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Lars Wadsö

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BORDERED PIT DIFFUSION

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ABSTRACT

I have calculated the diffusion through aspirated and non aspirated pits. It seems that the resistances of the margo and the torus are of minor importance to the total diffusion of the non aspirated pit. For the aspirated pit however, the resistance of the torus is naturally of greater importance.

CONTENTS

1. RESULTS

I have calculated the diffusion through aspirated and non aspirated pits. It seems that the resistances of the margo and the torus are of minor importance to the total diffusion of the non aspirated pit. For the aspirated pit however, the resistance of the torus is naturally of greater importance.

If I make my calculations with a high diffusion coefficient for the cell wall (like values from Stamm (1959) at higher moisture content) the total resistance of the aspirated pit is surprisingly low.

With the help of some mathematical tricks it is possible to show that the margo resistance is very low when the margo is as open as it looks in most pictures.

2. DIFFUSION

2.1 Vapour diffusion

Water vapour is transported from regions of high vapour content to regions of low vapour content. The mechanism for this is called diffusion, and is a result of a natural phenomenon. All molecules have thermal motion in a random directions. If there is a region of higher water vapour concentration more molecules will have a direction of movement out from that region, than into it. This is only because there are more water molecules if the vapour concentration is higher. Because this loss of molecules, the number of molecules in that volume will be reduced. When all regions have the same concentration of water vapour, there is no net tranport of molecules.

Thermal motion and concentration differences are the driving forces but there is another component that determines the rate of diffusion: the resistance to movement. This is a function of the molecular surrounding, and is in most cases impossible to determine theoretically.

When quantifying the phenomenon of diffusion it is possible to use one of several different definitions of a diffusion constant. I will use the following in this paper (conforming to ISO-standard 9346):

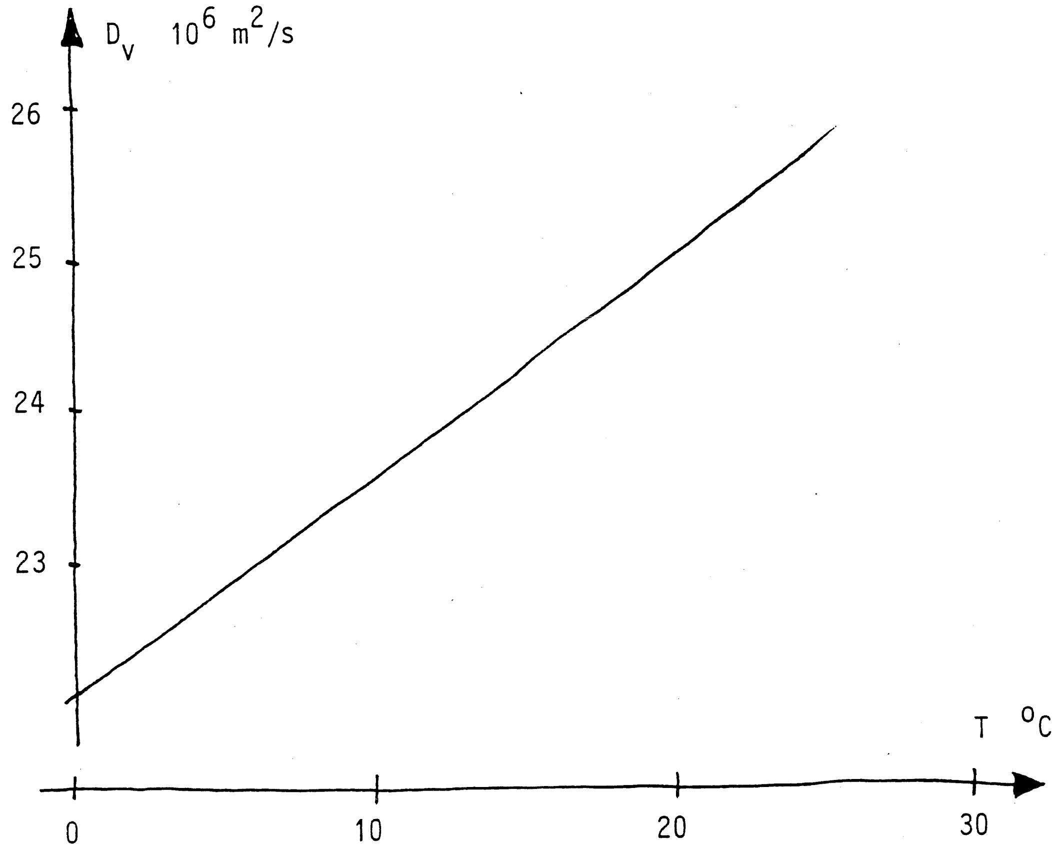
$$-g = D_v \, dv/dx$$
$$-g = \delta_v \, dv/dx$$

g	flow	$kg/(m^2 s)$
D_v, δ_v	diffusion constants	m^2/s
v	vapour content	$kg(vapour)/m^3(air)$
x	distance	m

Strictly speaking, the unit of the diffusion constant is $(kg\ m\ m^3)/(m^2\ s\ kg)$, but this can be shortened to m^2/s. In for example polymer technology you often see units like $(g\ cm)/(cm^2\ s\ bar)$, but as I use a gradient which corresponds to the flow unit I use, these two cancels out (except for a "m"). This is of course also because I use SI-units throughout this paper.

