Capillarity in wood and related concepts: a critical review

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Capillarity in wood and related concepts; a critical review

Lars Wadsö
Capillarity in wood and related concepts; a critical review

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December 29, 1995

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Contents

1 Nomenclature 3

2 Introduction 3
  2.1 Limitations etc. 5
  2.2 Definitions 5
  2.3 Materials classification 5
  2.4 Wood capillarity in practice 6

3 The classical relationships 8

4 The wood-water system 12
  4.1 Surface tension (surface energy) 12
  4.2 Contact angle 13
  4.3 Wettability 15
  4.4 The porous system of softwoods 16
  4.5 The cell walls 22
  4.6 Pit aspiration 23
  4.7 Wood components soluble in water 27
  4.8 Theoretical models 27
  4.9 Experimental model systems 31

5 Drying of wood 34
  5.1 General drying theory 34
  5.2 Drying models for wood 35
    5.2.1 General overview 35
    5.2.2 Wood drying models with capillary pressure 36
    5.2.3 Skaar's model 38
    5.2.4 Comstock model 40
    5.2.5 Čudinov model 40

6 Capillary absorption of wood 43

7 Conclusions 43

8 Recommended reading 46

9 References 46
1 Nomenclature

In this paper the directions in wood are named as follows:

**Longitudinal**: the direction along the length of the trunk of the tree (fiber direction).

**Radial**: The direction from the pith (the center of the trunk) to the bark.

**Tangential**: the direction along the growth-rings (perpendicular to the radial direction)

**Transversal**: either tangential or radial.

A surface is named after the direction it is facing (the direction of a normal vector of a surface), e.g. the bark faces in the radial direction. Note that this is not the common terminology in wood science.

Most symbols used are given on the next page.

2 Introduction

This introduction is rather lengthy and includes various items that are of interest to put the capillary phenomena in wood in correct settings.

Capillarity in wood is not a trivial subject. Van Brakel (1975) remarks that "the situation is not as bad for other transport phenomena as it is for capillary rise...". Probably because of this capillarity has received very little attention compared to the much less complicated diffusion.

The purpose of this review is to present what is known about capillary phenomena in wood and discuss how it should be measured and modelled. I particularly stress that wood cannot be modelled as any (general) porous media as its geometry is quite unique among porous materials.

The mechanisms of free water movement in wood can be divided into the following four part processes (Čudinov 1985):

- The flow paths.
- The physical processes governing the movement.
- The states of the moving water.
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>area</td>
<td>m$^2$</td>
</tr>
<tr>
<td>$D$</td>
<td>diffusion coefficient</td>
<td>m$^2$/s</td>
</tr>
<tr>
<td>$F$</td>
<td>flow rate</td>
<td>kg/(m$^2$.s)</td>
</tr>
<tr>
<td>$g$</td>
<td>gravitational acceleration</td>
<td>m/s$^2$</td>
</tr>
<tr>
<td>$h$</td>
<td>height (maximum capillary rise)</td>
<td>m</td>
</tr>
<tr>
<td>$k, K$</td>
<td>permeability coefficients</td>
<td></td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>pressure difference</td>
<td>Pa</td>
</tr>
<tr>
<td>$r$</td>
<td>capillary radius</td>
<td>m</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K or °C</td>
</tr>
<tr>
<td>$u$</td>
<td>moisture content</td>
<td>kg/kg</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>$x$</td>
<td>distance, length</td>
<td>m</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>angle with respect the vertical</td>
<td></td>
</tr>
<tr>
<td>$\eta$</td>
<td>viscosity</td>
<td></td>
</tr>
<tr>
<td>$\Psi$</td>
<td>capillary potential</td>
<td>m</td>
</tr>
<tr>
<td>$\rho$</td>
<td>density</td>
<td>kg/m$^3$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>surface energy, surface tension</td>
<td>N/m</td>
</tr>
<tr>
<td>$\theta$</td>
<td>contact angle</td>
<td></td>
</tr>
</tbody>
</table>

Indices:
- $s$ solid
- $l$ liquid
- $v$ vapor
- $\text{sat}$ saturation
The conditions for movement.

This review addresses questions that are raised in connection with these four processes.

2.1 Limitations etc.

This study is mainly limited to capillarity in softwood timber such as all different species of the genera Pinus (pines), Picea (spruces), Larix (larches), Abies (firs) and Pseudotsuga (Douglas firs). Hardwoods have a quite different morphology. The emphasis is not, as it usually is, on timber treatment (impregnation), but on the use of wood in contact with liquid water as rain, condensation etc.

2.2 Definitions

As the present text is an introduction to different aspects of capillarity in wood it is proper to introduce a subject by defining the basic concepts. Here I have used The Random House College Dictionary (1988) to find these definitions: capillarity is "a manifestation of surface tension by which the portion of the surface of a liquid coming in contact with a solid is elevated or depressed, depending on the adhesive or cohesive properties of the liquid". The word capillary is derived from the Latin word "capill(us)", hair.

By adhesive is meant "the molecular force of attraction in the area of contact between unlike bodies that acts to hold them together". Cohesion is "the molecular force between particles within a body that acts to unite them".

Water wets glass because water molecules are more attracted by the molecules at the hydrophilic ("having a strong affinity for water") glass surface than by other water molecules. Water in contact with silicon or any other hydrophobic ("having little or no affinity for water") material will show the opposite behavior: the water molecules are not attracted by the silicon surface and tries to avoid all contact with it (affinity is defined as "the force by which atoms are held together...").

2.3 Materials classification

Materials can be divided into three groups depending on their drying behavior (after van Brakel 1980). This classification is valuable in understanding
the differences between different types of materials used in capillary experiments.

**Capillary-porous media** have a clearly recognizable pore space but only negligible amounts of bound water. Such materials (packings of sand, glass beads, crushed minerals, nonhygroscopic crystals, polymer particles, some ceramics) do not shrink during drying.

**Hygroscopic-porous media** has both a clearly recognizable pore space and a large amount of physically bound water. This type of materials often shrink during drying. Typical examples are wood, textiles, clay and molecular sieves. A further subdivision can be made into materials with both macro- and macropores (e.g. wood) and materials with only micropores (e.g. silica gel).

**Colloidal (nonporous) media** has no pore space so all sorbed water is physically bound. Soap, some polymers (e.g. nylon and many adhesives) and various food products (e.g. raisins) are examples of this type of material.

### 2.4 Wood capillarity in practice

Why is it of interest to study capillary phenomena in wood? This question is best answered by a number of examples where capillarity plays a role in wood technology:

1. During drying of green wood the interplay between capillary pressure - permeability and diffusion will determine where the evaporation in wood takes place. If all open pores on the surface are emptied before pores inside the material have begun to empty, then the drying will be slower than if capillary pressures can suck the water from inside the wood to the surface, replacing it with air.

2. In dried wood it is found that the concentration of soluble compounds is increased at the surface (Boutelje 1990, Theander et al. 1993). These molecules may serve as nutrients for microbial growth on the wood surface. The deposition of molecules presumably takes place at the interface between the liquid and the gas phases during drying. The
soluble molecules may also be able to diffuse in response to concentration gradients and osmotic pressures caused by differences in concentration may also induce viscous flow. Where the soluble compounds are found in the dried wood depends on where the evaporation (or cell wall sorption) takes place.

3. In telegraph poles, harbor constructions and other wood structures in contact with both water and air there will be a transport of water from the water source to the air. This process may transport significant amounts of substances that will be deposited in the transition zone between the liquid phase and the vapor phase (Baines and Levy 1979). These substances could either increase the susceptibility to microbial attack, e.g. nitrogenous compounds, or reduce the risk of attack, e.g. natural or artificial fungicides.

4. The success of a treatment (impregnation) of wood with fungicides depends to a large extent on that the pressures are high or low enough to overcome the capillary forces resisting absorption. In some methods the impregnation liquid is actually supposed to be transported into the wood by capillary forces only.

5. The properties of water borne coatings in contact with a wood surface will be partly controlled by the ability of the wood to absorb water and other components from the coating. A too high absorption on parts of a wood surface, such as can be found in ponded wood, will make the coating (esp. stains) uneven.

