Swelling of Cellulosic Fibers in Aqueous Systems: A Review of Chemical and Mechanistic Factors

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Factors affecting the swelling of cellulosic fibers are considered in this review. Emphasis is placed on aqueous systems and papermaking fibers, but the review also considers cellulose solvent systems, nanocellulose research, and the behavior of cellulosic hydrogels. The topic of swelling of cellulosic fibers ranges from effects of humid air, continuing through water immersion, and extends to hydrogels and the dissolution of cellulose, as well as some of its derivatives. The degree of swelling of cellulose fibers can be understood as involving a balance between forces of expansion (especially osmotic pressure) *vs.* various restraining forces, some of which involve the detailed structure of layers within the fibril structure of the fibers. The review also considers hornification and its effects related to swelling. The expansive forces are highly dependent on ionizable groups, pH, and the ionic strength of solution. The restraining forces depend on the nature of lignin, cellulose, and their detailed structural arrangements.

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INTRODUCTION

The swelling of cellulosic fibers can have profound effects on such applications as absorbent paper products (Botkova *et al.* 2013; Hubbe *et al.* 2013; Ma *et al.* 2015), nanocellulose products (Torstensen *et al.* 2022), and products made from dissolving grades of cellulosic fibers (Okugawa *et al.* 2020, 2021). Less dramatic but still very important effects are observed in other paper products (Larsson and Wågberg 2008; Figueiredo *et al.* 2016). During the manufacture of paper, there is often a positive correlation between the swelling of cellulosic fibers (especially for kraft fibers) and the development of paper strength (Jayme and Büttel 1968). This phenomenon is mainly connected to the increased fiber flexibility that is associated with the swelled structure and consequently the increased number of fiber-fiber bonds in the fiber network. On the other hand, with increasing swelling of cellulosic fibers, the amount of water carried past the press section of a paper machine is increased (Hubbe and Heitmann 2007; Hubbe *et al.* 2020). The need to evaporate such water can slow down the rate of production and increase the net expenditure of energy.

Background: Structural Character of Cellulose and Matrix Polymers

The swelling of cellulosic fibers and their networks is normally quantified as liquid (water) mass uptake per mass of fiber, rather than quantified by a length or volume increase. A main reason is that several important steps in fiber swelling do not involve geometric or dimensional changes. To be able to discuss swelling behavior of cellulose and pulp fibers, one needs to take account of the structure of not only cellulose, but also cell wall matrix polysaccharides, *i.e.*, hemicelluloses and pectins. Cellulose has a simple primary structure consisting of anhydrous β-glucopyranosides connected with 1,4 glycosidic bonds, and a degree of polymerization that can reach several thousands (Heinze 2015). The structure of this monomer can be described as being like a discus, in which there are hydroxyl groups peripherally oriented, whereas there are apolar groups facing the tops and bottoms (Fig. 1) (Seeberger 2015).
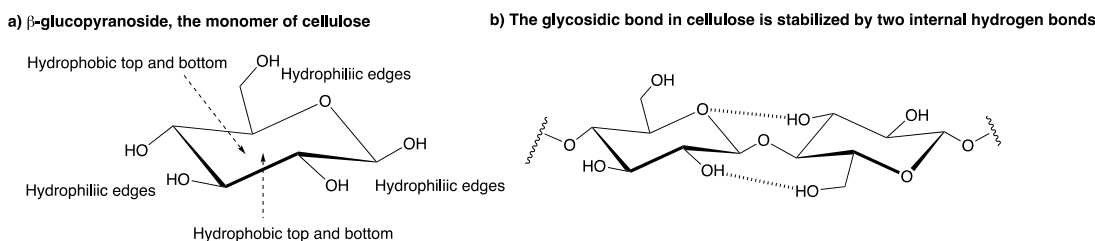
Fig. 1. Representation of the repeat unit in a cellulose chain: (a) β-glucopyranoside, (b) 1,4 glycosidic bonds, depicting also intra-chain hydrogen bonds

The glycosidic bond in the cellulose chain allows the possibility to form two stabilizing hydrogen bonds on each side, and these stabilize the structure into a two-fold helix, *i.e.*, a flat and almost straight structure, with hydroxyls exposed to the sides and a hydrophobic character facing upwards and downwards (Kovalenko 2010). In natural cellulose, *i.e.* cellulose I, chains with the same direction, *i.e.*, having the reducing endo towards the same direction, are lined up beside each other. They are connected with multiple hydrogen bonds, forming sheets in a secondary structure. These sheets are located

on the top of each other and held together by van der Waals bonds in a tertiary structure. For steric reasons, one residue is not located exactly over another but displaced both in chain direction and side direction. Thus, cellulose is forming a crystalline structure (Glasser *et al.* 2012), which is important for the development of superior mechanical properties of the polysaccharide (Ioelovich 2016).

The exact shape of the crystal, the quaternary structure, is a matter of debate; cellulose is synthesized by an enzyme complex located in the cell membrane, and the chains are present in aggregates, meaning that several chains are synthesized in parallel, thereafter forming extended crystals, which together constitute microfibrils (Saxena *et al.* 2005). The size, *i.e.*, the number of cellulose chains, and maybe also the shape of the microfibril, therefore depend on the size and shape of the aggregate of cellulose synthases. In some non-plant sources of cellulose, *i.e.*, bacteria, tunicates, and certain algae, the microfibrils can be very large and sometimes have a rather flat structure (Moon *et al.* 2011). In higher plants, the microfibrils are believed to be rather small; recent results suggest 18 chains (Jarvis 2018), but earlier both 28 and 36 chains have been suggested (Cosgrove 2014).

What then is the cross-sectional shape of a fibril in higher plants? The answer is not known with certainty, but a common suggestion is the honeycomb shapes presented in Fig. 2. Although other shapes also have been suggested, it is inevitable that the microfibril will have both hydrophobic and hydrophilic surfaces exposed (Mazeau 2011). These two surfaces have distinctly different properties, and it seems as if the hydrophobic side is attractive for adsorption of hemicelluloses, as will be further discussed below (Heinonen *et al.* 2022; Kong *et al.* 2022). Proteins that specifically bind to cellulose, such as the cellulose binding module of fungal aerobic cellulases, seem to bind to the hydrophobic surface by forming sandwich structures between the hydrophobic top of glucopyranside residues and aromatic amino acids, *i.e.* tyrosine and tryptophan (Arola and Linder 2016). Issues related to the differing affinities of different crystal planes of cellulose will be considered in more depth later in the article.
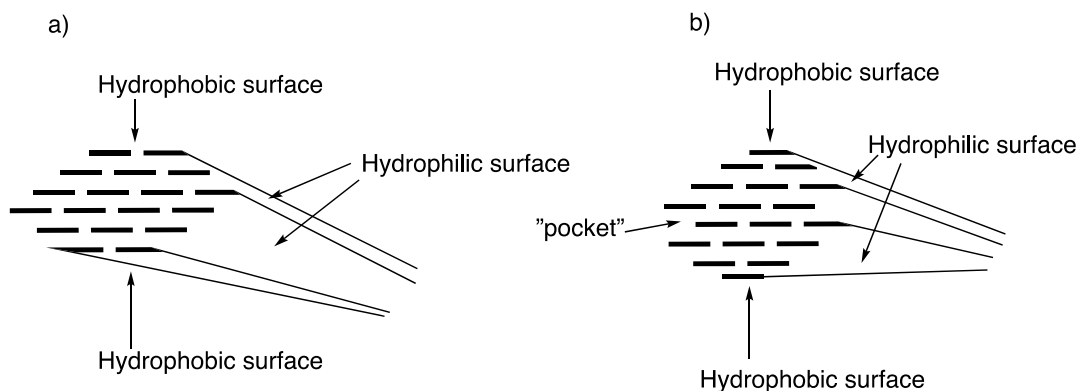
Fig. 2. Likely cross-sectional shapes that have been proposed for the microfibrils of cellulose within higher plants. a) Honeycomb (diamond) model. This model is favored by many scholars; note that both hydrophilic and hydrophobic surfaces are exposed. b) An alternative "double fibril" model. Here the hydrophobic surfaces are smaller, but instead "pockets" are created.

The contrasting hypothetical cross-sectional shapes of the initial cellulose microfibrils that form during biosynthesis can be expected to have implications related to how the units self-assemble into larger structures at later stages of biosynthesis. A recent

review of the fundamentals of self-assembly of lignocellulosic materials showed how idealized shapes, not unlike those shown in Fig. 2, might be expected to govern patterns of self-assembly (Hubbe *et al.* 2023). For instance, one might speculate that the "pocket" depicted in Part B of the figure might provide some kind of evolutionary advantage in the ability of plants to form strong cell walls. However, many fundamental questions remain unresolved concerning the mechanisms of cell wall formation in plants.

The cellulose microfibril should not be understood as being a stiff, static, and perfect crystal; rather, cellulose consists of a mixture of highly crystalline and more unordered cellulose domains. The unordered cellulose is partly located on the surface of the fibril. In the presence of water or similar liquids, there is probably some movability of the superficial cellulose chains on the fibril – but there are indications that there also are segments of the fibrils in which the unordered structure goes deeper into the fibril than the single layer indicated in Fig. 3 (Brestkin and Frenkel 1971; Nishiyama *et al.* 2003; Fernandez *et al.* 2011). The unordered cellulose is generally more reactive towards hydrolysis with acid or cellulolytic enzymes (cellulases) and probably also for chemical derivatization (Wang *et al.* 2014a; Ioelovich 2021). Most likely, an unordered segment in a fibril might allow the fibril to bend more easily, and the movability of the superficial cellulose chains might play an important role for interaction with water or another component. A honeycomb organization of the microfibril with moving superficial cellulose chains will give the microfibril a cylindrical appearance – something that seems to be supported by electron microscopic pictures of cell walls.
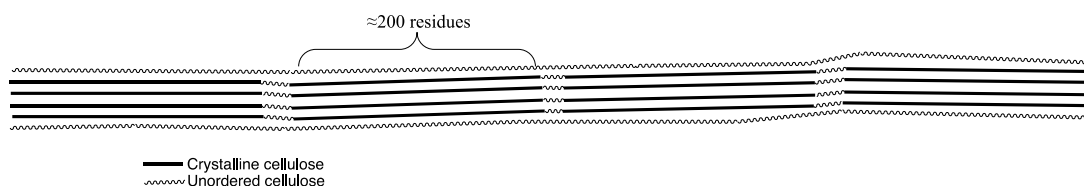

Fig. 3. The central part of the microfibrils might in general be rather crystalline, whereas surficial cellulose might be more flexible and unordered. There are most likely also short segments where the unordered cellulose goes deeper (Brestkin and Frenkel 1971; Fernandes *et al.* 2011).

With some exceptions, such as the seed hairs of cotton, cellulose does not appear as a single polysaccharide component in higher plants; the plant cell wall generally contains other polymeric carbohydrates, which are often called matrix polysaccharides. These are divided into two groups, the *hemicelluloses* and the *pectins* (Scheller and Ulvskov 2010). Hemicelluloses have a main chain in which the monosaccharide residues are connected with β-1,4 glycosidic bonds. The hydroxyl group on the C4 is peripherally located (as in glucose, Fig. 1). This allows the polysaccharide to adapt to the same two-fold structure as in cellulose, although other conformations also are possible. Examples are glucomannans, arabinoxylans, and xyloglucans. Pectins are cell wall polysaccharides that cannot adapt to such a two-fold helix. Examples include β-1,4 galactans, α-1,5 galacturonans, and rhamnogalacturonans (Alkorta *et al.* 1998; Ebringerová *et al.* 2005; Scheller and Ulvskov 2010).

Recent data suggest that both hemicelluloses and pectin can interact, such that they bind to cellulose surfaces, but that they do so in different ways; hemicelluloses can align themselves both parallel and antiparallel with cellulose chains in the microfibrils. In a sense, they may appear to "crystalize" onto the cellulose domains. By contrast, pectins bind

in more nonspecific way. Not surprisingly, the hemicelluloses appear to be more firmly attached to the cellulose microfibrils. Generally, matrix polysaccharides appear to prefer to bind to the hydrophobic surfaces of fibrils (Fig. 2) (Heinonen *et al.* 2022; Jarvis 2023).

The composition of matrix polysaccharides differs greatly between different phylogenic groups, but also between different cell wall layers. These differences start with the secondary wall, which is dominant in terms of both mass and volume (Harris 2006). The most studied of these are the woody eudicolyledons (hardwoods, *i.e.* "eucots"), monocotyledons, and conifers (softwoods, *i.e.* the dominating phylum of gymnosperms) (Daly *et al.* 2001). In woody eucots, xylans are the most common secondary cell wall polysaccharides, but glucomannans also are present in significant amounts (Salmén 2022). In monocots, xylans dominate almost totally, whereas in conifers, galactoglucomannans are the most common, followed by rather large amounts of arabinoxylans (Moreira and Filho 2008; Peng and She 2014). The primary cell walls have a more complex composition, and in addition to xylans, also xyloglucans and pectins (rhamnogalacturonan and polygalacturonic acid) are common (Hayashi 1989; Brett *et al.* 2005; Caffall and Mohnen 2009). The latter polysaccharides can also be present in the middle lamella. Berglund *et al.* (2020) presented evidence that different hemicelluloses can influence the elastic modulus and stretch to breakage of cellulose-based films in contrasting ways.

In summary, the cellulose itself probably mainly exposes surfaces rich in hydroxyls, thereby opening up for the ability to interact with water and other molecules, often leading to hydrogen bonding. In addition to this, there are possibilities for hydrophobic interactions and van der Waals interactions on the hydrophobic sides of a fibril (Fig. 2). A more unordered cellulose, when it is in a swollen state, will is likely to have proportionally more hydrophobic surfaces exposed. Charges, on the other hand, do not occur on pure natural cellulose (which is a homoglucan), so salt bridges do not occur directly between natural cellulose molecules (Kontturi *et al.* 2006). Anionic structures, *i.e.*, carboxylic acids, hypothetically may be induced on the cellulose polymer, by technical processes, such as bleaching. The matrix polysaccharides (the hemicelluloses) will most likely be forming layers around microfibrils, connecting them, or embedded in them, adding more of unordered structures with richer possibilities for hydrophobic interactions and van der Waals forces. Furthermore, certain matrix polysaccharides, *i.e.*, xylans, polygalacturonic acid, and rhamnogalacturonan, contain anionic carboxylic acids, thereby making plant fibers negatively charged. Xylans have been suggested to act as a kind of dispersant for cellulose microfibrils by adding charge to them by associating with the surfaces (Berglund *et al.* 2020). A similar role has been observed for glycerol (Moser *et al.* 2018b). Especially the cationic groups in pectins often form salt bridges to calcium ions, thereby crosslinking chains by means of "eggbox structures" (Fig. 4) (Cao *et al.* 2020). These structures function as crosslinkers to polysaccharide chains and have importance for the rigidity of pectin-rich tissues, such as middle lamella of the phloem in certain herbs, *e.g.* flax and hemp. Removal of calcium from pectin leads to a swelling and weakening of pectin rich tissues, and it increases their accessibility for enzymatic degradation; this approach has been considered for chemical retting of bast fibers (Henriksson *et al.* 1997). Addition of calcium salts may on the other hand decrease swelling (Thakur *et al.* 1967). In line with this, *Eucalyptus* wood with high content of calcium is more recalcitrant to kraft pulping (Vegunta *et al.* 2022).
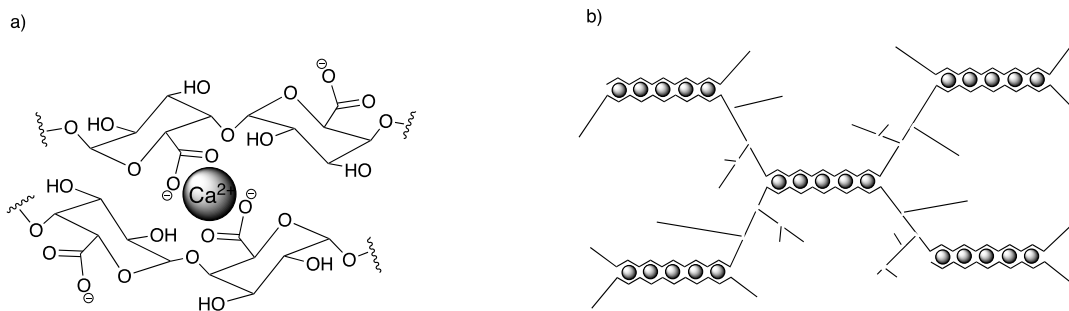
Fig. 4. Complexes formed between carboxylic anions and calcium(II) ions are known as "egg boxes". They are believed to play a central role in the rigidity of pectin-rich tissues (Heinze 2016). a) Chemical structure of an eggbox, *i.e.*, complex between two uronic acids and a calcium ion, thereby crosslinking two polysaccharide chains; b) Schematic presentation of the role of egg boxes in pectin structures; the calcium ions crosslink the "smooth" regions rich in galacturonic acids (Cao *et al.* 2020)

Steps in Swelling

The process of swelling of cellulosic fibers can be envisioned as a continuum of overlapping steps. To begin, equilibration of dry cellulosic fibers, paper products, or other such materials with increasing levels of relative humidity results in increasing moisture uptake and slight changes in macroscopic dimensions (Larsson and Wågberg 2008; Gamstedt *et al.* 2015; Joffre *et al.* 2016). Greater proportional effects of relative humidity on dimensions have been found when examining the thickness dimension of thin films of nanocellulose (Rehfeldt and Tanaka 2003; Shrestha *et al.* 2017; Torstensen *et al.* 2018). Wetting by pure water results in much larger mass uptake and swelling of dimensions (Scallan 1983; Solhi *et al.* 2023). A key focus of this review article will be on ways in which the pH and ion contents of such solutions affect the degree of swelling and how such effects can be understood based on chemistry, physics, and colloid science. Further aspects of the swelling mechanisms are revealed by considering evidence from more extreme situations, including the behavior of cellulose-based hydrogels (Ganji *et al.* 2010; Chang and Zhang 2011; Ma *et al.* 2015) and solvent systems for cellulose (Budtova and Navard 2016). For instance, some of the greatest observed degrees of swelling of cellulosic material are associated with the last steps before dissolution in the presence of specialized solvent systems (Cuissinat and Navard 2006; Zhang *et al.* 2013; Budtova and Navard 2016).

The Riddle of Cellulose's Insolubility in Water

In addition to the practical importance of swelling, as already described, the results of investigations into the swelling of cellulose fibers also can provide evidence into fundamentals of how the cellulosic material is being held together. As will be described further in this article, hydrogen bonding plays a central role not only in the bonding within cellulosic fibers, but also with respect to their interactions with water (Medronho *et al.* 2012; Norgren *et al.* 2023; Sjöstrand *et al.* 2023). If that were the only type of bonding, however, then it would be hard to explain the insolubility of cellulose in most aqueous conditions (Bergenstråhle *et al.* 2010; Budtova and Navard 2016). As been discussed above, cellulose chains and microfibrils display hydrophobic surfaces at specific planes, and these might interact with each other by van der Waals forces. When water is present, the cellulose is kept together, in part, by hydrophobic interactions, which involves an

entropic effect of the solvent (Ghosh *et al.* 2002; Glasser *et al.* 2012). Thus, this article will consider effects such as the orientation of cellulose macromolecular chains, which have differing affinity for water on different sides. This amphiphilic character is demonstrated by the differing wettability characteristics of the different faces of cellulose crystals (Yamane *et al.* 2006). In addition, the contrasting microfibril angles in different sublayers of a cellulosic fiber, as will be shown later, sometimes tend to restrain the swelling of other layers within the same fibers.

Sections of this Article and Recognition of Earlier Review Articles

This review article is organized into the major sections of quantification of swelling, factors affecting the swelling of cellulosic matter, theoretical aspects of swelling of cellulosic matter, applications of swelling of cellulosic material, and some closing comments. From a developmental and materials science perspective, the articles to be cited point to two main strategies that have been used to modify the swelling degree of cellulose-based materials intended for different applications. Chemical approaches, including the forming or attachment of different ionizable functional groups on cellulosic surface, can be used to increase the osmotic pressure that tends to increase swelling, subject to various aqueous conditions. Chemical delignification, along with physical treatments such as mechanical fibrillation (*i.e.* refining), can be used to alter or decrease physical restraints to the swelling of the same materials. However, as will be discussed, the restraining tendencies of cellulosic structures are also highly dependent on any history of drying, which can decrease the swelling ability, *i.e.* effects of hornification (Fernandes Diniz *et al.* 2004; Salmén and Stevanic 2018; Sjöstrand *et al.* 2023; Sellman *et al.* 2023).

Aspects of the swelling of cellulosic fibers have been considered in some earlier review articles, and these are listed in Table 1. Based on the items in this list, there appears to have been an acceleration of interest within the last two years.

Table 1. Earlier Review Articles Dealing with Aspects of Swelling of Cellulosic Fibers and Related Materials

Main Topics of Earlier Review Articles	Citation
Effects of acid groups and osmotic pressure on pulp swelling	Scallan 1983
Comparison of properties of chemical cellulose pulps	Young 1994
Thermal aging of paper and loss of swelling ability	Kato & Cameron 1999
Pore dimensions of swollen cellulosic fibers, *e.g.* kraft fibers	Alince 2002
Decreases in cellulosic fiber swelling due to drying history	Hubbe *et al.* 2007b
Cellulose-based hydrogels, including their swelling behavior	Chang & Zhang 2011
Theoretical aspects of cellulose insolubility and solubility	Medronho *et al.* 2012
Theoretical aspects of cellulose aggregation & hornification	Pönni *et al.* 2012
Absorbent products incorporating cellulose and its derivatives	Hubbe *et al.* 2013
Cellulose-based superabsorbent hydrogels	Ma *et al.* 2015
Cellulose in NaOH-water-based solvents	Budtova & Navard 2016
Cellulosic fiber swelling in composite applications	Gamstedt 2016
The role of hydrogen bonds in cellulose	Wohlert *et al.* 2022
Colloidal aspects of nanocellulose, including swelling	Benselfelt *et al.* 2023
Theoretical aspects of cellulose insolubility and solubility	Norgren *et al.* 2023
Nanocellulose-water interactions, comprehensive review	Solhi *et al.* 2023

QUANTIFICATION OF SWELLING

The swelling of cellulosic fibers and networks is often defined as the amount of liquid (often water) mass uptake per mass of fiber. Another way to define swelling is based on dimensional changes. However, such dimensional changes may be insignificant or hard to quantify in many situations of interest. Thus, in the literature, various different definitions and evaluations methods have been employed.