It should not be forgotten that m^2/s is like an abbreviation for the real unit. We should not try to understand m^2/s (I have at least not found any explanation for what x square meters per second is), but think of it as a convenient unit.

For water vapour in air the diffusion constant (D) has been accurately determined. It is indepentant of concentration and only slightly dependant on temperature (Nevander and Elmarsson 1981):



In this paper I have used a value of 25 10^{-6} m^2/s.

2.2 Bound water diffusion

There is also a transport of water through the cell walls and the membranes of the bordered pits. This transport is however not in liquid or vapour phase, but is a tranport of water molecules that are bound to the polymer molecules with hydrogen bonds.

In this paper the diffusion coefficient used for bound water diffusion is based on vapour content. This is only because the calculations are easier to make if all diffusion coefficients have the same dimensions. As the major part of the calculations are for vapour diffusion, the vapour content is a natural choice for the gradient of the diffusion coefficient.

One can differ between diffusion (vapour flow only) and permeability (both vapour and liquid flow). What should I then call the transport of bound water as it is neither vapour, nor liquid? I chose to call it diffusion because the process of bound water transport is basically the same as that of vapour diffusion.

The diffusivity of the bound water is not known as well as the vapour diffusion coefficient. I have therefore made calculations using three levels for the diffusion coefficient:

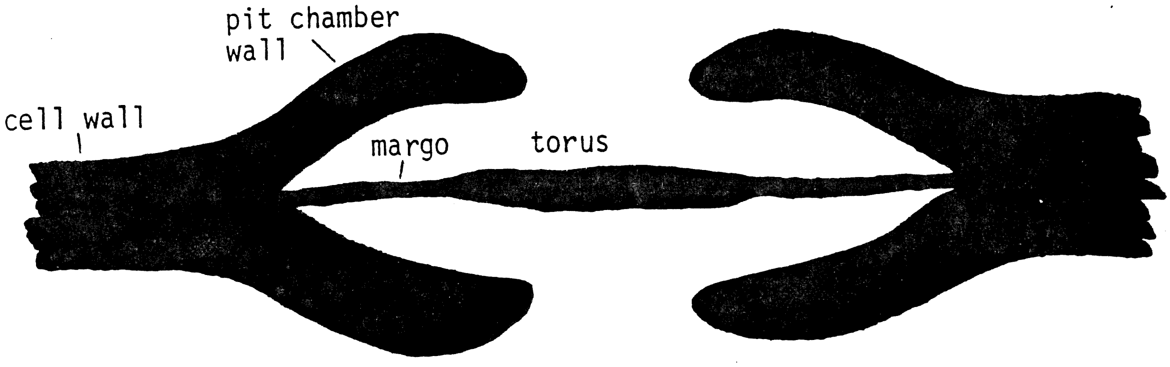
10^{-9} m^2/s	dry amorphous cellulose (at 25% RH) (Wadsö 1988)
10^{-7} m^2/s	wet amorphous cellulose (at 75% RH) (Wadsö 1988) or dry cell wall (Stamm 1959, 1960)
10^{-5} m^2/s	wet cell wall (Stamm 1959, 1960)

Further studies will show which of these values that are right.

