

**PAPER**

Chemical, colloidal and mechanical contributions to the state of water in wood cell walls

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**Abstract**

The properties of wood depend strongly on its water content, but the physicochemical basis for the interaction of water with cell wall components is poorly understood. Due to the importance of the problem both in the context of wood technology and the biological function of swelling and dehydration for growth stresses and seed dispersal, a wealth of descriptive data has been accumulated but a microscopic theory of water-biomolecular interactions is missing. We develop here, at a primitive level, a minimal parameter-free, coarse-grained, model of wood secondary cell walls to predict water absorption, in the form of an equation of state. It includes for the first time all three—mechanical, colloidal and chemical—contributions, taking into account the cell walls microstructure. The hydration force around the elongated cellulose crystals and entropy of mixing of the matrix polymers (hemicelluloses and lignin) are the dominant contributions driving the swelling. The elastic energy needed to swell the composite is the main term opposing water uptake. Hysteresis is not predicted but water uptake versus humidity, is reproduced in a large temperature range. Within this framework, the origin of wood dissolution and different effects of wood treatments on water sorption can be understood at the molecular level.

1. Introduction

Water is an essential component of the wood cell walls that controls its mechanical performance both in sustaining and generating forces. Elastic modulus and hardness depend on the state of hydration [1, 2] and it is well known that dehydration generates anisotropic shrinkage which is relevant for wood as an engineering material. But water uptake is also essential for biological functions by generating growth stresses in trees [3] or by providing seed mobility [4]. While hygromechanical properties of wood have been extensively studied [5, 6], the physicochemical basis for the interaction of water with cell-wall components are poorly understood. Previous approaches mostly had the central objective of long-term wood protection against moisture uptake. Increasing wood life-time in the field, in fact, is a long-term technological problem related to both dimensional stability and resistance to biological degradation of wooden products. Cheap, effective but extremely toxic creosote impregnation has been in use for over 300 years. However, it was banned in the European Union for consumer use in 2003 and industrial use in 2013. As a replacement for this coal-tar based treatment, wood research has focussed on alternative impregnations and chemical modifications to limit the water uptake. The effectiveness of the methods is normally assessed by measuring the water uptake by the modified/treated wood as a function of the water activity. For this reason, a vast amount of experimental data (sorption isotherms) were and are still being collected, and a lot of mathematical models (more than 70, according to [7]) have been proposed to describe the sorption of water by wood. However, most of these are parametric models and they results from the lack of first principles frameworks considering wood cell walls material as a hybrid containing cellulose crystals and a tri-component interstitial gel, composed of water/hemicelluloses and lignin. Taking into account the microstructure at chemical, colloidal (mesoscopic) and macroscopic scales as proposed recently [8] allows for

the replacement of a multi-parametric approach with an equation of state (EOS), which is derived from the conservation of free energy. Here, starting from the molecular level via the meso-scale to the macroscopic one, we use a force balance approach to develop, a minimal, parameter-free, model of wood secondary cell walls to predict water absorption, in the form of an EOS. EOSs are derivatives of the free energy versus structural parameters changes. In physical chemistry literature, EOSs are expressed as osmotic pressure versus distances and/or density determined by scattering, while in chemical engineering and wood technology, the EOSs are expressed as equilibrium water content versus relative humidity, but these two representations are equivalent [9]. Modelling as an EOS, including molecular forces as long range interactions (LRI) [10] and taking into account microstructures, was first applied to bilayer membrane stack of phospholipids [9] and then to colloidal crystals of latexes [11], hexagonal lyotropic liquid crystals [12], cross-linked gels [13], DNA [14, 15], collagen [16], polysaccharides [17] and PEG [18]. All of these EOSs became crucial to predict/understand the systems stability versus solvent chemical potential. We apply here the same methodology to the secondary cell walls of soft wood tissues taking into account the chemical, physicochemical and macroscopic elastic term.

Our aim is to establish the simplest possible EOS at the 'primitive level' (water as a homogenous continuous medium) for wood cell walls as model system. We avoid treating any non-measurable quantities as parameters and combine molecular forces with macroscopic elasticity under the assumption that they additively contribute to the total force.

2. Physicochemical basis

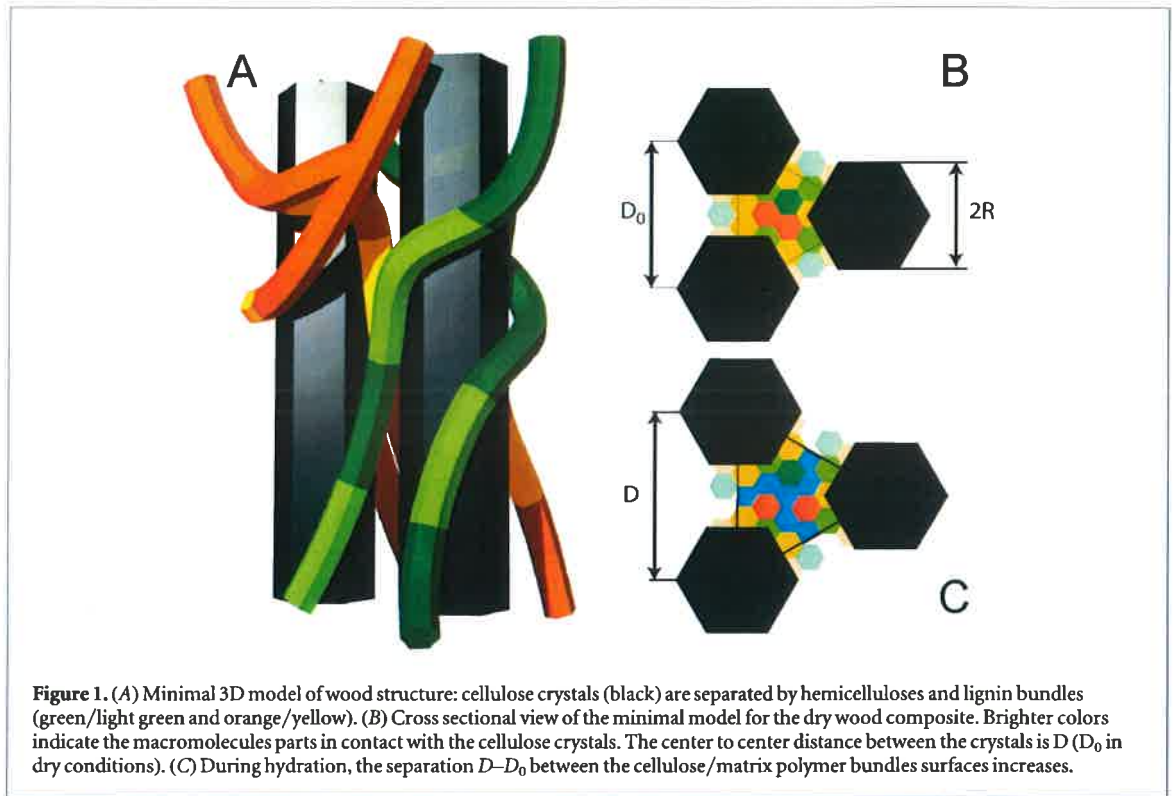
To model a minimal EOS the microscopic/molecular contributions to the total energy are decomposed here in chemical first neighbour enthalpy and colloidal LRI including water mixing entropy acting at nano-scale. These are combined with the macroscopic elastic terms using a constitutive equation developed for fibre reinforced nanocomposites. The secondary cell walls are modeled here as stiff, inert nanocrystals of cellulose all parallel to each other embedded in a softer, hygroscopic matrix of amorphous polysaccharides (hemicelluloses) and lignin. At the microscopic (colloidal) level, we consider the hydration repulsion and the mixing entropy term of the water as a solute in the swelling matrix between the cellulose crystal as main repulsive terms. Dominant attractive forces are taken in this work as an attractive mechanism linked to the adsorption enthalpy of matrix polymers cross-linking to crystalline cellulose fibers as well as the elastic energy stored in the composite while swelling.