6. The ability of a coating on an external panel or window frame to keep the wood dry depends on an interplay between capillary forces - permeability, which tries to get the water through the paint film and spread it in the wood, and diffusion, which is the process responsible for the drying out of moistened panels. Paints that allow a high degree of capillary absorption are not suitable as exterior paints. The same probably applies to paints which cracks easily, exposing the wood to capillary water. Cracks in the wood material (drying cracks, micro cracks) are also possible pathways for liquid water into wood.

7. Capillary forces also play a role when other liquids than water come into contact with wood surfaces. Wood adhesives should preferably wet the wood surface and penetrate a short distance into the wood to
give the adhesive bond maximum strength. Such a process is at least partly controlled by capillary forces. Other examples are oil and solvent based impregnations and solvent based coatings.

3 The classical relationships

I like to start from the beginning by giving the classical capillary relationships. These are based on the concept of adhesion and cohesion between different phases (solid, liquid, gas). It should be noted that this static theory can correctly describe capillary phenomena, but it was developed nearly 200 years ago, and later work has supplemented this theory by thermodynamic and dynamic molecular theory (Rowlinson and Widom 1982). The static theory makes no use of the fact that pressure is caused by molecular movement and collisions as such ideas were not proved until later in the 19th century. The classical static theory cannot say anything about what goes on at the molecular level, but is a correct way of dealing with capillary systems on a higher level on which solids, liquids and gases can be considered as continuums.

Water tends to form spherical drops in the absence of other forces. This is a manifestation of that the molecules within the water show strong attractive forces, whereas (almost) no such forces act between the water molecules and the air. Within the liquid the forces acting on the water molecules are balanced (the same from all directions), but at the surface there are no attractive forces from the air. There must therefore be a positive pressure in the liquid phase that balances these unbalanced attraction forces (otherwise the surface molecules would be accelerated into the water drop).

If there is an over-pressure in the drop there must be a force acting within the surface that is responsible for it. This surface tension \( \sigma \) [N/m] is this force which is acting in the liquid surface to balance the pressure caused by the difference in attraction between liquid-liquid and liquid-gas. It should be noted that the surface tension can also be seen as a surface energy, e.g. an energy per unit surface [J/m²=N/m].

In the absence of any other forces (e.g. gravity) a spherical drop of a liquid having the radius \( r \) [m] will have the surface area \( 4\pi r^2 \) [m²]. An infinitesimal amount of liquid added to such a drop will cause an increase of \( dA = 8\pi r dr \) in surface area for an increase in the radius of \( dr \). An increase in surface area will require energy to overcome the forces which acts against such an
increase. The following equation will then apply:

\[ \sigma \cdot dA = \Delta p \cdot Adr \]  \hspace{1cm} (1)

Here, \( \Delta p = p_l - p_v \). This leads to a relation for the over-pressure in the drop (for the cases with one or two principal radia):

\[ \Delta p = \frac{2\sigma}{r} = \sigma \left( \frac{1}{r_1} + \frac{1}{r_2} \right) \]  \hspace{1cm} (2)

Equation 2 will also apply to the opposite case with an air bubble in water if \( \Delta p = p_v - p_l \).

The strength of the cohesive forces within a liquid in relation to the strength of the adhesive forces between liquid and solid will determine the contact angle (\( \theta \)) at the liquid-solid interface. This is defined as zero for a liquid that completely wets a surface.

Using \( \sigma \) and \( \theta \) the following balance of forces applies to the equilibrium capillary rise \( h \) in a tube of radius \( r \):

\[ \cos \theta \cdot 2\pi r \sigma = \rho gh \pi r^2 \]  \hspace{1cm} (3)

The height is then:

\[ h = \frac{2\sigma \cos \theta}{\rho gr} \]  \hspace{1cm} (4)

The difference in pressure \( \Delta p = p_v - p_l \) over the meniscus at equilibrium is \( \rho gh \)

\[ \Delta p = \frac{2\sigma \cos \theta}{r} \]  \hspace{1cm} (5)

The above three equations will also apply for two planes the distance \( r \) apart.

At equilibrium conditions the Kelvin equation gives (van Brakel 1975):

\[ p_v = p_{sat} \cdot e^{\Delta p M / \rho RT} \]  \hspace{1cm} (6)

Hence, when transport takes place in a partly saturated porous medium, the presence of a capillary potential gradient is accompanied with a vapor pressure gradient. The difference between \( p_v \) and \( p_s \) can, in general, be neglected when \( |\Delta p / \sigma| > 10^7 \text{ m}^{-1} \) (van Brakel 1975).

For capillary rise in a tube under action of capillary forces only the Washburn-Rideal equation gives (Hergt and Christensen 1972):

\[ h^2 = \frac{r \sigma \cos \theta}{2\eta} \]  \hspace{1cm} (7)
Here, \( t \) is the time [t] from the start of the experiment.

The velocity of the capillary rise in a capillary of radius \( r \) when the gravitational acceleration is taken into account is given by Yata (1989) as:

\[
\frac{dh}{dt} = \frac{(p_1 - p_2)r^2}{8\eta} = \frac{r\sigma \cos \theta}{4h\eta} - \frac{r^2\rho g}{8\eta}
\]  

(8)

If the capillary leans away from the vertical by an angle of \( \alpha \) this velocity will be increased and the rate of absorption (e.g. in g/m\(^2\)s) will be increased (\( h \) is measured along the capillary, Yata 1989):

\[
\frac{dh}{dt} = \frac{r\sigma \cos \theta}{4h\eta} - \frac{r^2\rho g \cos \alpha}{8\eta}
\]  

(9)

A capillary constant (length) \( a \) [m] can be defined as

\[
a = \sqrt{Rh}
\]  

(10)

For water \( a \) is 3.93 at 0°C and falls steadily to zero at the critical point. This length determines the scale of many capillary phenomena, such as the shape of hanging drops (Rowlinson and Widom 1982).

The surface tension \( \sigma \) used above is the surface tension between liquid and gas. If we call this \( \sigma_{lg} \), we may also define two other surface tensions: \( \sigma_{sg} \) between solid and gas, and \( \sigma_{sl} \) between solid and liquid. These three \( \sigma \)'s are better called surface energies, as they give the energy in J/m\(^2\) needed to create these three interfaces. According to Adamson (1967) the following relation relates these three \( \sigma \)'s to each other:

\[
\sigma_{lg} \cos \theta = \sigma_{sg} - \sigma_{sl}
\]  

(11)

The equation is limited to ideal homogeneous surfaces which are in equilibrium with each other.

It is thought (Scherer 1990) that the state of a liquid capillary surface (e.g. \( \Delta \rho, r, \sigma \) and \( \theta \)) does not influence the rate of mass transport from the liquid surface to the gas phase.

"There is a tendency in the literature to consider all mass transfer as diffusion" (van Brakel 1980). However, two principally different types of mass transfer should be considered. Diffusion is "restricted to transport mechanisms based on the distribution of molecules within a single phase" (van Brakel 1980). Fick's law of diffusion is written as:
Here $\phi$ is any applicable potential (vapor content, vapor pressure, concentration etc.). Diffusion can take place both in the vapor and the liquid phase.

The second type of mass transfer is by *viscous flow* where one phase is moved as a response to gradients in total pressure. Darcy's law for viscous flow is written as:

$$F = -k \frac{dp}{dx} \tag{13}$$

For the vapor phase Eq. 13 covers convection. For liquid flow, $dp$ may be due to capillarity, gravity, osmotic forces and others.

For $N$ circular tubes of radius $r$ Poiseuille's law, a special case of Darcy's law, is:

$$F = -\frac{N \pi r^4 \Delta p}{8 \eta L} \tag{14}$$

The last two equation applies to laminar flow, i.e. when the Reynolds' number $Re<Re_{cr}$. For capillary processes the flow will always be laminar.