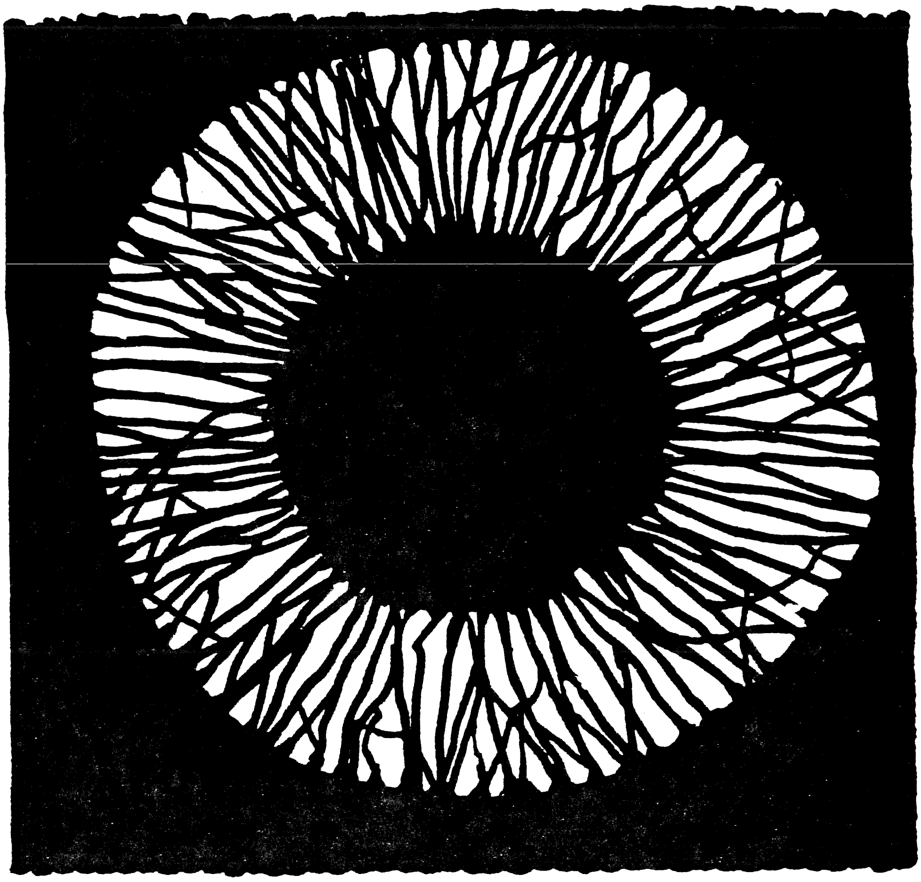
The torus has a thickness (x) between 0,21 μm and 0,28 μm (Bolton and Petty 1978). Therefore the diffusivities above will give approximate resistances (Z_v) of 200; 2 and 0,02 s/m when Z_v is computed like x/δ_v. In the computer program the margo and the torus are representated by resistances.

3. THE STRUCTURE OF THE BORDERED PIT

The bordered pit pore is a complicated structure found in the walls between fibres and between fibres and ray tracheids. A cross section of a bordered pit lookes like this:

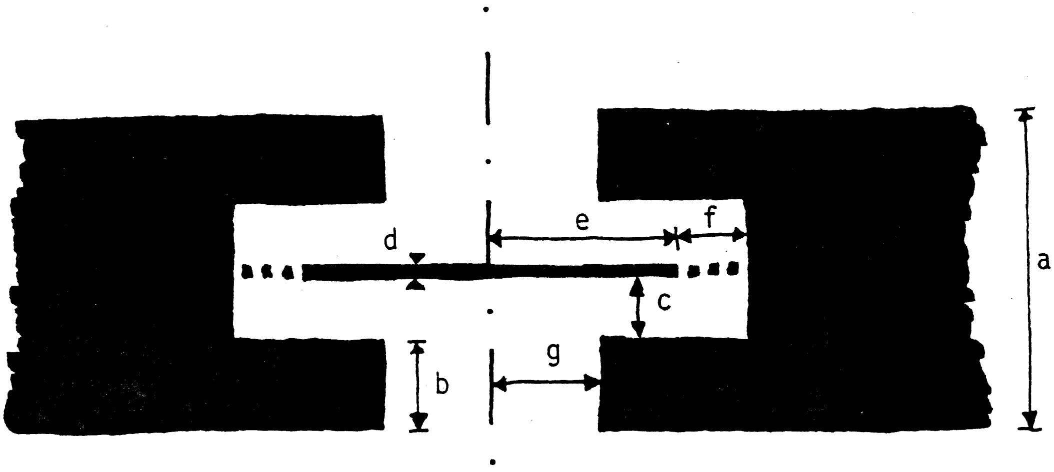


Viewed from inside the lumens it would look like this if the pit chamber wall was torn away, revealing the margo and the torus:



It is not clear if the margo really is as permeable as it looks in this picture (more about that in chapter 4).

To make the computer flow calculations I have to simplify the structure (next page):