Commonly used methods to quantify the swelling of cellulosic fibers and related materials can be placed into the categories of water retention value (and related tests), methods involving measurements of the concentrations of soluble polymers in solution, methods based on observed changes in dimensions of objects, methods based on permeability, and a variety of lesser-used approaches (Gallay 1950). These are described in the subsections below. As a general summary, each of the existing methods to be considered for evaluation of swelling involves areas of uncertainty and approximation. Methods that rely upon the dimensions of swollen cellulosic material typically suffer from uncertainty in defining the boundary between the material and the surrounding aqueous (or other) medium. Methods that depend on the sizes of selected probe molecules tend to be blind to the presence of some pores that may be larger than the probe. And some, such as the WRV tests to be described next, can be regarded as practical, but not firmly grounded in theory.

Water Content Assessment

Water retention value

The water retention value (WRV) test (Welo *et al.* 1952; Marsh *et al.* 1953; Jayme and Büttel 1964, 1968; Cheng *et al.* 2010), which involves centrifugation of a damp plug of fibers, is specified in standard methods (SCAN-C 62:00, 2000; TAPPI UM 256 1981; ISO 23714:2014). The basic assumption is that when a specified centrifugal acceleration is applied to the damp plug of fibers, the acceleration will remove water that was either between the fibers or within the fiber lumens. The idea is that the effective forces acting on the fibers will squeeze each of the fibers, such that any water contained within the lumen space will come out *via* the pit openings. An analogy can be made to the squeezing of a tube of toothpaste. By contrast, it is assumed that any water contained within the mesopores or micropores within the cell walls of fibers will be prevented from escaping by sufficiently large capillary forces (Welo *et al.* 1952). Different fiber starting materials will of course showcase varying fiber properties, and the remaining water will be located differently based on fiber morphology.

As a general rule, WRV tests have a reputation of providing useful comparisons between chemically delignified pulp samples that have been refined to different levels. However, high levels of external fibrillation can contribute to the WRV values in a way that does not fit with the usual definition of swelling. For example, a well-fibrillated thermomechanical pulp (TMP) fiber may have a WRV value that suggests about twice the level of swelling in comparison to the results of soluble exclusions tests (see later discussion). In addition, TMP tends to maintain its WRV over cycles of papermaking and repulping (Alanko *et al.* 1995). Because TMP has a composition similar to wood, its cell walls lack the porosity and swelling ability of kraft fibers, especially after the latter have been refined.

A related test method of water removal is drainage, which can be measured in Degrees Schopper Riegler (°SR) or Canadian Standard Freeness (CSF). Drainage is more

related to liquid water passing between fibers but has been shown to correlate linearly with WRV. However, it is important to note that slopes of linear correlations are different for different pulp compositions (Sjöstrand *et al.* 2019).

To carry out a WRV test, a well-defined amount of pulp fibers is formed into a plug, which is then centrifuged under specified conditions of centrifugal force, time, and temperature. One weighs the material immediately after centrifugation. The procedure is done in such a way as to allow water released from the fibers to pass through a screen and not return. A second weight is determined after the same plug of fibers has been completely dried, preferably according to ISO 638 (2008) or a similar method.

Different results can be obtained from WRV tests, depending on the level of centrifugal acceleration (Cheng *et al.* 2010). The WRV values tend to decrease with increasing centrifugal acceleration and time of spinning. As described in the cited article, smaller particles of cellulose gave rise to larger WRV values, which is consistent with the presence of generally smaller capillary opening within the material. Based on this principle, WRV has been employed as a way to characterize the degree of fibrillation of highly fibrillated cellulose materials, *i.e.* micro- or nanocellulose (Gu *et al.* 2018). Effects of carboxymethylation (Laine *et al.* 2003) and TEMPO-oxidation (Maloney 2015) of cellulosic fibers also have been evaluated with WRV.

Although the WRV test has been used for many years as a practical way to estimate the amount of water held within the cells walls of ordinary cellulosic fibers, especially when they are being used to manufacture typical grades of paper, there is evidence that some other categories of water can be involved, especially when polymeric chemical additives are being employed. For example, if one were to assume that the WRV test senses only water present in mesopores, then one would expect that relatively small cationic polymers, having easy access into such pores, would have a big effect on the WRV results. In principle, the small cationic polymers would be expected to diffuse into tiny pores in the cell walls and neutralize surface charges, leading to pore contraction due to the decreased osmotic pressure. However, the opposite was found by Swerin *et al.* (1990), and Ström and Kunnas (1991). They observed that a high-molecular-mass cationic polymer product had a much bigger effect on WRV than a low-mass version. It has been argued that such results are consistent with a charged patch type of interactions among external fibrils and polyelectrolytes at the fiber surfaces (Hubbe and Panczyk 2007b; Hubbe *et al.* 2008). Alternatively, the same effects might be attributed to complexation among oppositely charged polyelectrolytes, where the cellulosic fibrils are regarded as if they were anionic polyelectrolyte strands (Hubbe 2019). In either case, the WRV results appear to be sensitive to details concerning such charged polymer additives.

Some modified versions of the WRV test have been demonstrated, seeking to broaden the range of information that can be obtained. For example, Hubbe and Panczyk (2007a) developed a modified WRV method (MWRV) in which a mass was placed on top of the damp plug of fibers before the start of centrifugation. Such a modification makes the test results somewhat more relevant to such situations as water removal in a wet-pressing operation. Notably, however, variations in pH and salt concentration were not found to have major effects on the results of the MWRV tests. Rather, increased refining increased the MWRV results, whereas drying history of the fibers decreased the MWRV values.

Some researchers have obtained WRV values when evaluating the properties of nanocellulose suspensions, but the justification and meaning of such tests can be questioned. To carry out such tests, a membrane is used to support the cellulosic material during centrifugation (Cheng *et al.* 2010; Gu *et al.* 2018). This approach makes it possible

to evaluate nanocellulose materials having small enough particle size to pass through the usual supports used in WRV tests. Since nanocellulose suspensions do not have any lumen spaces or inter-fiber spaces, one cannot claim that the applied centrifugation is meant to remove water from such spaces. Rather, it seems likely that the WRV results from testing of nanocellulose suspensions will be related to surface area and fineness of the material, which are expected to contribute to both capillary forces and resistance to flow.

Solute Concentration Tests

Another basic way to gain information about the amounts of water that are contained within the mesopore structure of cellulose fiber cell walls involves the evaluation of concentrations of probe macromolecules in solution (Stone and Scallan 1966, 1967, 1968; Scallan and Carles 1972; Alince 1991). The idea is based on an assumption that a water-soluble polymer of a certain molecular mass will be prevented from entering a pore if it is smaller than a critical size, perhaps related to the radius of gyration of that macromolecule. Three ways of carrying out such tests are possible, as described below.

Fiber saturation point

To determine the fiber saturation points of cellulosic materials in aqueous suspension, one selects a water-soluble polymer having a lack of attraction to cellulosic surfaces and a suitably high and narrow distribution of molecular mass such that it can be assumed that little of the macromolecule will be present in the mesopores of a typical chemical pulp (kraft, sulfite, *etc.*) specimen (Stone and Scallan 1966, 1967; Alince 1991). Dextran molecules having molecular mass of about one million Daltons or greater have been used for such tests. Rather than providing a physical barrier to entrance of the probe polymers, one relies upon the fact that the probability that such a polymer will diffuse into a given space depends strongly on whether or not the freedom of motion of polymer segments will become constrained, thus affecting the entropy content and the free energy (Alince 2002). The concentration of the probe polymer in the bulk of solution will tend to be increased, compared to what can be calculated based on the known added quantity. The calculation involves the total amount of solution present, including solution that happens to be within mesopores and micropores of the cell walls of fibers. One then calculates the volume that is associated with the pores too small to permit access. As noted by Scallan and Carles (1972), the obtained fiber saturation value results are often in reasonable agreement with WRV test results, at least when testing ordinary papermaking fibers within typical ranges of mechanical refining.

Inverse size-exclusion chromatography

Size exclusion chromatograph (SEC) has emerged as an effective and practical way to evaluate the molecular mass distributions of polymers in solution (Burgess 2018). The method is based on the principle that the time required for a given macromolecule to elute through a packed column will depend on whether or not it is small enough to spend time within the pores of a selected packing material. Very small probe molecules will require the longest elution times, since they will be spending more time, on average, within parts of the liquid that are not available for larger macromolecules. Inverse size exclusion chromatography (ISEC) measurements are similar, except that one employs a known probe macromolecule, having a narrow molecular mass distribution, and the quantity to be determined is the pore size or pore size distribution of a solid material, *e.g.,* a swollen cellulosic substance (Yao and Lenhoff 2004). The ISEC method was employed, using a

series of different molecular mass fractions, by Berthold and Salmén (1997a) to help understand how the process of kraft pulping and bleaching affect the pore size distribution. In general, it was found that there was a substantial increase in the volume of mesopores (*i.e.*, pores from 2 to 50 nm in diameter) following chemical pulping, with even greater porosity after both pulping and bleaching. Follow-up work showed how such distributions were shifted due to partial closure of intermediate-sized pores (mainly mesopores) in the course of drying and rewetting (Berthold and Salmén 1997b).

Polyelectrolyte adsorption

Because cellulosic materials typically have a negative charge – due to the presence of axabinoxylan or pectin or by chemical modification of cellulose (natural cellulose is, as discussed above, uncharged) – cationic polyelectrolytes will be expected to interact strongly with them. It has been proposed to use cationic polyelectrolytes of known molecular mass to probe the pore structures of cellulosic fibers (Alince and van de Ven 1997; Alince 2002). By employing a highly branched polymer, the cited work reached the conclusion that mesopores within the swollen cell walls of bleached kraft fibers were relatively uniform and about 80 nm or larger in diameter. However, much smaller sizes have been determined by other methods, such as NMR (Li *et al.* 1993). Studies have shown that factors affecting permeation of cationic polyelectrolytes from aqueous into porous materials are complex (Wu *et al.* 2009). As described in the cited review article, cationic polymers at first may be drawn into small pores in a snake-like fashion; however, the progress of cationic polymers into such pores is likely to be strongly affected by kinetic factors, including essentially trapped non-equilibrium conditions. Further information about cellulose porosity was obtained indirectly by sensing electrokinetic effects that originate from those areas of bleached kraft fibers (Hubbe *et al.* 2007a).

Table 2. Methods to Evaluate Swelling Based on Dimensional Changes

Specimen Type	Method	Citation
Kraft fibers & paper	Environmental scanning electron microscopy	Enomae & Lepoutre 1998
Regenerated cellulose fibers	Environmental scanning electron microscopy	Karlsson *et al.* 1998
Regenerated cellulose fibers	Optical & electron micrographs, with use of adsorbed colloidal particles	Kasahara *et al.* 2002a,b
Ultrathin cellulose film	Ellipsometry	Rehfeldt & Tanaka 2003
Ultrathin cellulose film	Grazing incidence X-ray diffraction	Kontturi *et al.* 2011
Nanofibrillated cellulose films (nanopaper)	High speed optical microscopy	Qing *et al.* 2013
Newspaper fibers & paper	Visual observation of light from prisms	Jablonsky *et al.* 2014
Unmodified spruce fibers	Synchrotron X-ray computed tomography	Gamstedt *et al.* 2015
Cellulose nanocrystal films	Polarized light microscopy with dynamic vapor sorption	Shrestha *et al.* 2017
Nanofibrillated cellulose films (nanopaper)	Positron annihilation lifetime spectroscopy to determine free volume pore size	Torstensen *et al.* 2018
Single nanofibrillated cellulose	Atomic force microcopy, under dry & aqueous conditions	Ottesen & Syverud 2020
Paper	White light interferometry & grid projection	Wong *et al.* 2023

Methods Based on Dimensional Measurements

Reported swelling methods involving dimensional measurements of cellulose-based materials have tended to be diverse, rather than following a standard. It appears that different kinds of specimens, or possibly different orientations of those specimens, will require different procedures. Table 2 summarizes such work, with attention to the nature of the specimens and the methods. Note that some of these methods were designed in such a way as to capture rapid changes in dimensions upon introduction of changes in humidity or immersion (Qing *et al.* 2013; Jablonsky *et al.* 2014; Shrestha *et al.* 2017). In addition, it has been possible to capture dramatic and to a large extent reversible changes in dimension by wetting and redrying by suitable methods (Kontturi *et al.* 2011).

Permeability

Though the degree of correlation between permeability and porosity (or fractional volume content of pores in a material) needs to be established in each case, permeability is sometimes used as a proxy for porosity measurements. In paper specimens, there is a general expectation that air permeability will decrease with increasing apparent density. However, the effect is not linear. This is shown in Fig. 5, which for the first time plots data reported by Vänskä *et al.* (2016). The cited authors varied the lignin content as well as the extent of mechanical refining. As shown in the figure, the logarithm of the time required for permeation of 100 cm^3 of air was found to be roughly proportional to apparent density. However, all of the results shown in the figure for the highest Gurley seconds values were beyond the upper limit of measurement. The densest sheets, representing high levels of refining, tended to act as near-perfect seals, suggesting molecular contact between adjacent fibers in the structure. In other cases, the correlation between permeability and density may be poor due to detailed differences in pore structure (Hantel *et al.* 2017). Nonlinear and complex relationships between paper permeability and density are also suggested by studies of the relative ease of removal of water during the paper forming process (Hubbe *et al.* 2020). The cited review article showed, for instance, that densified surface layers may have a dominant effect on permeation behavior.
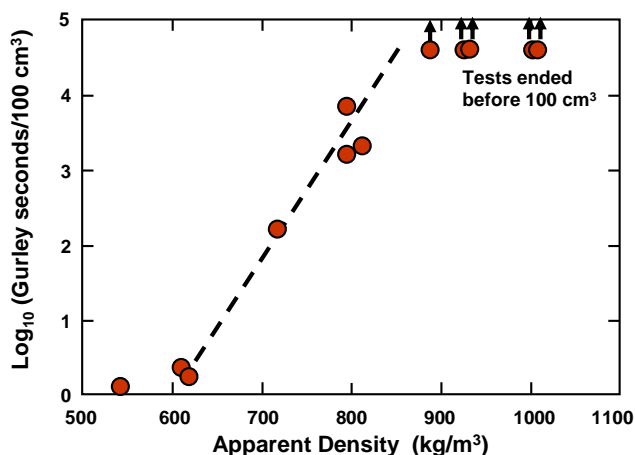

Fig. 5. Plot prepared here for the first time from the data of Hantel *et al.* (2017), showing the logarithm of air permeation times for paper prepared with different delignification degree and mechanical refining levels, leading to the apparent density values shown for the resulting paper

Surface Area and Porosity Using Specialized Drying Approaches

One of the most trusted approaches to determining the surface area and pore sizes of materials is by adsorption of very cold nitrogen or argon gases at low pressures (Bardestani *et al.* 2019). When the goal is to study the pore structures of cellulosic materials, one of the key challenges is the fact that such tests require the usage of completely dry samples. It is well known, however, that substantial and partly irreversible closure of pores (*i.e.* hornification) occurs when cellulosic materials are dried using conventional evaporation, especially in cases where the lignin has been removed (Fernandez Diniz *et al.* 2004; Hubbe *et al.* 2007b). Geffertova *et al.* (2013) found that repeated cycles of paper forming, drying, and reslurrying of the pulp in preparation for the next cycle without additional refining tended to increase the air permeability of sheets. This is consistent with the increasing stiffness and lack of compliance of hornified fibers. To minimize such effects during determination of pore sizes in wet specimens, it is recommended to replace the water in the specimens with another solvent and then employ critical point drying (Kang *et al.* 2018). In other words, evaporation takes place at the location within a phase diagram where solid, liquid, and gas phases meet each other. Such approaches can avoid development of high surface tension forces and extensive hydrogen bonding in the course of drying. Once the specimens have been dried, then one can use the Brunauer-Emmett-Teller (BET, 1938) method to obtain the surface area, based on gas adsorption isotherms (Sing 2001; Bardestani *et al.* 2019). Related methods can provide estimates of pore-size distributions (Barrett *et al.* 1951; Bardestani *et al.* 2019), though such determinations require simplifying assumptions (Groen *et al.* 2003).

These BET-related methods require that the sample is dried. Even when using specialized drying methods, there still will be some risk of pore collapse, which will influence the result. Therefore, there is interest in methods for measuring the cellulose surface area without drying. One such method is based on adsorption of the colorants methylene blue and Congo red (Inglesby and Zeronian 1996). This method requires a high content of sulphate ions to make the adsorption possible. This is problematic, since it can lead to aggregation of fibers and collapse of pores. Moser *et al.* (2018a) developed a method based on adsorption of the polysaccharide xyloglucan on the cellulose, which does not require increased ionic strength. The content of non-bound xyloglucan can easily be detected, since it forms a strongly colored complex with iodine.

FACTORS AFFECTING THE SWELLING OF CELLULOSIC MATTER

The emphasis of this section is to consider evidence about what parameters affect swelling of cellulosic fibers. Though some theoretical aspects may be unavoidable, in light of such emphasis, the goal will be to consider articles that employed an empirical approach, rather than to focus on theories, which will be covered in the subsequent main section.

Aspects related to experimental design and selection of conditions need to be considered carefully when attempting to understand published work related to the swelling of cellulosic fibers. With many exceptions, typical experiments related to the swelling of cellulosic materials have involved one-at-a-time variation of certain parameters *e.g.*, pH. The conditions that are held constant, in such experiments, can be numerous and quite specific to the interests of the researchers. Those conditions may not necessarily match those employed by other researchers. As will be illustrated by some of the cases considered

in this article, some findings will appear to have general validity, whereas other findings may be limited to special circumstances.

In general, as will be described in this section, there has been great progress in understanding different aspects that contribute to swelling behavior (Benselfelt *et al.* 2023; Sellman *et al.* 2023; Sjöstrand *et al.* 2023; Solhi *et al.* 2023). Factors that influence the extent of swelling include not only the chemical composition and aqueous conditions, but also the details of the layered structures that make up a cellulosic fiber.

Fiber Structural Details Resulting from its Biosynthesis

Many key attributes affecting the swelling behavior of cellulosic fibers have their origin in the nanostructures and microstructures that are established during biosynthesis. For a full understanding of those details, readers are referred to other sources (Brown and Saxena 2000; McNamara *et al.* 2015; Manan *et al.* 2022).

Some important aspects, relative to swelling behavior, can be emphasized. First, it has been shown that cellulose chains during their biosynthesis are essentially extruded towards the outside of cell membranes in parallel, essentially continuous manner (Brown and Saxena 2000; Tobias *et al.* 2020). As mentioned earlier, they almost immediately join together in nascent crystalline form in groups of about six, thus becoming microfibrils. Although the term "microfibrils" does not contain the term "nano," it has become well established in the literature (Doblin *et al.* 2002) as a descriptor for these features that have nano-sized thicknesses. The process is depicted schematically in Fig. 6, part A. The nanofibrils may then join in parallel with other such groups, thus becoming larger fibrillar structures. In close succession, hemicellulose is also formed, and then lignin, thus surrounding and connecting the cellulose nanofibrils or microfibrils. In that manner, nature forms a nanocomposite structure in which the relatively stiff cellulose fibrillar elements are embedded in a double matrix of hemicellulose and lignin. Figure 6, part B illustrates the diffusion of monolignol compounds into the nascent cellulosic substance during the biosynthesis process.

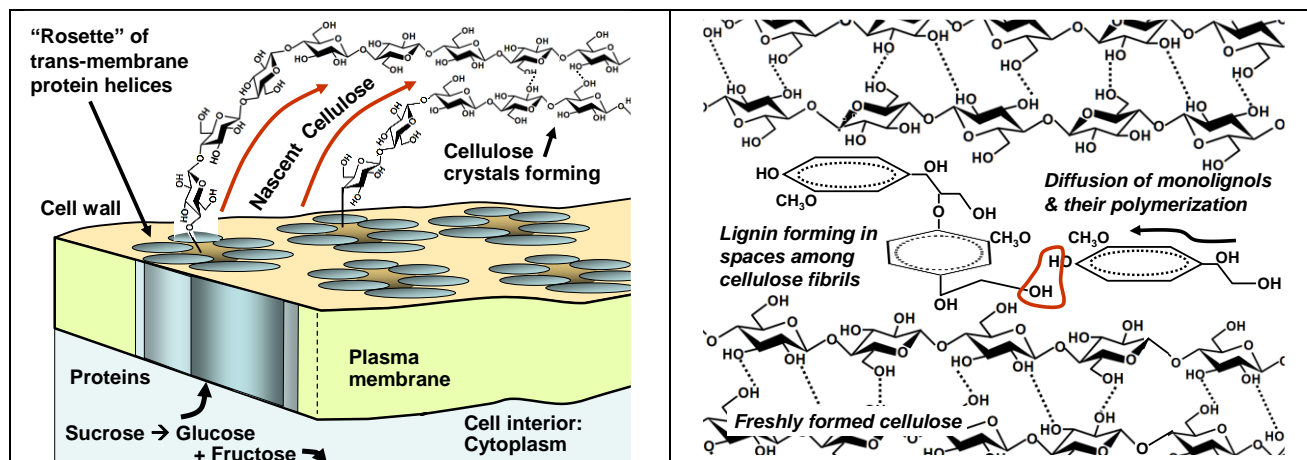**Fig. 6.** Schematic diagram of key biosynthetic events in the formation of lignocellulosic fibers. A: cellulose biosynthesis; B: lignin biosynthesis occurring within spaces of the just-formed cellulose nanofibrils or microfibrils.