Capillary absorption is often modelled by the so-called extended Darcy equation (Hall 1994):

$$F = -K(u) \frac{d\Psi}{dx} \tag{15}$$

which for a system tilted an angle $\alpha$ with respect to the vertical will be:

$$F = -K(u) \frac{d}{dx} (\Psi + x \cos \alpha) \tag{16}$$

Here, $\Psi [m]$ is the capillary potential per unit weight of liquid, i.e. the height to which the liquid will rise at equilibrium:

$$\Psi = \frac{\Delta p}{\rho g} \tag{17}$$

Van Brakel (1975) does not write $k$ as a simple function of the moisture content $u$, but states that "both $k$ and $\Psi$ are dependent in a non-unique way on the liquid content, $u$, of the porous medium". This probably means that $k$ is influenced by the moisture content, but that this is not the only factor on which it is dependent.
For a real porous material like wood, \( \Delta p \) is a complicated function of the pore space geometry. Hence, for capillary liquid transport, one need not only a model for the transport coefficient \( K \), but also for (part of) the driving force, i.e. the capillary pressure (van Brakel 1975, Hall 1994).

In the above equations for capillary transport, \( \Psi \) are often replaced with the pressure potential or the gravitational potential, or any sum of these as long as they are similarly defined. The equations can then be used for mixed problems (Hall 1994).

### 4 The wood-water system

In this part is reviewed what is known about the part-processes and parameters needed to understand and model capillary flow in wood.

#### 4.1 Surface tension (surface energy)

The surface tension \( \sigma \) of pure water in air is well known (Table 1). Bramhall (1979) gives the following relation for \( \sigma(T) \) [mN/m]:

\[
\sigma = 75.6 - 0.1625T
\]  

In this equation \( T \) should be entered as °C.

The surface tension of water is higher than that of all other liquids except mercury. Table 2 shows the surface tension of some other common pure liquids.

The surface tension of water can change appreciably with the addition of surface active substances (surfactants). The influence of the impurities normally found in water in wood, such as water-soluble wood extractives, is not well known. Bolton and Petty (1980) argue that the value could be as low as 40 mN/m.

Yata (1989) measured longitudinal capillary absorption on 42 woods as a function of the surface tension (water and water with added wetting agents with \( \sigma \) of 71, 47, 42, 37 and 31 mN/m). For the sapwood of softwoods the surface tension did not influence the rate of absorption much, but for the heartwood of softwoods the penetration was increased several times when water was replaced with a liquid with \( \sigma=42 \) mN/m. Also for the hardwoods an increased rate of absorption was observed when \( \sigma \) was lowered (maximum rate with \( \sigma=31 \) mN/m). It was also observed that the heartwood of 13
Table 1: The surface tension of water as a function of temperature (CRC 1993).

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>surface tension, ( \sigma ) (10(^{-3}) N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>75,64</td>
</tr>
<tr>
<td>10</td>
<td>74,23</td>
</tr>
<tr>
<td>20</td>
<td>72,75</td>
</tr>
<tr>
<td>30</td>
<td>71,20</td>
</tr>
<tr>
<td>40</td>
<td>69,60</td>
</tr>
<tr>
<td>50</td>
<td>67,94</td>
</tr>
<tr>
<td>60</td>
<td>66,24</td>
</tr>
<tr>
<td>70</td>
<td>64,47</td>
</tr>
<tr>
<td>80</td>
<td>62,67</td>
</tr>
<tr>
<td>90</td>
<td>60,82</td>
</tr>
<tr>
<td>100</td>
<td>58,91</td>
</tr>
</tbody>
</table>

woods had no open capillaries for penetration. For the pines in this study the result were as follows: the heartwood of *Pinus desiflora* and *Pinus koraiensis* absorbed less than 0,15 g/cm\(^2\)h, but *Pinus pentaphylla*, *Picea jezoensis* and *Picea sitchensis* had higher heartwood absorption than this value. It was also observed that the rate and amount of absorption was increased by leaning the specimen away from vertical towards the horizontal direction. This effect was higher in woods with large capillaries (i.e. ring-porous hardwoods) as would be expected from theoretical considerations (Eq. 9). Figure 1 shows the effect of decreased \( \sigma \) and of leaning the sample.

### 4.2 Contact angle

A number of measurements of wood-water contact (\( \theta \)) angles have been made on wood surfaces. There are, however, several problems associated with these measurements:

- The contact angle shows hysteresis (Gray 1962).
- It is influenced by the roughness of the wood surface (Gray 1962).
Table 2: The surface tension of some common liquids at 25°C (CRC 1993).

<table>
<thead>
<tr>
<th>liquid</th>
<th>surface tension $(10^{-3} \text{ N/m})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>485.48</td>
</tr>
<tr>
<td>CCl₄</td>
<td>26.43</td>
</tr>
<tr>
<td>CH₃OH</td>
<td>22.07</td>
</tr>
<tr>
<td>C₂H₅OH</td>
<td>21.97</td>
</tr>
<tr>
<td>C₃H₆O</td>
<td>23.46</td>
</tr>
</tbody>
</table>

Table 3: Contact angles at different conditions. Values shown with standard deviations from 60 measurements.

<table>
<thead>
<tr>
<th>symbol</th>
<th>conditions</th>
<th>value</th>
<th>cos $\theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_0$</td>
<td>air-filled wood</td>
<td>55±9</td>
<td>0.57</td>
</tr>
<tr>
<td>$\theta_u$</td>
<td>water-filled wood</td>
<td>19±6</td>
<td>0.95</td>
</tr>
<tr>
<td>$\theta_w$</td>
<td>wood substance</td>
<td>21±6</td>
<td>0.94</td>
</tr>
</tbody>
</table>

- Wetting of a wood surface is always accompanied by penetration of liquid into the wood.
- A fresh wood surface is rapidly aged and contaminated (Gray 1962). Herczeg (1965) found that glycerol-wood contact angles increased from 43 to 65 after 45 hours exposure to "laboratory atmosphere".
- The contact angle of a liquid drop on wood is not constant with time (Liptáková and Kúdela 1994).
- The surface of the wood substance is not homogeneous (Gray 1962).
- A wood surface consists of wood substance and lumens, the latter of which may be filled with air or water (Liptáková and Kúdela 1994).

It is clear that the contact angle measured on a wood surface is not directly applicable to a wood substance surface, e.g. in a wood lumen. Liptáková and Kúdela (1994) tried to solve this problem by a method which separated the effect of permeation and the non-wood substance part of a wood surface. They defined three different contact angles which are shown in Table 3.

As seen in the table there is a big difference between air-filled wood and the other two materials. It may be concluded that the wetting of wood substance by water is so good that it is a very good approximation to give the contact angle as 0.

Water-wood contact angles reported in literature, e.g. Nguyen and Johns (1978), are often for air-filled wood (short time measurements).
Figure 1: Two figures from Yata (1989). a. The absorption (retension) into Hinoki (Chamaecyparis obtusa) heartwood as a function of surface tension. b. Difference in absorption between vertical and inclined samples of Sugi (Cryptomeria japonica). The inclined samples were almost horizontal.

Gray (1962) found all different types of behavior when he measured contact angles on 19 species of wood at different conditions. Green (undried) wood showed less wettability (higher contact angle) than dried wood. Sanded wood gave higher contact angle than unsanded wood. Different species also gave quite different results.

Bailey and Preston (1969) found that when comparing the permeability of softwood heartwood to petroleum distillate and water the important factor was the angle of contact with the wood surfaces (and not the viscosities).

4.3 Wettability

Wettability is the ability of a liquid to wet and to be absorbed by a material. It is often assessed by measuring the work needed to first slowly immerse a sample and then slowly bring it out from a liquid. A wettability index is then defined as the area under the force-time curve measured by a prescribed procedure. This index is used in the study of gluability and other technical processes.

In a study by Casilla et al. (1984) it was found that the wettability of four
Asian meranti species (*Shorea* sp. and *Parashorea* Sp.) in a large number of liquids was very influenced by the pH of the liquids. There was also a linear correlation between wettability index and liquid surface tension. A wood with incrustations (deposited extractives in the wood) gave much lower wettability than a wood without such hindrances to permeability.