2.1. Geometric model

To express the energy changes as a function of the water content and the composition of the cell walls, and to link them to structural changes the cell walls undergo while swelling, a geometrical model is required. We build our geometric model (see figure 1) starting from a structural model proposed by Altanaer *et al* in which the nanocrystals of diameter $2R$ equal to 2.5 nm [19] are embedded in a gel matrix of hemicelluloses and lignin [20]. The composition of typical soft wood secondary cell walls (adult wood), in dry conditions, can be approximated as 50% cellulose, 20% hemicelluloses and 30% lignin [21]. For the sake of simplicity, we consider the cellulose crystals as hexagonal and arranged in an hexagonal lattice, with a center to center distance D . The hemicelluloses and lignin are treated as linear macromolecules which are in contact with the cellulose crystals in specific points named contact points (brighter regions of the polymers in figure 1). Whether the hemicelluloses and lignin fill the space between the microfibrils or they separate larger bundles of packed microfibrils (often called macrofibrils) is still not clear. Although this is an important detail to build a correct geometrical model for the system, as we lack definitive data, we will assume that the non-cellulosic component of wood cell walls are homogeneously distributed in between the cellulose microfibrils. This is a reasonable assumption as the typical microfibrillar distance changes with hydration and because the hemicelluloses are supposed to drive the swelling by water. Also, here, we consider cellulose crystals as single, water inert, units. This can be justified considering that they are insoluble and very stable in hydrated environment because of strong intermolecular H-bonds and hydrophobic interactions [22]. Under these assumptions, we can picture the wood cell structure as depicted in figure 1, where the black hexagonal prisms represent the unswellable cellulose crystalline domains, while the orange and green prisms depict the non-cellulosic macromolecular constituent. The moisture content can be expressed as a function of the cellulose nanocrystals separation D and the amount of non-cellulosic content as:

$$MC = \frac{\rho_w}{\rho_{cw}} \left(\phi_c \left(\frac{D}{2R} \right)^2 - 1 \right) \quad (1)$$

where ρ_w and ρ_{cw} are respectively the densities of water and the cell walls material, ϕ_c the volume fraction of the cellulose component of the cell walls and R is the apothem of the cellulose crystals that are considered hexagonal prisms.



The center to center distance between cellulose crystals at 0 MC (i.e. in dry conditions) can be readily calculated as:

$$D_0 = \frac{2R}{\sqrt{\phi_c}} \quad (2)$$

As measured by small angle x-ray and neutron scattering (SAXS and SANS), the average distance between the crystals increases with hydration [19, 23] reaches about 4.2 nm in the wet state. In our model, D then becomes larger and larger as the water is taken up and the average surface separation of the cellulose-matrix bundles, $D - D_0$, increases. Taking the density of the wood cell walls material to be about 1.5 g cm^{-3} , the water density as 1.0 g cm^{-3} , a 50% content of cellulose for secondary cell walls and 1.25 nm as the radius of the cellulose crystals, their separation would be about 3.5 nm in dry conditions and 4.2 nm around the fiber saturation point (MC ≈ 0.3) which is in good agreement with the above mentioned x-ray and neutron scattering data.

Also, the total volume fraction of water, i.e. the ratio between volume of absorbed water and the total volume of cell walls and water, can be expressed as:

$$\phi_w = 1 - \frac{1}{\phi_c} \left(\frac{2R}{D} \right)^2 \quad (3)$$

The definition of this geometrical model sets a framework to carry out the the calculation of the molecular force balance. Here, all the derivatives are taken versus the same dimension at nano-scale, the spacing D and considered for a unit length h of the lattice.

The choice of D as the easily observable spacing between cellulose fibers allows a convenient graphical representation of the different terms in the molecular forces balance equilibrating at each relative humidity (RH). In osmotic pressure units, i.e. Π versus D , this representation has been used in biophysics considering for example the case of DNA gels [15]. This can be converted in partial molar free energy versus solvent volume fraction, which is useful to extend the treatment to other solvents than pure water [24], or in a sorption isotherm which is more commonly used in wood chemical engineering, where the moisture content is plotted versus RH, i.e. the water activity. The conversion between the different units is carried out here assuming the partial molar volume of water to be constant (18 g cm^{-3}). As shown on figure A1, as unit cell for calculations we use an infinite hexagonal prism with a central axis on cellulose crystals. This Voronoi polyhedron allows for the complete tessellation of the macroscopic wood cell wall.

2.2. The constitutive equation

The relationships between D and Π can be formalized using a constitutive equation adapted from [8] where microscopic chemical, mesoscopic colloidal and macroscopic elastic term are combined (respectively m , c and e superscripts):

$$dG^m(D) + dG^c(D) + dG^e(D) - \nu_m \Pi(RH) dN = 0 \quad (4)$$

3. Force balance

We now start to evaluate the different terms to be considered in the force balance. All the intermediate quantities we consider here are derived from geometry as deduced from micro-structural determinations and thermodynamic quantities available in literature.

3.1. Hydration force

The hydration force is a general repulsive mechanism associated with ordering of water at an interface [25, 26]. The contact pressure Π_0 is associated to the binding free energy difference between a water molecule coming from bulk with respect to one in the first layer close to a surface [27, 28], and the decay length of the exponential at the primitive level $\lambda \approx \sqrt[3]{0.03 \text{ nm}^3}$ is linked to the partial molar volume of water [27]. Recently, a successful generalization towards a universal exponential effective solvation including hydrophobic and hydrophilic terms in the form of an algebraic scalar, Hy , has been introduced [29]. The cell walls used here as model systems have a balanced hydrophile and hydrophobe interaction in between hemicellulose and lignin, so the dominant term is the hydration force between cellulose crystals. In the absence of salt, the secondary hydration force can be neglected, and we consider the primary hydration repulsion with a full Hy parameter taken as -1 [30].

The pressure is exerted on the planes of the prisms as shown in figure 1 and translates as an exponential variation with the surface separation $D - D_0$ as shown on figure 1(C). The contact pressure at $D = D_0$ is not a parameter, but can be derived from the initial slope of the gravimetric sorption isotherm on wood and taken as $\approx 5.8 \text{ kJ mol}^{-1}$ (see [31] and appendix A.3).

The energy per unit length h related to the hydration force between 2 hexagonal prisms of apothem D_0 can be expressed as:

$$\frac{\Delta G^{HF}}{h} = \frac{\overline{\Delta G}_0}{3} \frac{\sqrt{3}}{3} D_0 \lambda e^{-\frac{D-D_0}{\lambda}} \quad (5)$$

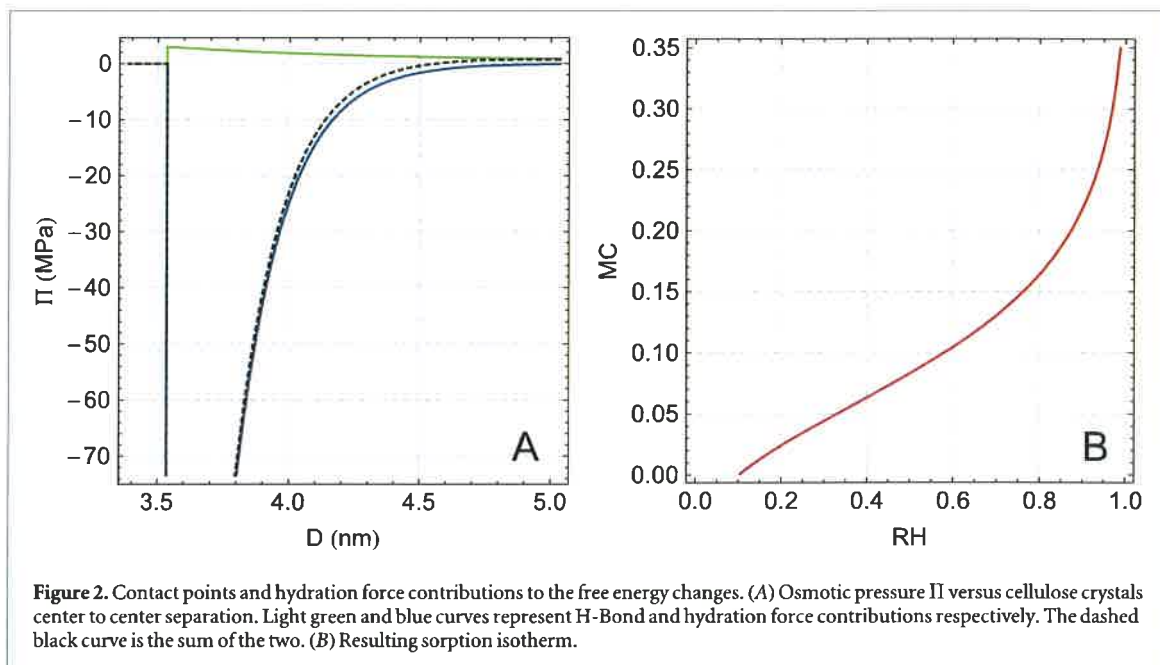
where $\overline{\Delta G}_0$ is the contact free energy density (energy per unit volume) related to the energy per mole spent to remove the last water layer between two surfaces, ΔG_0 , and λ is the typical decay length for the hydration force which we took as 0.19 nm , according to [32]. Note that, under the assumption that water molecules in the last water layer have a molar volume of \bar{v} , it holds $\overline{\Delta G}_0 = \Delta G_0/\bar{v}$. The pressure term can be readily obtained by derivation with respect to D :

$$\frac{d\Delta G^{HF}/h}{dD} = -\frac{\overline{\Delta G}_0}{3} \frac{\sqrt{3}}{3} D_0 e^{-\frac{D-D_0}{\lambda}} \quad (6)$$