Another key aspect that will affect the swelling behavior of cellulosic fibers, related to their biosynthesis, is the layered nature of the cell walls, and in particular the microfibril

angles within the cell walls. Figure 7 depicts a typical cellulosic fiber, as it might be present in a wood specimen. As shown, each fiber has a thin primary (P) layer, and within that are three secondary (S) sublayers, of which the S2 sublayer is by far the thickest, such that it tends to dominate the structural aspects of fibers. The microfibril angle within the S2 sublayer often is within the range of 2 to 25 degrees, *i.e.,* close to being aligned with the fiber and with the axis of the plant (Barnett and Bonham 2004; Donaldson 2008). Substantially higher values of the S2 sublayer fibril angle are found in such wood species as juniper (Hanninen *et al.* 2012); such wood species tend to be much more flexible and resistant to breakage, but less able to grow high.
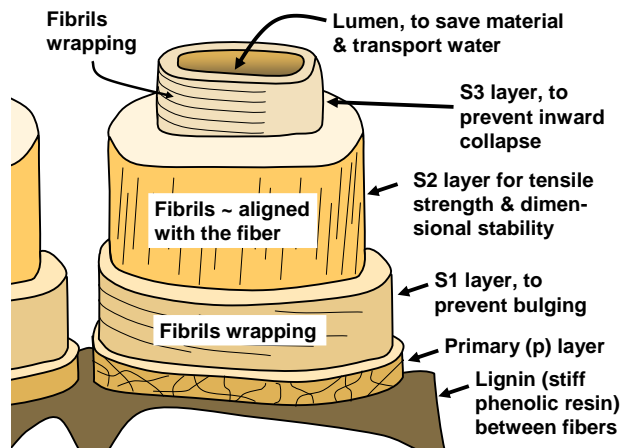
Fig. 7. Sketch of lignocellulosic fiber, including layered structure, typical microfibril angles, and lignin distribution

The thinner S1 sublayer wraps itself around the S2 sublayer, such that it tends to restrict outward swelling of the S2 sublayer (Barnett and Bonham 2004). On the inside of the structure, adjacent to the lumen space, the S3 sublayer is likely oriented such that it tends to prevent inward collapse of the S2 sublayer. Between adjacent fibers, the "middle lamella" region is rich in lignin, thus providing a stiff, decay-resistant matrix to the composite structure. Studies suggest that at least part of the hemicellulose within a typical cellulosic fiber acts as a covalently bonded connector between lignin and cellulose (Lawoko *et al.* 2003).

Disassembly of Woody Material

In view of the theme of restraining factors and forces that tend to oppose the swelling of cellulosic fibers, it is important to keep in mind some of the widely employed technologies that are being used to prepare such fibers for papermaking, nanocellulose, and other applications. Many such processes can be regarded as disassembly processes, whereby either some components are removed or the fibers are mechanically separated from each other. Such treatments may weaken the ability of structures within the fiber to restrain swelling tendencies.

Delignification

Terms including "pulping" and "chemical pulping" are used to denote the widely employed methods of removing lignin (often with partial removal of hemicellulose) as part of the preparation of cellulosic fibers for papermaking and other applications (Mboowa

2021). It has been shown that removal of lignin from a cellulosic fiber, still in its undried state, leaves behind a structure having substantial mesoporous character (Stone and Scallan 1967; Berthold and Salmén 1997a,b). In other words, there are pores having diameters in the range of about 2 to 50 nm. Berthold and Salmén (1997a), who employed inverse size exclusion chromatography, found that delignification resulted in development of about 1.1 to 1.2 mL/g of new pore volume for water-swollen never-dried bleached and unbleached kraft pulps. Confirmatory evidence of increased pore volume after chemical pulping has been obtained by WRV testing (Jayme and Büttel 1968; Laivins and Scallan 1993). For example, Carlsson *et al.* (1983) showed that the WRV, a measure of swelling, increased from an initial value near to 115% (mass water per mass solids) up to the range 160 to about 250 %, depending on the pH. Scallan and Tigerström (1992) showed that such results could be interpreted as being due to a decreased elastic modulus of the cellulosic fiber material with the removal of the lignin, thus decreasing the ability of the fiber structures to resist swelling.

Presumably this development of mesopore spaces in wood fiber cell wall as a result of chemical pulping could be attributed to the presence of lignin-rich nano-domains having such dimensions in the original wood. Such domains are illustrated in Fig. 8, which is a redrawn version inspired by Fengel and Wegener (1989). Note that lignin is envisioned in the sketch as surrounding a microfibril (*i.e.*, an assemblage of nanofibrils), the center portion being mostly cellulose, and with hemicellulose acting as an intermediary between the cellulose and the lignin. As mentioned in the Introduction, it should be understood that pectins also are expected to play a role (Alkorta *et al.* 1998; Ebringerová *et al.* 2005; Scheller and Ulvskov 2010). The idea of lignin occupying nano-sized domains is supported by the relatively large size of the lignin macromolecules that have been isolated by alkaline pulping methods (Gupta and Goring 1960).
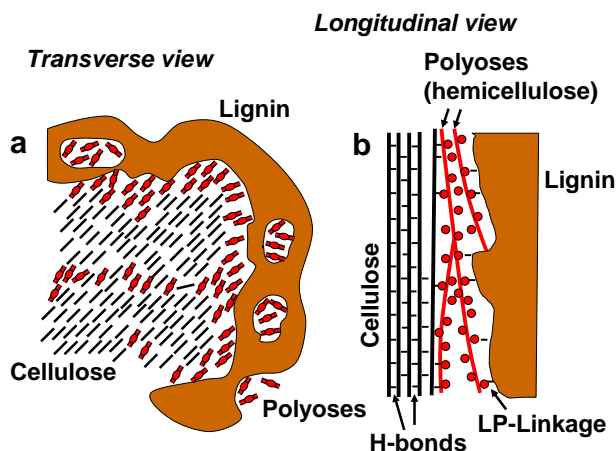
Fig. 8. Depicture of woody material at the nano-scale, whereby cellulose and lignin tend to occupy different nano-domains, and the hemicellulose tends to be located between the cellulose and lignin

Lignin-carbohydrate complexes in intact wood

Another important feature that is shown in Fig. 8 is a type of linkage that can be expected to play a contributing role in inhibiting swelling of intact wood specimens. Note the label "LP-Linkage" that appears at the lower right of the figure. This label refers to covalent attachments between hemicellulose and lignin, *i.e.,* lignin-carbohydrate

complexes (LCCs) (Lawoko *et al.* 2003). The presence of such bonds helps to explain how it is possible for the hemicelluloses, which are the most hydrophilic main component of wood, to remain securely adherent, at a molecular level, to lignin, which is much more hydrophobic. Thus, wood retains its inherent strength and integrity, even when it is soaked during rainy seasons or immersion in water. In intact wood, lignin forms connections with different matrix polysaccharide molecules in a way that crosslinks the structure. This prevents wood fibers from extensive swelling in water (Henriksson 2017). Such limitations to swelling can be regarded as an attribute of "woody" matter, *i.e.* secondary xylem. During chemical pulping, the lignin-polysaccharide networks are in large part dissolved (Lawoko *et al.* 2005).

The moisture content of intact wood specimens has been shown to rise in approximately linear fashion with increasing relative humidity (RH) from about zero to about 0.3 mass fraction at about 95% RH (Fredriksson 2019). Further exposure of the material to liquid water gave rise to a dramatic rise to about 2.5 mass units of water per mass unit of solid. It is reasonable to expect that such values are constrained by such factors as the pore volume within cell lumens, vessels, some swelling of hemicellulose, and the presence of LCCs that prevent what otherwise might be a form of delamination at the nanoscale of wet wood. As noted by Fredriksson (2019), under dry conditions, much of the water is associated with wood material *via* hydrogen bonding, whereas under saturated conditions capillary forces draw water into the structure.

Mechanical refining of pulp

To prepare cellulosic fibers for papermaking, their aqueous suspensions are typically passed through mechanical devices called refiners (Gharehkhani *et al.* 2015). Often this operation is carried out at consistency (filterable solids) levels of 4 to 10%. In a modern pulp refiner, flocs of fibers experience repeated compression and shearing events as the rectangular "bars" of a rotor repeatedly cross a corresponding set of bars on a stator.

There are two main classes of refining practices – refining of mechanical pulps and refining (sometimes called "beating") of chemical pulps such as kraft pulps. A key difference lies in the fact that mechanical pulps are generally fed into the refining system in the form of wood chips, whereas the chemical pulps already have been liberated as individual fibers due to the breakdown and dissolution of the lignin. The equipment, processes, and various options for pulp refining have been discussed elsewhere (Li *et al.* 2011; Gharehkhani *et al.* 2015; Kerekes 2015). As noted by Lahtinen *et al.* (2014), both main classes of pulp refining generally result in a fibrillated appearance of the material. In other words, some unraveling takes place of the outer fibrillar layers due to the repeated compression and shearing event. Kraft pulps were found to fibrillate relatively easily and quickly, yielding large values of WRV (*e.g.* 380%). This effect is consistent with the breakdown and removal of cellulosic strands encircling the dominant S2 sublayer of pulp fibers. Increases in WRV due to refining can be largely attributed to delamination within the cell walls, *i.e.,* internal fibrillation (Przybysz *et al.* 2017). By contrast, mechanical pulps did not reach as high levels of WRV and there was substantial fragmentation of fibers, in addition to visible fibrillation (Lahtinen *et al.* 2014). The fines fraction of refined pulp has been shown to hold onto a disproportionate amount of the water detected by WRV and related tests (Laivins and Scallan 1996; Olejnik *et al.* 2017).

Figure 9 presents a schematic view of how the cross-section of a kraft pulp fiber is expected to change over the course of extensive mechanical refining. The manner in which

fibers are packed together in the woody tissue of a tree gives rise to the rectangular shape of unrefined wood-derived fibers, as depicted on the left side of the figure.
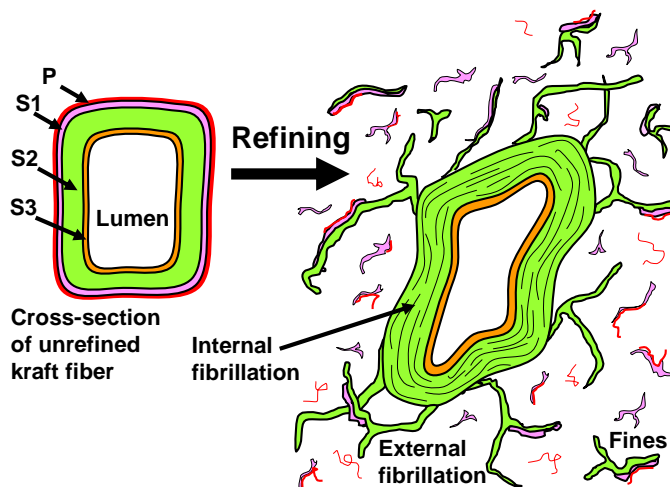

Fig. 9. Schematic view of (left) the cross-section of an unrefined kraft pulp fiber, showing the layered structure of the cell wall and (right) an intentionally exaggerated view of the same fiber's cross-section after mechanical refining, featuring swelling of the partly delaminated S2 sublayer, mechanical breakdown and either removal of fibrillation of the outer layers, and partial or complete collapse and closure of the lumen space. Figure previously used by Debnath *et al.* (2022)

Repeated shearing and compression events as the fiber passes through one or more mechanical refiner stages is expected to impart swelling. In this illustration, the bright green S2 sublayer is depicted as becoming thicker, presumably in the course of internal partial delamination, with the intake of water. The breakdown of the outer layers of the kraft fiber, as well as some of the S2 sublayer, may partly result in attached cellulosic fibrils extending outward from the main part of the fiber. When such fibril material becomes detached during the course of refining, they become part of the fines component of the fibrous slurry. These narrow cellulosic materials will be in contact with large amounts of water, leading to the question as to whether this can be regarded as another contribution to swelling.

Preparation of nanofibrillated cellulose

Considerably greater increases in apparent swelling can be achieved if mechanical compression and shearing of cellulosic material is continued way beyond the levels associated with ordinary papermaking, *i.e.,* with the production of microfibrillated (MFC) or nanofibrillated cellulose (NFC) (Eichhorn *et al.* 2010; Lavoine *et al.* 2012; Hubbe *et al.* 2017). The resulting materials, often consisting of highly branched and diverse strands of cellulose having diameters less than about 100 nm, typically have no restraints on their swelling. When the amount of water is kept in a suitable range, hydrogels are formed (Hubbe *et al.* 2013). However, in violation of the usual expectation for a proper hydrogel, such mixtures can continue to take up more water until they become viscous non-gelled suspensions (Hubbe *et al.* 2017). By contrast, a proper hydrogel will be composed of hydrophilic (usually negatively charged) polymer segments with sufficient covalent cross-linking to prevent their dissolution (Ganji *et al.* 2010; Hubbe *et al.* 2013).

A variety of mechanical devices, as well as different chemical and enzymatic treatments, can be employed to prepare nanofibrillated cellulose and related products from a variety of cellulosic materials. From a practical standpoint, there can be advantages of simply using ordinary pulp refining equipment, which is a mature technology employed at paper mills throughout the world (Gharehkhani *et al.* 2015). By carrying out very large numbers of repeated passages through such refiners, gel-like MFC suspensions can be obtained (Chen *et al.* 2016; Shafiei-Sabet *et al.* 2016). At a laboratory scale, various homogenizer devices can be used effectively to achieve different degrees of fibrillation by varying the number of passes. For instance, Pääkkö *et al.* (2007) used a high-pressure homogenizer to convert oxidized cellulose into nanocellulose suspensions having exceptionally high viscosity at a given solids content. Others have used devices in which a pair of jets collide directly, causing suspended cellulose particles to become fibrillated (Dimic-Misic *et al.* 2016). Finally, friction-grinding equipment can be used as a way to prepare highly fibrillated cellulose suspensions at the lab scale (Hassan *et al.* 2011). Products of such shearing devices, as long as they are kept in their wet state, can swell with water without any upper limit. However, such mixtures may pass from being gel-like to being liquid-like at some point, since typically there are no permanent attachments between the adjacent particles while they remain in a wet condition.

Aqueous Conditions

Colloidal science considers the forces of interaction between materials at very short distances in aqueous media (Hubbe and Rojas 2008; Benselfelt *et al.* 2023). Thus, many of the factors related to water that affect swelling of cellulosic materials fall within that field. Here the attention will be on the evidence, considering in what ways the swelling has been found to depend on pH, the nature of charged groups on cellulosic materials, the concentrations of salts, and effects due to various multivalent ions.

Table 3. Reported Effects of pH on the Swelling of Cellulosic Materials

Specimen Type	Reported Effects	Citation
Cellulose gels	High WRV values were observed in pure water in the pH range from 6 to 10.	Grignon & Scallan 1980
Unbleached & bleached kraft	Reswelling ability after drying was much greater with increasing pH value during drying, but only when the carboxyl group content was high.	Lindström & Carlsson 1982
Unbleached & bleached kraft	Strong increases in WRV of unbleached kraft were observed with increasing pH, but little pH effect in case of bleached kraft pulp.	Lindström & Kolman 1982
Delignified spruce	WRV increased by about 70% with increasing of pH from 3 to 10.	Carlsson *et al.* 1983
Microcrystalline cellulose	Only a slight increase in water uptake was found with increasing pH; larger particles swelled to a greater degree.	Ang 1991
Acrylic acid-deriva-tized cellulose	Fiber perimeter doubled when changing the pH from 2 to 5.	Karlsson *et al.* 1998
Succinylated cellulosic fibers	Fiber perimeter increased by about 18% or 40% when the pH was raised from 3 to 11.	Gellerstedt *et al.* 2000
TEMPO-oxidized cellulose fibers	The increase in WRV on changing from pH 3.5 to 9 was much greater for high-charge fibers.	Sjöstedt *et al.* 2015

pH and fiber charge

Most effects of pH on the swelling of cellulosic materials can be attributed to the degree of dissociation of ionizable groups, especially carboxylic acid groups, which will be considered in more detail later. Table 3 summarizes some key findings related to observed pH effects. As shown, it has generally been found that swelling increases with increasing pH. The results are in agreement with the relationship between pH and dissociation of carboxylic acid groups (Herrington and Petzold 1992).

As mentioned in Table 3, the findings of Lindström and Kolman (1982) provide a good reference point, since they involve ordinary unbleached and bleached kraft pulps. Their main findings are shown in Fig. 10. As indicated in part A of the figure, only minor pH effects were observed in the case of bleach kraft pulp. When comparing pH effects during refining in the absence of salt (distilled water), an increase in WRV from about 172 to about 182% was observed when the pH was raised from about 3 to 5. But when the WRV was retested in pH=4 buffer solution, all of the values were about the same, regardless of the pH. In addition, no effect of pH on WRV was detected when refining was carried out in the presence of salt (0.1 N NaCl). Part B of Fig. 10 shows a different story when evaluating the corresponding unbleached kraft pulp. Increasing pH during refining yielded relatively large increases in WRV, at least up to pH=10. The decrease observed above pH=10 in the absence of salt is consistent with the higher ionic strength that is required to reach those high pH values. Ionic strength effects will be discussed next. Note that the effects of pH on WRV were still apparent for the unbleached kraft pulp even after the pulp had been rinsed and adjusted to pH=4 with a buffer.
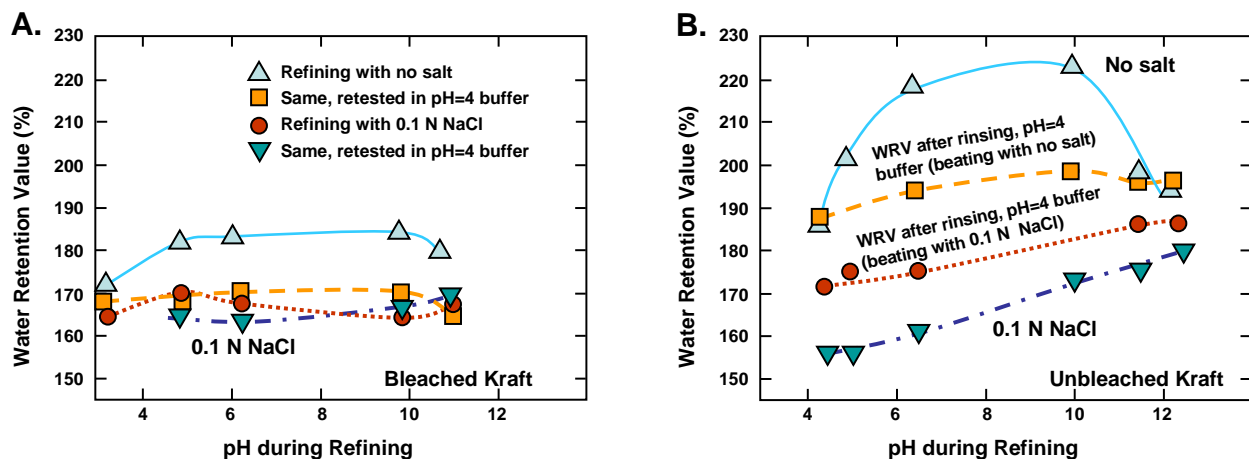
Fig. 10. Redrawn figures from Lindström and Kolman (1982) showing effects of pH during refining of (A) bleached kraft pulp and (B) unbleached kraft pulp. Refining was at the pH values shown either with no salt of 0.1 N NaCl. WRV measurements were done either in the same solution or after rinsing with pH-4 buffer solution

Salts

Simple monovalent salts, such as NaCl, are known to suppress osmotic effects that otherwise would promote swelling, as will be discussed later in the article. Empirical evidence of such effects is widely available. For instance, Fig. 10 shows a case in which the presence of 0.1 N NaCl decreased the ability of a certain amount of mechanical refining to increase the WRV of both bleached and unbleached kraft pulps. In the case of the bleached kraft pulp, the effect of salt disappeared after the pulp specimens had been rinsed

and resuspended in mildly acidic buffer solution, but in the case of the unbleached kraft pulp, which tends to bear a higher density of carboxylic groups (Lloyd and Horne 1993; Lindgren *et al.* 2002; Hubbe *et al.* 2012), the effects of salt during refining were still apparent in the pH=4 buffer solution.

Effects of salt can be expected to be more dramatic in cases where the cellulosic materials have been treated to increase its charge density of carboxylic acid groups. Thus, large decreases in WRV were observed upon salt addition to pulp fibers that had been treated with carboxymethyl cellulose (CMC) (Laine *et al.* 2002). In the cited study it is notable that the charged groups were associated with the cellulose merely by an adsorption process of the CMC onto the fibers, with no covalent attachment. The effect was greater, per unit of adsorbed CMC, when the molecular mass of the CMC was large. The authors attributed those results to an extended, bulky conformation of CMC chains attached externally to the cellulosic fibers. Related effects were found by Karlsson *et al.* (2018), who studied carbohydrate gels that had been carboxymethylated to different degrees. Salt effects became important at pH values of about 7 and higher. Salt-free gels having high carboxylate content reached WRV values up to about 140%, whereas the corresponding WRV values in the presence of 10 mM NaCl were about 73%.

Cation valence

The ability of positively charged ions to suppress the swelling of negatively charged cellulosic materials increases strongly with increasing valence (Scallan 1983; Lindström 1992; Maloney 2015; Kummala *et al.* 2018). Such effects were shown in particular by Scallan and Grignon (1979). Higher-valence metal ions suppressed the fiber saturation point (FSP) values of sulfite and kraft pulp fibers to a greater extent. The suppression of swelling was highly correlated with decreases in the strength of paper sheets formed form the respective fibers. Similar effects of cationic valence on swelling and fiber strength were reported by Katz *et al.* (1981). Notably, the hydrogen ion, associated with low pH, had effects similar to those of the trivalent aluminum ion. This is consistent with the findings of Scallan and Tigerström (1992), who showed that exchanging sodium ions in place of hydrogen ions led to large increases in the swelling of pulp fibers.

Benselfelt *et al.* (2019) found that the ions that were most effective for lowering the swelling of negatively charged nanofibrillated cellulose were those that developed strong complexation. Of the divalent ions, the magnesium ion had the minimum deswelling effect, whereas barium (a highly polarizable divalent ion) and copper (a much less polarizable ion than magnesium) had greater deswelling effects. A similar relationship was found in the case of monovalent cations (Benselfelt *et al.* 2023), such that the greatest swelling was observed for Li^+, somewhat less for Na^+, and the least for Cs^+. These effects were observed in the case of negatively charged nanocellulose films.

Cationic polyelectrolytes

Cationic polyelectrolytes likewise have been shown to decrease the swelling of cellulosic materials in suspension (Swerin *et al.* 1990; Ström and Kunnas 1991; Zhang *et al.* 2002; Aarne *et al.* 2012). Thus, it was found that a low-mass quaternary ammonium polymer (polybrene) was able to suppress the swelling of hardwood kraft fibers to lower WRV values than treatment with high-mass poly(diallyldimethylammonium chloride) (polyDADMAC) (Aarne *et al.* 2012). The polyDADMAC was able to achieve a relatively high decrease in WRV (from about 355% to about 250% in the case of highly refined fibers) at a lower added amount, making it a more efficient deswelling agent. Ström and

Kunnas (1991) found, likewise, that higher-mass polyethylenimine (PEI) was both more efficient (requiring a lower dosage) and more effective (reaching a lower WRV) in comparison to a lower-mass PEI product. Aarne *et al.* (2012) found that adsorption of polybrene onto bleached hardwood kraft pulps mainly decreased the swelling of the larger pores in the cell walls, having initial diameters in the range of about 27 to 220 nm.

