)$$

Because of the small strain setting, we are neglecting the dependence of $V$ and $k$ on $N$. Large strains could in principle be considered in a framework similar to what was used in a previous work ([19]). From the latter expression, Eq. (1) can be rewritten as

$$\frac{dg^c}{d\phi} = \Pi - \frac{1}{9}kE\phi, \quad (12)$$

where we have defined the free energy change per unit volume as $g^c = G^c/V$. This expression provides a way to determine the chemical potential of water in the wood tissue starting from mechanical measurements. If the chemical potential is known, it defines the sorption isotherm of the wood cells under free swelling, with $k$ defined by Eq. (10a), or when no swelling in the axial direction is allowed, with $k$ defined by Eq. (10b), giving a description of the actuation and stress generation of the wood cells. Also, the model presented here can be generalized in the case of arbitrary boundary conditions to describe, for instance, the hygroelastic effects (i.e., the change in moisture content under a given applied stress) or the dependence on the MFA of the generated stress under restrained swelling.

*A representative case: compression wood.*—A relation between the axial strain in a free swelling experiment and the eigenstrain $\eta$ can be derived as

$$\epsilon_x = \eta(1 + \nu)\frac{[1 - \nu + f(2n^4 - n^2)]}{1 - \nu^2 + f[1 - 2(1 + \nu)m^2n^2]}. \quad (13)$$

Using the parameters $f$ and $\nu$ as given in the caption of Fig. 2 and the microfibrillar angle $\mu \approx 50°$, as measured by x-ray diffraction [18], we extract $\eta$ from this equation by measuring $\epsilon_x$ as a function of relative humidity in a tensile stage coupled to a humidity chamber [18]. Through Eq. (2), $\eta$ can be directly related to the water volume fraction $\phi$ in the tissue. This finally results in a relation between $\phi$ and RH, as shown in Fig. 3(a).

In the same figure, these values of $\phi$ calculated from mechanical experiments are compared with those obtained gravimetrically. The calculated volume uptake compares satisfactorily with the measured ones, indicating that the model captures the volume changes due to the water uptake remarkably well. For this reason we can confidently use Eq. (11) to assess the mechanical energy needed to swell the wood cell of a given $\eta$. To do so, we require a reasonable value for the Young's modulus of the matrix surrounding the cellulose fibers $E$. Using Eq. (13), this can be evaluated from the measurement of the Young's modulus $Y_e$ of the wood cell tissue at constant $\phi$ in a simple tensile test. As $E$ changes with the water content, the measurement was repeated at different $\phi$'s.
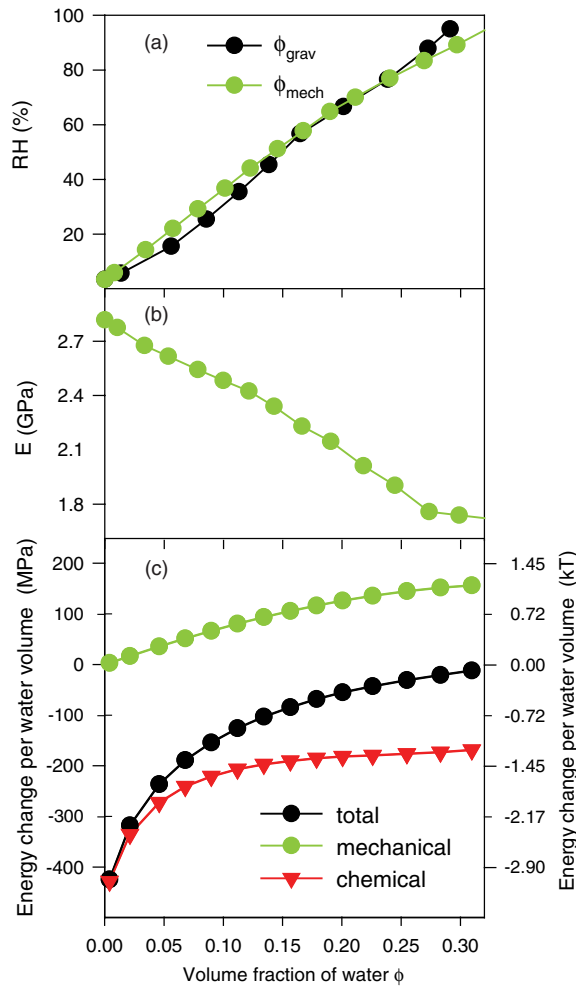
FIG. 3 (color online). (a) Comparison between the calculated volume fractions of water $\phi$ as a function of the relative humidity (RH). Green: from mechanical experiments. Black: from gravimetric measurements. (b) Dependence of the Young's modulus of the matrix $E$ on the water volume fraction. (c) Balance of energy density changes according to Eq. (12). Green: elastic energy. Black: total energy. Red: calculated chemical energy. The values are reported for a compression wood tissue with a measured $\mu$ of 50° and using $f = 15$, $\nu = 0.4$.

The calculated $E$ values are reported in Fig. 3(b) and both the absolute values and their change with moisture compare with typical values reported in literature for wood polymers [20,21]. The significant lowering of $E$ with hydration (in this case it reduces to about 60% of the dry value close to saturation) is typical for solid materials dominated by H bonds [22,23], as the wood polymers are, and is due to the reduction of the effective density of H bonds with increasing water content. Using these values for $E$ we calculated the free energy change required to swell the wood cells using Eq. (11). The resulting curve is plotted in Fig. 3(c) (green), together with the total energy (black) and the free energy change term due to the molecular interactions of water with the wood cell molecular

components (red). The latter was calculated through Eq. (12). The elastic term of the free energy change reaches fairly high values, that are about half of the chemical potential of water in the gas phase at very low relative humidity and exhibits changes, at average to high volume fractions, on the order of 1.2 kT. The chemical free energy change decreases steeply for values of $\phi$ in the 0–0.15 range, but keeps stable afterward at an average value that corresponds to $\sim$1.2 kT. Taking into account that configurational entropy gains at these volume fractions (larger than 0.15) are typically lower than 1/2 kT this free energy difference seems to arise from a different bonding state of water in the confined spaces of the wood tissues with respect to the bulk phase. Taking 9.5 kT as the value for the H-bond enthalpy in bulk water at room temperatures [24], the water absorbed in the wood tissues, for volume fractions higher than 0.15, is then characterized by a 15% stronger H-bond network with respect to the bulk liquid. This energy difference of 1.2 kT is in between the one at the high density liquid to low density liquid transition (about 0.5 kT at 200 MPa [25]) and that at the freezing point (around 2.5 kT). This would suggest that the main driving force for water absorption in non living plant tissues is a phase transition of water to a liquid state, characterized by a stronger H-bond network, occurring when $H_2O$ is confined within the macromolecular components of the wood cell wall material.

With the energy balance presented in this Letter, we attempted for the first time to describe quantitatively the chemical potential of water in the wood cell walls taking into account the mechanics of the swelling cells. The model, in general, is suitable to describe quantitatively the actuation as well as the volume changes coupled to deformation for composite materials constituted by a soft, swelling, material reinforced by stiff, inert, fibers and allows us to extract the thermodynamics functions from mechanical experiments.

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