Since in a unit cell we count 6 couple interactions belonging each to 2 cells, this term has to be multiplied by 3 in the force balance (*vide infra*, equation (10)).

3.2. Binding of polysaccharides and lignin to the cellulose crystals

At the colloidal scale, the main cohesive term opposing to dissolution and swelling of wood is the binding of matrix polymers to cellulose crystals. In general, the monomers are considered to have a difference in free energy when in the gel and when in contact with one cellulose crystal. In figure 1 the cross-linking network of lignin (orange) and hemicelluloses (green) are shown approximately to scale with cellulose crystals (black). Each 'contact point' is shown as brighter sections of the relative polymer. When water is taking apart cellulose nanocrystals, the number of contact points per unit length of matrix polymers decreases and this has a cost in free energy, as the total number of contact points per unit volume decreases. The analytical expression for this term and its derivation are detailed in the appendix A.4. Here, we consider only lignins to bind on cellulose crystals. In fact, although the binding of hemicelluloses to cellulose crystal has been (macroscopically) demonstrated on bacterial cellulose/mannan based polysaccharides systems [33], the interaction energy has never been measured and recent observations from molecular dynamic simulations seem to indicate that, at the molecular level, water molecules adsorbed at the cellulose interface and push away from it hemicellulose chains. On the other hand, lignin is largely constituted by aromatic moieties which interact with carbohydrate rings in hydrated environments. This interaction (sugar-aromatic stacking) is fundamental for molecular recognition of



carbohydrates, and has been extensively characterised in recent years. The enthalpy per contact point for sugars/ aromatic ring has been measured to be about $2.5 k_{\text{BT}}$ [34] in water.

The presence of contact points is then an attractive term in the force balance since it favours de-swelling, but is rather small compared to the hydration repulsion term (see figure 2(A)). Adding up the attractive mechanism due to cross-linking and the hydration force, one can calculate a partial equation of state combining the chemical term and the one due to mesoscopic microstructure (as detailed in section 3.6). These are shown in figure 2. In figure 2(A) the partial EOS is shown as a partial equation of state in pressure-distance usual form. With this partial EOS, the main features of swelling are not well captured: swelling goes well beyond 30% in MC (see figure 2(B)), and the water uptake at low humidities is significantly underestimated. The EOS calculated in terms of partial free energy vs. volume fraction is reported in figure C1(A).

3.3. Van der Waals

Another attractive term that is often of importance for colloidal complex fluids and structures, as for example for the adhesion of Gecko on vertical walls [35], is the Van der Waals term. In this case, the Van der Waals force computed between cellulose crystals acting across the inter-crystalline hydrated matrix has been found to be negligible, by at least two orders of magnitude (see appendix A.5).

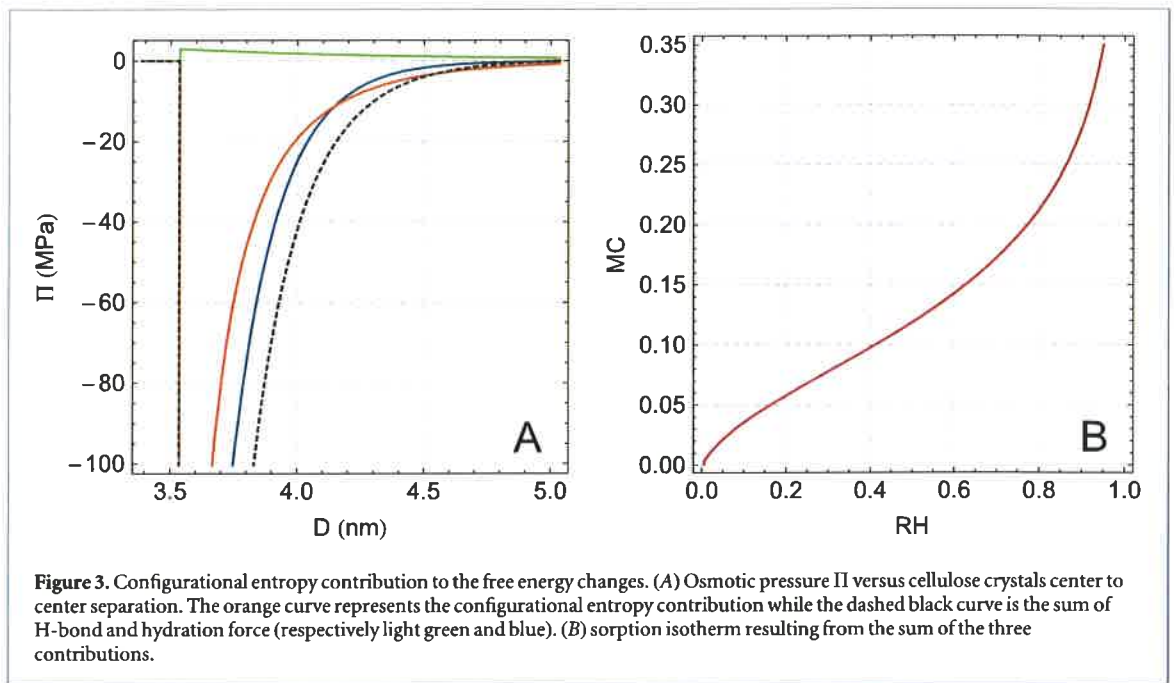
3.4. Mixing entropy

Mixing entropy is universal and dominated by the smallest molecule, in this case water, which is dispersed in an amorphous binary polymer mixture of hemicelluloses and lignin. This is also the dominant term in water uptake in ultra-flexible microemulsion near spontaneous emulsification [36]. For wood cell walls entropic contribution becomes important as was observed by Di Renzo *et al* [24] in swelling experiments in other solvents. The systematic maximum in excess swelling measured there appears always around 50% in mole fraction and underlies the importance of the mixing entropy in the force balance [37]. We estimate the partial free energy of mixing per mole from the classical expression given by Flory for the partial entropy of mixing, under the assumption that the polymer chains are of infinite length:

$$\frac{d\Delta G^S/h}{dD} = \frac{d\Delta G^S/h}{dN} \frac{dN}{dV} \frac{dV}{dD} = \sqrt{3} D \frac{RT}{\bar{v}} (\ln \phi_w^m + 1 - \phi_w^m + \chi_0 (1 - \phi_w^m)^2) \quad (7)$$

Where ϕ_w^m is a function of D as defined in equation (A.1) and χ_0 is the Flory interaction parameter at low polymer volume fractions. Here, we take χ_0 as 0.5 which is the value reported for many polysaccharides at water volume fractions larger than 0.2 at around room temperature [38]. Although the value of the interaction parameter depends on the composition, we consider it constant, as at low solvent volume fractions it accounts for direct solvent/solute interactions. In our model, this is already taken into account in the hydration force term as well as in the contact points term.