Anions acting as swelling agents

Though it has received less attention in published articles, certain ions having the same (*i.e.*, negative) charge as the cellulosic material have been shown to increase swelling, in contrast to, for instance, the chloride ion. Thus, Fält and Wågberg (2003) observed significantly higher WRV values of unbleached kraft pulp in the presence of sodium sulfate at a 0.1 M concentration, in comparison to NaCl. The effects were shown to correlate to the results of tests with quartz crystal microbalance with dissipation (QCM-D) (Fält *et al.* 2003). Thus, the Na_2SO_4 solution gave rise to a looser, presumably more swollen cellulosic film. Sodium bicarbonate solutions have shown related effects (Kahar *et al.* 2013), but effect of the pH of those solutions makes such findings harder to interpret.

Bendzalova *et al.* (1996) reported that treatment of wood chips with "swelling agents" including amines, carbonates, and chlorides before high-yield pulping at high temperature led to higher swelling. The WRV of the resulting pulp was increased from about 100% in the case of water to almost 500% in the case of sodium carbonate. Related results were found with measurements of the fiber saturation point, but only a fair correlation was observed between the two different measurements of swelling. It is possible that such effects bear a relationship to the ionic liquid solvent systems to be described later; thus, higher swelling may be associated to combinations of positive and negative ions that do not have a tendency to form crystals.

Attributes of the Cellulosic Material

Many factors that affect the swelling of cellulosic materials fall into the category of attributes of the cellulosic materials themselves. Some of these attributes, being so central to the discussion, have already arisen when considering aspects of biosynthesis, delignification, mechanical refining, and the effects of aqueous conditions. The purpose of this subsection is to consider such aspects as chemical composition, aspects of microstructure, chemical modifications, effects related to delamination, effects related to the crystalline nature of cellulose, and effects on swellability related to drying.

Cellulose fibrillar orientation

The form of an especially dramatic manifestation of swelling, called ballooning (Cuissinat and Navard 2006; Zhang *et al.* 2013; Budtova and Navard 2016), has been attributed to the differing orientations of cellulose microfibrils in the different layers of a cellulose fiber cell wall. Aspects of ballooning will be considered in more detail later in this article when considering solvent systems for cellulose. Figure 11 provides a schematic illustration of the ballooned structure of a typical kraft pulp fiber that has been subjected to swelling in cold, moderately concentrated (7.6%) NaOH solution (Cuissinat and Navard 2006), especially in the presence of thiourea and urea (Zhang *et al.* 2013). Because most of the mass of the cell wall is contained within the S2 sublayer of the fiber, that sublayer accounts for most of the observed swelling. But the S2 sublayer is wrapped by the very thin primary (P) layer and the S1 sublayer, both of which have at least some cellulose fibrils oriented to encircle the fiber. In particular, the predominant microfibril angle in the S1

sublayer of Norway spruce wood species has been measured as 89 degrees, implying that it wraps the fiber perpendicular to the fiber axis (Andersson *et al.* 2000). Apparently, the swelling of the thick S2 sublayer causes it to burst through parts of the P and S1 layers, and that outer cellulosic material slides and is forced into narrow bands (Cuissinat and Navard 2006). Le Moigne and Navard (2010) described the "rolling up" of the outer cellulose layers into collars.
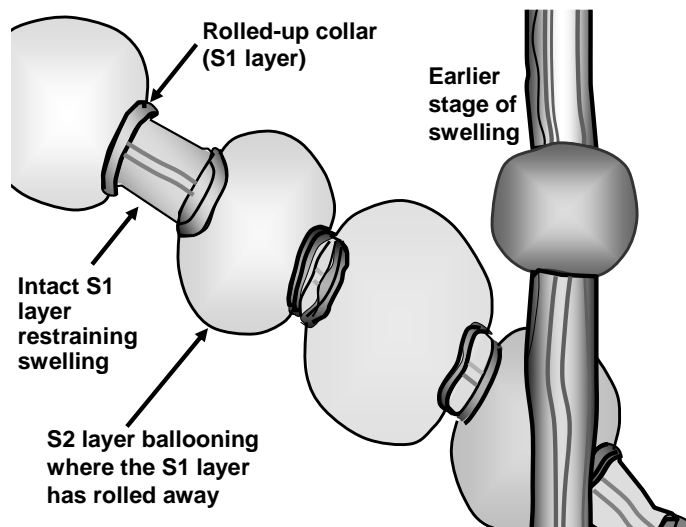

Fig. 11. Features of fir kraft fibers highly swollen ("ballooned") in NaOH-water solution, at different stages of the swelling process (redrawn in simplified form from Cuissinat and Navard 2006)

Confirmation of the mechanism just described comes from the fact that the ballooning phenomenon does not arise in some other notable forms of cellulose. For instance, regenerated cellulose fibers and filaments prepared after complete dissolution do not show ballooning phenomena. On the other hand, ballooning is still seen when studying intact plant-based cellulosic fibers that have been chemically derivatized (nitrocellulose, cyanoethylcellulose, cellulose xanthate fibers) (Cuissinat *et al.* 2008).

The orientation of crystals in a film of cellulose nanocrystals (CNCs) has been shown to affect the nature of swelling (Shrestha *et al.* 2017). Only isotropic swelling was observed when self-organized cellulose nanocrystal (CNC) films were exposed to high humidity conditions. By contrast, films composed of shear-oriented CNC particles showed increases in film dimensions of 0.02 and 0.30% in the parallel and perpendicular directions, respectively (Shrestha *et al.* 2017). This is consistent with the fact that plant fibers typically swell very little in their length directions, while they show various degrees of swelling perpendicular to their axes (Solhi *et al.* 2023).

Lignin content

As was shown already in the context of conventional delignification (*i.e.* chemical pulping) by breaking down and dissolving lignin from plant material, the resulting wet material contains substantial pore volume. To further explore such effects, Bai *et al.* (2022) used a combination of phosphoric acid and hydrogen peroxide to treat sugarcane bagasse. The treatment was found to remove essentially all of the hemicellulose and about 98% of the lignin. The void volume was increased by a factor of about ten relative to the untreated bagasse.

Such effects suggest two contributing mechanisms, the first of which is the fact that spaces are left behind after the removal of the solubilized material. The second mechanism is related to the relatively stiff, hydrophobic nature of lignin, in comparison to the other main components of woody material. Presumably after that stiff material is gone, the remaining structure will be more compliant and thus able to swell. It is also possible that the breakage of covalent bonds associated with LCC may play a role.

Hemicellulose content

Various work has shown that removal of both lignin and different levels of hemicellulose tends to increase swelling of the resulting fibers. The situation considered by Bai *et al.* (2022), as discussed above, was special, since the treatment had removed not only the lignin, but also all of the hemicellulose. A number of studies have considered effects in which the level of hemicellulose remaining in the fiber material was systematically varied. For example, Katz *et al.* (1981) progressively removed more hemicellulose from spruce and aspen mechanical pulps by NaOH treatments of differing severity.

The fiber saturation point was found to increase in a linear fashion in each case with the increasing content of acidic groups, which are mainly associated with the hemicellulose component. Likewise, work by Pejic *et al.* (2008) showed that removal of hemicellulose, along with some lignin from hemp fibers increased the capillary rise but decreased the WRV.

These WRV findings are consistent with the hydrophilic nature of hemicellulose and its tendency to swell in water. Another way to estimate effects of hemicellulose in pulp specimens is to compare the carboxylic acid group contents, of which the hemicellulose xylan is typically the main contributor. Zanuttini and Marzocchi (2003) showed that the WRV of chemi-mechanical pulps increased to an accelerating degree with increasing acidic group content.

Palasingh *et al.* (2021) discovered a unique effect with xylans, a hemicellulose component from hardwood pulps, were added to other polysaccharides as combined binders in the preparation of nanocellulose films. Though both components of the binder mixture were hydrophilic, the combination proved less susceptible to swelling. The effects were tentatively attributed to nanostructural effects.

Cellulose chemical modification with charged groups

Studies have shown that increasing amounts of ionizable groups in cellulose lead to greater swelling in water. Such findings are highlighted in Table 4. Such findings have been demonstrated, for instance, when cellulose is oxidized, giving rise to carboxyl groups. Hashemzehi and Sjöstrand (2022, 2023) prepared gel-like suspensions of extremely swelled fibers from commercial pulps by a combination of chemical treatments of oxidation and deep eutectic solvents, and even if the structure became extremely swollen, fibers were still visible in polarized light microscopy. Similarly, Table 5 highlights the findings of studies in which covalent reactions were employed to attach charged groups to cellulose, with evaluation of effects on swelling.

Table 4. Oxidation of Cellulose and its Effects on Swelling

Main Findings	Citation
The swelling of unrefined TEMPO (2,2,6,6-tetrametyl-1-piperidinyloxy radical)-mediated oxidation of bleached hardwood kraft pulp over a wide range was essentially unchanged relative to the original pulp.	Kitaoka *at al.* 1999
Peroxide treatment as the final stage of a bleaching sequence led to higher swelling of the pulp and denser, stronger paper sheets.	Toven 2003
Increasing oxidation of cellulose with nitrogen(IV) oxide in CCl_4 caused increased swelling in water	Zimnitsky *et al.* 2004
TEMPO-oxidized bleached kraft bamboo pulp showed higher WRV with increasing oxidation.	Zhang *et al.* 2012
TEMPO-mediated oxidation made it possible to achieve target swelling levels with less refining.	Brodin & Theliander 2013
Periodate-oxidized cellulose fibers swell homogeneously while maintaining their cellulose I crystal form; this is consistent with damage to the outer layers of the fibers.	Sim *et al.* 2014
TEMPO-oxidized nanofibrillated cellulose achieved 3.6 mL/g inter-particle water (*vs.* 0.7 to 1.7 mL/g for fibers).	Maloney 2015
TEMPO-oxidized fibers showed higher swelling with increasing charge content at pH=10, but not at pH=3.5.	Sjöstedt *et al.* 2015
Drying of TEMPO-oxidized nanofibrillated cellulose resulted in reduced swelling ability.	Torstensen *et al.* 2018
Pretreatment of cellulose with phosphoric acid and hydrogen peroxide led to inter-crystalline swelling and removal of lignin; the combination favored enzymatic saccharification.	Bai *et al.* 2022
Swelling of TEMPO-oxidized nanofibrillated cellulose films was similar to that of cellulose nanocrystal films.	Torstensen *et al.* 2022
Periodate oxidation in combination with deep eutectic solvent led to increased swelling of cationized cellulose fibers.	Hashemzehi & Sjöstrand 2022, 2023

Note: TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy

Table 5. Derivatization or Mixing of Cellulose with Negatively Charged Groups or Adsorption of Such Groups and its Effects on Swelling

Main Findings	Citation
Carboxymethylation of cotton generally increased swelling in water, but it was not the only factor.	Racz & Borsa 1997
Succinylation of cellulosic fibers resulted in increased swelling, especially at higher values of pH.	Gellerstedt *et al.* 2000
Topochemical attachment of CMC to the outer surface or bulk carboxymethylation of bleached softwood kraft pulp increased WRV, leading to higher paper strength.	Laine *et al.* 2002
Grafting of carboxymethylcellulose (CMC) onto bleached softwood kraft fibers gave higher swelling and enhanced paper strength.	Laine *et al.* 2003
Powdered carboxymethyl cellulose presence in paper strips led to more rapid wicking, as well as swelling, which were modeled.	Masoodi *et al.* 2012
Carboxymethylation of softwood kraft fibers led to their ballooning due to heterogeneous swelling.	Sim *et al.* 2014

Cellulose chemical modification with uncharged groups

       Though the reasons are somewhat different, derivatization of cellulosic materials with uncharged substituent groups also has been shown to affect swelling in water. Such findings are highlighted in Table 6. Based on such findings, it appears that a moderate level of substitution with uncharged groups can interfere with possible hydrogen bonding interactions between adjacent cellulosic surfaces. However, at higher levels of substitution, the hydrophobic nature of the attached groups can have a dominant effect, thus rendering the material significantly more hydrophobic and thereby decreasing swelling in water at higher levels of substitution.

Table 6. Derivatization of Cellulose with Uncharged Groups and its Effects on Swelling

Main Findings	Citation
Maximum swelling of acetylated ramie cellulose fibers was with 0.25 moles of acetic acid per glucose unit.	Vermaas & Hermans 1947
Low levels of acetylation (*e.g.* 10 to 15%) of pine and eucalyptus kraft pulps helped reswelling after drying. Effects were attributed to less inter-chain association.	Higgins & McKenzie 1963
Once-dried pulp fibers showed maximum swelling at about 5% content of acetyl groups.	Ehrnrooth *et al.* 1977
Esterification of cellulose fibers with fatty acids decreased swelling with increased alkyl chain length, whereas the degree of substitution had little effect.	Freire *et al.* 2006

Hornification's effect on swelling

       Effects of drying of cellulosic materials on subsequent swelling in water already have been mentioned in the course of discussing some other factors (Fernandes Diniz *et al.* 2004; Salmén and Stevanic 2018). The term hornification, as mentioned earlier, is widely used to refer to such loss of swelling ability, and the most commonly used method to quantify hornification is water retention value (WRV) tests (SCAN-C 62:00, 2000; TAPPI UM 256 1981; ISO 23714:2014), which involve centrifugation. The most severe effects of this nature are associated with conventional air-drying of cellulosic material from which lignin and much of the hemicellulose has been removed (Hubbe *et al.* 2007b). Such susceptibility is consistent with the compliant nature of kraft fibers, especially after mechanical refining, the presence of pores in the mesopore size range, and the fact that freshly exposed cellulosic surfaces are no longer isolated from each other by layers of lignin. Drying of paper also gives rise to strong capillary forces, which draw cellulosic surfaces into molecular contact (Page 1993; Wohlert *et al.* 2022), thus promoting the establishment of dense areas of hydrogen bonding.

       The mechanism of this phenomenon was proposed to be driven by chains of hydrogen bonds (Sjöstrand *et al.* 2023), although this does not account for the temperature dependence reported in several publications (Luo and Zhu 2011; Salmén and Stevanic 2018; Sellman *et al.* 2023). In fact, there are some disagreements in the literature on the mechanisms for hornification, probably due to the fact that multiple mechanisms can be simultaneously contributing to the reduced swelling during drying cycles. The hornification effects have been shown to decrease when using liquids other than water (Sjöstrand *et al.* 2023; Hashemzehi *et al.* 2024), and in some cases even *negative hornification* was achieved (Hashemzehi *et al.* 2024). Negative hornification is when the fiber swelling is higher when fibers are dried from a solvent compared with a never-dried

fiber reference. It has been demonstrated that negative hornification may occur during the drying of cellulose from specific solvents, which is particularly evident with less polar solvents. The underlying idea behind this phenomenon is that the presence of the solvent could lead to increased cellulose swelling by disrupting cellulose-cellulose bonds during the drying process. This disruption might expose and expand the inter- and intrafibrillar structure more than that found in a never-dried pulp.

Cellulose is typically bonded together in layers by hydrogen bonds, with hydrophobic interactions and van der Waals forces maintaining the layers' cohesion. Similar interactions could occur between cellulose fibrils (Medronho *et al.* 2012). The hypothesis from Hashemzehi *et al.* (2024) suggests that when a non-polar solvent infiltrates cellulose surface (Norgren *et al.* 2023), it potentially weakens the hydrophobic interactions, thus leading to possible cellulose swelling, ultimately resulting in negative hornification. Supporting this idea, the weakening of non-polar interactions has been proposed to play a role in cellulose dissolution (Lindman *et al.* 2010). Additionally, other factors might contribute to this phenomenon, such as the solvent's interaction with the polymer itself. For instance, the cellulose chains might become stiffer upon contact with certain solvents, further contributing to a more open structure.

Higher temperature during drying of pulps from water has been shown to result in stronger hornification (Welf *et al.* 2005). This phenomenon was especially stronger for drying temperatures over 100 °C. Sjöstrand *et al.* (2023) suggested that this is due to two different mechanisms. For the highest temperature, dehydration might give rise to covalent crosslinking of fibers. This is supported by a yellowing of these fibers. The temperature dependence under 100 °C is more puzzling, since hydrogen bond chains and thereby osmotic pressure are expected to decrease at higher temperatures; a possible explanation is that higher mobility on superficial cellulose chains (Fig. 3), as introduced by Salmén and Stevanic (2018). This allows cellulose surfaces to interact more firmly and with more hydrophobic interaction and van der Waals interactions. That the latter interactions might be important in hornification is supported by the results of von Schreeb *et al.* (2024); in that study microcrystalline cellulose was highly swollen by a partial dissolution in alkali, followed by precipitation, thereby creating a very swollen and amorous form of cellulose. The highly swollen cellulose became much more strongly hornified than the original material, and it was suggested that this was due to that the more amorphous cellulose had more hydrophobic surfaces exposed (von Schreeb *et al*. 2024). Table 7 highlights some key findings of studies showing how the drying of cellulosic materials has been found to affect subsequent swelling in aqueous media.

Table 7. Findings Related to the Hornification of Cellulosic Materials, *i.e.* the Loss of Aqueous Swelling Ability Due to a History of Having Been Dried

Main Findings	Citation
Drying of pulp fibers led to a loss of swelling ability and reduced paper strength after recycling.	Lyne & Gallay 1950
Shrinkage and reswelling were quantified for bleached spruce sulfite fibers upon drying and rewetting.	Page & Tydeman 1963
The loss of pore volume was demonstrated by solute exclusion tests, leading to a model in which lamellar pores close in a semi-irreversible manner during drying.	Stone & Scallan 1966
Transverse shrinkage of pulp fibers was quantified by soft X-ray analysis, showing about 0.5% shrinkage at 1.5% moisture content, 2% shrinkage at 1% moisture content, and over 7% at dryness.	Tydeman *et al.* 1966

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The drying of a wood pulp fibers was described as involving the following conceptual steps: (a) water removal from the fiber surface, with no deformation of the fiber, (b) water removal from the lumen, with collapse to a more ribbon-like shape, (c) water removal from the fiber wall, with the start of shrinkage, (d) development of wrinkling and transverse shrinkage, and (e) transverse shrinkage of the bonded regions within a paper sheet.	Nanko and Ohsawa 1989
The authors proposed that the formation of zones of hydrogen bonding, especially in the absence of lignin or hemicellulose "spacers" between the cellulosic surface, is responsible for loss of swelling ability.	Laivins & Scallan 1993
This thesis presents a wide-ranging discussion of hornification and its causes, including the closure of slit-like pores in the cell walls of fibers.	Nazhad 1994
The fines content of bleached kraft pulp, especially the fines generated during mechanical refining, were found to be highly susceptible to hornification.	Laivins & Scallan 1996
Loss of WRV of bleached kraft pulp was mainly attributable to water loss in the solids range 45% to 70%, which corresponds to the loss of free water.	Weise *et al.* 1996
The presence of hemicellulose, in general, tended to inhibit hornification during repeated drying of bleached kraft pulps.	Oksanen *et al.* 1997
Carboxymethylation of cotton, which renders it more swellable, gave rise to greater loss of swellability upon drying.	Racz & Borsa 1997
Similarities in effects of thermal aging and drying were reviewed, noting that both treatments led to a loss of swelling ability of fibers from paper.	Kato & Cameron 1999
Laser confocal microscopy showed losses in swelling occurring starting and solids contents in the range 30 to 35% during wet-pressing.	Weise & Paulapuro 1999
The term "cellulose fibril aggregation" is used to denote the coalescence of adjacent cellulosic material during drying, leading to loss of swelling ability, especially when the content of hemicellulose is low.	Hult *et al.* 2001
Hornification effects could be inhibited by treatment with swelling liquids, having diminishing effects in the following order: 12% NaOH > formamide > dimethyl sulfoxide = 2% NaOH = ethylene glycol	Tze and Gardner 2001
Additives such as cationic starch positively affected strength of sheets prepared with unbleached softwood kraft pulp, and the effects persisted in the course of recycling, but hornification was still evident.	Zhang *et al.* 2002
The review article emphasizes formation of lactone bridges as an alternative explanation for the reversible nature of hornification.	Fernandes Diniz *et al.* 2004
A co-crystallization mechanism to explain hornification is supported by ^{13}C NMR spectral evidence.	Newman 2004
The state of swelling of unbleached kraft pulps was correlated with their bonding ability. Drying greatly decreased WRV test results.	Forsström *et al.* 2005
Drying at increased temperature resulted in increased loss of swelling ability, whereas parallel tests with heating in the absence of drying did not hurt subsequent swelling.	Welf *et al.* 2005
Partial removal of xylan adversely affected the strength of unbleached and bleached kraft fibers that were dried.	Moss & Pere 2006
Hemicellulose adsorption onto kraft pulp helped decrease loss of absorptivity upon drying.	Köhnke *et al.* 2010
Swelling, as measured by WRV, decreased as a result of drying of bleached kraft pulp regardless of temperature.	Letkova *et al.* 2011
Wet-pressing of various chemical pulps induced loss of swelling ability.	Luo *et al.* 2011
Increasing time and temperature of drying increased the hornification of bleached hardwood kraft pulp.	Luo & Zhu 2011
Never-dried cellulose pulps of various kinds were more reactive to NaOH-water solvent system, but not NMMO.	Spinu *et al.* 2011
Cycles of drying of kraft pulp, without subsequent refining steps, led to increased air permeability, which is consistent with a stiffening of fibers due to pore closure.	Geffertova *et al.* 2013
Effects akin to hornification were observed when newsprint paper was subjected to accelerated aging, *i.e.* 98 °C at 50% relative humidity for various time periods.	Jablonsky *et al.* 2014

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The loss of swelling ability of unmodified plant fibers, when dried, was attributed to hydrogen bonding, despite the presence of lignin.	Ferreira *et al.* 2017
Loss of swelling ability increased with increasing temperature of drying; unexpectedly, such loss was greater if the process was halted at 80% dryness.	Salmén & Stevanic 2018
High-temperature drying of NFC films caused loss of free-volume pore size according to positron annihilation lifetime spectroscopy.	Torstensen *et al.* 2018
Coalescence of adjacent cellulose surfaces, *i.e.* fibril aggregation, accompanying the initial drying of pulp (moisture contents 10 to 15%), was confirmed by X-ray scattering tests.	Paajanen *et al.* 2022
The WRV of bleached kraft pulps decreased with cycles of drying. *Eucalyptus globulus* pulp showed less adverse effect that some other pulp types.	Simões *et al.* 2023
It was proposed that cellulose surfaces need to come close together in order to form hydrogen bonds that are responsible for loss of swelling ability. Acetone drying led to higher reswelling ability, which was proposed to be due to lack of chains of hydrogen bonds.	Sjöstrand *et al.* 2023
The review article cites sources indicating that hornification is not limited to delignified pulps.	Solhi *et al.* 2023
The process of hornification is proposed to be linked to a diffusion mechanism, and influenced by the time and temperature required for the surface interactions.	Sellman *et al.* 2023
Water as a solvent significantly influences the hornification process due to its capacity to create hydrogen bond bridges, while alcohol's weaker ability to engage in such interactions resulted in considerably lower hornification. A trend of reduced hornification when employing solvents with reduced polarity was shown, supporting the theory of hydrogen bond chains. The interaction between hydrophobic surfaces on cellulose via hydrophobic interactions emerges as another potential explanation for this phenomenon.	Hashemzehi *et al.* 2024

Crystal form of cellulose and related effects

By means of preparing regenerated cellulose products, technologists have been able to change the crystal form and other aspects of the material. Table 8 shows studies in which such differences in crystal type suggest that it may have played a role in swelling. It is important, when viewing such findings, to keep in mind that such transformation in crystallinity leads to profound changes that are not limited to just the crystalline zones. For this reason, caution should be exercised in drawing conclusions.