Pecina and Paprzycki (1988) found that the wettability decreased for heat treated wood up to 190°C. At higher temperatures it increased due to breakdown of the cell wall components.

Gray (1962) and Herczeg (1965) discussed wettability in the more scientific terms of free energy of wetting and contact angles.

### 4.4 The porous system of softwoods

This section contains information on the porous system of softwoods relevant to capillary phenomena and permeability. Figure 2 shows the classical illustration of a typical softwood structure. The following structures are seen (symbols in brackets refer to the figure):

- **Tracheids** (cells, fibers) are the main components and make up more than 90% of the mass of a softwood. There are two types: large thinwalled early-wood fibers [3, 3a] and smaller thickwalled late-wood fibers [4, 4a]. These two types of tracheids are formed during the early and late part, respectively, of the growing-season.

- **Bordered pits** [S] connect tracheids with each other. Most bordered pits are found on the tangential surfaces (facing in the tangential direction) of the early-wood fibers. The early-wood bordered pits are also larger than the late-wood bordered pits. When wood dries most bordered pits are closed by aspiration.

  Figure 3 shows the tangential surfaces of earlywood and latewood fibers. The length of the fibers are approx. 100 times their thickness (2-3 mm compared with 20-40 μm).

  Figure 4 shows the complex structure of a bordered pit. The margo (margo strands) and the torus constitute a valve-like structure. The composition of the margo and the torus are similar for the genera *Picea* (spruces), *Pinus* (pines), *Larix* (larches) and *Pseudotsuga* (Douglas firs), but there are differences seen on the inner side of the pit chamber (Liese and Bauch 1966)
Figure 2: A schematic drawing of the porous system of softwood timber taken from Howard and Manwiller (1969) and shows a Loblolly pine (P. taeda) sample with the approximate size of 0.5×0.5×0.5 mm³.
Figure 3: Tangential surfaces of earlywood and latewood tracheids. a are bordered pits between tracheids, b are bordered pits to ray tracheids, and c are pits to ray parenchyma (Howard and Manwiller 1969).
Figure 4: Cross section of a bordered pit and measured dimensions of such pits in Scots pine (*Pinus sylvestris*) (Petty 1972).
Rays [9, 10, 11] are pathways in the radial direction which are built by a large number of cells of two types: parenchyma cells [K] and tracheid cells [J].

The main reason for refractory behavior (the very low permeability found in some woods, e.g. spruce) is due to the structure of the ray cells. In refractory woods the ray parenchyma cells communicate with each other and the longitudinal tracheids only through very small pits. Investigations by Liese and Bauch (1966) show a very good correlation between ray tracheid area (not ray area) and radial water uptake in species from the four genera given above.

Resin canals [2] are intercellular spaces lined with epithelial calls [E] in which liquid resins flow in the living tree. When the tree dies and the wood is dried the resin will dry, but the canals may still serve as pathways for liquid transport. In Pinus, Picea, Larix and Pseudotsuga there are both longitudinal and horizontal resin canals.

Several studies have been made in which liquids have been either sucked into wood by capillary tension or vacuum, or pressed into wood by overpressure. Below a summary is made of the findings in some of these studies:

Buro and Buro (1959) studied the penetration of colored water and hot paraffin wax into small samples of Scots pine (Pinus sylvestris). They remarked that a flow of a liquid through wood may have to zig-zag, using flow-paths in all directions even if the net flow is only in one direction. Therefore all flow paths are of interest to the flow in all directions. In the longitudinal direction the tracheids, the bordered pits and the resin canals are the main penetration paths. No difference was found between the permeability of earlywood and the latewood of the sap wood. In the heartwood the latewood was not permeable at all for water or paraffin wax. Both these liquids did, however, enter slightly into the heartwood earlywood. The longitudinal and radial resin canals in the sapwood were accessible for water, but not for paraffin; neither of these liquids entered into the resin canals of the heartwood. In the radial direction the liquids could also penetrate through the rays, but this had mainly a local effect (to distribute the flow). The position of the torus in the bordered pits (aspiration) was not the only factor influencing the permeability of these, as also substances deposited in the pits limits the flow.
Wardrop and Davies (1961) passed solution with copper salts through small specimens of radiata pine (Pinus radiata). "The penetration proceeded from tracheid to tracheid via the bordered pits and spread 'laterally' through the rays. The ray parenchyma appeared to be more readily penetrated than the ray tracheids. The resin canals were also effective in facilitating longitudinal penetration. The path of penetration was similar in both sapwood and heartwood".

Erickson and Balatinecz (1964) forced liquid monomeric styrene into Douglas-fir (Pseudotsuga menziesii) where it was polymerized into a solid. Injection was made in the three principal directions. "In the longitudinal direction, the bulk flow was through the tracheids. Some penetration of resin canals occurred. Liquid also moved into many of the ray tracheids and spread laterally be this means. In radial impregnation the liquid moved mainly in the ray tracheids. Ray parenchyma cells were mostly impermeable. The liquid moved from the ray tracheids occasionally into longitudinal tracheids. Radial intercellular spaces between ray parenchyma cells and longitudinal tracheids sometimes contained liquid. In tangential impregnation, the penetration was comparatively slow. Movement was through tracheid bordered pits and into and across ray tracheids to some extent". It was also concluded that "sapwood showed a larger number of penetrated cells than the heartwood". It was observed that the treatment was uneven as all cells do not contribute equally to flow (some cells appear impermeable). Liquids may thus form a discontinous system between the surface and the interior of the wood and pockets of liquid and air may exist. A similar study was made by Moore et al. (1983) who, however, was mainly interested in the technique itself.

Bailey and Preston (1969) pressure impregnated sections of Douglas fir (Pseudotsuga menziesii) with silver nitrate and hydrazine hydrochloride solutions. It was shown that for the longitudinal flow the open bordered pits fored ready paths from tracheid to tracheid. The closed (aspirated) bordered pits "can be impenatrable". No movement occurs across the pit membranes between tracheid and ray cells. In the radial direction the ray cells are of little signifiance in penetration. During impregnation Bailey and Preston found that aqueous liquids move through bordered pit membranes and "transient capillaries" in the cell wall. They could, however, not say if this was by diffusion or mass flow.
Hergt and Christensen (1972) exposed veneers to liquid water for very short periods of time (max. 8 s) and measured the water uptake. They found that the absorption took place in two steps: first a rapid wetting of the surface and then a slower capillary penetration. Solvent extraction of the wood increased the absorption in some species.

Trenard and Gueneau (1984) pressure impregnated Scots pine (*Pinus sylvestris*) and Silver fir (*Abies alba*) with liquid gallium at 50°C. The liquid metal penetrated into the longitudinal tracheids and subsequently into the rays through the cross-field pitting. The reverse did not occur as radial flow through rays was negligible.

Cote (1990) states that the tracheids are the principal conductors. For an impregnation to reach all parts of a wood movement between these and from these to surrounding elements is essential. Two possibilities exist for this: the bordered pit pairs and the "transient capillaries" of the swollen cell wall. The transient capillaries are only found when the wood cell walls are swollen by polar liquids. Another less significant pathway in softwoods is the interconnected system of resin canals. Although the resin might be hardened in many instances these canals appear to be effective pathways.

Richter and Sell (1992) vacuum impregnated white fir (*Abies alba*) with an epoxy resin and also studied capillary rise with colored water. The primary pathways were the longitudinal tracheids, and the bordered pit pairs dominantly influenced the impregnation. Wood rays were not primarily involved in the transport of impregnation fluid, and normal heartwood was mostly impermeable. In sapwood the liquids preferably extended into the latewood zones, whereas in earlywood only isolated groups of tracheids proved to be permeable. Pit aspiration is thus not a homogeneous phenomenon, even within a growth ring.

4.5 The cell walls

The cell wall may play an important role for the capillary behavior of wood. Most experiments on capillary behavior are made on capillary-porous media (cf. the introduction) in which the solid material only acts as a limitation of the pore space. In wood, however, the cell wall can also transport water as bound water or capillary water in microscopic pores in the cell wall. Nothing,
however, seems to be known how this should influence the capillary behavior of a material.