The scaling of this contribution with the center-to-center separation between the cellulose crystals is presented in figure 3(A). The entropic force is larger than the hydration force at very low water contents (where it



diverges) while it is lower at intermediate ones. Interestingly, at larger hydrations ($D > 4.1$ nm) it becomes comparable with the hydration force but decays slowly, so that it becomes dominant for very large hydrations. The dashed curve in figure 3(A) is the sum of all chemical—i.e. nearest neighbour—and mesoscopic LRI terms

The correction to the EOS introduced by taking into account the mixing entropy of water is shown on figure 3(B). The picture becomes now closer to measurements in the low moisture content regime, and the typical sigmoid shaped adsorption isotherm that has been the object of dozens of ‘ad hoc’ parametrizations emerges. Still, the behaviour at high humidities largely overestimates the experimental one for wood cell walls. The EOS calculated in terms of partial free energy vs. volume fraction is reported in figure C1(B).

3.5. Mechanical energy stored in the composite

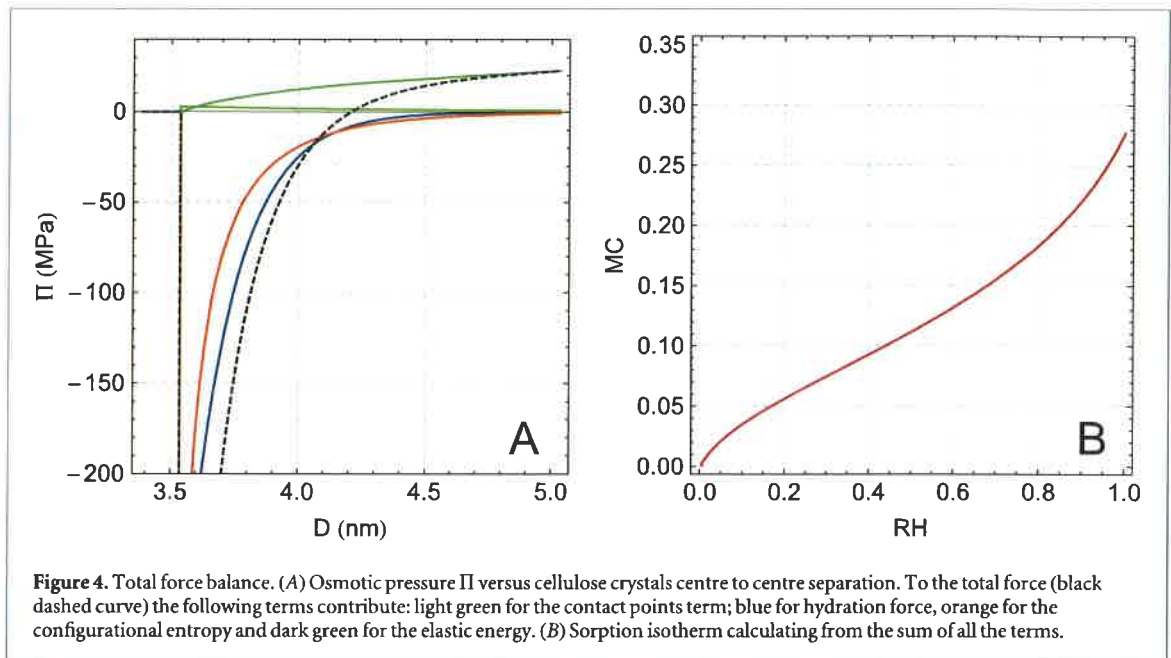
Also from a macroscopic point of view, secondary cell walls of wood tissues can be modelled using a minimal mechanical model: we consider solvent sorption in a composite material constituted by a stiff, inert component and a softer swelling matrix [39]. In this model, the fibers act as an external constraint with respect to the volume change (i.e. swelling) of the matrix. Without any constraints, the matrix would swell isotropically and no elastic energy would be stored at all. The stiff crystalline fibers, which are considered to be at rest in dry conditions, however, act as stiff springs and counteract this isotropic swelling. As a result, the material swells mostly in the directions perpendicular to the fibers and elastic strains are introduced. The associated elastic energy can be computed using a simple analytical model and depends on the winding angle and the relative amount of cellulose microfibrils as well as on the Young’s modulus of the matrix. Following the approach in [8], we know the total elastic energy per unit height stored in the unit cell of the composite during the swelling of can be expressed as:

$$\frac{\Delta G^{El}}{h} = \frac{1}{2} \frac{\sqrt{3}}{2} D^2 \frac{1}{9} k E \phi_w^2 \quad (8)$$

Where k is a constant depending on the microfibrillar angle (see equation (10a) in [8]), E is the moisture dependent Young’s modulus of the matrix surrounding the cellulose fibrils (which has been estimated to decrease from about 2.8 GPa in dry conditions to about 1.7 GPa around the fiber saturation point) and ϕ_w is the water volume fraction as defined in equation (3). The pressure term related to equation (8) is then:

$$\frac{d\Delta G^{El}/h}{dD} = \sqrt{3} D \frac{1}{9} k E \phi_w \left(1 - \frac{\phi_w}{2}\right) \quad (9)$$

This equation reveals that the force required to bring the cellulose crystals to a distance D is proportional to $kE/9$, which can be seen as an effective spring constant. In figure 4(A), the derivative of elastic energy stored in the composite with respect to the water content is reported for a very low microfibrillar angle (0–10 degrees) and compared to the other terms. The effective pressure term obtained in this way represents a second term restraining the swelling but it is significantly larger than the contact points term described above, especially at high hydrations.



3.6. The total force balance

Assuming that all the terms described so far combine in an additive way, we can now balance the forces in a unit cell and compute the EOS and the water sorption isotherm from equation (4) by combining equations (A.3), (6), (3), (A.8) and (9) as follows:

$$\frac{RT}{\bar{v}} \ln(RH) = \frac{\sqrt{3}}{3} \frac{1}{Dh} \left(3 \frac{d\Delta G^{HF}}{dD} + \frac{d\Delta G^S}{dD} + \frac{d\Delta G^{CP}}{dD} + \frac{d\Delta G^{El}}{dD} \right) \quad (10)$$

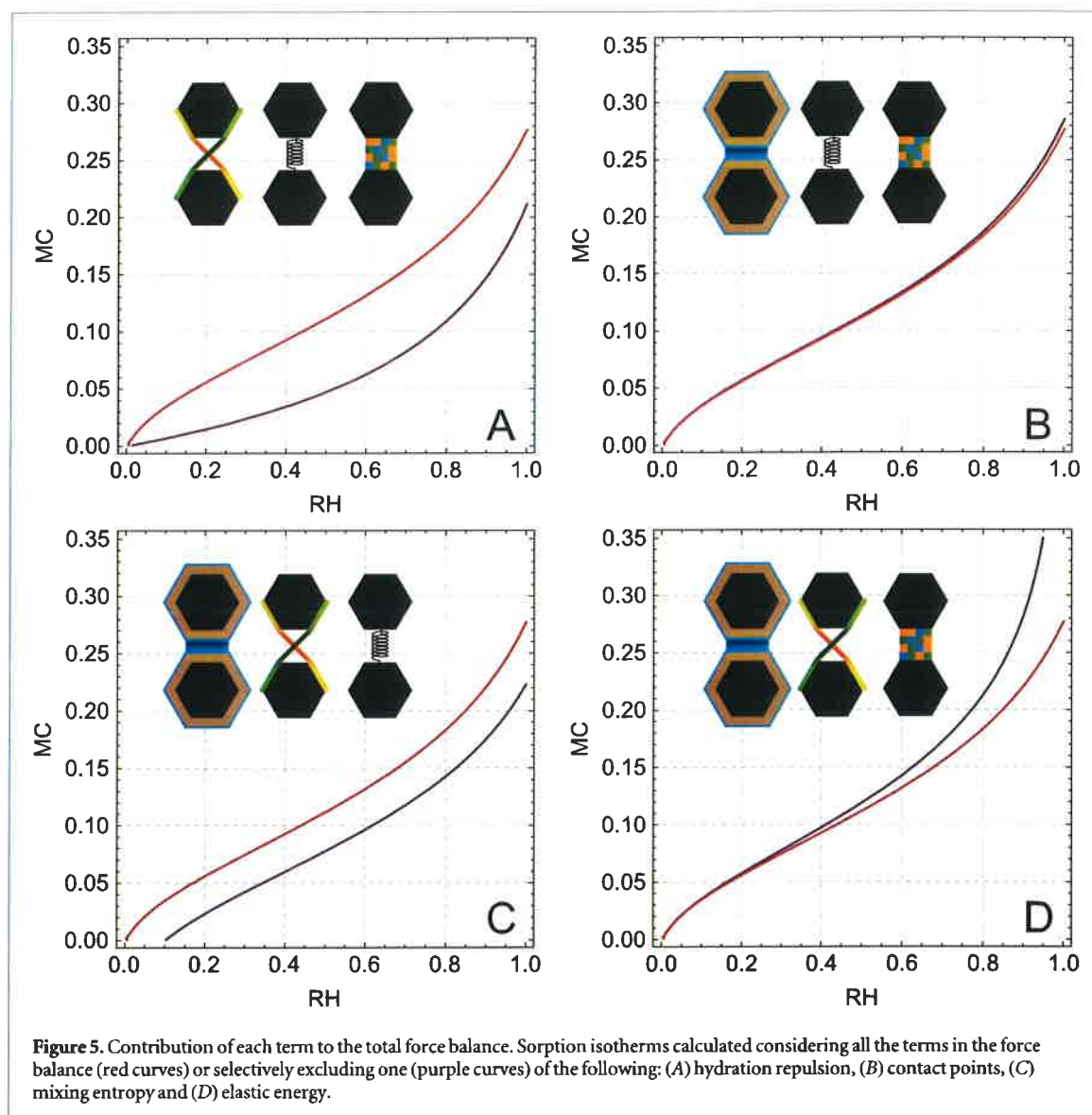
As mentioned above, here we omit the Van der Waals term because it is at least one order of magnitude smaller than the smallest term in equation (10) and therefore negligible.