Table 8. Cellulose Crystal Type as a Possible Factor Contributing to Swelling in Aqueous Media

Main Findings	Citation
Conversion of cotton fibers to cellulose II, by treatment with LiOH or KOH, at ambient temperature led to increased swelling during the treatment and this affected the resulting fiber tensile properties.	Sreenivasan *et al.* 1989, 1993
Sodium carbonate treatment of rice straw appeared to change the crystal form to cellulose II and also to lead to swelling, which promoted enzymatic saccharification.	Kahar *et al.* 2013
Treatment of hemp fibers with NaOH (mercerization leading to cellulose II) swelled the fibers, increasing their accessibility to enzyme action.	George *et al.* 2015
Pretreatment of cotton fabric with NaOH/urea solution, thus changing cellulose I to cellulose II, increased WRV.	Gao *et al.* 2020

Transformation of cellulose I to cellulose II occurs upon dissolution and regeneration of cellulose. The change also takes place after treatment with sodium

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hydroxide in mercerization of cellulose and subsequent removal by washing, even though the fibers remain intact during such processing. In the mercerization, sodium ions are incorporated in the structure as "alkali cellulose". Studies have shown that alkali concentrations of 8 to 10% may transform a substantial part of the cellulose to cellulose II (Dinand *et al.* 2002; Schenzel *et al.* 2009). It has also been discussed that some steps in the pulping and/or bleaching processes may result in a higher amount of cellulose II and a higher degree of hornification (Ferreira *et al.* 2020).

THEORETICAL ASPECTS OF SWELLING OF CELLULOSIC MATTER

Adsorption, Wetting, and Permeation

Having considered, in the previous section, various evidence related to factors that affect swelling, the focus of this section will be on finding general explanations. These can be broadly assigned to the categories of thermodynamics, physical constraints, chemical effects, and kinetic effects. Thermodynamics considers ways in which physical systems arrange themselves to reach a minimum state of free energy, taking account of heats of interaction and a preference for freedom, *i.e.* maximization of entropy (Ganji 2010; Alexandersson and Ristinmaa 2018). Physical constraints can be considered in terms of the mechanics of materials, including the modulus of elasticity and other materials properties. Chemical effects include osmotic pressure (Grignon and Scallan 1980). Chemical effects also include consideration of solvent systems that have been optimized for the swelling of cellulose, up to its complete dissolution. Kinetic effects include consideration of diffusion-related processes and capillary wicking rates, in addition to considering trapped non-equilibrium states.

At a basic level, the interaction of water and cellulose can be regarded as a type of adsorption (Brunauer *et al.* 1938). As described in the cited article, even without considering the possibility of swelling, it is possible to account for many features of such interactions, including multilayer adsorption at very high levels of relative humidity. A further advance in understanding was achieved by thinking in terms of the interactions within clusters of water molecules (Frank and Wen 1957). When considering the polar nature of the -OH groups at cellulosic surfaces, Berthold *et al.* (1996) considered the relationship between such groups and the number of adsorbed water molecules.

The basic thermodynamics of water adsorption onto cellulosic materials has been reviewed (Eklund and Lindström 1991). Briefly stated, thermodynamics considers the equilibrium processes of water and cellulosic materials. Such processes will proceed in such a way as to minimize the Gibbs free energy of the system, which contains an enthalpy (heat) term and an entropy (randomness) term. Thus, at equilibrium, the chemical potential (Gibbs free energy per monomeric unit) of an adsorbed water molecule will equal that of a non-adsorbed one. The approach has been developed further to predict the pressures and relative rates of evaporation from curved menisci, such as when a pore is fully or partly filled with water (Thomson 1871; Fisher *et al.* 1981; Galvin 2005). Eklund and Lindström (1991) show how such concepts can be used to explain or predict adsorption behavior onto porous materials, including paper.

In general, for interaction between water or humid air and fibers, a change in Gibbs free energy ΔG is the driving force, as given by:

$$\Delta G = n_w \Delta \mu_w + n_f \Delta \mu_f, \tag{1}$$

In Eq. 1, n_w and n_f are the molar quantities of water and fiber, respectively and $\Delta\mu_w$ and $\Delta\mu_f$ are the change in chemical potential for water and fiber, respectively. The swelling of cellulosic fibers and fibrous networks, the change in Gibbs free energy ΔG_{swell} consists of several contributions and can be summarized as,

$$\Delta G_{swell} = \Delta G_{sorption} + \Delta G_{mixing} + \Delta G_{ionic} + \Delta G_{network} + \Delta G_{capillarity} \qquad (2)$$

in which $\Delta G_{sorption}$ is from both specific and non-specific moisture and liquid sorption. This contribution is from general moisture sorption to surfaces, as from moisture adsorption and desorption isotherms (Eklund and Lindström 1991), as described above. ΔG_{mixing} is the change in Gibbs free energy from mixing, with contributions from osmotic pressure and Gibbs-Donnan equilibria, and in general to which Flory-Huggins theory can be applied (Burchard 2003). ΔG_{ionic} is from electrostatic interactions, such as depicted by the DLVO theory and specific ionic interactions (Derjaguin and Landau 1941; Verwey and Overbeek 1948; Benselfelt *et al.* 2023). The $\Delta G_{network}$ term comes from restrictions to swelling from the fiber lamellae structure (see above), whereas $\Delta G_{capillarity}$ comes from wetting along and inside fibers and networks as well as from capillary work, in which a ΔP term, in most cases, is the Laplace capillary pressure but it can also comprise an external pressure. The latter two contributions are discussed below as well as osmotic contributions. However, for detailed discussions of Eq. 2, readers are encouraged to study the references cited above. Recently, an approach based on calorimetry data and MD simulations has been suggested by Benselfelt *et al.* 2024, in which cellulosic fibers could be considered as polyion-polydipoles showing considerable entropy-driven interactions in water.

The individual or overall change in Gibbs free energy can be negative or positive. A negative value indicates a spontaneous process, whereas a positive value implies that a process would cost energy to occur. In a larger context, swelling is governed not only by thermodynamic considerations but also kinetic ones, and it further depends on domain sizes and interacting distances.

More and more, the understanding of the forces that govern how biological structures are assembled has developed. The term self-assembly of biological systems is by no means young (Kushner 1969), but it has grown in importance as self-assembly more and more serves as inspiration when materials and products are innovated and developed. The assembly of lignocellulosic materials is now studied with great effort. Plant organisms that are constituted by such materials show a vast number of properties that are of interest.

Self-assembly, from a physical and chemical point of view, is governed by thermodynamics, which involves entropy and enthalpy (Hubbe *et al.* 2023). In self-assembly, a metastable state is preferable from an energy point of view. From a metastable state, the system can then overcome the entropic drive to maximize degrees of freedom. This circumstance is observed in nature in several examples, such as cell membranes, RNA/DNA, and cellulose (Etale *et al.* 2023).

In many cases, water acts as a mediator for the assembly and stabilization of biological molecular systems (Dargaville and Hutmacher 2022). Thermodynamics is essential here. Water produces an environment that can drive metastable configurations and long-range molecular order, encompassing not only the hydrogen bonding, but also van der Waals forces. These become more important as the hydrogen bonding moieties of molecules force the more apolar parts closer together, animal cell membranes being one example (Cresswell *et al.* 2021; Furman *et al.* 2021).

The thermodynamics of the complete system becomes vast when considering numbers of molecules involved, their interaction, and all structures engaged. Thus, the task of modelling such systems in detail becomes very challenging (Shen and Gnanakaran 2020). The number of molecules that can be modeled to a sufficient degree of accuracy, when using more detailed modeling methods such as molecular dynamics, are often quite small (Araujo *et al.* 2018; Chen *et al.* 2022; Wohlert *et al.* 2022). This means that very long range and large systems effects can be difficult to capture, in particular their summative effects on a higher structural scale (Sinko *et al.* 2015; Salem *et al.* 2022; Thybring *et al.* 2021, 2022).

Crystal/microfibril level

Some important questions arise with respect to events that occur within the size ranges of crystals and microfibrils. These include, how far do the order effects reach (Jarvis 2023; Lindman *et al.* 2017). With this respect, what is the relevance of structural features of cellulose? With respect to heterogeneity – the structural heterogeneity should disrupt the reach of order effects. But how large are the entropic gains? What could be overcome?

Removing water and putting it back again

The OH-groups present on cellulose will have to bind to something else. If they bond to other OH-groups in an orderly manner, this will tend towards increasing order and thus larger sizes of crystals. The bonds involved in such self-assembly are not easily opened again. Structure prevails. Long range order induces strain, stiffening the structure. These ideas have been supported by various research (Maloney *et al.* 1998a,b; Salmén and Stenovic 2018; Grunin *et al.* 2020).

Chemical effects

With respect to chemical heterogeneity, a question arises as to whether in a similar manner, structural heterogeneity should induce disturbance. Chemical pulping is in some sense a method to remove the heterogeneity, leaving room for continued crystallization of the cellulose (Pönni *et al.* 2012; Brännvall *et al.* 2021; Hult *et al.* 2003; Kihlman *et al.* 2013; Pönni *et al.* 2014). Examples of where chemical disturbance can be overcome have been described (Östblom *et al.* 2006).

Kinetic effects

A further question is whether crystallization and morphological changes (on a nano scale) can be observed *in situ*. It is known that crystallinity can be developed during pulping, and it can be characterized using various methods. Water bonding changes can be observed. Deuterated water has been used, since vibrations, measured as peaks in IR spectroscopy, can be assigned to bulk water and surface water (Rowland *et al.* 1995; Engquist *et al.* 1997; Östblom *et al.* 2006; Habibi *et al.* 2010; Suchy *et al.* 2010; O Neill *et al.* 2017; Sinko *et al.* 2015; Han *et al.* 2019; Nishiyama *et al.* 2019; Borrero-Lopez *et al.* 2023; Greca *et al.* 2023). Stresses tend to induce a long-range order on a fibrillar level and eventually impact fiber strength (increase stiffness).

Osmotic Pressure

Ionic strength and charge density

The osmotic pressure that develops within hydrophilic polymeric material immersed in water is a major contributing factor in swelling (Ganji *et al.* 2010). Proctor (1914) may have been the first to clearly explain osmotic effects as controlling the swelling behavior of hydrogels. Hydrogels generally can be described as loosely crosslinked polymer chains that contain ionizable groups. A historical breakthrough in the understanding of many swelling behaviors in aqueous systems with cellulosic materials can be attributed to a decision to regard those systems as versions of hydrogels (Grignon and Scallan 1980; Scallan and Tigerström 1992). As described by these authors, the extent of swelling then can be estimated by considering a balance between osmotic pressure, which favors swelling, and restraining forces, which are due to the properties of the material, crosslinking effects, and various related factors. As noted by Scallan (1983), it is mostly the carboxylic acid groups within cellulosic materials that contribute to such swelling effects, though one needs to keep in mind that other ionized groups, such as sulfonate groups, can likewise be expected to contribute. A testament to the strength of osmotic forces is the fact that a sufficiently high substitution of cellulose with carboxyl groups can cause it to become converted to nano-sized cellulose fibrils, *i.e.* NFC, without need for intensive shearing (Sjöstedt *et al.* 2015). Osmotic forces also play a role in steric stabilization, a mechanism by which hydrophilic polymer chains extending from a surface keep those surfaces from colliding and adhering to each other (Zauscher and Klingenberg 2000).

The osmotic pressure can be calculated based on the following equation (Ganji *et al.* 2010),

$$\pi = RT\left[\Phi\sum_i \overline{C_i} - \phi\sum_i C_i\right] \tag{3}$$

where Φ is the osmotic coefficient of the gel phase and ϕ is the corresponding quantity for the external aqueous solution. Likewise, $\overline{C_i}$ is the concentration of the ith ionic species in the gel phase and C_i is the corresponding value in the external solution phase. At equilibrium, one can expect a balance between the osmotic pressure and any elastic forces tending to limit swelling in the material (Grignon and Scallan 1980). The osmotic coefficient of the gel phase is given by Eq. 4 (Ganji *et al.* 2010),

$$\Phi = \left\{\phi_P + \frac{n_p}{n_m\alpha}\right\}\bigg/\left\{1 + \frac{n_p}{n_m\alpha}\right\} \tag{4}$$

where n_p is the molarity of the polymer, n_m is the molarity of the monomer, and α is the degree of ionization as a fraction. Various expected dependencies of swelling effects follow from these basic equations. Thus, swelling is expected to increase with increasing density of the ionic groups on the polymer chains or lamellar surfaces, *etc.*

Charge Effects

Effects of pH can be explained by the fact that a sufficiently low pH will cause protonation of carboxylate groups, thus decreasing the expressed charge density. The pK_a value, which is the pH at which there are an equal amount of charged and uncharged groups, is typically about 3.3 for carboxyl groups associated with hemicelluloses (Laine *et al.* 1996; Hubbe *et al.* 2012). Higher values of pK_a are associated with carboxyl groups with other neighbor groups, *e.g.*, those associated with lignin, as well as fatty acids and resin acids in the pulp. As the pH is adjusted to become increasingly higher than the pK_a

value of the predominant acidic groups, an increasingly higher proportion of those groups will be in their deprotonated, negatively charged form.

The effects of pH typically are spread out over a relatively wide interval. On an external surface or on a small molecule, each successive unit of pH increase above the pK_a value results in a tenfold decrease in the remaining uncharged carboxylic acid groups. Thus, at about pH=6 or higher, one can regard such carboxyl groups in typical cellulosic materials as being mainly in their negatively charged form. But swelling often continues to increase over a wider pH range (Lindström and Carlsson 1978; Lindström and Kolman 1982; Carlsson *et al.* 1983; Gellerstedt *et al.* 2000; Karlsson *et al.* 2018). The explanation lies in the fact that pH values can be markedly different in the interior of a material that behaves like a hydrogel (Grignon and Scallan 1980). The reason for such a difference can be explained based on a Donnan distribution of ions (Laine and Stenius 1997). Within the hydrogel, the ionic groups include those that are immobile – attached to the polymeric material. Those groups do not exist outside of the hydrogel. Differences in the concentrations of specific ions inside and outside of structure resembling a hydrogel are required because nature will not allow a buildup of net charge at any location. Thus, within the hydrogel there will be an equal number of positive and negative ions present, which will include the bound ions. As a practical consequence of the Donnan equilibrium, the pH is often two or three points lower within a cellulose-based hydrogel than outside, though the difference becomes less with increasing salt addition (Grignon and Scallan 1980).

The increasing concentrations of simple salts, such as NaCl, strongly decreases osmotic pressure values, thus decreasing swelling effects. As noted already, such effects have been widely reported for cellulosic materials (Grignon and Scallan 1980; Laine *et al.* 2002; Karlsson *et al.* 2018). Corresponding effects have been shown in swollen nanocellulose films (Ahola *et al.* 2008; Reid *et al.* 2016, 2017; Benselfelt *et al.* 2023), and in ultrathin cellulose films regenerated onto the surfaces of quartz crystal microbalance surfaces (Fält *et al.* 2003).

An alternative, and possibly equivalent way to account for the effects of surface charge and salt concentrations, with respect to the swelling of cellulosic materials, is based on repulsive forces between like-charged surfaces. These forces were first theoretically calculated by Dejaguin and Landau (1941) and Verwey and Overbeek (1948), who together are recognized for developing the so-called DLVO theory. The notable feature of this theory is the principle that the repulsion effect arises not directly from the charges on the facing surfaces, but rather due to the overlap of the adjacent layers of counter-ions, *i.e.* clouds of sodium or potassium ions, *etc.*, which balance the net charge on the surfaces.

Such an effect is illustrated pictorially in Fig. 12. In the figure, the pink area represents cellulosic material, and the gap in that material is supposedly filled with aqueous solution. The forces are expected to be strongest when the physical distance between the surfaces is approximately 0.5 to 2 nm, *i.e.* wide enough to physically accommodate a double layer, but not too much larger than that. The DLVO theory predicts a decreasing range of electrostatic repulsion with increasing salt in systems related to cellulosic materials (Hubbe and Rojas 2008), which is in line with predictions based on osmotic pressure calculations.
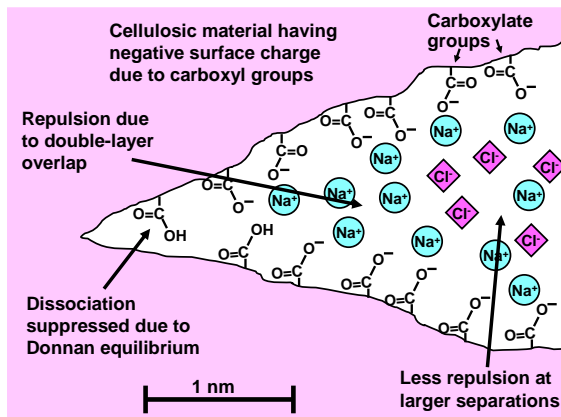
Fig. 12. Simplified qualitative representation of the potential swelling effect due to repulsive forces between facing cellulosic surfaces having the same sign of net charge, shown here as originating from the presence of carboxylic acid groups, where the counter-ions are shown as Na$^+$, and where the co-ions are shown as Cl$^-$

Complexation

As was discussed earlier in the article, multivalent cations, including various metal ions and cationic polyelectrolytes, have been shown to suppress swelling of cellulosic materials to a greater extent than monovalent cations, such as Na$^+$ (Scallan 1983; Swerin *et al.* 1990; Lindström 1992; Aarne *et al.* 2012; Maloney 2015; Kummala *et al.* 2018). For example, it has been noted that such forming such complexes in nanocellulose gels can greatly suppress swelling (Benselfelt *et al.* 2023). In addition, although separately each polyelectrolyte may be water-soluble, a well-formed film composed of complexed polyelectrolytes can be water-resistant with relatively low permeability to liquids and gases (Hubbe 2021).

Many of these effects can be placed within the category of polyelectrolyte complexation (Ström and Kunnas 1991; Chang *et al.* 2011). One of the key findings when two charged polyelectrolytes are mixed with each other is that the minimum swelling coincides with a state of equal interactions between opposite charges on the two kinds of polyelectrolytes (Chang *et al.* 2011). Notably, the stoichiometry of interaction between a strong polyacid and strong polybase in solution approaches a strict 1:1 ratio of charged groups in the relative absence of salt ions (Chen *et al.* 2003). PECs are known to undergo an unusual "antipolyelectrolyte effect" in which the degree of swelling increases with increasing salt addition (Dautzenberg and Jaeger 2002; Valencia and Pierola 2007). This effect can be attributed to the fact that the salt, within a certain range of concentration, weakens the complexation between the chains before sometimes causing the PEC to come apart. Such systems can have the unique ability to absorb and remove salt from brine solutions (Ayoub *et al.* 2013).