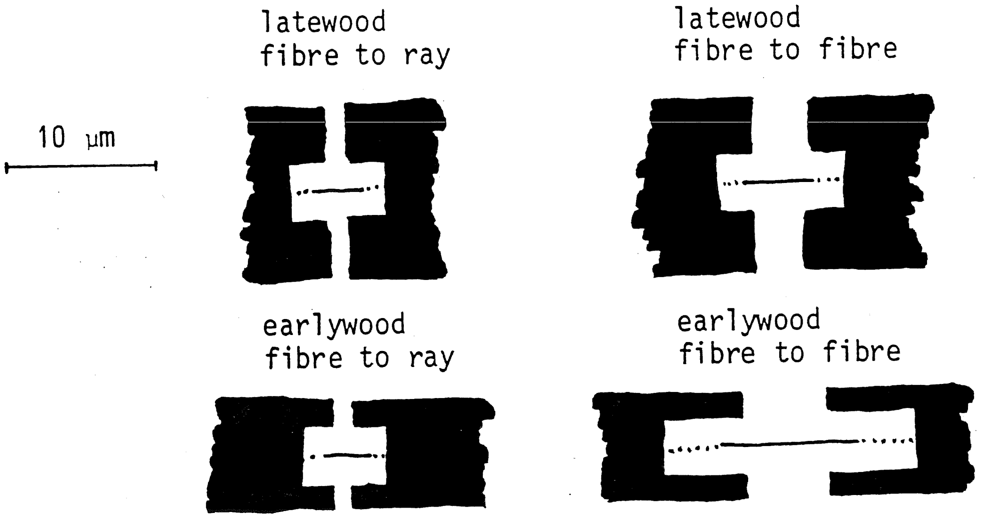
For each type of bordered pit I below give the values for a-g that I have used. I must stress that these values are not (in most cases) mean values. They shall be wieved more like probable or possible values that I use to get approximate flow resistances of the different pits.

I have used values for Pinus sylvestris and Picea abies without separating one from the other. I believe the pits look very much the same in these two swedish trees. The number of pits does however differ a lot (but that is not the subject of this paper).

unit: μm	a	b	c	d	e	f	g
fibre to fibre (earlywood)	7	1,5	2	0,21	4,2	4,2	2,7
fibre to fibre (latewood)	12	4	2	0,28	2	2	1,5
fibre to ray tracheid (earlywood)	7	1,5	2	0,21	1,5	1,0	0,6
fibre to ray tracheid (latewood)	12	4	2	0,28	1,5	1,0	0,6

Data for the fibre to fibre pits are from Bolton and Petty (1978). For the fibre to ray tracheid pits I have used the same data and made approximations of the pit openings from photographes taken by Ingvar Johansson (Swedish Institute for Wood Technology Research, Stockholm). I would like to stress that these dimensions are only approximate.

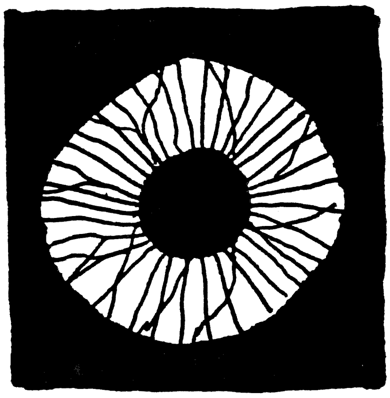
Below I have drawn the different bordered pits to the same scale, so that we can compare their sizes:

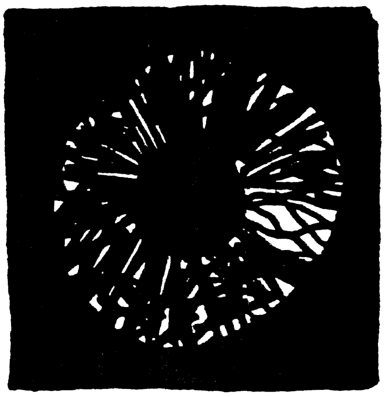


4. RESISTANCE OF THE MARGO

I think the margo is the most important part of the unaspirated bordered pits, at least if we are interested in diffusion. Therefore it would be interesting to know the fractional porosity of the margo. This is however not so easy as it is very hard to know if the margos we can see in microscopes are artifacts of the preparation or the real margos.

On the next page are two examples of margos with different fractional porosity:





In the left picture the torus is held by the margo strands. If it lookes like this in the wood, then the resistance to flow of the margo is negligible, as I explain in appendix A1.

On the other hand it is possible that the margo strands are artifacts. Above right is a drawing of a photograph of the margo made with a special technique which seems to leave the margo intact (Bolton 1976).

As it is hard to tell which one of these photographs that shows the margo as it really looks, I have made calculations using three different margo resistances:

1. Tarkow and Stamm (1960a) measured the diffusion of carbon dioxide through Sitka spruce and concluded that the resistance to flow through the pit membrane pores is 40 times greater than for free vapour diffusion. They attributes this to the pores in the margo being so small that their diameter is less than the mean free path of the water molecules.

2. Petty (1973) uses an equation for the diffusion coefficient as a function of the size of the margo pores, and finds that the margo resistance should be three times what it would have been with the normal diffusion coefficient.

3. I find that the resistance of the margo should be very low by using the mathematical method of conformal analyses (appendix 1) plus the the fact that the mean free path can be written like (Atkins 1979):

$$\lambda = 1/\sigma\sqrt{2}\quad kT/p$$

λ	mean free path	(m)
σ	collision cross section	(m^2)
k	Boltzmann constant	($1,38\ 10^{-23}$ J/K)
T	temperature	(K)
p	pressure	(Pa)

The collision cross section for H_2O, N_2 and O_2 is between $0,23\ 10^{-18}$ and $0,31\ 10^{-18}\ m^2$. This will give a free mean path of $0,1\ 10^{-6}$ m which seems to be much smaller than most pores, at least in the left pictures on the preceding page.