**Bailey and Preston (1969)** found silver grains in the cell walls after their impregnation with silver nitrate, indicating "the presence of channels in the wall in both sapwood and heartwood though much less marked in heartwood than in sapwood. Removal of extractives from heartwood increases the abundance of Ag grains in wood subsequently treated". These extractives were found to make the heartwood hydrophobic and only slowly absorbing.

**Kellogg and Wangaard (1970)** measured the cell-wall density of 18 species. Wood-substance density values ranged from 1497 to 1517 kg/m$^3$ for hardwoods and from 1517 to 1529 kg/m$^3$ for softwoods. Earlier Christensen and Hergt (1968) had measured cell wall densities of Klinkipine (Araucaria hunsteinii) and Radiata pine (Pinus radiata) as 1434 and 1437 kg/m$^3$, respectively. The accuracy of these measurements is difficult to assess as different organic liquids or mercury were used under different pressures after different extraction procedures etc.

Kellogg and Wangaard calculated that voids in the dry cell walls of these 18 species occupied from 1.64 to 4.76% of the cell-wall volume.

**Cote (1981)** also discuss the "theoretical and still poorly defined 'transient capillary' which enlarges or contracts during swelling or shrinkage of wood".

### 4.6 Pit aspiration

The lumens in a softwood are connected by pit pores with a special structure (Fig. 4). The torus of the pore is supported by margo strands. In the living tree with liquid-filled lumens this construction may not have any function. If, however, a lumen loses its liquid content through drying or by accident, the pit will be closed by the torus. This phenomenon is called aspiration.

A large number of studies have been made on different aspects of the aspiration process. We are here interested in studies concerned with the effects of aspiration on permeability. Several of these studies have been made by comparing the effects of different drying methods. Solvent drying is made by gradually exchanging the water in green wood with other liquids which do not cause pit aspiration when they evaporate.
Figure 5: Proposed mechanism of pit aspiration according to Hart and Thomas (1967) (taken from Siau 1984).

**Bailey** (1913) was the first to recognise that pit aspiration is an important factor in determining wood permeability.

**Hart and Thomas** (1967) proposed the model for pit aspiration seen in Fig. 5. When the liquid front recedes through the pit the openings between the margo strands are so small that very high capillary tensions will develop in the liquid phase. As drying proceeds the torus will be pulled along by the surface tension of the water until it touches the walls of the pit border. There it will be bonded to the pit border and the pit will be effectively closed.

**Comstock and Cote** (1968) found that the permeability of red pine (*Pinus resinosa*) and eastern hemlock (*Tsuga canadensis*) was reduced by normal drying procedures to only a small fraction of the green permeability. The reduction was more severe at higher drying temperatures, but still very large even after drying at -18°C. When the sap was re-
placed with surfactant solutions with low surface tensions and organic liquids with high surface tensions it was found that the former, but not the latter, did cause pit aspiration. It was concluded that high surface tension alone does not cause aspiration. A critical factor is also the ability of a liquid to promote adhesion between the torus and the pit border.

Petty and Puritch (1970) measured permeabilities of *Abies grandis* wood dried by solvent exchange and normal air drying. In the paper is also described a method to calculate the number of lumens and pits which are conducting from gas permeability measurements at different pressures and mean pressures. In solvent-dried wood 83% of the tracheids were conducting. In air-dried wood only 32% of the latewood tracheids were conducting. The earlywood tracheids were not conducting at all. The authors also calculated the number of conducting pit membrane pores per conducting tracheid to be 27000 for solvent-dried wood and only 600 for air-dried wood. From these results it was concluded that most pit pores are aspirated in air-dried wood.

Thomas and Kringstad (1971) studied Loblolly pine (*Pinus taeda*) and concluded that pit aspiration will only occur when the evaporating liquids has the following properties:

- a molecule able to form hydrogen bonds and possessing both hydrogen donor and acceptor properties.
- the ability to swell wood nearly as great or greater than water.
- a surface tension and contact angle relationship such that the initial capillary tension force is sufficiently high to begin pit membrane displacement.

Meyer found that percentage pit aspiration, tracheid length and number of pits per tracheid determines gas permeability in two samples of Douglas-fir (*Pseudotsuga menziesii*). By light-microscope studies it was found that the percentage of aspirated pits in sapwood was 32%, 55%, 88%, 93% and 98% for green, solvent-dried, freeze-dried, air-dried and oven-dried samples, respectively. Longitudinal gas permeability was found to be a function of percent pit aspiration.
Table 4: Pressures needed to aspirate pit pores and corresponding dimensions of the smallest components of the bordered pits (Bolton and Petty 1978).

<table>
<thead>
<tr>
<th></th>
<th>P / atm</th>
<th>r / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>earlywood</td>
<td>5.4</td>
<td>0.3</td>
</tr>
<tr>
<td>latewood</td>
<td>680</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Petty (1972) measured the dimensions of the bordered pit components of Scots pine (*Pinus sylvestris*). The results are summarized in Fig. 4.

Bolton and Petty (1978) calculated the force needed to deflect the torus of early- and late-wood membranes. The very large capillary tensions needed to deflect the thicker latewood torii explains why the degree of aspiration in dried spruce and pine is almost complete in the earlywood, but often much less in the latewood. Their result is given in Table 4.

Cote (1981) emphasizes wood ultrastructure as an important domain for wood-water phenomena. Aspirated pit membranes does not allow free passage of particles, but liquids may move through the structure by diffusion.

Johansson and Nordman (1987) used a microscopic technique to count the number of aspirated bordered pit in Norway spruce (*Picea abies*) and concluded that the pits aspirate quickly when they are drained of liquid and that the aspiration is irreversible. It was also found that hydrophobic extractives contributed to the irreversibility of the aspiration.

The following two equations have been proposed in connection with pit aspiration. Stamm, Clary and Elliot (1968) gave the following equation for the number ($N$) of pits traversed in series through a given length ($L$) of wood, where the maximum ($f_{\text{max}}$) and average ($f_{\text{av}}$) fiber lengths are known:

$$N = 1 + \frac{4(L - f_{\text{max}})}{3 \cdot f_{\text{av}}}$$ (19)

Meyer gave an equation for the proportion of fluid-filled tracheids at various levels within a permeability sample. If $n$ is the number of pits per tracheid and $q$ the probability that a pit is aspirated, then the probability that a liquid arrives at level $i + 1$ in a certain tracheid is

$$p_{i+1} = p_i (1 - q^{n/4}) [2 - p_i (1 - q^{n/4})]$$ (20)

It should be noted that pit aspiration causing lower permeability is a phenomena seen mostly in softwoods. In a study by Tesoro and Choong (1976) the water permeability was measured on the heartwood and the sapwood.
of 12 different wood species. In all hardwood samples the permeability increased after drying, whereas in the softwood samples the permeability was very much decreased due to pit aspiration.

An increase in penetration can be obtained due to the action of microorganisms (fungi, bacteria) which mainly perforate the thin structures of the pits. Ponding and wet storage for long periods of time may result in such degradation.

4.7 Wood components soluble in water

The sap of a living tree contains water-soluble substances which could influence the capillary properties of water. An extreme example is the sap of the sugar maple (Acer saccharum) which contains up to 5% sucrose in spring time.

We are here interested in the amounts of substances that exist in the sap of the living tree or that will dissolve when wood is moistened by capillary action. A large number of different substances are of interest (Browning 1967): sugars and oligosaccharides, polysaccharides (pectic substances, starch, arabinogalactans), glycosides, cyclitols, organic acids, proteins, and alkaloids. The pectic substances and the proteins are water soluble, but are not dissolved to a significant extent by water in wood as they are hidden in the wood cell wall.

The surface tension of water can change appreciably with the addition of surface active substances (surfactants). The influence of the impurities normally found in water in wood, such as water-soluble wood extractives, is not well known. Bolton and Petty (1980) gave a value as low as 40 \(10^{-3}\) N/m.

4.8 Theoretical models

Models and theories of capillary phenomena should always be used with great caution as it is extremely difficult to make reliable models of such a complex phenomena as capillarity. It should be noted that there is still an active discussion as to the explanations of results of even some of the simplest possible capillary experiments.