The mechanism by which polyelectrolyte complexation takes place is illustrated in Fig. 13. At left in the figure, one visualizes two separate polyelectrolytes, presumably being combined as dilute solutions from different containers. Each of these separate kinds of polyelectrolytes, in salt-free solution, has mainly two types of ions – those bound to the chain and a set of oppositely charged monovalent ions (the counter-ions) that have more freedom of motion. As depicted in the figure, when a pair of oppositely charged ions forms a polyelectrolyte complex (PEC), a direct pairing takes place between ions attached to the contrasting macromolecular chains. Because the polyelectrolyte chains, in addition to the charged groups attached to them, are already highly constrained in terms of possible

movements, only a relatively small amount of freedom of motion (entropy) is lost by such pairing. On the other hand, the former counter-ions of both signs of charge now are able to circulate freely within essentially all of the aqueous solution in the system. Thus, the PEC process tends to be driven to completion by a combination of two energy terms. These are namely the increased entropy mainly due to the more fully liberated former counter-ions and the heat of interaction associated with forming relatively stable ion pairings along the chains.
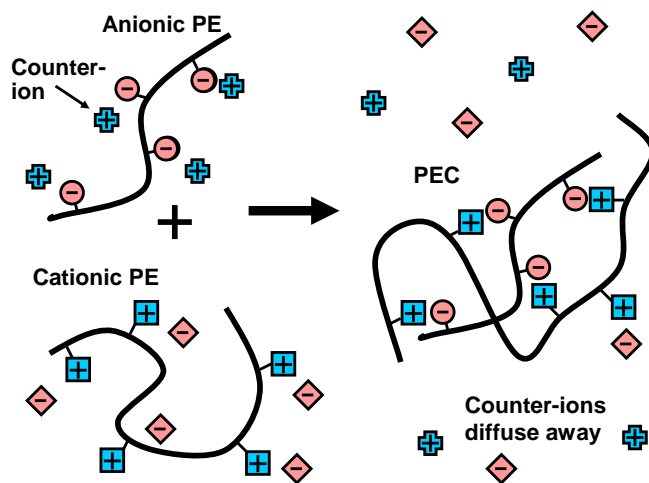

Fig. 13. Schematic representation of the interaction between two initially separate solutions of oppositely charge polyelectrolytes to form polyelectrolyte complexes, with the pairing of chain-bound charge groups and increased freedom of the fully liberated former counter-ions

It has been proposed that certain chemical additive programs that are widely employed during the industrial production of paper involve deswelling mechanism related to the polyelectrolyte complexation just described (Hubbe 2005). During the papermaking process, water needs to be removed from a layer of fiber slurry as it travels over a continuous loop of a mesh screen (or in the gap between two such screens). It had become well known that the dewatering process could be promoted by the additional of cationic polymers, with optimum results associated with adding the needed amount to just neutralize the net colloidal charge (Horn and Melzer 1975). Such observations are consistent with some effects of cationic polyelectrolytes on swelling (Swerin *et al.* 1990; Ström and Kunnas 1991; Zhang *et al.* 2002; Aarne *et al.* 2012), as mentioned earlier in this article. However, even greater dewatering effects have been observed in papermaking systems when treatment of the pulp furnish with a cationic polymer (usually either a very-high-mass cationic acrylamide product or cationic starch) is followed by either the sodium form of montmorillonite (commonly called bentonite) or various forms of colloidal silica (Andersson *et al.* 1986; Langley and Litchfield 1986; Andersson and Lindgren 1996; Hubbe 2005). As depicted in Fig. 14, the loops of cationic polymer are expected to collapse onto the surfaces of the small negatively charged particles, thus giving rise to a contraction and deswelling of the polyelectrolyte coils, *i.e.* a self-wringing sponge effect (Debnath *et al.* 2022).
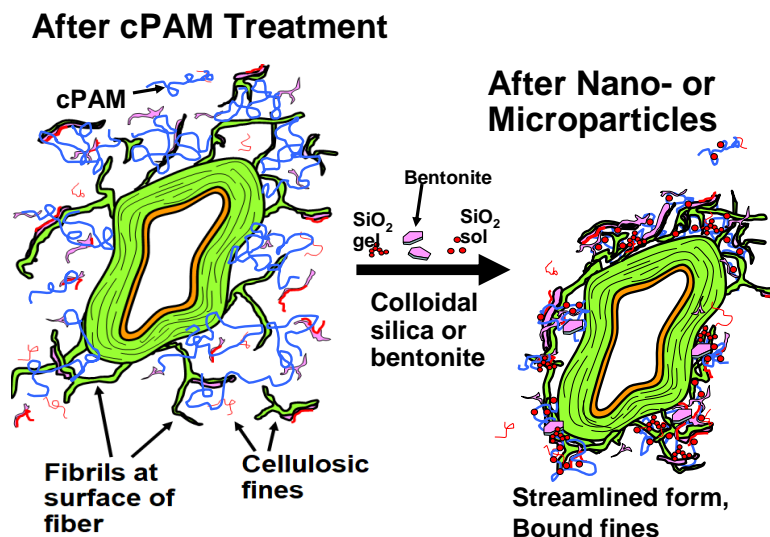
After cPAM Treatment

Fig. 14. Schematic illustration of a proposed deswelling effect when a fibrillated cellulosic fiber (shown in cross-sectional view) has just been treated with cationic acrylamide copolymer of very high molecular weight (left view) and subsequently is treated with an optimal level of a negatively charged particulate entity with very high surface area, *e.g.* colloidal silica, or a sodium montmorillonite (bentonite) product

Structural Restraining and Loosening of Restraints

The word "structure" can be regarded as a starting point for understanding and possibly quantifying the forces that restrain the swelling of cellulosic materials, for instance in opposition to the osmotic pressure effects just described. The cellulose macromolecule, often in the form of fibrils composed of those macromolecules, has a very strong resistance to stretching in its lengthwise direction (Iwamoto *et al.* 2009). It has been proposed that the elastic modulus of cellulose can be modeled in terms of the force-distance relationships that include a hydrogen bonding term (Kroon-Batenburg *et al.* 1986).

The high resistance to stretching of cellulose fibrils can provide strong restraint of swelling, depending on structural arrangements. Thus, Dufresne (2012) showed that the presence of stiff, relatively long cellulose nanocrystals tended to decrease the swelling of hydrophilic matrix polymers in a composite film exposed to water. The crystalline nature of cellulose and its degree of crystallinity can be expected to govern its swelling and its mechanical properties that may serve to resist swelling (El Seoud *et al.* 2008). An indirect demonstration of the forces within cellulose fibers that serve to limit swelling comes from measurements of the swelling of nanocellulose films (Rehfeldt and Tanaka 2003; Moriwaki and Hanasaki 2023). The cited authors pointed out that nanopaper films, composed of NFC, swell in the direction perpendicular to the fibrils to a much greater extent than ordinary cellulosic fibers. The explanation is that such films often lack extensive connections already established between the cellulose fibrils, including intertwined crystalline zones of the cellulose, covalent bonding to adjacent lignin domains (Lawoko *et al.* 2003), and an intertwined, relatively dense structure involving collaboration among the cellulose, hemicellulose, and lignin, as will be considered next.

Role of lignin

The lignin component of wood and many cellulosic fibers has a reputation as being relatively stiff. It follows that lignin, to the extent that it has not been removed by a

chemical pulping operation (Fardim and Tikka 2011), can play a major restraining role with respect to the swelling of the polysaccharide components of the fiber. Evidence of such a role comes from studies showing how the thermal softening of lignin can enable fiber swelling (Eriksson *et al.* 1991). On the other hand, Wang *et al.* (2021) showed that incorporation of lignin into a nanopaper structure by hot-pressing was able to decrease swelling by 94%. Likewise, high levels of modulus of elasticity were achieved when lignin was used as a binder in particleboards, along with a reduction in water swelling (Mathiasson and Kubat 1994).

Another factor that can contribute to lignin's general negative effect on fiber swelling is its generally hydrophobic character, especially in its natural form (Notley and Norgren 2010; Borrega *et al.* 2020; Lisy *et al.* 2022). Ekeberg *et al.* (2006) showed that it is possible to separate kraft lignin into fractions having differing degrees of hydrophobicity, which indicates its heterogeneous nature in high-yield kraft fibers. As noted by Borrega *et al.* (2020), the water-wettability of lignin surface can be strongly affected by the often nano-particulate nature of lignin. Reduction in the pH, which occurs during the process of washing unbleached kraft pulp, can precipitate small lignin particles back onto the fiber surfaces, leading to nano-scale roughness. It has been shown that roughness on a very fine scale tends to amplify differences in wettability (Wenzel 1949; Hubbe *et al.* 2015).

The elastic modulus of lignin tends to decrease with increasing content of water, which appears to function as a plasticizing agent (Cousins 1976; Back and Salmén 1982; Eriksson *et al.* 1991). The Young's modulus of different lignin specimens can range from about 2 to 7 GPa (Cousins 1976), depending on the moisture content and various changes that may occur during isolation or processing. These values are in the general range that has been predicted by quantum chemical calculations (Elder 2007). Back and Salmén (1982) showed that the softening temperature of native lignin decreased from about 200 to 115 °C as water content was increased in the range of zero to about 2.5%. Further increase in water content was found to merely remain external to the native lignin domains. However, it was found that derivatization of lignin, especially sulfonation, increased its swelling ability, which continued to depress the softening point of the lignin with much higher moisture contents of the modified lignin (Back and Salmén 1982).

Polysaccharides and hydrogen bonding issues

The mechanisms by which the polysaccharide components of woody materials can contribute to restraint of swelling often depend on hydrogen bonding in some way. It follows that such contributions will depend on such factors as the relative humidity or state of immersion in aqueous media. Assaf *et al.* (1944) used the term "avid" to describe the attraction of water molecules from the air onto and into dry cellulose, due to hydrogen bonding opportunities. Already at that time it was understood that the non-crystalline portions of cellulose, in addition to the hemicellulose, which is fully amorphous, take up most of that water. When forming nano-paper from NFC under ideal conditions, it is possible to achieve films that are sufficiently dense and defect-free that they can serve as superior barriers to oxygen and oils (Dufresne 2012). However, such barrier properties become progressively degraded with increasing relative humidity (Aulin *et al.* 2010).

A key principle regarding hydrogen bonds is that they generally have about the same energy content in a range of different circumstances. These include their presence in liquid water, in interactions between water molecules and cellulosic surfaces, and in air-dried or strongly dried cellulose material, including paper (Medronho *et al.* 2012). All such hydrogen bonds have an energy content of about 5 kcal/mole (21 kJ/mole).

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Considerable progress has been achieved in differentiating between various states of water that may exist within cellulose-based materials over a range of moisture contents. These categories of water include bulk water, freezing bound water, and non-freezing bound water (Tait *et al.* 1972; Froix and Nelson 1975; Maloney *et al.* 1998a,b; Capitani *et al.* 1999; Park *et al.* 2007; Gao *et al.* 2015). In addition, some water molecules could, in principle, be present in cellulosic materials in the form of chemical complexes (Joubert *et al.* 1959); however, such a category might be regarded as the same thing as non-freezing bound water. Differential scanning calorimetry has revealed that some of the more tightly bound water requires a higher expenditure of heat to induce evaporation (Park *et al.* 2007). As noted by Paajanen *et al.* (2022), coalescence due to hydrogen bonding or other interactions between adjacent cellulose chains may sometimes have the effect of opening up larger domains of bulk water within a swollen cellulosic material. Under some drying conditions, increased amounts of the remaining water may become less mobile, thus showing lower rates of diffusion in comparison to bulk water (Salmén and Stevanic 2018). The unique behavior of bound water can include changes in mobility, as detected by NMR methods (Lindh *et al.* 2017).

Crystallinity as an impediment to swelling

The crystalline domains within cellulosic materials are understood to be non-swelling, and they also may restrain swelling of adjacent cellulosic structures (Roberts 1996; Solhi *et al.* 2023). Large differences in swelling have been reported when comparing amorphous *vs.* crystalline thin films of cellulose (Aulin *et al.* 2009). Ottesen and Syverud (2020) found a correlation between crystalline content and aqueous swelling of NFC. Paajanen *et al.* (2022) reported that the swelling within wood microfibril bundles involved increased thickness of water layers between the adjacent cellulosic fibrils.

Related observations have been made for various regenerated cellulose materials. Chaudemanche and Navard (2011) observed much greater swelling of outer parts of lyocell cellulose filaments. The observations were attributed to a suspected lower crystallinity of the surface layers. Isogai and Atalla (1998) observed different propensities of different cellulose samples for dissolution in cold NaOH solution. These differences were attributed so such factors as the types of crystals (cellulose I *vs.* cellulose II, for instance) and differences in cellulose molecular weight in some specimens. Those results were consistent with those of Kontturi *et al.* (2011), who found that certain highly amorphous thin cellulose films swelled dramatically in water and were soluble in dilute NaOH solution.

The insolubility of crystalline cellulose domains in water

Though many of the hydrogen bonds that hold cellulosic structures together can be readily replaced by similar bonds with water molecules, there is one area of exception. Crystalline domains within cellulose remain stubbornly resistant to the effects of water. There appear to be two contributing explanations for such behavior. One involves cooperative effects of multiple hydrogen bonds acting in an organized fashion. The other involves van der Waals forces and hydrophobic interaction. Cooperative effects due to multiple hydrogen bonds acting together can be understood based on statistics. A single hydrogen bond, in an aqueous system, will have an average lifetime of less than a picosecond (Rapaport 1983). In such a pattern of bonding, though the existence of any one bond may be transient, the chance that all of the bonds would release simultaneously is essentially zero (Hubbe *et al.* 2023). Such situations, especially when macromolecules are involved, easily can lead to trapped non-equilibrium states rather than perfect crystals or

uniform gels (Claesson *et al.* 2005; Hubbe 2021). During biosynthesis of cellulose, as shown earlier in Fig. 6, it appears that the details are set up in such a way as to achieve a high degree of perfection of the crystalline domains, such that the result may be regarded as being close to a theoretical goal represented by defect-free crystals.

Another useful way to view the situation is through the lens of self-assembly (Hubbe *et al.* 2023). In the case of cellulosic microfibrils and other cellulosic surfaces, one can envision the possibility of zipper-like processes of hydrogen bond formation. Thus, Budtova and Navard (2016) suggested that such as zipping process can lead to insolubility of cellulose. Newman (2004) proposed that such a mechanism could account for irreversible loss of swelling ability when some cellulosic materials, such as kraft fibers, are dried. The concept was that the facing surfaces undergo a form of co-crystallization as the boundary between them dries out. This topic has been explored further by others (Pönni *et al.* 2012; Sjöstrand *et al.* 2023). Zhang *et al.* (2018) who proposed a mechanism by which cellulose dissolution can be promoted by relocation of cellulose chains so that they are "out of place" with respect to an otherwise possible zipper-like repair process. It was proposed that some cellulose solvent systems depend on such disorganizing effects to favor a net unraveling and dissolution.

As noted by Yamane *et al.* (2006), the cellulose crystal presents contrasting hydrophilic or hydrophobic character, depending on which face is being presented. This makes sense due to the fact that the hydrophilic –OH groups on cellulose face in the equatorial direction from the anhydroglucose repeating units of the polymer. Such an organization among adjacent chains means that in one direction the interactions are dominated by hydrogen bonding, whereas in the orthogonal direction, they are not. Rather, van der Waals forces and hydrophobic interactions are dominant in that direction. Such a dual-nature of how cellulose is held together has been discussed as a way to explain why it has been relatively difficult to find effective solvent systems for cellulose (Lindman *et al.* 2010; Glasser *et al.* 2012; Medronho *et al.* 2012; Budtova and Navard 2016). Reid (2017) proposed that van der Waals forces played a dominant role in the formation of certain CNC thin films; such a concept was helpful for explaining why observed swelling in that case has not been affected by salt ions. Hydrogen bonding has received dominant attention that hydrogen bonding has received as an explanation for many of the properties of cellulosic materials, including paper (Norgren *et al.* 2023). In that situation it is easy to overlook that the importance of van der Waals forces has been recognized for a long time (Warwicker and Wright 1967).

Sheet-like cellulose structures

A sheet-like nanostructure of water-swollen cellulose had been proposed by Stone and Scallan (1966, 1968) based on their observations of pore dimensions and the effects of drying. Such effects have been discussed by Nazhad (1994) in the context of accounting for loss of swelling ability when chemical pulp fibers are dried. In addition, electron micrographs of cross-sections of highly swollen cotton fibers under intermediate solvent conditions (ethylene diamine and $ZnCl_2$) appear to show separated sheet-like lamellas at the nano scale (Aravindanath *et al.* 1992a,b). Such an outcome is consistent with the concept described above, in which the bonding within cellulose chains is dominated by water-resistant van der Waals forces in one of the orthogonal directions (Khazraji and Robert 2013). The cited authors backed up such a characterization with molecular modeling. Based on the models and findings mentioned above, one can envision swollen cellulosic materials as potentially having slit-like, readily expandable pores that each can

fill with quite a lot of water, thus accounting for the ability of such fibers to take up much more water compared to their dry mass (Parham and Hebert 1980).

Accounting for High Swelling Systems

When technologists have the aim of dissolving cellulose, for instance with the use of specialized solvent systems, there are some factors that can become increasingly relevant. These include the molecular weight of the cellulose and its arrangements at the nano scale. Thus, treatments that break down the cellulose molecule can be important in cases where the goal of swelling the cellulose may include dissolution.

Depolymerization by chemical means

Thermodynamics dictates that dissolution of otherwise uniform polymeric materials will become more difficult with increasing molecular weight. Such effects can be expected to have parallel effects on swelling. The reason is that polymeric materials with increasing chain length gain less and less translational entropy upon their dissolution (Flory 1953; Medronho *et al.* 2012). The degrees of freedom within segments of a dissolved polymer are low due to the fact that each repeating unit is not free to move away from its immediate neighbors.

It has been shown that low molecular weight cellulose tends to be more readily soluble in specialized solvent systems, such as aqueous NaOH, which will be discussed in more detail later. Isogai (1996) found this in NMR studies. The cellulose employed was microcrystalline cellulose (MCC), in which the acid-destruction of non-crystalline zones of cellulose leads to decreased molecular weight. Since each cellulose chain needs to fit completely within a crystal domain of the remaining material after the acid hydrolysis, the molecular weight tends to have a limiting minimum value, *i.e.*, a leveling-off value. Parallel tests carried out with cotton linters, using the same NaOH solvent system, showed low levels of solubility.

Certain treatment conditions may induce a combination of cellulose swelling and simultaneous breakdown in mass, such that the two effects can lead to confounding of effects. For instance, placement of kraft fibers in –butyl-3-methylimidazolium hydrogen sulfate solutions gave rise to simultaneous swelling and breakdown (Mao *et al.* 2016). The breakdown of molecular mass was especially noticed at the highest temperature considered for treatment in that work. Likewise, treatment of bagasse fibers with phosphoric acid and hydrogen peroxide led to intergranular swelling, at the same time as hydrolytic breakdown (Bai *et al.* 2022). The combination of swelling and breakdown appeared to have favorable effects on subsequent enzymolysis, leading to the recovery of glucose in that study.

Cellulase treatment

Enzymatic hydrolysis of cellulose also has been shown to promote swelling in some cases. Thus, cellulase was used as a pretreatment or post-treatment in the preparation of lignin-containing NFC (Bian *et al.* 2019). The pretreatment led to higher values of WRV, consistent with higher swelling. Those results suggest that the cellulase pretreatment had the effect of weakening the material, making it more susceptible to the mechanical fibrillation process. By contrast, post-treatment with the cellulase led to lower WRV than the control sample (no cellulase). It is known that post-treatment of fibrillated cellulose with cellulase may essentially dissolve and remove some of the slenderest fibrils, leading to faster drainage rates during paper formation (Gruber and Gelbrich 1997; Kim *et al.* 2006). Biodegradation of single crystals of cellulose has been shown to lead to swelling

(Wang *et al.* 2012). This process was followed under aqueous conditions by means of atomic force microcopy. It was found that significant swelling took place only after substantial hydrolysis had been completed. Josefsson *et al.* (2008) showed that cellulase treatment could increase the swelling within cellulose ultrathin films. The effects were detected using the dissipation mode of the quartz crystal microbalance method (QCM-D). Thus, endoglucanases are able to create new end groups within the cellulose structure, making the material softer, with less restriction on swelling, whereas cellulases of cellobiohydrolase type lowered the swelling probably by degrading exposed structures (Josefsson *et al.* 2008).

Sublayer wrapping within cellulosic fibers

Some findings related to the layered structure of plant-derived cellulosic fibers already have been considered, but here the focus is on such findings specific to study of high levels of swelling. Some key findings of this type are included in Table 9. As shown, the restraining effects due to various cellulose layers can take many forms. In particular, the manner in which outer layers wrap around inner layers of cellulose fibrils in plant-derived cellulosic fibers tends to constrain fiber swelling in directions perpendicular to the axis. Ballooning, in fact, represents a partial failure in such a restraining action, whereby swelling within the thick S2 sublayer causes it to burst through the P and S1 layers, in a process that might be called herniation.

Table 9. Findings Related to How the Layered Structure of Cellulosic Fibers May Act to Restrain Swelling in the Presence of Cellulose Solvent Systems

Main Findings	Citation
Conversion of cotton cellulose from cellulose I to cellulose II in alkaline media occurs at different rates in different cell wall layers.	Aravindanath *et al.* 1992a
Swelling of cotton in a mixture of ethylenediamine and zinc chloride leads to sheet-like delamination within in cell wall.	Aravindanath *et al.* 1992b
The swelling of both cotton and viscose cellulose fibers in alkaline solution displays strong heterogeneity, which can be attributed to a nonuniform distribution of reagents.	Jaturapiree *et al.* 2008
In the course of their dissolution, the fibrils within native cellulosic fibers rotate and contract lengthwise.	Le Moigne *et al.* 2010
The core of lyocell regenerated cellulose filaments are buckled in the course of swelling of the outer parts of the filaments upon immersion in N-methylmorpholine N-oxide and water mixtures.	Chaudemanche & Navard 2011
Pretreatments such as hydrothermal, ethanolic acid, or both, enhanced subsequent alkali-based dissolution of cellulose, which is consistent with the weakening of the cellulose layers.	Kihlman *et al.* 2013
Ballooning phenomena are described in detail for different solvent systems including aqueous NaOH with optional thiourea, and urea. There was uniform swelling with all three components present.	Zhang *et al.* 2013
Ballooning phenomena were not observed if softwood kraft fibers were mechanically refined (leading to external fibrillation) before carboxymethylation, leading to relatively uniform swelling. This was attributed to degradation of the S1 layer.	Sim *et al.* 2014
This review article describes in detail how the outer layers of a cell wall roll up into collars that periodically constrain the drastic swelling of cellulose fibers from plants in various solvents.	Budtova & Navard 2016
Nanopapers, in which the fibrils are not constrained by encircling fiber layers, swell drastically perpendicular to the plain of the sheet, which contrasts with the limited swelling of ordinary paper.	Moriwaki & Hanasaki 2023

Some revealing features of the ballooning phenomenon were shown in micrographs of NaOH-water swollen bleached fir kraft fibers (Cuissinat and Navard (2006). Representative images from that work, which had been obtained by optical microscopy, were shown earlier in simplified form, in Fig. 11.

Crosslinking effects

In addition to the layered structures that are either present within cellulosic fibers or that develop in the course of their dissolution, another effect that can restrict fiber swelling is crosslinking. Such effects are well known in the field of hydrogels (Chang and Zhang 2011; Salam *et al.* 2011; Hubbe *et al.* 2013; Ma *et al.* 2015). But some studies have shown that some of the same reagents can be utilized to constrain the extents of swelling of cellulosic fibers (Gamstedt 2016). For example, Almgren *et al.* (2010) treated bleached birch kraft fibers with butanetetracarboxylic acid. The treated fibers were heated for 15 minutes at 150 °C, which would be expected to lead to formation of di-ester crosslinks, probably *via* initial dehydration to form the five-carbon-ring-type anhydride groups. The crosslinked fibers were less susceptible to swelling. Similar findings, based on treatments with butanetetracarboxylic acid and citric acid, were found to decrease the swelling of paper (Caulfield 1994). Steps in the likely mechanism, for the case of citric acid, are shown in Fig. 15. Note that a higher level of heating is required for both of the reactions shown at the left of the figure, involving the formation of successive dicarboxylic anhydride rings. Once such rings are formed, the activation energy for reaction with an –OH group (for instance on cellulose or other polysaccharide) will be lower (Nguyen and Pham 2020), and somewhat less vigorous conditions can be employed to complete the ester formation. It is worth noting, however, that the final structure in the depicted reaction contains a free carboxylic acid group, which can be expected to contribute to a swelling effect when the pH is raised to near or above its pK_a value.
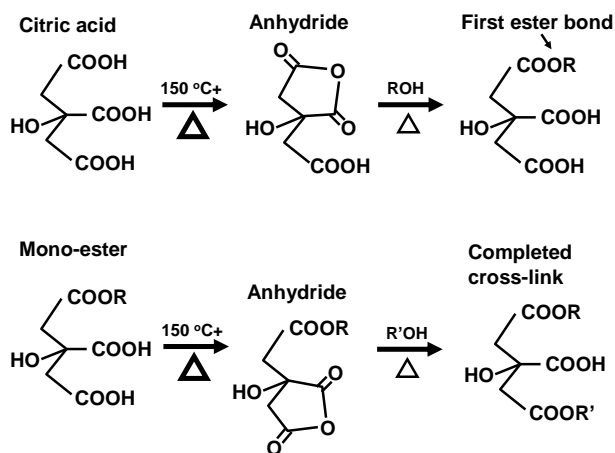

Fig. 15. Steps in a reaction of citric acid that can lead to crosslinking of a poly-alcohol, such as cellulose, which is here represented by the groups ROH and R'OH

Solhi *et al.* (2023), in their review article, suggested that crosslinking agents can be used to preserve the integrity of chiral nematic films prepared from CNC. In such applications, the crosslinks would limit swelling and keep the film from excessive swelling, which could be a step towards the individual nanoparticles from going back into aqueous

suspension and losing the striking optical affects often associated with chiral nematic character.