For use in a computer program these effective diffusivities are made into resistances (Z_v). I then assume that the margo has the same thickness as the torus (mean value of the values given by Bolton and Petty (1978) for earlywood and latewood).

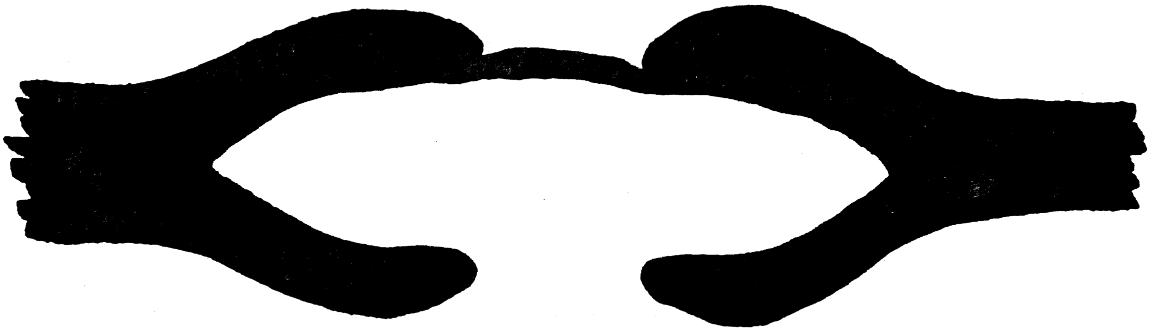
$$Z_v = x\ /\ D \qquad \text{unit: s/m}$$

I then get the following values by using the assumptions above:

1. $Z_v = 0,4$ s/m
2. $Z_v = 0,03$ s/m
3. $Z_v = 0$ s/m

5. ASPIRATION OF THE PITS

The bordered pits are said to be aspirated when they are closed:



It has been proved (Comstock 1968, Thomas and Kringstad 1971, Bolton and Petty 1977) that the pits aspirate when the water front recedes as the wood is dried the first time. This is because the surface tension can pull the torus against the pit border. The polar water molecules then acts as a coupling agent so that the pit continues to be closed even after the liqud water has disappeared. By some process that is not very well understood the pits do probably not deaspirate even if all the water (including the bound water) is evaporated, or if the moisture content is raised again.

It is safe to assume that at least a large majority of the pits do aspirate as the wood dries. It is however not certain that there are any unaspirated pores at all in normaly dried wood. Johansson and Nordman-Edberg (1987) has made an interesting study in which they show that it is not 90 or 95% of the pits in their material that are aspirated, but 99,9% or 100%. Their studies are on Picea abies, and there might be differences between different wood species.

Philips (1933) measured 2-11 unaspirated pits per fibre and Petty and Puritch (1970) concluded from their measurements that 3-6 pits per fibre were open (the total number of pits are approximately 100 in an earlywood fibre and 20 in a latewood fibre). I think these articles are very interesting as the number of open pits is crucial for the diffusivity of wood. It is probably a great difference between having a few unaspirated pits and having none.

I have also made some calculations for the case of a pit being aspirated. I have then used the three different torus resistances I mentioned in chapter 2.1.

6. COMPUTER RUNS

I have used a computer program written by Bengt Eftring (Department of Building Construction, Lund Institute of Technology). It is called TEMP2 and works by the explicite forward difference method, simulating heat or moisture flow in rectangular or cylindrical structures.

Below is a table of the parameters that I have varied:

pit type (see chapter 3)	earlywood fibre to fibre latewood fibre to fibre earlywood fibre to tracheid latewood fibre to tracheid			
margo resistance (unit: s/m)	0,4	0,03	0	
torus resistance (unit: s/m)	infininity	200	2	0,02
state	aspirated	unaspirated		

I have also made a few special runs with a non-zero diffusion coefficient of the cell wall, and with part of the lumen void included. These are not included in the table.

