

Describing non-Fickian water-vapour sorption in wood

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Moisture transport and sorption in wood may not be accurately described by Fick's law of diffusion. The problem of making a model of non-Fickian behaviour (NFB) for wood is discussed. Some measurements in which NFB in wood is clearly seen are also reviewed. Four criteria, which must be satisfied by a model describing sorption in wood cell walls, are presented: (1) the model should not only describe the response to step changes in vapour pressure; (2) it should be able to predict sorption with more than one time scale; (3) the sorption rate should not depend on the thickness of the cell wall; (4) small rapid changes in vapour pressure should give slower fractional weight change than large rapid changes. A review of models of NFB in synthetic polymers indicates that there is presently no model of NFB which fulfills the above criteria. More measurements of the sorption behaviour of the cell wall are needed to construct such a model for wood. This model can then probably be used, together with a Fickian diffusion model, to model the sorption behaviour of whole wood.

Nomenclature

Some notations are only described where they are used.

c	concentration in a material	kg m^{-3}
D_c	diffusivity with c as potential	$\text{m}^2 \text{s}^{-1}$
D_p	diffusivity with p as potential	$\text{kg}/(\text{m s Pa})$
F	flux	$\text{kg m}^{-2} \text{s}^{-1}$
p	partial vapour pressure	Pa
t	time	s
x	distance	m

1. Introduction

Diffusion is usually assumed to obey Fick's law, i.e. primarily, that the flux is proportional to the gradient in concentration (or any other relevant potential). Fick, who derived the law which bears his name, tested his assumptions by measuring diffusion of aqueous sodium chloride [1]. In such a simple system Fick's law is quite accurate.

There are, however, diffusion processes which cannot be described by Fick's law. One such case is glassy polymers absorbing solvent vapours [2, 3], which may show very non-Fickian behaviour. The present work aimed to show that Fick's law does not accurately describe water-vapour transport in wood. The possibilities of applying the models used for synthetic polymers to wood are discussed.

If diffusion is assumed to obey Fick's law, it is usually implied that the following three equations describe the process

$$F = -D_p(p) \frac{\partial p}{\partial x} = -D_c(c) \frac{\partial c}{\partial x} \quad (1)$$

where F ($\text{kg m}^{-2} \text{s}^{-1}$) is the flux, p (Pa) is the vapour pressure, c (kg m^{-3}) is the penetrant concentration in

the material investigated, and D_p and D_c are the diffusivities associated with p and c , respectively. Equation 1 is written for both p and c , as either one of these may be used.

$$c = c(p) \quad (2)$$

Equation 2 is the equilibrium sorption isotherm, i.e. the relation between concentration and vapour pressure. The sorption hysteresis is seldom taken into account in transport calculations.

$$\frac{\partial c}{\partial t} = \frac{\partial F}{\partial x} \quad (3)$$

Equation 3 is the continuity equation which should always hold true in systems without chemical reactions.

The diffusivity of a polymer can be measured by two different principles: the steady-state cup method and the transient sorption method. In the cup method the flow through a specimen at steady state is measured. In the other type of measurement, the sorption method, the weight change of a sample is measured, following a step change in the external conditions (vapour pressure, relative humidity). From the weight change curve, usually plotted as a function of the square root of time, the diffusivity may be evaluated. In this paper these two methods are referred to as the "cup" and the "sorption" methods.

If Equations 1–3 hold true for a transport process, it is here called "Fickian". Sorption measurements then have the following characteristics when surface resistance and other external disturbances are neglected [4]. (1) The initial slope is linear when plotted as a function of the square root of time. (2) Curves for samples of different thicknesses are superimposed when plotted as a function of time divided by the

square root of the thickness of the sample. If properly evaluated, cup and sorption measurements should also give essentially the same diffusivity if Fick's law holds true (minor differences may be found if the diffusivity is concentration dependent).

A diffusion phenomenon which cannot be described by Equations 1-3 is said to be "non-Fickian". Ample evidence of non-Fickian behaviour (NFB) is found in the polymer literature, usually in the form of anomalous sorption curves (see e.g. [2, 3]). Sorption measurements are much more easily disturbed by NFB than are cup measurements.

This paper presents an analysis of the prospects of constructing a model of NFB in wood. This is done both by discussing the experimental evidence for NFB in wood and by examining models of such phenomena in polymers.