Solvent Systems

While the main focus of this review is on swelling, rather than dissolution, the effects of cellulose solvent systems can be regarded as an extreme manifestation of swelling. Many findings related to solvent systems already have been described in connection to other factors affecting swelling. Here the effects of some different solvent systems will be considered.

Swelling agents and solubility principles

Certain so-called swelling agents have been shown to induce swelling but not dissolution of cellulose. Highlights of such treatments and their results are given in Table 10.

Table 10. Swelling Agents for Cellulosic Fibers and their Reported Effects

Main Findings	Citation
Treatment of wood chips with amines, carbonates, and chlorides before high-yield pulping exhibited higher saturation points.	Bendzalova *et al.* 1996
Treatment of pulp fibers with swelling agents decreased the loss of swelling ability accompanying drying. Effectiveness, in decreasing order, was 12% NaOH > formamide > dimethyl sulfoxide = 2% NaOH = ethylene glycol.	Tze & Gardner 2001
The swelling of cellulose fibers by aprotic solvents was able to be well fitted based on solvent properties, especially when using the number of moles of solvent per anhydroglucose units as the way to express swelling. Dipolar actions were dominant.	El Seoud *et al.* 2008; Fidale *et al.* 2008
Fe-tartaric acid-NaOH complex solution swelled viscose, lyocell, or modal fibers, depending on concentration and time.	Vu-Manh *et al.* 2010a,b
Swelling of cellulose in different solvents was correlated with Hansen solubility criteria.	Chen *et al.* 2015

As is evident from the work of Chen *et al.* (2015), it makes sense to consider solubility principles as a way to predict, or at least to qualitatively judge, the potential for different media to swell cellulose. A practical approach to such analysis, which has become widely used in science and industry, is that of Hansen (2007). Such analysis is grounded on three types of interaction between the solvent and various candidate substances to be added. As illustrated in Fig. 16, the first is the Hildebrand parameter, δ_D, which is the square-root of the cohesive energy density of the material (either the solvent or the candidate for dissolution). The second parameter, δ_P, has to do with the extent of polar nature. The third parameter, δ_H, has to do with the capability for hydrogen bonding. In principle, if there is a good match between the solubility parameters of a certain solid and a certain solvent, then one would anticipate favorable swelling and a higher chance of solubility. The hypothetical example shown in Fig. 16 represents a case where the solubility spheres of cellulose and prospective solvent do not overlap, meaning that solubility is not expected. Though, based on the analysis of Chen *et al.* (2015), it makes sense to regard the Hansen method as a good starting point, the approach has limitations. In particular, the Hansen method does not have a way to deal with differing affinity characteristics of

different parts, ends, or faces of a given molecule or material. Such details tend to become more important when dealing with large molecules, *e.g.* polymers such as cellulose.
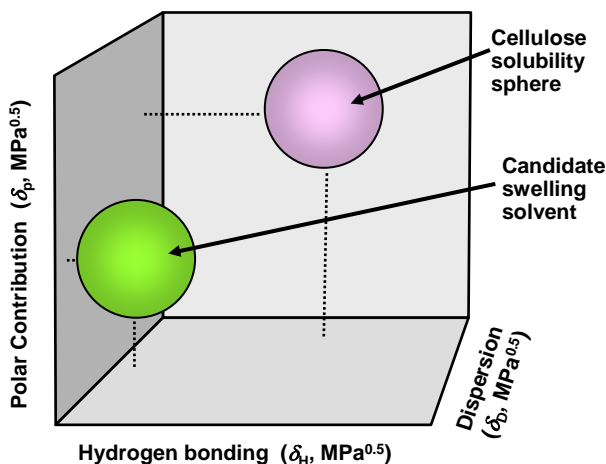

Fig. 16. Concept of solubility spheres, obtained by tests with probe liquids to determine the likely Hansen solubility parameters corresponding to solubility

In principle, mutual solubility can be promoted when one of the substances has Lewis acidic character and the other has Lewis basic character (van Oss *et al.* 2001; Jia *et al.* 2008). Van Oss *et al.* (2001) proposed that such interactions could make a contribution even in some aqueous systems. Such a term is not included in the Hansen system. Boluk (2005) came to the conclusion that Drago acid-base theory could help to account for hydrogen bonding interactions related to spruce kraft pulp and mechanical pulp. Pure cellulose, *i.e.*, alpha cellulose, appeared to have a balanced acid-base character. El Seoud *et al.* (2008) used Gutmann's donor and acceptor numbers to consider the solubility of a variety of different cellulose materials. The inclusion of these values, along with other parameters, allowed them to make more accurate predictions of cellulose solubility.
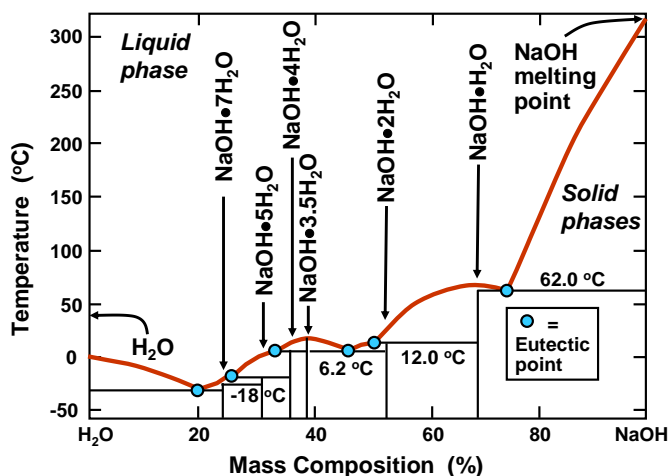

Fig. 17. Phase diagram for NaOH hydrates as a function of temperature and mass composition, also showing several eutectic points (blue circles)

NaOH as a cellulose swelling agent and solvent

The ideal conditions for dissolving cellulose in NaOH solution involve a concentration of about 7.6% and a temperature of about –5 °C (Cuissinat and Navard 2006). These rather specific conditions appear to result in the most favorable hydrated species of ions in a eutectic-like liquid (Budtova and Navard 2016). Figure 17 shows a NaOH-water diagram, which has been redrawn based on the work of Cohen-Adad *et al.* (1960). Note that a liquid phase is present for conditions of temperature and mass composition above the red line, and different NaOH hydrates will be represented at equilibrium in several solid phase mixtures, which are represented below the red line.

As mentioned earlier, it is likely that such hydrates tend to shift the position of recently unraveled cellulose chains. In principle, such a mechanism could inhibit the continual reassembly of cellulose crystallites, thereby allowing dissolution to proceed (Isogai and Atalla 1998; Zhang *et al.* 2018). Table 11 gives highlights from studies focusing on NaOH solution as a cellulose solvent or swelling agent.

Table 11. NaOH Solutions and the Swelling and Dissolution of Cellulose

Main Findings	Citation
Cotton was swollen in NaOH solution, followed by centrifugation. Results depended on prior degradation of the cellulose.	March *et al.* 1953
The swelling ability of cotton followed the order LiOH > NaOH > KOH at 4.5 M concentration and zero °C.	Iyer *et al.* 1989
LiOH and KOH treatments of cotton began at lower concentration with the KOH.	Sreenivasan *et al.* 1989
Alkali treatment of recycled cellulose fibers, followed by high shear treatment, led to higher paper strength, suggesting increased swelling and conformability.	Bhat *et al.* 1991
NaOH treatment helped to restore bonding ability to recycled kraft pulp, but at the expense of slower dewatering.	Young 1994
NaOH treatment during fiber recycling led to fiber swelling and higher paper strength.	Gurnagul 1995
Cotton fibers were swollen with 5 M KOH and NaOH. The NaOH gave greater changes in crystallite orientation.	Sreenivasan *et al.* 1995
Different cellulose crystal forms exhibited differing solubilities in NaOH solutions, as shown by NMR analysis.	Isogai 1996
Carboxymethylation levels of cotton had minor effect on the swelling in NaOH solution.	Racz & Borsa 1997
Best cellulose dissolution was with 8 to 9% NaOH, freezing, and then thawing at 20 °C in 5% NaOH.	Isogai & Atalla 1998
Maximum swelling of lyocell twill fabrics was with 9% NaOH.	Ibbett & Hsieh 2001
Recycled hardwood bleached kraft fibers were swollen, to deceasing extent, in 12% NaOH > formamide > dimethyl sulfoxide = 2% NaOH = ethylene glycol.	Tze & Gardner 2001
Aqueous NaOH treatment led to an increase in void volume, but smaller pore sizes of native cellulose.	Crawshaw *et al.* 2002
Fibrillation of various cellulose fibers decreased in the order LiOH > NaOH > KOH, and it increased with concentration.	Zhang *et al.* 2005
Details of ballooning were compared for an NaOH solvent system with cotton and wood fibers. Urea improved solvent quality. Zinc chloride accelerated the dissolution process.	Cuissinat & Navard 2006
Mercerization of cellulose fibers resulted in greater porosity, as detected by diffusion of fluorescent whitening agent.	Bui *et al.* 2007
Lyocell treatment with NaOH solution led to inter-fibrillar swelling.	Ozturk & Bechtold 2007

Various fibers were swollen and dissolved in NaOH solution or NMMO. Ballooning was seen in all plant fibers.	Cuissinat & Navard 2008
Swelling treatments led to non-uniform dimensional changes.	Jaturapiree *et al.* 2008
Ultrathin cellulose films were highly soluble in NaOH solution, which was attributed to lack of hierarchical morphology.	Kontturi *et al.* 2011
A two-step process was used to dissolve regenerated cellulose; NaOH was used in the first step, and urea was added in the second step.	Qi *et al.* 2011
Ballooning phenomena were studied for NaOH in combination with optional thiourea and urea.	Zhang *et al.* 2013
Swelling treatment with 5% NaOH improved the enzyme accessibility of hemp fibers.	George *et al.* 2015
Swelling of cellulose in NaOH followed by HCl regeneration led to easy diffusion of acid and chloride ions, leading to saccharification.	Sun *et al.* 2015
This comprehensive review article focuses on NaOH-based solvent systems for cellulose, including a historical evolution of concepts.	Budtova and Navard 2016
Treatment with 4 to 18% NaOH solution before mechanical refining moderately increased the resulting WRV of bleached kraft pulps.	Choi *et al.* 2016
A model predicts periodic decrystallized regions during NaOH treatment.	Nakano 2017
At pH 11, the swelling of cotton in aqueous glycine was maximized.	Remadevi *et al.* 2017
Alkali swelling of kraft pulp fibers made it possible to produce high-bulk paper products.	Choi *et al.* 2018
Various types of cellulose fibers were swollen over a range of NaOH concentration. Viscose swelled the most and wood-derived fibers the least.	You *et al.* 2021
Freeze-thaw treatment in the course of mercerization led to efficient swelling, allowing the process to proceed with just 5% NaOH rather than 15%.	Cao *et al.* 2022
Kraft pulp was swollen in cold NaOH solution, blended to form highly fibrillated cellulose, and then formed into dense, transparent paper.	Tian *et al.* 2022

NaOH with thiourea and or urea

It has been discovered that the solubility of cellulose in cold NaOH solution becomes even greater in the presence of optimized amounts of urea and thiourea (Yan *et al.* 2007; Zhang *et al.* 2013; Budtova and Navard 2016). The effect is supposedly attributable to weakening of hydrophobic interactions between the cellulose chains by the additives (Medronho *et al.* 2012). Zhang *et al.* (2013) found that adding thiourea to a NaOH system produced similar but more expanded balloons of swollen cellulose compared to NaOH alone.

Viscose

The viscose process, based on carbon disulfide treatment of the sodium form of cellulose, apparently does not involve true dissolution of cellulose, but rather a transient derivatization to cellulose xanthate (Lenz *et al.* 1993; Budtova and Navard 2016). The derivatization becomes reversed in the next step of the process wherein the viscous solution is converted back into cellulose. Steps in this chemical transformation are illustrated in Fig. 18. Lenz *et al.* (1993) found that the ability of viscose fibers to become fibrillated was correlated with the degree of orientation of its crystallites. In general, the drawing process employed while regenerating viscose fibers favors increased tensile strength, but also the ability to swell or delaminate perpendicular to the axis. Okugawa *et al.* (2020) reported that regenerated cellulose fibers are much more sensitive to water, in comparison to native

cellulose fibers. This is consistent with the lack of, for instance, an S1 sublayer wrapping the structure. Okugawa *et al.* (2021) proposed that swelling takes place in the amorphous zones between axially oriented microfibrils of cellulose in a regenerated cellulose filament.
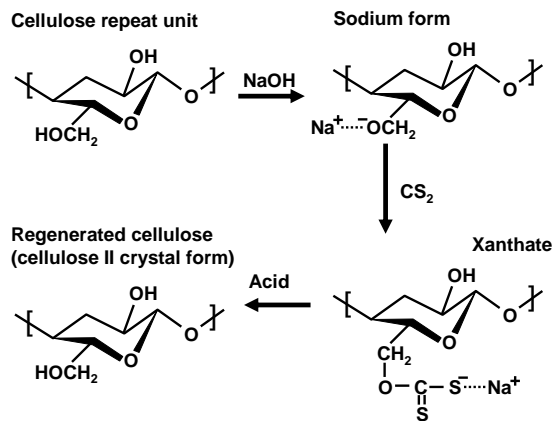

Fig. 18. Steps in the viscose process for preparation of regenerated cellulose (*e.g.* rayon) from cellulose (*e.g.* high-purity bleached kraft pulp or cotton)

NMMO

Partly due to environmental concerns about the viscose process, there has been a motivation to implement alternative ways to prepare regenerated cellulose products. The N-methyl-morpholine-N-oxide (NMMO) solvent process, yielding a regenerated cellulose product called lyocell, is regarded as a more eco-friendly alternative (Jiang *et al.* 2020). A likely mechanism to explain the ability of NMMO to dissolve cellulose is suggested in Fig. 19. As shown, it has been proposed that the NMMO replaces some of the key hydrogen bonding connections that connect the cellulose chains (Jiang *et al.* 2020). Though it is understood that a complete solubilization mechanism also likely will involve van der Waals interactions, that aspect is not considered in the depicted scheme.
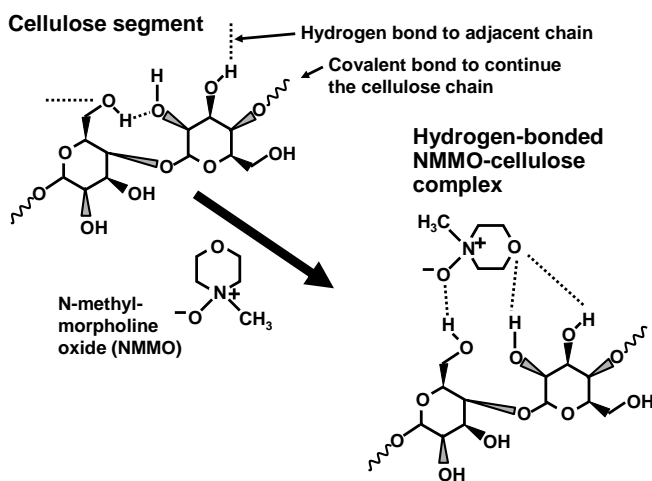

Fig. 19. A mechanism that has been proposed for NMMO's effectiveness for swelling and dissolving cellulose (redrawn based on scheme shown by Jiang *et al.* (2020)

Chaudemanche and Navard (2011) reimmersed lyocell fibers back into NMMO and studied the patterns and rates of swelling. Their results led them to the conclusion that the lyocell fibers were more porous in their outer layers, leading to high swelling in the NMMO solvent. However, Cuissinat and Navard (2006) described NMMO as a dissolution inhibitor. Cuissinat and Navard (2008) and Cuissinat *et al.* (2008) showed that NMMO treatment of a wide range of plant fibers consistently led to the ballooning effect described earlier. Lokhande (1978) attributed the effectiveness of NMMO as a swelling agent for cotton fibers to its combination of a relatively high Hildebrand parameter and a high polarity parameter, according to the Hansen (2007) approach. Sayyed *et al.* (2018) showed that dissolution of hardwood acid sulfite pulp in NMMO could be promoted by ultrasonication.

Phosphoric acid

Though phosphoric acid has been known as a cellulose solvent option since the 1930s (Budtova and Navard 2016), its usage tends to reduce the cellulose molecular weight due to acid hydrolysis. Possibly it is due to that attribute that the system has seldom been described in published articles. Y. H. P. Zhang *et al.* (2006) found that swelling of cellulose in phosphoric acid, followed by rinsing, rendered the material more susceptible to enzymatic hydrolysis. X. M. Zhang *et al.* (2018) showed that phosphoric acid was able to convert crystalline zones of cellulose to amorphous character and to impede the ongoing repair mechanism for the crystal zones. As was noted earlier, phosphoric acid has been used in combination with hydrogen peroxide as a swelling system to enhance enzymatic hydrolysis (Wang *et al.* 2020; Bai *et al.* 2022).

Ionic liquids

An ionic liquid can be defined as a salt that has a melting point below the boiling point of water.

Table 12. Ionic Liquids and the Swelling and Dissolution of Cellulose

Main Findings	Citation
Cupriethylene diamine (or cuene) has been used as the medium for testing of the molecular mass, by means of evaluating the viscosity of its solutions.	Vidal *et al.* 1991
A non-alkali aqueous mixture, bearing similarity to an ionic liquid (LiCl/urea/water) was used to swell regenerated cellulose.	Tatarova *et al.* 2010
Two ionic liquids, 1-butyl-3-methylimidazolium chloride/dimethyl sulfoxide ([bmim]Cl)/DMSO and 1-ethyl-3-methylimidazolium chloride/dimethyl sulfoxide ([emim]Cl)/DMSO, were used to swell and dissolve palm biomass.	Rahman *et al.* 2012
A series of methylimidazolium ionic liquids were used to swell bagasse. Results were sensitive to alkyl chain lengths.	Wang *et al.* 2014b
There authors noted that ionic liquids as solvents of cellulose were already known in the 1930s.	Budtova & Navard 2016
The ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate was used to swell and dissolve kraft pulp fibers. Substantial hydrolysis was noted at the highest temperature.	Mao *et al.* 2016
Swelling of rice straw by ionic liquids was quantified using atomic force microscopy.	Xu *et al.* 2018
The ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMI-M][OAc]) was less and less effective with increasing water content.	Chen *et al.* 2020

In principle, ionic liquids represent combinations of positive and negative ions that have a mismatch in key properties such that they do not fit well together in a crystal form. Some of them have been shown to be able to swell or dissolve cellulose. Such findings are summarized in Table 12. The mechanism by which ionic liquids swell and dissolve cellulose has been reviewed (Li *et al.* 2018a; Khoo *et al.* 2021). Li *et al.* (2018a) proposed that the key to effectiveness of such solvent systems may lie the optimization of separate interactions with cellulose by the two types of ions. Khoo *et al.* (2021) emphasized the advantage of using an ionic liquid having a tendency to catalyze the breakdown of cellulose molecular weight; those authors were focused on an end goal of further converting the cellulose to biofuels. Molecular dynamic simulation work suggests that ionic liquids induce a progressive decrease in hydrogen bonding (Ishida 2020), which seems compatible with the zipper-like mechanism suggested by others for the action of cellulose solvents (Budtova and Navard 2016).

Kinetic Aspects of Swelling

In many current and potential applications, the rate at which the swelling of cellulosic materials occurs will affect success of a process. Time is required for such processes as diffusion, changes in conformation of soluble polymers, zipping and unzipping processes, and capillary flow.

Hysteresis in dry cellulosic materials

To begin with relatively dry cellulosic materials, researchers have found strong hysteresis effects when cellulosic paper takes up or loses water from or to the atmosphere (Ramarao and Chatterjee 1997; Nilsson *et al.* 1998; Hill 2009; Shrestha *et al.* 2017). Such effects are evidence that the material is not at a true equilibrium; rather, rate-determined processes govern the properties. For example, Shrestha *et al.* (2017) found that the amount of water present in a thin film of cellulose nanocrystals (CNC) at a specified relative humidity was often about 0.02 g water per g cellulose lower during the adsorption tests than during the subsequent desorption steps in the procedure. These findings are shown replotted in Fig. 20.
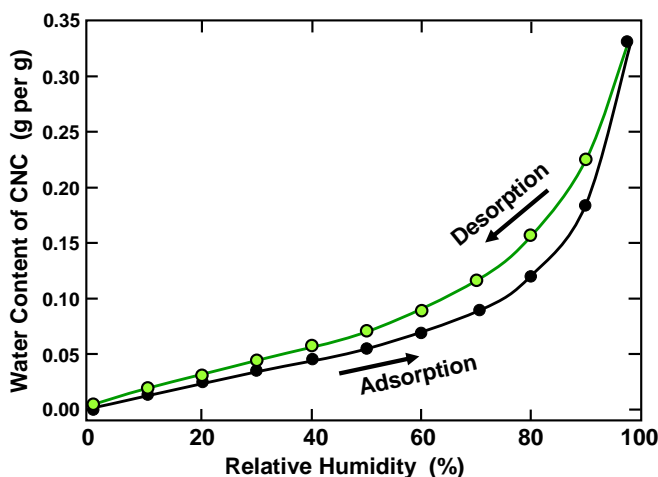

Fig. 20. Example of a hysteresis during adsorption of water vapor into a cellulose nanocrystal (CNC) film during increasing relative humidity, followed by desorption during decreasing relative humidity (redrawn from Shrestha *et al.* (2017)

Such findings support the view that water-cellulose interactions can depend on cooperative effects involving multiple hydrogen bonds. Whereas a single hydrogen bonding site on cellulose might be expected to be in pure equilibrium with changes in relative humidity, a sufficiently large group of such sites may require larger changes in relative humidity to prompt a change from local a "bonded area" condition to a condition in which cellulose-to-cellulose hydrogen bonds have been replaced in that region by cellulose-to-water hydrogen bonds, *etc.*

More recently, an approximate match to adsorption-desorption equilibria, as shown in Fig. 10, has been achieved by molecular dynamics simulation (Chen *et al.* 2019b). However, better fits were achieved when taking into account the coupled deformation of the soft material in the course of adsorption and desorption of water molecules (Chen *et al.* 2019a, 2020). This approach takes into account the adsorption-induced stress that contributes to swelling. Calculations based on either finite elements or analytical analysis based on a uniform strain assumption both were able to account for hysteresis loops in plots of water content of cellulose *vs.* relative humidity (Chen *et al.* 2020). Notably, the analyses just described did not consider capillarity, which was justified by an assumed presence of only nano-sized pores too small for development of a meniscus.