One and two-dimensional models are often unreliable (van Brakel 1980) as capillary phenomena usually take place in three dimensional networks which cannot be modelled with less degrees of freedom.
There exist a large number of non-pore and pore space models. Van Brakel (1975) gives an overview of these, from which much of the following is taken.

Non-pore space models includes empirical correlations, continuum models, statistical dynamic models, irreversible thermodynamic models etc. In these transport coefficients are derived from very general parameters, e.g. porosity. All these models have in common that they are not based on a full description of the actual porous system under investigation. The main problem with these types of approaches is that different types of porous materials behave very differently and none of the proposed models have been shown to be realistic (van Brakel 1975).

It is quite obvious that porosity cannot be the main factor determining the permeability of wood as it is well known that the main resistances to flow are the pit pores which only contributes to a minute fraction of the total porosity. For random sphere packings and similar systems this approach may, however, be of more use, but it seems that even here there exists large discrepancies between predictions and experimental results (van Brakel 1975).

The moisture (or liquid) content \( u \) is often used as the driving force for capillary liquid transport (for wood, see e.g. Nadler et al. 1985). This, however, cannot be correct. "In no sense of the term can the liquid content be regarded as the driving force" (van Brakel 1975). The capillary pressure or any other similar potential (cf. Eq. 15) is the only sensible driving force, but it is of course not as easy to determine as the moisture content.

The main reason that capillary transport is treated as diffusion is probably the great impact the heat transport theory had on mass transport theory. In the early papers by Sherwood (1929ab, 1930, 1932) and Newman (1931ab) the equations for heat flow was used on diffusion problems. This made it possible to make calculations of drying rates and other mass flow problems. As this theory is so convenient it has been used even when it clearly is physically incorrect.

As early as 1937 Ceaglske and Hougen in a paper on the drying of granular solids (e.g. sand) stated this very clearly as: "The drying rate of a granular substance is determined not by diffusion but by capillary forces. The moisture distribution cannot be calculated correctly from diffusion equations but depend on the complex suction-water concentration relation of the substance. This relation is dependent upon particle size, degrees of packing, and distribution of pore spaces and hence must be determined by experimental methods. In the drying of a granular solid the rate of water flow is deter-
mined by capillary forces and not by moisture concentration gradients; the flow may be in the direction of increasing concentration”.

Even if \( u \) cannot be the correct driving force for capillary transport it may in some special cases, e.g. wetting of one material under quite constant conditions, be of practical use. It seems that van Brakel (1975) is close to the truth when he states that different capillary phenomena (at present) require different approaches. One problem often encountered in capillary processes is the way in which the liquid replaces the air. There are fundamental differences between drying, where the evaporating water and the replacing air is transported in different directions, and drainage where both phases are transported in the same direction.

Anomalous behavior is sometimes described as being caused by one of a number of other factors which, in general, are very difficult to study:

1. The existence of liquid water with other properties than normal water.
2. The occurrence of film (surface) flow.
3. Disjoint pressures.

It is normally, e.g. for renderings on facades, that small capillaries can suck water from larger capillaries. Similar phenomena in drying were seen by Ceaglske and Hougen (1937). In wood there are larger pores (the lumen) and smaller pores (the bordered pits). Both these structures are so small that they theoretically can suck water from each other. However, it is not trivial to explain how the larger lumen can start to suck water from a bordered pit situated in the cell wall; there is no obvious way for the meniscus to move from the small opening of the pit to the much larger lumen. Some other mechanism, e.g. film flow or bound water flow, is probably active to overcome this obstacle as we know that capillary rise in wood is far greater than just a single cell length of a few millimeters.

Pore space models can be divided into one-, two- and three-dimensional models. In the following the division of van Brakel (1975) is used, but only those models useful for modelling capillary phenomena in wood are mentioned. Figure 6 shows these models.

One-dimensional models for softwood transport in the longitudinal direction should be composed of a tube with restrictions. One such model which, however, is not very realistic for wood is 1515 (cf. Fig. 6). LW1 denotes
Figure 6: Pore space models applicable to wood (the figures are taken from van Brakel (1975, with his numbering) or drawn by myself (LW#)).

one which would be more useful for wood. It is doubtful which value a one-dimensional model has. It cannot capture the total blockings of part of the flow path and the roundabouts taken by the flow path to pass such obstacles.

True two-dimensional models are often used as they are attractingly complex at the same time as they may be drawn on a paper. In some cases, such as a close packing of spheres, a two dimensional model is clearly useless for flow in the plane of the paper as there will be no flow paths through the system. Van Brakel (1975) gives examples of two-dimensional models with the flow in the third dimension. These models are restricted three-dimensional models. For wood 233 could be used (with the flow in the normal direction to the plane of the paper), but this model cannot model the constrictions in the main flow directions, only those at right angle to the main flow direction.

Three-dimensional pore space models are very complex, especially as a realistic model for wood cannot have a repeated cell structure (i.e. the number of aspirated pores have to be varied etc.). Model 343 shows one simple model and 351 one which is more general.

From the review of van Brakel (1975) it seems that no pore space models have been applied on wood. Some of the drying models below (e.g. Comstock 1970 and Plumb et al. 1985) are, however, some type of pore space models.

Pseudo-pore space models (the term given by van Brakel 1975) are simple tube arrangements "used in ad hoc explanations, for didactic purposes or as a conceptual model of a formal model of some transport phenomena". These
cannot be multiplied in any simple way to obtain an extended pore space. A
typical example is the ink bottle pores (LW2) and other pore arrangements
used to explain hysteresis. The so called independent domain theory (see e.g.
Morrow 1970) uses such pseudo-pore models when it divides the pore space
into a number of regions that behave independently and assigns two radiiuses
to each domain: one for capillary condensation and one for capillary evapo-
ration. The theory has been used to explain hysteresis (cf. ink bottle pores),
but this is probably not mainly a function of pore geometry (most surfaces
in simple pores show capillary hysteresis and all hygroscopic materials show
the independent domain theory and its successors intend to solve is that of
giving an account of the accessibility of an arbitrary region in the pore space.
This is not a property of the pore space alone."

According to van Brakel (1975) the concept of "pore size distribution" is
misleading as there does not exist any pores with well defined lengths and
recognizable walls. This is certainly true for normal porous media, but wood
is different. As wood consists of a quite ordered array of large pores of well
defined lengths and walls, coupled together with small openings, pore sizes
do actually have a meaning for wood. It is however doubtful if pore size
distributions (as measured by mercury porosimetry) are of any use.

Plumb et al. (1985) writes: "In contrast to the random packing of many
porous media, such as sand, wood cells are organized in a very regular pat-
tern. This fact makes it very attractive to utilize a mechanistic model of
wood structure to identify capillary porous properties — permeability and
capillary pressure". It seems that wood is quite unique in being a well orga-
nized porous material. Figure 7 gives one picture of the softwood structure
as would be used in such modelling.

4.9 Experimental model systems

It is in many cases advantageous to study different phenomena separetely
by using model systems in which one or a few processes may be isolated.
For other porous media many such studies have been made with glass beads
or micro-porous glass, but for wood only one such study, which is discussed
below, has been found. It is probably not of very much interest to use systems
with very different geometries from that of wood to try to understand wood
behavior. Heizmann (1970) presents one such study in which experiments
with glass beads are compared with similar experiments with a number of
Figure 7: Typical softwood structure (Rosen 1987).
different woods. The results (e.g. "moisture distributions...could be calculated by an exponential function") do, however, not give much information of what is going on in the wood.

Ceaglske and Hougen (1937) dried moist sand. By placing coarse and fine sand in different arrangement they showed that small pores are able to pull the water out of larger pores and a material with small pores on its surface will show relatively quick drying. "To retard rate of drying, sprinkle coarse sand on top; to hasten drying, sprinkle a layer of fine wet sand on top" (Ceaglske and Hougen 1937). Such simple experiments are often of greater value than experiments with all complicating factors included at the same time.