2. Evidence of NFB in wood

Wood is porous hygroscopic material, i.e. it sorbs water vapour from the air. If Fick's law is to be used for a larger specimen of such a material, there must always be instantaneous local equilibria between the vapour and solid phases in the specimen (Equation 2). The sorption in the cell wall must, therefore, be much faster than the diffusion into the sample.

Christensen and Kelsey [5-7] measured water-vapour sorption on single cell walls in the absence of air. Some of their results are shown in Fig. 1 as sorption curves. It is seen that the sorption rate is definitely finite at high relative humidities (RH). At the highest RH-range, approximately 24 h is needed to reach 50% of the fractional weight increase. The only measurements reported were in absorption, but Christensen remarked that similar results had also been seen for desorption [5]. She also found that sorption rates were nearly identical for cell walls of very different thicknesses [7]. She concluded that the diffusion in the cell wall was very much faster than the sorption

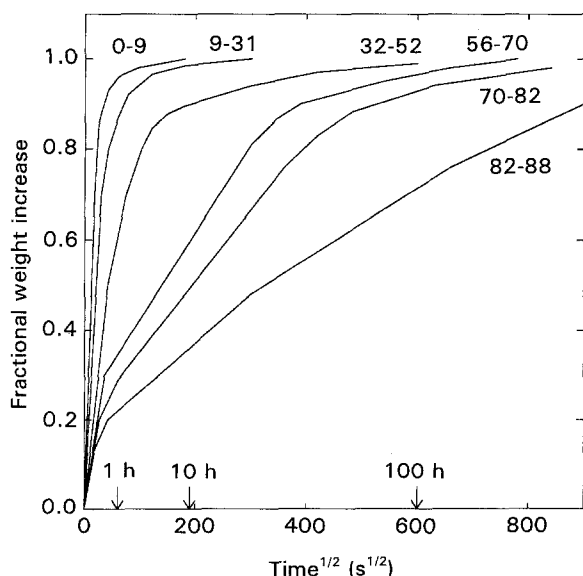


Figure 1 Sorption measurements on single cell walls in the absence of air [6]. Numbers on each curve are initial and final relative humidity (%).

rate of the cell wall material. The sorption rates were also shown to be dependent on the size of the step in RH. Larger steps gave higher sorption rates. This is seen in Table I.

Comstock [8] obtained different results from cup and sorption measurements on whole wood samples. At high RH the transient sorption measurements gave lower diffusivities than steady-state measurements. Absorption also seemed to be slower than desorption at high RH. Similar results have been obtained by Kelly and Hart [9] and Skaar *et al.* [10].

Some previous sorption measurements [11, 12] are also presented here as part of the discussion. They were made at 23 °C in absorption on pine sapwood (*Pinus silvestris*). Fig. 2 shows measurements of absorption from 54%-75% RH. The samples are described in Table II. Simulated curves for the same samples are also shown. These are based on cup

TABLE I Sorption measurements on single cell walls in the absence of air [7]. The table gives the times to half the concentration changes. Series A contains 12 equal steps of 1.5% moisture content (kg moisture/kg dry wood), series B contains 6 steps of 3% etc. The maximum moisture content of 18% corresponds to approximately 90% RH.

Final moisture content (%)	Time to half sorption (h)					
	A	B	C	D	E	F
1.5	0.07					
3.0	0.11	0.05				
4.5	0.16		0.06			
6.0	0.49	0.13		0.06		
7.5	0.95					
9.0	3.6	0.66	0.24		0.06	
10.5	18					
12.0	14	5.3		0.29		
13.5	18		1.1			
15.0	28	9.6				
16.5	-					
18.0	27	30	14	11	0.64	0.17