The resulting graph in figure 4(B) shows that the relative moisture content versus relative humidity predicted by the model exhibits the characteristic sigmoidal shape, without divergence at high humidity as found for wood cell walls. At low to intermediates water contents, the dominant terms are hydration repulsion and mixing entropy, while the attractive terms are relatively small. At larger hydrations, the attractive cohesive terms, in particular the elastic one, start to be comparable in magnitude with the repulsive ones (see figure 4(A)) and the swelling is effectively limited. The contribution to the total EOS calculated in terms of partial free energy vs. volume fraction are reported in figure C1(C).

This is easier to appreciate from figure 5, where we present the sorption isotherms calculated by suppressing selectively one of the four interaction terms to emphasise the ranges and the effects of every term to the sorption behaviour.

The broad bump at low humidity is due to the predominance of hydration repulsion and, to a minor extent, of the entropic term. This feature, in fact, does not show up if either one of these contributions is suppressed, as shown in figures 5(A) and (C). This initial slope at high osmotic pressure is rationalised for wood cell walls as it was for lipid bilayers and DNA gel swelling, i.e. via the contact term of the hydration pressure. This is not a parameter in the model, but has been assessed using the experimental value corresponding to the adsorption energy of the first water layer as proposed by Marčelja and Radić [27]. The universality of this interpretation of hydration of interfaces as well as of the associated decay length has been recently reviewed [25]. The main term opposing swelling is clearly the elastic energy term, that starts to have a visible effect from about 0.5 of water activity by effectively decreasing water uptake. Without this term, swelling would almost diverge, as the contribution from binding of matrix polysaccharides does not affect the sorption behaviour, as it can be seen comparing figures 5(B) and (D).

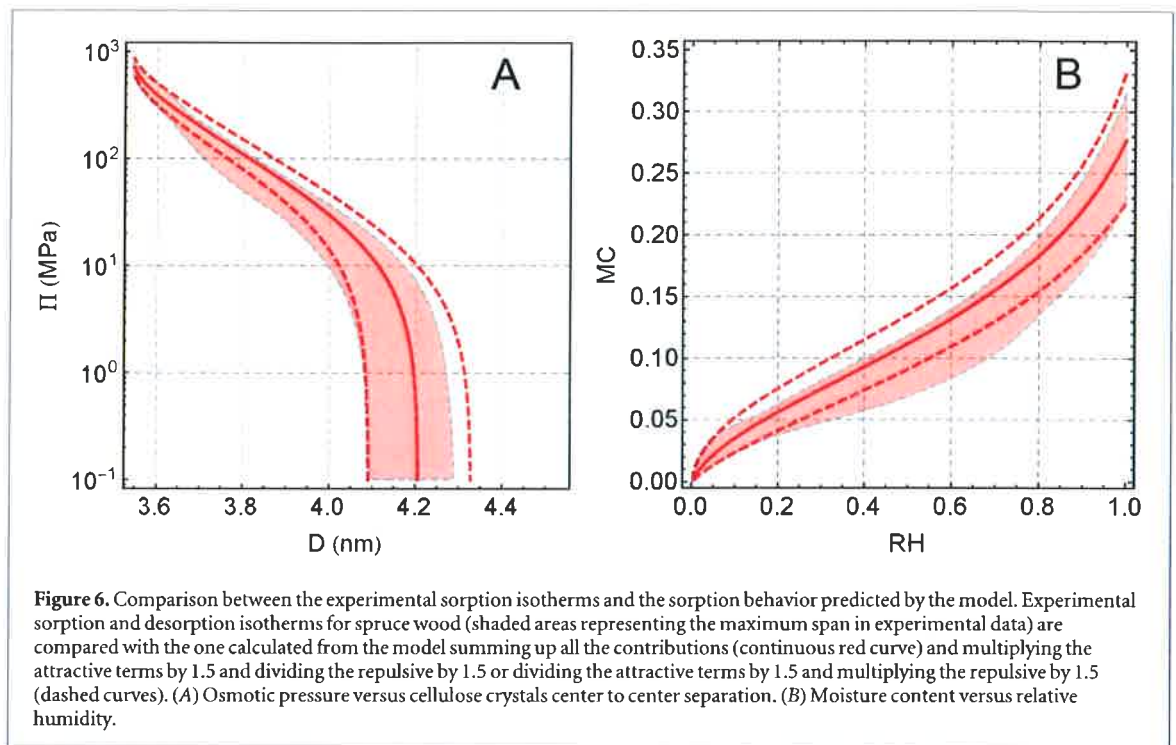
It is worth stressing that there are no free parameters in the formulation of the model and the curve shown in figure 4(B) is derived merely from geometrical and thermodynamics data. For this reason, the model can, at least in principle, be used to predict the sorption isotherm of wood tissues with different composition or with others MFAs.



4. Discussion

The comparison of the result from this model with literature data is shown in figure 6, where the sorption isotherms are presented in terms of MC versus RH (figure 6(A)) as well as osmotic pressure versus interaxial spacing D between cellulose crystals axes (figure 6(B)). The curves have been calculated assuming incompressibility of fluids involved as well as constant partial molar volumes of constituents. The continuous curve represents the sorption isotherm calculated *ab initio* as shown in figure 4. To account for inaccuracy of literature data used to produce the model isotherm, we present in figure 6 also two limit isotherms assuming 50% uncertainty of the quantities involved (dashed lines). As the variability in sorption data for wood is quite large, the experimental data are plotted as a shaded area.

Qualitatively, the sorption isotherm predicted by the model captures the main features of the experimental ones. Numerically, the value for the maximum swelling predicted by this multi-scale model presented here falls in the range of the experimental values. However, at low water chemical potentials small changes in forces are associated with large changes in the equilibrium distance D and the maximum swelling can change significantly if some of the force terms are not derived from careful experiments or accurately evaluated. Therefore, even if the computed curve captures the qualitative behaviour of the experimental one, the level of accuracy of the model to precisely predict the behavior at high hydration of several types of wood needs to be refined, for instance by improving the description of the mechanical energy stored in the composite. Also, we neglected here the interaction between the two matrix polymers (hemicelluloses and lignin) and did not take into account the topology of the lignin network. However, as this is still not well characterized, we could not correct for it. Moreover, our minimal primitive model does not predict hysteresis effects, that can be attributed to slow