Engøy et al. (1991) made drying experiments with a wood model system consisting of 100 μm PMMA optical fibers placed in one layer between glass microscope slides. This system shows resemblance to the porous system of a softwood in that there are large pores with an aspect ratio of 100 and that the ratio between the largest and the narrowest pore diameters are approx. 5. As there is some surface roughness in the glass slides there are also many possibilities for the water to go from one pore to another. The experiment was conducted by drying the model system which was initially filled with water.

The observations in this study can be summarised as follows:

- Evaporation takes place from all menisci and is independent of the pressure state of the water in the menisci.
- Larger pores empty first as they cannot support as small radius of curvatures as can smaller pores.
- In drying horizontal pores the largest pores drain completely before the second largest pore start to drain. In experiments with vertical pores the gravity force will make the pores drain more or less simultaneously.
- At the end of an experiment, when all pores have been drained of a contiguous liquid phase, there is still a discontinous system of droplets.
5 Drying of wood

5.1 General drying theory

Drying of porous materials is generally agreed to follow the stages described by Sherwood (1929ab, 1930, 1932): constant rate period (CRP), first falling rate period (FRP1), and second falling rate period (FRP2). In all these periods capillary phenomena play a role even if Sherwood and many later researchers have treated all phenomena as diffusion. Theory and most measurements have been made on materials that have geometries very unlike wood. Most porous materials (clays, gels, glass beads, powders etc.) have random pore sizes within certain distributions. Many such materials are submicroporous, e.g. they have pore-radiuses on the nm-scale. Wood (softwoods) is very different in many respects: 1. It mainly consists of two types of larger elongated pores (early- and late-wood lumens) connected by smaller pores (pit-pores). 2. The cell-wall material itself is very hygroscopic.

In spite of these differences I here summarises the conventional drying theory and the three drying periods (following Scherer 1990). During the CRP the rate of evaporation from the surface of the drying body is constant because the surface is wet. This period can continue for a long time because 1. The drying body may shrink from the tension in the liquid caused by the meniscii formed at the surface (e.g. gels may shrink to a tenth of their original size (Scherer 1990). 2. Small dry spots on the surface does not decrease the rate of drying because there is an effective diffusive transport within the boundary layer. Suzuki and Maeda (1968) found that in some cases the decrease in fractional area of wetted surface had little effect on the mass transfer coefficient. 3. Liquid films may form on the outer exposed surfaces. To which extent this can contribute to the effective area of evaporation is unclear (van Brakel 1980).

The FRP1 starts when the shrinkage stops and the meniscii are forced into the drying body. Most of the evaporation of the liquid is still at the surface, but it has to be transported there from below the surface. Part of the transport to the surface will be by diffusion. The rate of drying will then decrease.

The difference between FRP1 and FRP2 is that during the latter all liquid has to evaporate below the surface of the solid, e.g. there are no continuous liquid paths to the surface. When there are continuous liquid paths in a region, the state is said to be funicular. The opposite, when only isolated pockets of
liquid remains is called *pendular*. It is only in the funicular state that liquid can be transported to the surface of a body by the low capillary pressures at the surface. When the paths are broken, i.e. in the pendular state, all the transport is by diffusion.

During the falling rate periods FRP1 and FRP2 a sharp drying front is often observed. Shaw (1986) has shown that this sharpness is caused by the pressure gradient in the unsaturated region. One pore cannot dry much ahead of the other pores before such a large capillary pressure is needed that other neighbouring pores are emptied first. However, this line of reasoning can probably not be applied to soft-woods. Shaw performed his experiments on silica spheres.

In a connected porous system in equilibrium the capillary tension has to be the same in all pores, and all menisci then have the same radius of curvature in the absence of gravity. When the surface begins to get dry the menisci have to retreat into the material. As a smaller pore can support a meniscus with a smaller radius of curvature (i.e. a higher capillary tension) the largest pore will empty first (Scherer 1990), the second largest will be emptied next etc.

Ceaglske and Hougen (1937) measured capillary pressure as a function of water content in sand and used this to model capillary transport in drying sand. Their paper is interesting as it contains a physically correct model of capillary transport in a porous material.

Many materials show substantial shrinkage during drying as a consequence of the great capillary tensions. This is not seen for wood but wood collapse during drying is caused by the same phenomenon.

### 5.2 Drying models for wood

#### 5.2.1 General overview

A large number of drying models for wood have been proposed. In most of these capillary forces are not taken into consideration (e.g. Bateman et al. 1939, Nadler et al. 1985, Haloui et al. 1992).

Rosen (1987) gives an overview of different models of wood drying that does not take capillary phenomena into account. He cites Stamm: "Moisture movement above the fsp [fiber saturation point], though not in itself a diffusion phenomenon, will be controlled by the diffusion below fsp, and will appear as if it were a diffusion phenomenon". This reasoning is not very
clear, but it is probable that it is possible to fit the solution to the diffusion equation to the drying curves. However, as these can more or less be described by one parameter (e.g. a time to half desorption) this is no good proof.

It is interesting to note that several workers using the diffusion equation to solve problems involving capillary phenomena are aware of that this equation is not the correct one. They find that it can be used to model the weight loss or weight increase of a wood sample, but that the moisture profiles calculated can not be correct.

5.2.2 Wood drying models with capillary pressure

Spolek and Plumb (1981) obtained a mechanistic relation between moisture content and capillary pressure with the help of the Comstock (1970) model as:

\[ \Delta p = 12400S^{-0.61} \]  

(21)

Here, \( S \) is the liquid saturation, i.e. the fraction of the pore volume that is filled with water. This relation was fitted to experimental results of suction measurements on Southern pine (\( Pinus \) sp.).

Dorri et al. (1985) modelled the drying of small wood particles. They found that at least for the larger particles the capillary flow had to be taken into account as the surface otherwise would dry out too quickly, "leading to a reduction in predicted drying rate". They assumed that the capillary radius in wood (probably: softwoods) could be described as:

\[ r = RS^{-0.333} \]  

(22)

Here, \( R \) is the radius of the lumen. Figure 8 compares the capillary pressures given by the above two equations. It is seen that there are large differences between the two equations.

Moyne and Perré (1991) and Perré and Moyne (1991) include a capillary pressure assumed to be dependent on temperature and moisture content. The function used for the capillary pressure is (\( S \) is degree of saturation, \( \epsilon \) is the porosity, and \( k_{\text{sat}} \) is the permeability at saturation):

\[ \Delta p = J(S)\sigma \sqrt{\frac{\epsilon}{k_{\text{sat}}}} \]  

(23)

This equation was proposed by Leverett (1941). The function \( J \) was correlated with Leverett's experimental data. Note that it is not a function of
Figure 8: A comparison between two equations for the capillary pressure as a function of moisture content in wood. Equation 3 with $\theta=0$ and $\sigma=72$ mN/m was used together with $R=20$ mum to convert $r$ to $\delta p$. Solid line: Spolek and Plumb (1981), dashed line: Dorri et al. (1985).

the pore geometry (radiuses etc), but it has to be measured for each material. No values of $J$ for wood are given in the papers.

Bramhall (1979ab) included ”capillary flow in response to net surface tension forces determined by the free water differential”. He notes that Eq. 3 (of this report) ”is of questionable value because the radius varies unpredictably over a wide range as drying progresses [...] there is as yet no known correlation between the tensions at these points and their MC or other measurable property [...] since free water concentrates at the tapered ends of tracheids due to the tendency for the radius of the meniscus to become a minimum value, the tension must be a function of MC”. Bramhall uses the following relation:

$$\text{Net retention force} = \sigma \frac{dW}{dx} \tag{24}$$

Here, $W$ is the free water content. This was obtained as a ”linear relationship” from ”the first two experiments”. No data is given in the papers.

Plumb et al. (1985) in their model of heat and mass transfer in wood during drying included liquid transport via capillary action. The authors are very clear in distinguishing wood from random packed porous media. In
tangential direction the model of Comstock (1970) was used. In the radial direction a new model was proposed which, however, is not described in any detail, but seems to include both ray cells, tapered tracheid cells, and pits connecting these.