Below is a table of all the important runs: R is the total resistance of the pore (in s/m^3) that can be used in $-g = 1/R \; \Delta v$ This resistance is a very good way to get an understanding of the importance of the pits. Note that Z_v (in s/m) is a resistance per m^2, whereas R (in s/m^3) is the total resistance of one pit (a component resistance).

	margo resistance s/m	torus resistance s/m	aspirated?	R s/m^3
Earlywood fibre to fibre	0	infinity	no	$13,4\ 10^9$
	0,03	infinity	no	$13,7\ 10^9$
	0,4	infinity	no	$16,1\ 10^9$
	0,4	0,02	no	$10,1\ 10^9$
	0,4	2	no	$15,0\ 10^9$
	0,4	200	no	$16,1\ 10^9$
Latewood fibre to fibre	0	infinity	no	$17,4\ 10^9$
	0,03	infinity	no	$18,1\ 10^9$
	0,4	infinity	no	$23,8\ 10^9$
	0,4	0,02	no	$15,8\ 10^9$
	0,4	2	no	$22,4\ 10^9$
	0,4	200	no	$24,7\ 10^9$
	-	0,02	yes	$15,9\ 10^9$
	-	2	yes	$86\ 10^9$
	-	200	yes	$7000\ 10^9$
Earlywood fibre to tracheid	0	infinity	no	$183\ 10^9$
	0,03	infinity	no	$186\ 10^9$
	0,4	infinity	no	$218\ 10^9$
	-	0,02	yes	$339\ 10^9$
	-	2	yes	$2080\ 10^9$
	-	200	yes	$142000\ 10^9$
Latewood fibre to tracheid	0	infinity	no	$325\ 10^9$
	0,03	infinity	no	$327\ 10^9$
	0,4	infinity	no	$356\ 10^9$

7 DISCUSSION OF THE RESULTS

From the above results we can draw two conclusions. The first is that the resistance of the non aspirated pit does not seem to depend very much on the margo or the torus. Changes of the resistance of these two parameters does not change the total resistance of the pit very much.

The second conclusion is that the resistance of the aspirated pit is greatly affected by changes is the permeability of the torus. This is of course not very surprising as the torus blocks the diffusion path in the aspirated pit. If the torus resistance is as low as 0,02 s/m, the aspirated pit has nearly the same permeance as the non aspirated pit. This is only natural as the total resistance of the air column in the pit is 0,5 s/m, i.e. much larger than the torus resistance in this case.

When viewing the calculations now afterwards, when they are completed, I think I can explain all the results by simply analysing the resistances of the different components. In other words: it is not necesary to redo these calculations for other values of the resistances and the dimensions.

Three typical values of the total latewood fibre to fibre tracheid pit resistance are:

low margo resistance low torus resistance	$16\ 10^9\ s/m^3$
aspirated pore with medium torus resistance	$60\ 10^9\ s/m^3$
aspirated pit with high torus resistance	$7000\ 10^9\ s/m^3$

How long will the flow path through a lumen be, if it shall have the same resistance to flow as the three pits above? The answer is given by x=RAD, where x is distance (m), R is resistance of pit (s/m^3), A is area of lumen (m^2), and D is diffusion coefficient of vapour in lumen (25 10^6 m^2/s).

R_{pit} s/m^3	x_{lumen} / m	
	earlywood 25 µm x 25 µm	latewood 5 µm x 20 µm
16 10^9	0,25 mm	0,05 mm
86 10^9	1 mm	0,2 mm
7000 10^9	100 mm	20 mm

These figures shows a large span: from only a little greater than the diameter of the lumen up to 40 times the length of the fibre (which is 1-3 mm long). It is of course of highest importance to know which of these pit resistances that should be used when making a model of the diffusion through wood.

One more interesting comparison can be made: how high are the pit resistances compared to the cell wall resistance? If we consider the diffusion in the tangential direction one cell wall can be viewed as having an area of 25 µm x 3 mm at right angle to the flow direction. If it has a thickness of 12 µm it will have a resistance of 12µm / (25µm 3mm δ_{cw}), where δ_{cw} is the diffusion coefficient of the cell wall material. If I calculate the resistance of the cell wall for the three different cell wall diffusivities I have explained in chapter 2.2, I get the following:

δ_{cw} m^2/s	R_{cw} s/m^3
10^{-9}	160 10^9
10^{-7}	1,6 10^9
10^{-5}	0,016 10^9

Except for the lowest δ_{cw} these resistances are surprisingly low, lower than the resistance of the pits.

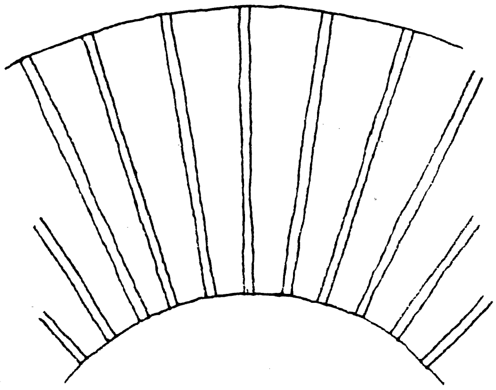
As I use three different levels for the diffusion coefficients of the cell wall there is a considerable span between the results. It is therefore hard to make any further conclusions. I hope however to be able to find more exact values of the diffusivities of the cell wall.