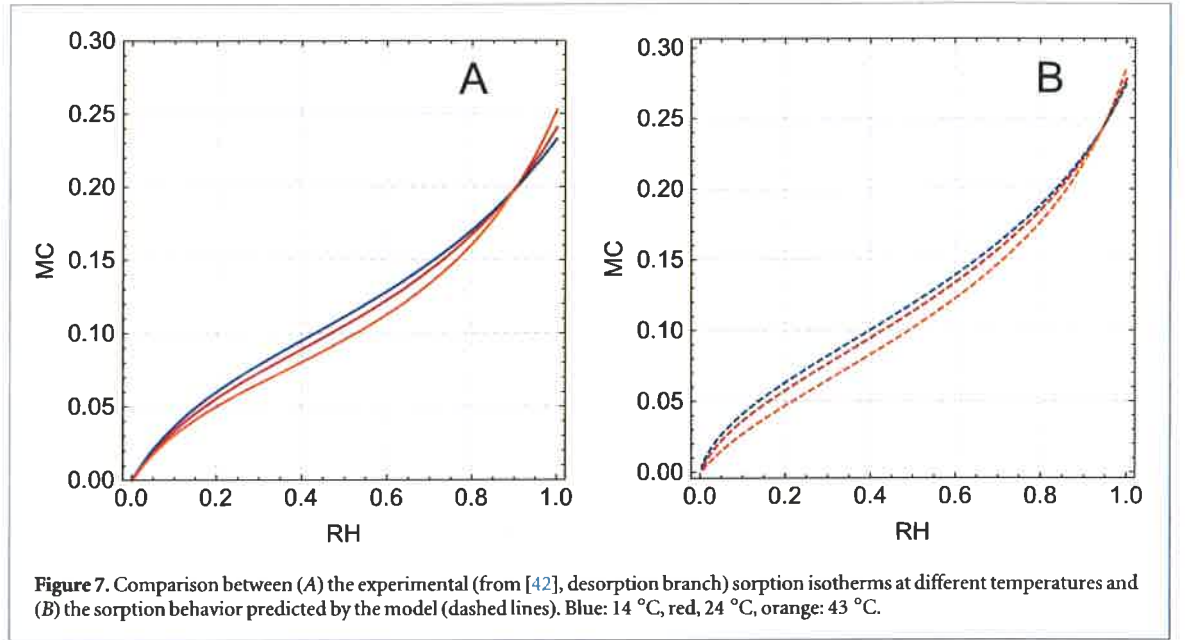
relaxation of some of the constraints imposed by deformation of the cross-linking the cellulose crystals, but more details are necessary to be able to predict hysteresis effects and their variation with chemical treatments.

Despite the intrinsic inaccuracy of the model, the order of magnitude of each contribution to the total energy seems to be correct, and it is now possible to appreciate how similar the wood tissues EOS (figure 6(A)) is to the one observed for other systems. For example, the EOS of multi-layered vesicles dispersed in an aqueous solution of known water activity [40] has been explained in term of decay of a repulsive force, counter-balanced by a strong attractive mechanism. The repulsive contribution is the hydration force and it is common to both systems, but while in the case of lipid vesicles the attractive term was the van der Waals force, in the case of wood this is 'replaced' by the elastic term. Also, the case of wood cell walls has several features in common with the case of DNA in the absence of condensing agents [15] and the entropic and the hydration force terms have been invoked to describe the water-holding in meat [41].

Developing models of EOS from first principles started with the perfect gas equation established by Boltzmann, but is useful only if it allows to predict changes in behaviours resulting from variation in physical or chemical parameters, i.e. if it has a predicting power. Here, we test the predictive power of the model by calculating the sorption isotherm for wood at different temperatures and comparing the results with available experimental data. The change in sorption behaviour with T , in fact, can be modelled without introducing any additional parameter by taking into account the T dependence of each term. As shown in figure 7, the distance in MC between the curves calculated for different temperatures seems to be reproduced in a large range (14 °C to 45 °C, data taken from [43]). Unlike parametric models, the EOS derived from the force balance predicts the observed the reversal in equilibrium moisture contents at very high RHs (larger than 0.9) between different temperatures (see figure 7). The observed trend results from the decrease of the contact free energy (which contains enthalpic and an entropic terms, see [31] and the appendix A.3) and the concomitant increase of elastic contribution due to the increase of the elastic modulus of the matrix at lower temperatures.

5. Conclusions

The model presented here is aimed to describe water uptake by wood cell walls, starting from structural and compositional data. To this aim, we developed a first principles EOS by balancing forces at the molecular, colloidal and microscopic levels. The EOS captures satisfactorily the experimental data at different T , and can explain qualitatively the behaviour of wood tissues subjected to different treatments. This represents a step forward in the understanding of fundamental forces driving wood swelling and allows to design new treatments aimed to improve wood preservation and to describe the physical chemistry of water actuation and stress generation in plant tissues. In the present stage of theory there is no difference between the matrix polymers. To describe the EOS of tissues with different composition, the difference between lignin, as a branched



hydrocarbon containing aromatic cycles and hemicelluloses as an almost linear semi-flexible polymer must be introduced at a more refined level than the minimal model introduced here. The same applies for hysteresis effects, which are beyond the minimal model.

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Appendix A. Further details of the model

A.1. Water volume fraction within the matrix

From the geometrical model presented in figure 1, the water volume fraction within the matrix polymers, used to assess the mixing entropy term, can be expressed as:

$$\phi_w^m = \frac{4R^2 - \phi_c D^2}{\phi_c (4R^2 - D^2)} \quad (\text{A.1})$$

A.2. Work of expansion of the unit cell

We consider prisms arranged in a hexagonal lattice with a center to center distance of D , and a unit cell containing 1 prism (see figure A1).

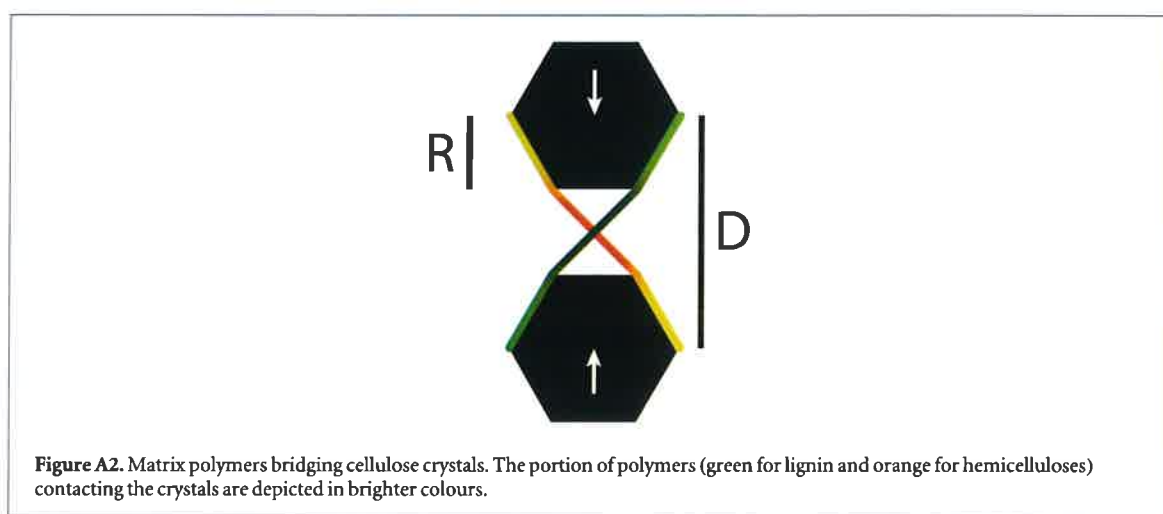
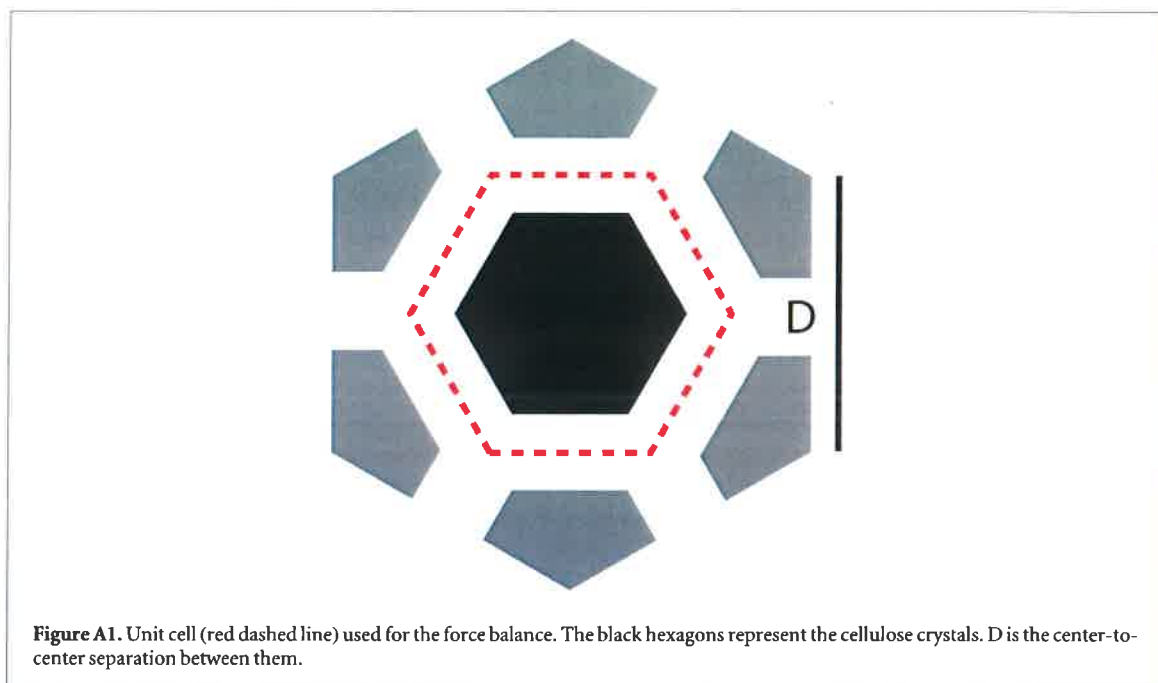
The work of expansion of the lattice $d\Delta G_{\text{tot}}$ at osmotic pressure Π for a small volume change is equal to:

$$d\Delta G_{\text{tot}} = \Pi dV = \Pi d\left(\frac{\sqrt{3}}{2} D^2\right) h = \Pi \sqrt{3} D h dD \quad (\text{A.2})$$

where h is the height of the unit cell which does not change during swelling (as the cellulose crystals are considered here almost unextensible). From equation (A.2),

$$\Pi = \frac{\sqrt{3}}{3} \frac{1}{D} \frac{d\Delta G_{\text{tot}}/h}{dD} \quad (\text{A.3})$$

It is worth noticing that, under the approximation that the molar volume of water does not change with hydration, dV is also equal to $\bar{v}dN$, where \bar{v} is the molar volume of water.



A.3. Hydration force

To make explicit the dependence of ΔG_0 on temperature (which is needed to model the temperature dependence of the sorption isotherms) we can decompose it in an enthalpic and an entropic term so that $\Delta G_0 = \Delta H_0 - T\Delta S_0$. Here, we took ΔH_0 to be about 20 kJ mol^{-1} , as reported in literature [44]. From the same reference, we evaluate ΔG_0 to be the experimentally observed 8.3 kJ/mol subtracted from 2.5 kJ mol^{-1} which is the contribution to the total free energy due to the mixing entropy at low MCs (around 0.05 to 0.1, where the surface separation is close to λ).

A.4. Contact points

The free energy change due to the decrease in number of contact points per matrix polymer unit length during swelling is obtained as follows. A contact point is defined as a portion of matrix polymers (a monomer) directly interacting with the cellulose crystals. We consider here that the matrix polymer can either adsorb on a cellulose crystal surface or lie in the inter-crystalline space, as in figure A2 .

Taking this as a geometric model, for each polymeric chain in a unit cell, we evaluate Λ , i.e. the portion of the chain in contact with a cellulose surface with respect to the total chain length (i.e. the ratio between the darker segments and the total chain length in figure A2), as:

$$\Lambda = \frac{2\sqrt{3}R}{3\sqrt{(D-2R)^2 + \frac{4R^2}{3}}} \quad (\text{A.4})$$

The number of monomers per unit length within the unit cell is:

$$\frac{N_{mp}}{h} = \frac{1}{h} \frac{V_0^{\text{mat}}}{V_m} \quad (\text{A.5})$$

Where V_0^{mat} is the volume between cellulose crystals of the unit cell in dry conditions ($\sqrt{3}\phi_c R^2/(1-\phi_c)$) and V_m is the volume of the matrix polymers monomer. Here we estimate the molecular weight of a monomer to be about 170 g mol^{-1} (which is in between the molecular weight of the glucose and the one of xylose, the main components of secondary cell walls hemicelluloses and close to the one of the most abundant monolignols monomer in soft wood) and its density to be around 1.4 g cm^{-3} (in between the density of hemicelluloses and lignin). Under this approximation, the number of monomers per unit cell in dry conditions is found to be about 15. If the volume fraction of lignin in the matrix is taken as $\phi_l \approx 0.5$, and only the lignin contact points are considered to contribute to the energy, the number of contact points per unit length within the unit cell, N_{cp} could be roughly estimated as:

$$\frac{N_{cp}}{h} = N_{mp} \phi_l \Lambda \quad (\text{A.6})$$

and the total energy term per unit length is found by multiplying the free energy difference of a single contact point ΔG_0^{CP} by the number of contact points per unit length at distance D . After substituting equations (A.4)–(A.6):

$$\frac{\Delta G^{\text{CP}}}{h} = \frac{N_{cp}}{h} \Delta G_0^{\text{CP}} = \frac{2R^3 \phi_l \phi_c}{(1-\phi_c) V_m \sqrt{(D-2R)^2 + \frac{4R^2}{3}}} \Delta G_0^{\text{CP}} \quad (\text{A.7})$$

As before, the pressure term can be derived by differentiation:

$$\frac{d\Delta G^{\text{CP}}/h}{dD} = - \frac{2R^3 \phi_c \phi_l (D-2R)}{(1-\phi_c) \left((D-2R)^2 + \frac{4R^2}{3} \right)^{3/2} V_m} \Delta G_0^{\text{CP}} \quad (\text{A.8})$$

A.5. Van der Waals

In hexagonal symmetry, containing anisotropic elements with cylindrical six-fold local symmetry, many different cases of organic materials have been considered recently by Podgornik *et al* [45]. For a rough estimation, we do not take into account variation of the Hamaker constant with the water content of the inter-crystalline gel. The case shown in figure 1 is very similar to the case that has been used for evaluating the equilibrium precursor material in the synthesis of common mesoporous silicates around hexagonally arranged cylinders [46]. In our case, for small separations, the energy per unit length for the case of 2 cylinders of radius R becomes [47]:

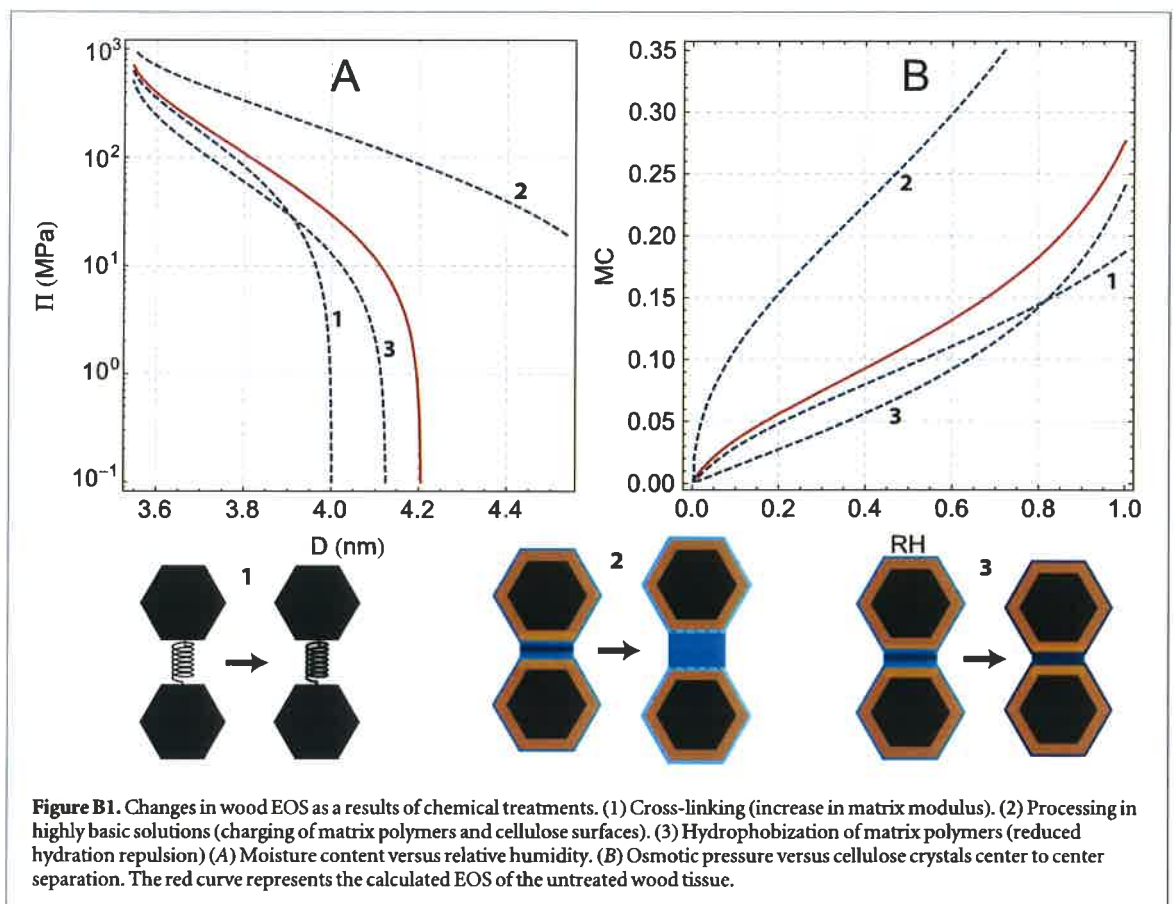
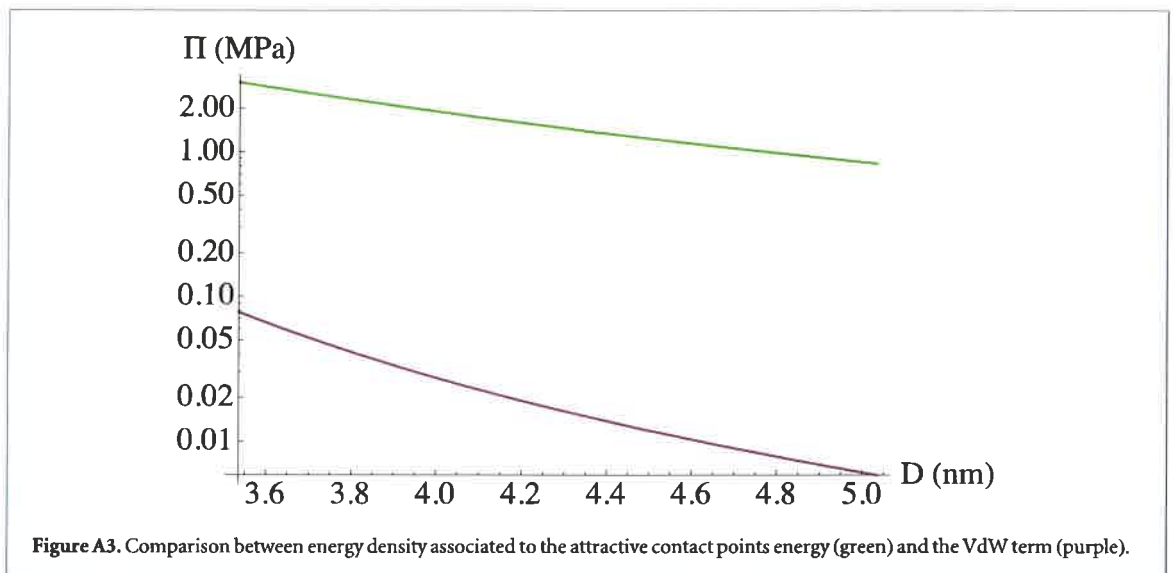
$$\frac{\Delta G^{\text{vdw}}}{h} = -A \frac{\sqrt{R}}{24(D-2R)^{3/2}} \quad (\text{A.9})$$

where A is the Hamaker constant and a cut-off distance is taken as the apothem of the black hexagons shown on figure 1.

We use a conservative value of $A = 0.6 \text{ kT}$ for cellulose crystals interacting through the gel. The results in free energy density are shown in figure A3. It can be seen by comparing the values of van der Waals cohesive energy to the cross-link term that cohesion due to Van der Waals is always negligible by more than an order of magnitude.

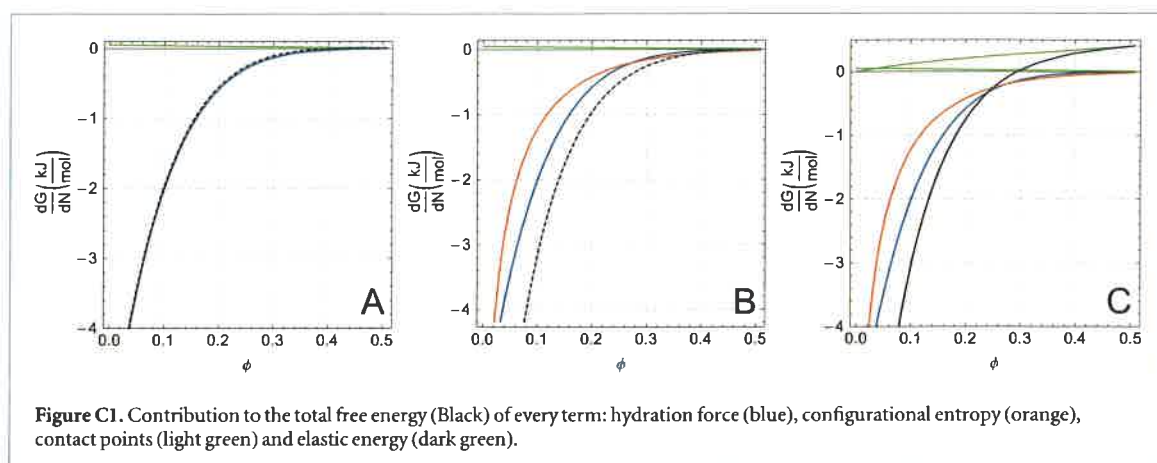
A.6. Temperature variations

Temperature is an explicit parameter in our model that appears in equation (6) through ΔG_0 , in equation (3) and in (10) so that the sorption isotherm can be trivially calculated at every T . However, it has to be stressed that also the Young's modulus of the matrix E in equation (9) exhibits a temperature dependence. Although this has not been directly measured, it can be assessed using the variation of the wood's modulus of elasticity Y with T , namely $E(T_1) = Y(T_1)/Y(T_0)E(T_0)$. Although this is species and moisture dependent, in most dynamic studies at constant moisture content, for several wood tissues, Y has been reported to decrease linearly with T with a rate of about 1% per Celsius.



Appendix B. Qualitative predictions of the model

The equation of state developed in this work is aimed to allow rationalisation as well as qualitative understanding of several processes that have been proposed for the impregnation or chemical treatment of wood. In figure B1, we have reported the effect expected from: (1) increasing the chemical cross-link between matrix polymers by chemical agents, such as glyoxal, which would result in an increase in the matrix Young's modulus (curve 1). (2) The Kraft delignification process [48] using concentrated sodium hydroxide, which results in (at least) doubling the hydration force via electrostatics at high ionic strength. A crude way to account for the effects of concentrated bases is to replace numerically the hydration force decay length with a Debye length of 0.5 nm as reported by Marčelja [49]. This results in winning two orders of magnitude in osmotic pressure for MC of about 30% (curve 2). The same is true in the case of concentrated NaClO and TEMPO (an oxidation catalyst for the



depolymerisation of hemicelluloses), as reported in the work of Isogai *et al* [50, 51]: here sodium hypochlorite charges the cellulose crystals and the wood tissues are brought to dissolution. (3) Hydrophobisation induced by acetylation of the cellulose crystals. This is a transformation of typically half of the surface of crystalline cellulose by esterification induced by mixed anhydrides: the effect of this treatment (as for instance in the patented Wood-Protect™ treatment) can be qualitatively modelled by a reduction of 50% of the contact pressure of the hydration force, all other parameters being constant.

Appendix C. EOS in terms of free energy versus volume fraction

In figure C1 (A),(B) and (C), the calculated EOS reported in figure 2, 3 and 4 are plotted in terms of partial free energy (kJ/mol) vs. volume fraction.

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