Stanish et al. (1986) used Darcy's law for liquid phase transport. The pressure in the liquid phase is the local gas pressure less the capillary pressure associated with the gas-liquid interface. The capillary pressure was taken from Spolek and Plumb (1981), cf. Eq.21.

5.2.3 Skaar's model

The drying front in a porous material is irregular on a microscopic scale even if it often looks quite sharp by naked eye (Shaw 1986). Skaar (Siau 1984) have described how, in principle, the drying of a number of wood cells proceeds. Figure 9 shows the stages of drying of a wood surface:

- Figs. 9b–d shows how the capillary tension reaches a maximum when the air-liquid interface has the same radius of curvature as the radius a the opening the meniscus has to pass through.

- In Fig. 9e the drying has just started from the wet surface.

- In Fig. 9f the surface is dry and the meniscii are at the entrances to the smaller pores connecting the lumens.

- In Figs. 9g–h the air bubbles in one of the lumen in the wood expands as there is a negative capillary pressure in the whole system. The evaporation continues from the meniscii, but they do not move inwards.

- In Figs. 9i–j: the same process for another lumen.

- In Figs. 9k–l there are no more air bubbles to expand, but as the drying from the meniscii continues the capillary pressure is decreased and the largest meniscus will retreat into the pore. At this stage there will be very high tension in the liquid phase which will be decreased each time a meniscus has travelled through a pore and starts to empty a lumen.

- In the last figures, Figs. 9m–n, is shown that the high capillary tensions can cause collapse in wood.

This model of drying raises a number of questions:
Figure 9: Skaar's model of transversal drying of wood (Siau 1984)
- Are there air bubbles in all/most/many/any lumens that will make these cells empty before the capillary front advances inwards?

- How deep in the wood can an air bubble expand? A limiting factor must be the high resistance to liquid flow to the surface from deep inside the wood.

- Does the drying proceed step-wise? Could this be measured by measuring the capillary pressure?

- What role does the transport of liquid water and water vapor through the cell wall play?

5.2.4 Comstock model

Comstock (1970) described a model for permeability of softwoods based on lumens connected with pits on their tangential surfaces on their tapered ends (Fig. 10). The realistic simplicity of this model have encouraged others to use it. Spolec and Plumb (1981) modelled how capillary forces can cause free water movement in the tangential direction with this model. The cells nearest the surface contains less water than the cells inside the wood. As the cell ends are tapered, a small amount of water in a cell end will give a small radius of curvature and a lower pressure. Furuyama and Kanagawa (1994) models wood drying with continuous liquid phase in a similar fashion.

As the lumens are tapered only at their ends this cannot be the only cause of liquid transport in wood. When the lumen are anything between half-filled and filled the capillary radiiuses does not decrease with moisture content.

5.2.5 Čudinov model

The moisture content profiles of drying wood may look very different depending on if the wood was initially water saturated or not. If the wood is initially saturated and contains no air a sharp drying front will be observed. If the initial conditions are a lower moisture content the drying profile will be more like that of a diffusion controlled process. Figure 11 shows this.

Čudinov (1985) has put forward a theory which explains this phenomena. In his model the pathways between the lumen (the bordered pits) are filled with water in those parts of the wood which are near the fiber saturation.
Figure 10: Comstock (1970) model of capillary transport

Figure 11: Drying profiles during two types of drying of a wood slab with thickness $D$: 1. The wood is initially unsaturated, e.g. the lumen contain both free water and air. 2. The wood was initially saturated at $u_{\text{max}}$. The fiber saturation point and the moisture content in equilibrium with the drying conditions are denoted by $u_F$ and $u_{gl}$, respectively (Čudinov 1985).
Because of this the air in a lumen will be trapped there. Water is removed from a lumen by liquid transport in water filled lumens to a place where the water can evaporate. As water is removed the pressure of the air will decrease. This under-pressure in the lumens which are above fiber saturation causes a flow of liquid water from the inner parts of the wood to these lumens. Note that in this model the gas phases of the lumens are not connected until the moisture content goes below the fiber saturation point. The liquid phases are, however, in contact, so the water may move from one lumen to another. According to Cudinov (1985) there should be a pressure minima in drying wood near the position of the fiber saturation point. Figure 12 shows how the water is transported. The leftmost cell is emptied of liquid water and is thus at fiber saturation.

If wood is initially saturated it contains no air and the whole drying process will be by diffusion from a drying front, but if wood is initially unsaturated the above model may explain why there is not any drying front. The model may partly also explain why wood does not dry homogenously.
as preferential liquid flow paths will be established, causing other parts of
the wood to be emptied of their liquid.

6 Capillary absorption of wood

There are unfortunately not many experiments with capillary absorption in
wood reported except those in which only a capillary coefficient is given.
Below is described one interesting experiment which has not been described
elsewhere in this report.

Yata (1987) studied the effect of initial moisture content on the rate of
penetration into seven woods. The wood was probably dried to 7% mois­
ture content and then conditioned to various moisture contents between 7
and 190% before the experiments. The rate of absorption was higher for dry
wood. Figure 13 shows results for Sugi (Cryptomeria japonica) and Hinoki
(Chamaecyparis obtusa).

7 Conclusions

1. Capillary phenomena play a role in nearly all processes in which liquid
water is present in wood.

2. Capillarity may be very different in different softwoods, e.g. is the per­
meability of the sapwood of pine and spruce very different.

3. Longitudinal flow in softwoods is mainly through lumens and bordered
pits in series.

4. Tangential flow is also mainly through lumens and bordered pits, but
many more pits have to be traversed per length compared to in the
longitudinal direction.

5. Radial flow is through different types of flow paths. The influence of
the ray cells is not clear.

6. The flow will utilise all structural elements possible and will zig-zag
when necessary.
Figure 13: Effect of changes of the initial moisture content on the penetration of water for 60 minutes into sapwood of Hinoki (Yata 1987). The ratio of water uptake was calculated with respect to the absorption at 11% moisture content in a separate experiments (as there are no data points at ratio=1.0). From another figure in Yata (1987) the water uptake of Hinoki sapwood after 60 minutes was 0.68 and 0.19 g/cm² for wood with initial moisture contents of 7 and 171%. 
7. Aspiration of bordered pits and incrustations in pits will drastically decrease the permeability. Normally most bordered pits in dried softwood are aspirated. In the heartwood deposited substances block pits.

8. Penetration and capillary suction is often uneven processes: two cells close to each other may have very different ability to absorb water. Larger parts of a piece of wood may also show decreased or increased permeability.

9. The importance of the cell wall to capillary phenomena is largely unknown. It is, however, known that there are micro-capillaries in the wet cell wall ("transient capillaries").

10. The driving force for capillary transport is capillary pressure or any other related "force". Moisture content cannot be the correct driving force.

11. Modelling capillary suction in wood is very complicated and it is doubtful whether any such models actually will be able to predict the behavior of wood in use. One of the main problems are the very variable material properties seen.

12. A model for capillarity in the longitudinal direction should be made up of lumens (in the fiber direction) and bordered pits of which a certain fraction is aspirated.

13. A model for capillarity in the tangential direction should be made up of lumens cross-sections and bordered pits of which a certain fraction is aspirated.

14. A model for capillarity in the radial direction probably has to be tailored to a certain wood as there are large differences between different authors (=different woods) on the influence of the rays.

15. There are very few published experiments with capillarity in wood, except those in which the placement a water soluble trace substance is investigated microscopically after drying. New methods, including the use of model systems, should be investigated.
8 Recommended reading

After reading a large number of papers it is not a difficult task to recommend a small number of papers which are among the best of these:

Ceaglske and Hougen (1937) contains a physically correct description of capillary transport in drying sand.

van Brakel (1975) is a brilliant, but very critical, review.

Petty and Puritch (1979) is an interesting account of how the flow resistances and number of open pits can be determined from permeability experiments.

Yata (1987) describes an interesting experiment.

Siau (1984) contains a good chapter on the softwood micro structure.

Engøy et al. (1991) describes a simple, but interesting experiment.

Richter and Sell (1992) contains lots of information on impregnation pathways in softwoods.

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49