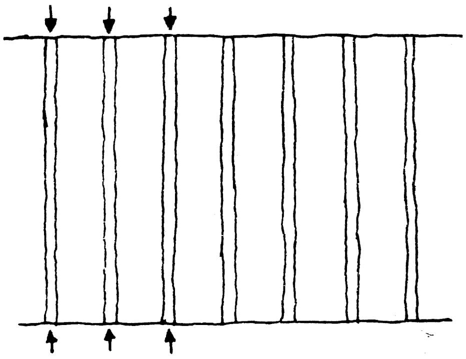
Petty (1973) found that 98% of the resistance to longitudinal diffusion was in the lumen, but that the pits controlled the resistance in the tangential direcion. His result agree with my calculations if there are are a few non aspirated pores in each fibre.

APPENDIX 1 CALCULATION OF MARGO RESISTANCE

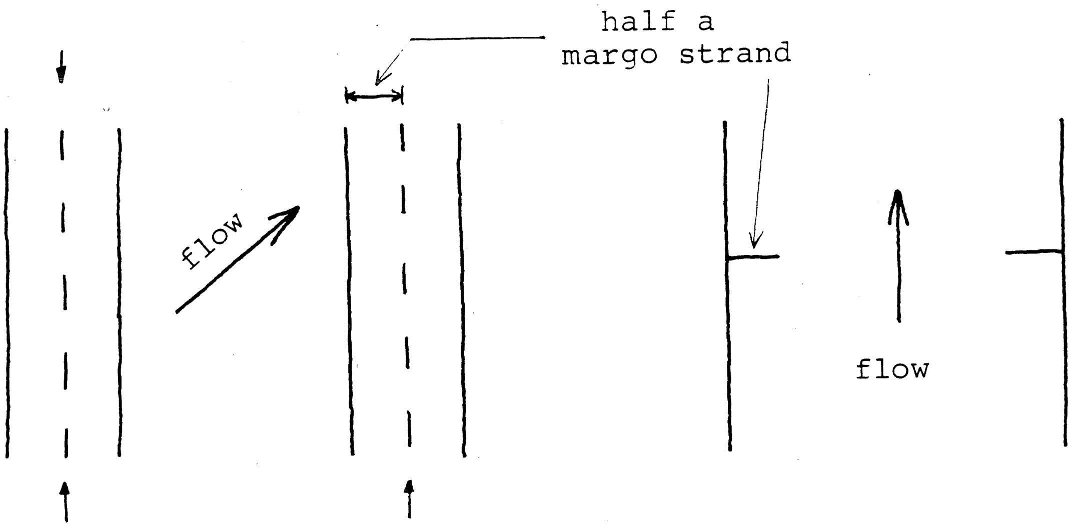
How much does the margo or the margo strands hinder the diffusion? This problem can be studied theoretically in a rather elegant way which I like to show in this appendix. I am indebted to Johan Claesson (Building Physics Group, Departement of Building Technology, Lund Institute of Technology) for showing me this.

In the case of the margo we approximate the margo strands with thin flat obstructions of the flow path, and calculate the mean distance between the strands. By doing this we can approximate the real margo with parallell strands:

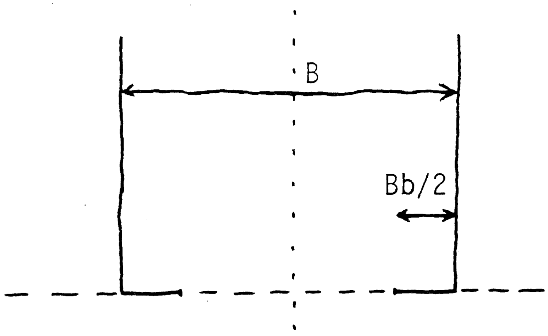




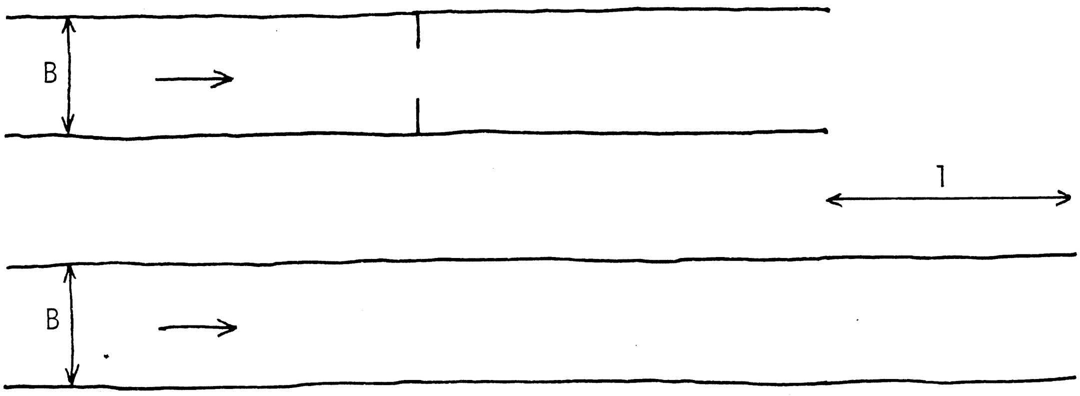
As we in the right case above have lines of symmetry (small arrows) we can simplify the problem even further, by looking only at that part of a flow path that is between two margo strands (including half a strand at each side). We then get a 2-dimensional diffusion problem in a plane perpendicular to the strands. Below are two drawings of this:



We need only consider half the structure, as the flow after the margo obstruction is a mirror image of the flow before the obstruction (B is the width of the flow path and b is the part of it that is blocked).



If we know what the margo strands or the margo pores look like, it is possible to calculate the extra resistances they give. A good way of quantifying the resistance is by calculating the equivalent extension of the diffusion path. Below is a drawing showing what I mean. The total resistance is the same in both cases and we want to calculate $y_o = l/B$, i.e. the lengthening measured in number of flow path width:



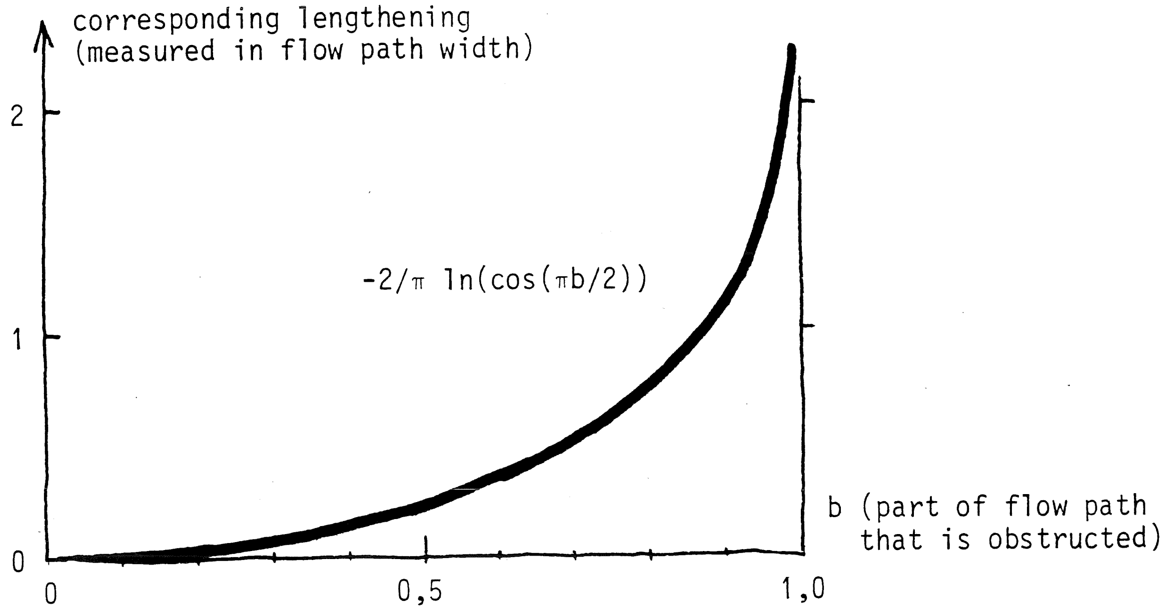
Both these structures give the same resistance to flow (i.e. give the same flow with the same gradient). In the top case the obstruction gives an extra resistance. In the bottom case the lengtening gives the same extra resistance.

It is possible to calculate the corresponding lengthening of the flow path by conformational transformation. A good explanation of the method is given by Nehari (on page 183-185 he explains the mapping that I have used).

The lengthening y_o calculated will be:

$$y_o = -2B/\pi \ \ln(\cos(\pi b/2))$$

Below I have plotted the function:



The distance between the margo strands is (calculated from Bolton and Petty 1978) 0,25 μm for earlywood and 0,4 μm for latewood. The strand thicknesses are 0,03 μm amd 0,1 μm. This means that 12% and 25% respectively are blocked (b=0,12 and 0,25). As we can see in the diagram the extension of the flow path corresponding to this is negligeble.

Even if the margo strands were 0,25 μm thick (like the torus) and covered 75% of the area, the equivalent extension would only be 0,15 μm. This might seem strange, but it is a result of that the diffusion in a natural way 'optimizes' the flow. The result of a thin 50% blocking will for example not give a 50% decrease in flow as the margo is only one of the many resistances that are coupled mainly in series.

These calculations are made under the assumption that the mean free path is not greater than most of the pores. If the pores are much smaller than 0,1 μm the resistance will be higher, but I belive that it will not change dramatically before the pores become even smaller.

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