Capillary suction

Fibers and fibrous networks constitute a capillary system. When such networks are exposed to water or other wetting liquids, the extent and the rate at which the liquid enters will influence the extent and rate of swelling. A previous section discussed the change in Gibbs free energy for swelling, in which contributions stem from capillarity, *i.e.* both surface tension-area wetting work, γA and capillary action pressure-volume work, $-\Delta PV$. The two quantities can be treated separately, but many studies dealing with fiber networks, such as paper, discuss such liquid-surface interactions together based on the Lucas-Washburn (L-W) relation, named after Lucas (1918) and Washburn (1921). An example of the type of situation considered by Lucas and Washburn is illustrated in Fig. 21.
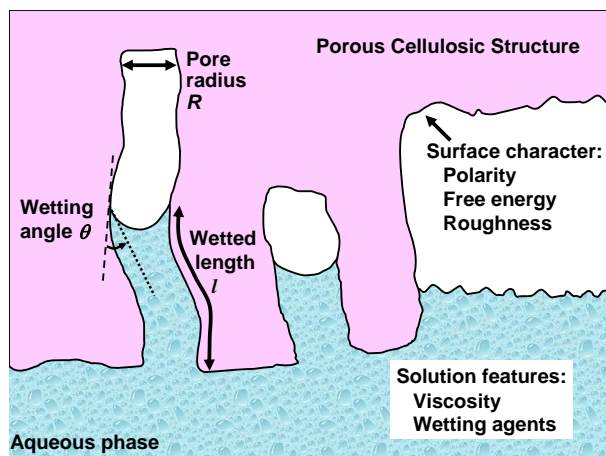

Fig. 21. Simplified geometry to estimate rates of wetting into a porous solid under the assumptions of a known radius of smooth cylindrical pores having constant contact angle

Simplifying assumptions include the presence of cylindrical smooth pores of one radial size and one angle of contact with solution having a known Newtonian viscosity.

Based on these assumptions, it is possible to calculate a contribution of capillary pressure to enter into a pore,

$$\Delta P_{\text{capillary}} = \frac{2\gamma \cos\theta}{R}R \tag{5}$$

where γ is the interfacial tension, θ is the contact angle within the pore, as defined in Fig. 21, and R is the assumed radius representing the capillaries. This pressure is balanced by a Hagen-Poiseuille flow resistance term related to the viscosity of the solution,

$$\Delta P_{\text{viscous}} = \frac{8\eta v l}{R^2} \tag{6}$$

where η is the dynamic viscosity of the solution, v is the average velocity of the fluid passing into the pore, l is the wetted length at the present time, and R is the same value already assumed for the pore radius. If one sets these two pressure terms equal to each other, then one can solve for the wetting length l at an elapsed time equal to t after immersing the dry porous material into the solution,

$$l = \frac{\sqrt{2R\gamma \cos\theta}}{4\eta}\sqrt{t}^2 \tag{7}$$

which gives a square-root time dependence. The L-W model does not consider effects of inertia and gravity, which can be of large importance. For pores in fibers and fiber networks, R and θ are not easily determined.

It is well known that the L-W model is too simplified to describe cellulosic fibers and network, but the model is still used with, in many cases, a good fit to determine the rate of capillary flow. Examples are by Kvick *et al.* (2017), in which also swelling of the pores during imbibition was included and by Salminen (1988), in which also other contributions are considered, such as the morphology and the effect of an advancing fluid front in pores due to fluid vapor diffusion, in front of the liquid.

Deviations from the Lucas-Washburn model are expected due to such factors as changes of contact angle as a function of time of contact, changes in morphology of the material due to swelling, adsorption or desorption of chemical contaminants, and various effects related to the roughness of real surfaces (Hubbe *et al.* 2015). Already Bosanquet (1923) introduced the inertial capillarity which gave a solution of two time-scales of the liquid flow, one of linear time dependence at short times and square-root dependence at longer times and which can explain the experimental observation that larger pores fill more easily than smaller pores (Quéré 1997; Gane 2005). The effect of gravity has been added, also presenting an analytical solution (Fries and Dreyer 2008).

The influence of the complex geometries in fibers and fiber networks (*e.g.* expanding or contracting pores, dislocations and obstructions) was pointed out by Kent and Lyne (1989). Variations in pore morphology have been experimentally verified (Senden *et al.* 2000). Studies have included various relevant well-defined geometries of the imbibed material (thin, thick, or deformable, such as swelling) of the flow situation (infinite or finite fluid reservoir, or drops) as well as if the fluid expands unidirectional, spherically or radially. To summarize their findings, the capillary rise proceeds as a function of $t^{1/2}$ for unidirectional capillary flow into a porous material (Marmur 2003). For an expanding pore, the rate is a function of $t^{1/4}$ or $t^{1/3}$) (Reyssat *et al.* 2008). The rate becomes a function of and goes as $t^{1/3}$ for flow imbibing spherically from a small orifice (Xiao *et al.* 2012) or from a fluid-saturated porous material into a capillary (Danino and Marmur 1994). The latter study also discusses flow from originally larger pores into smaller pores as an

explanation for a lower flow rate than would be expected. For the special case of fluid drops into porous materials (Oko *et al.* 2014, 2016) was $t^{0.8}$ for an isotropic material but $t^{0.2}$ for paper. The slower rate in a fiber network is a result of a rough liquid front during capillary flow, which is a similar effect as the presence of obstructions for flow inside a porous network.

When fibers and fiber networks imbibe a wetting fluid by capillary suction, there are, as seen, a number of different effects that can both increase and decrease the capillary flow rate. This can in fact give a final result resembling a $t^{1/2}$-dependence. This means that the Lucas-Washburn model may still apply. Knowing variability of the imbibing and swelling material is of large importance to further understanding capillary and swelling processes.

The relation between sorption in fibers, with accompanied fiber swelling, to the fluid uptake into the porous network between fibers, giving a swelling of the porous network, can be understood (Bristow 1986) based on experiments using oil as a non-swelling fluid and water as a swelling fluid. Zhmud *et al.* (2000) compared different theoretical approaches, corroborated with experiments, and discussed the important effect of liquid surface tension and surfactancy. Roberts *et al.* (2003) visualized the liquid advancing front using cryo-microscopy in papers. They described the liquid flow as being more along fiber surfaces and *via* fiber-fiber cross-points, rather than in the pores.

Several studies have started from Darcy's law of fluid motion in porous media (Scheidegger 1974; Lyne 2002) in generalized form and in specific patterns of flow, *e.g.*, flow in a pipe.

$$Q = -\frac{kA}{\mu L}\Delta P \tag{8}$$

In Eq. 8, Q is the liquid flow rate, k is the permeability, A is the cross-sectional area, μ is the dynamic viscosity, L is the length penetrated by liquid, and ΔP is the pressure difference. This makes it possible to avoid the experimental issue of determining R and θ is avoided because the material properties are instead permeability and porosity. Permeability and capillary pressure can be estimated for an experimental system (Carman 1937; Marmur 2003). Approaches may also start from Navier-Stokes equations to include inertia and gravity effects. This may lead to equations that are too complex to be analytically solved, but instead numerically, or dimensional analyses may be used to conclude if some factors can be neglected. This was used in the case of small imbibing drops (Oko *et al.* 2014), in which both inertia and gravity terms were much smaller than the pressure term, and the complete equation was simplified to Darcy's law.

Masoodi and Pillai (2010, 2011) used Darcy's law to model the rates of wicking of liquid into paper-like materials. A new contribution of that work was to account for simultaneous swelling of the porous material in the course of wetting. Mark (2012) used Darcy's law to model edge wicking into paperboard to also include the effect of an external (hydrostatic) pressure. Pejic *et al.* (2008) found that wicking of water into hemp fibers was increased by removal of lignin and some of the hemicellulose; those results are consistent with changes in wettability and pore sizes. Welo *et al.* (1952) used such principles to understand the WRV test, in which a centrifugal dewatering is used to estimate the amounts of water remaining in mesopores in the cell wall. Wohlert *et al.* (2022) emphasized the importance of capillary forces, acting during the evaporation of water from paper, in drawing cellulosic fiber surfaces into molecular contact so that hydrogen bonds could then form in the contact zones. As noted earlier, that aspect of capillary forces, in combination

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with drying, has been found to close up mesopores in a semi-irreversible manner, leading to lower levels of water sorption if and when the material is wetted again.

Diffusion-controlled processes

Diffusion processes often can be at the root of time-dependent phenomena related to the swelling of cellulosic materials (Ganji 2010). As noted by Alexandersson and Ristinmaa (2019, 2021), processes of adsorption and diffusion often control the rate at which water will invade and change the properties of cellulosic materials. Reid *et al.* (2017) and Shrestha *et al.* (2017) concluded that diffusion was the controlling process in the uptake of water into thin films of CNC. Conversely, water that is very closely associated with cellulose in tiny pores and gel structures can exhibit a slower rate of diffusion (Torstensen *et al.* 2022).

Table 13. Molecular Dynamics Simulation Studies of the Swelling of Cellulosic Materials

Main Findings	Citation
Simulation of the swelling of cellulose I crystals predicts a tendency for a right-handed twisting, which remained persistent.	Yui *et al.* 2006
Calculations were made of the mean force for separating cellulose oligomer chains, taking into account hydrogen bonds and hydrophobic interactions.	Bergenstråhle *et al.* 2010
Simulations of cellulose I beta crystals in ammonia solution predicted a change in end-to-end distance of cellulose molecular chains relative to non-ammonia media, which was interpreted as evidence of swelling.	Huang *et al.* 2014
MDS calculations based on an amorphous cellulose phase showed the relationship between water content and swelling, as well as changes in stiffness of the solid material and diffusion rates of the water molecules. A critical change was found at 10% moisture.	Kulasinski *et al.* 2014
MDS analysis quantified the role of hydrogen bonds, which were shown to be maintaining the crystal structure of the cellulose and contributing 12% of the stiffness of the crystal. Swelling effects were not considered or reported in this work.	Djahedi *et al.* 2016
Simulation of the transformation of cellulose I to cellulose II was carried out for partially decrystallized cellulose subjected to NaOH solution.	Nakano 2017
Swelling in ionic liquids resulted in a decrease in cellulose crystallinity, as shown by NMR and molecular dynamics simulation.	Xu *et al.* 2018
The use of MDS is discussed relative to hydrogen bond interactions and swelling of lignocellulosic materials. Such simulations can approximately predict adsorption-desorption equilibration as a function of changing relative humidity.	Chen *et al.* 2019
MDS analysis indicated increased diffusion dates of ammonia within cellulose, which was taken as evidence of swelling. The MDS findings were confirmed by other observations.	Huang *et al.* 2019
MDS simulation of a pair of cellulose crystals, one attached to a wall and one free to bend, showed establishment of molecular contact between the two crystals in the course of vacuum drying, thus supporting a common interpretation hornification, *i.e.* the loss of swelling ability when porous cellulosic materials are dried.	Ogawa *et al.* 2020
Simulations were used to account for observed loosening of the packing of cellulose microfibrils (in the moist range) and deformations to the crystals (in the relatively dry range).	Paajanen *et al.* 2022

Mathematical modeling of swelling

Kinetic effects related to the swelling of cellulosic material often can be expressed in terms of mathematical models, but such models can be complex. For example, Masoodi *et al.* (2012) showed that a finite element model was able to account for rates of wicking into paper-like media. Their model allowed for concurrent swelling. Geffert *et al.* (2017) showed that swelling of cellulosic materials could be well described by a combination of two models, namely a generalized hydroscopicity model and a simple bounded growth model. Sayyed *et al.* (2021) noted that swelling of cellulose pulp in NMMO solution often follows a second-order rate expression. In other words, the rate slows with time, tending toward a final saturated condition. As noted by the authors, a deceleration in a process of swelling might be attributed to a plugging up of diffusion pathways, keeping the water or other liquid from being able to swell some isolated zones.

Molecular Dynamics Simulations

Further perspectives on swelling mechanisms can be gained by carrying out molecular dynamics simulation (MDS) studies. Such studies related to the swelling of cellulosic materials are highlighted in Table 13. As shown, in most of these studies, the MDS work was done to either confirm or shed additional light on the findings from other methods. Unlike those studies listed in Table 13, most publications dealing with MDS and cellulose do not provide information related to swelling, since such evidence is often absent or indirect. Studies listed in Table 13 represent some exceptions in which authors discussed their findings in relation to swelling.

APPLICATIONS OF SWELLING OF CELLULOSIC MATERIALS

This section highlights selected examples in which the swelling behavior of cellulosic materials, as well as its control, can have important effects in various applications. Rather than attempt to cover all potential applications, the objective here is to illustrate different ways in which the swelling of cellulosic materials can be important for industry and society.

Pulping of Cellulosic Fibers

In the course of preparing cellulosic fibers for papermaking, the dominant process involves breakdown and removal of the lignin component of wood, mainly using the kraft process (Fardim and Tikka 2011). The kraft process involves placing wood chips in a pressured vessel called a digester. The pulping liquor, which is a solution of sodium hydroxide and sodium hydrogen sulfide, needs to be able to diffuse into the wood chips, and this can be affected by swelling – either as a result of pretreatments or due to the alkaline nature of certain pulping liquors. The pretreatment of wood chips with alkaline aqueous solution has been shown to swell the wood and to promote permeability of pulping reagents (Minor and Springer 1993). The cited authors attributed part of the effect to saponification of ester groups in the wood. It has been proposed that the swelling of wood, brought about by a combination of temperature and immersion in water, is also a key to effective preparation of mechanical wood pulps (Fjellström *et al.* 2012). Such swelling helps the fibers to come apart with less damage on loss of fiber length. As discussed earlier, *Eucalyptus* wood with high content of calcium is pulped more slowly, which partly could be due to a decreased swelling (Vegunta *et al.* 2022),

Pulp Refining Optimization

Swelling is also important when using mechanical refining to get kraft fibers ready for formation into paper (Gharehkhani *et al.* 2015). As was noted earlier in a different context, a strong correlation has been found between the swollen nature of papermaking fibers, as represented by WRV, and their dry-strength properties (Jayme and Büttel 1968). The effect has been attributed to an expectation that a swollen fiber will be more conformable and better able to develop molecular contact between the cellulosic surfaces, leading to high levels of hydrogen bonding (Page 1969).

Absorbent Products

Swelling is a necessary process in cellulose-based absorbent products. Not only does the material need to swell in order to contain the absorbed fluid, but the material needs to be strong enough and have sufficiently strong capillary effects to hold onto that fluid. Ordinary cellulose can absorb 3.5 to 10 times its weight of water, depending on various details of composition and preparation (Aberson 1969; Parham and Hebert 1980; Ang 1991). Fluff pulp, which typically is comprised of bleached softwood kraft fibers, is widely used in disposable absorbent products, such as diapers (Parham and Hebert 1980). Such products also contain super-absorbent hydrogels, which optionally can be prepared with carboxymethylcellulose (CMC) as a component (Ganji *et al.* 2010; Chang *et al.* 2011; Hubbe *et al.* 2013; Ma *et al.* 2015). Moriwaki and Hanasaki (2023) noted that nanopaper sheets, composed of NFC, became immediately transformed to hydrogels upon contact with water. Sun *et al.* (2015) achieved related effects by first swelling cellulose at low temperature in NaOH and then very rapidly regenerating it by exposure to HCl solution; the resulting material acted like a hydrogel. As an alternative, Karlsson *et al.* (1998) achieved high levels of swelling by graft polymerization of regenerated cellulose fibers with acrylic acid.

Dissolving Pulp Manufacture

The ability of fibers to swell upon immersion in a cellulose solvent is a key criterion for high-quality dissolving grades of cellulose pulps, since this makes it easier for the cellulose to be chemically derivatized. This ability can be judged, for instance, by swelling in a dilute cupriethylenediamine (CUEN) aqueous solution (Arnoul-Jarriault *et al.* 2016). Such a solution is a diluted version of the medium that is often used for viscometric assessment of cellulose molecular mass. Pulps having a rapid ability to swell and dissolve in various solvent systems are known as "reactive". It has been shown that reactivity can be increased by such treatments as TEMPO-mediated oxidation of the fibers (Gehmayr *et al.* 2012). Part of the concept of reactivity can be addressed as accessibility and refers to the ease of which reactive sites of the molecule can be reached by reaction chemicals and/or solvents and depends on several physical and chemical properties of the pulp (Li *et al.* 2018b).

Bioenergy

Swelling ability also can be important when using enzyme-based strategies to prepare biofuels. For example, it has been shown that swelling of hemp fibers with 5% NaOH solution promoted subsequent enzymatic saccharification (George *et al.* 2015). Related studies using different swelling agents have been reported (Bendzalova *et al.* 1996). Once sucrose has been prepared from cellulose in such a way, it can then be

converted to biofuels such as ethanol and butanol by fermentation. Contrary results have been reported, in which increased swelling of pulp xylan led to less enzymatic hydrolysis (Buchert *et al.* 1993). The latter results suggest that certain enzymes have evolved to favor their action on dense cellulosic material, including crystalline cellulose rather than artificially swollen versions. However, as noted earlier, it has been shown that the loss of swelling, due to drying of cellulosic material, generally has a negative effect on rates of enzymatic saccharification (Luo and Zhu 2011; Duan *et al.* 2015).

CLOSING COMMENTS

This review article has focused on factors affecting the swelling of cellulosic fibers, published findings related to such effects, mechanistic explanations, and some published examples of current or potential applications. The word "swelling," as used in the related literature, was found to cover a wide range of phenomena. As illustrated in Fig. 22, these phenomena can range from the slight dimensional changes associated with changes in relative humidity. Successively greater swelling occurs when the cellulosic material is immersed in water, and even more so when immersed in a select group of agents able to strongly swell and even dissolve cellulose. The mechanistic explanations for forces encouraging swelling range from adsorption, to osmotic pressure, and to disruption of the mechanical structures that ordinarily would limit swelling, such as the outer layers of plant-derived cellulose fibers.
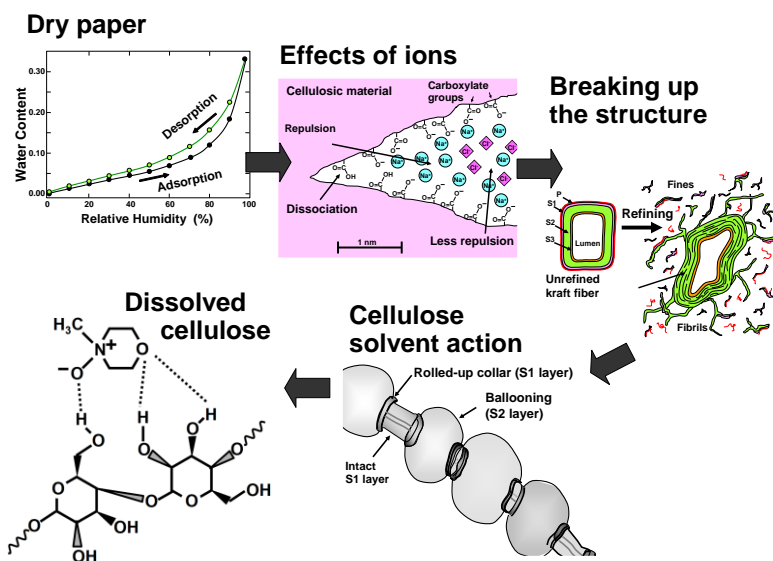

Fig. 22. Envisioning cellulose swelling as a continuum of overlapping processes, using some earlier figures to provide examples

Some principles that were shown, in this review, to help explain some of the cited findings, can be summarized as follows:

- Crosswise swelling of cellulose fibers and other cellulose-based structures is typically several times greater than axial swelling; such behavior is consistent with a model in which slit-like spaces between sheets of cellulosic material can open up

and accommodate water, depending on such factors as osmotic pressure and the application of mechanical shearing.

- Swelling of cellulosic fibers in water is positively influenced by the polar nature of cellulose, as well as hemicellulose, and by osmotic effects that arise from the presence of ionizable groups such as -COOH.

- Cellulose's non-solubility in water, which clearly acts to restrain swelling in many cases, is related to its typically high level of crystallinity, which can further by attributed to a dense and regular pattern of hydrogen bonding, in combination with hydrophobic (van der Waals) association acting in a perpendicular direction.

- The microfibril angles within different layers of the cell walls of plant fibers, as well as the presence of lignin and lignin-polysaccharide complexes all play important roles relative to the restraint of swelling.

- Very high levels of swelling, even leading to dissolution of cellulose, can be achieved by a variety of cellulose solvent systems. At least some of these systems simultaneously attack the hydrogen bonding within the cellulose domains and also weaken the van der Waals associations between the non-polar faces of adjacent cellulose chains or sheets.

The study of aspects of the swelling of cellulosic materials continues to provide opportunities for new researchers. Because the field is diverse in many ways, it is hard to place limits on the kinds of research that will be useful in the years ahead. On the one hand, there will be a need for fundamental research. Although such theories as osmotic pressure and its controlling factors are by now well established, the general theories often do not take into account the structural details of real cellulosic fibers. The need for developmental scientists and engineers, working to implement aspects of research in industry, can be expected to grow. An expected growing focus on photosynthetically renewable materials is likely to promote more emphasis on the practical usage of cellulose-based materials in a wide range of products, ranging from absorbents to enzymatically produced biofuels, to packages, and to medical devices. In many applications, greater swelling may be the goal, whereas in others it may be an advantage to limit swelling. As has been shown by the articles cited in this review, by varying the manner in which cellulosic fibers are prepared and by controlling the environmental to which they are exposed, it is possible to achieve a wide range of outcomes relative to swelling and its restraint.

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