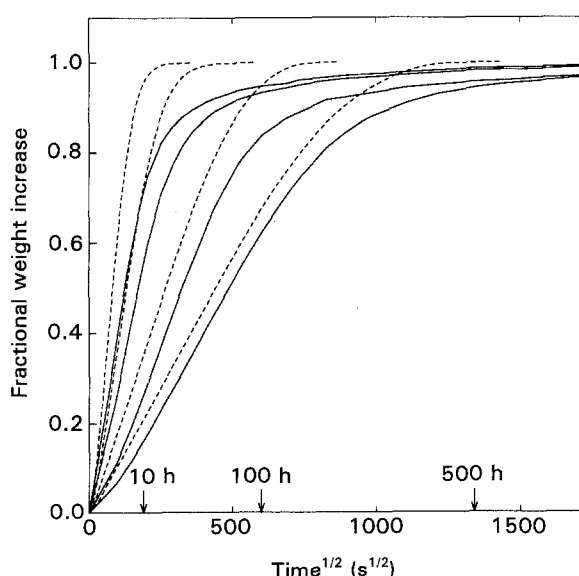


Figure 2 Sorption measurements from 54%-75% RH on whole wood samples: experimental curves [12] (—) compared with simulated sorption curves (---). The samples are described in Table II.

TABLE II Data on pine sapwood specimens used in the sorption measurements shown in Figs 2 and 3 [12]. The specimens are arranged in order of decreasing rate of absorption. This order is the same for both the measured and the simulated curves in Figs 2 and 3

Sample number	Flow direction	Half thickness (mm)
1	Longitudinal	6.7
2	Longitudinal	11.4
3	Tangential	4.8
4	Tangential	8.1

measurements made on duplicate samples [13]. Cup measurements are measurements of flow through a sample at steady-state. It is thought that such measurements are not very influenced by NFB which is an unsteady-state phenomenon related to sorption. The simulations are made with a computer program which is based on Fick's law (Equations 1–3) [14]. It is seen that the measured curves show lower absorption rates than the simulated curves. This is natural if the absorption in the cell wall is a limiting factor.

Fig. 3 shows curves in the higher interval from 75%–84% RH. Here the difference between experimental and calculated curves is very large. Note that after the first rapid weight increase all experimental curves have the same slope. A similar slope is also seen in the corresponding curve in Fig. 1.

The report by Hunt [15] that swelling is a much faster process at high RH than absorption, should also be mentioned. He proposed that this was caused by the sorbed moisture being sorbed in different ways and having different properties. A fast sorbing fraction is seen in Figs 1 and 3.

In Figs 2 and 3, it is seen that wood does not behave according to Fick's law in a sorption measurement. It would be valuable to describe this in a model of NFB in wood. Such a model could be the basis for calculations in wood drying, building physics and other fields of science, where it is important to predict the moisture behaviour of wood.

3. Requirements for a model of NFB in wood

Different materials transport and sorb penetrants in different ways. It is not very useful to try to apply a model made for one material to another material in which transport and sorption are governed by different processes. Therefore, some differences between wood, synthetic polymers and other materials are pointed out, before the requirements for a model of NFB in wood are discussed.

A simple division of materials into three groups can be made according to their drying behaviour [16]:

- (A) non-hygroscopic porous materials (e.g. sand);
- (B) hygroscopic porous materials (e.g. wood, concrete);
- (C) hygroscopic non-porous materials (e.g. soap).

The sorption behaviour of most polymers is like that of group C, i.e. they are non-porous, but sorb pene-

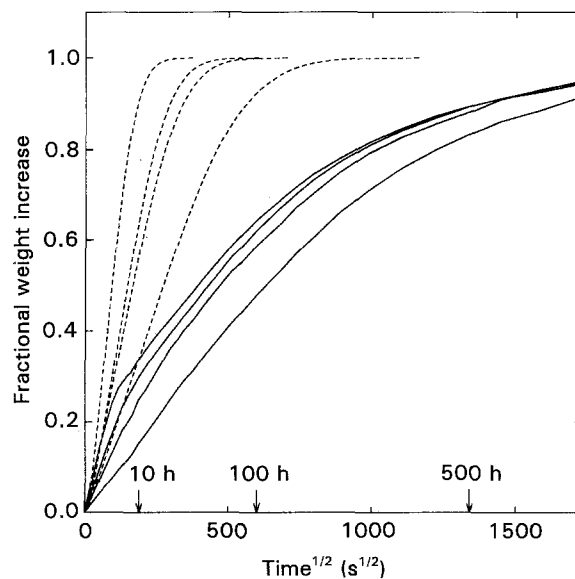


Figure 3 Sorption measurements from 75%–84% RH on whole wood samples. Experimental curves [12] (—) compared with simulated sorption curves (---). The samples are described in Table II.

trants (not necessarily water). Wood is made up of polymers, but is a material in group B, because it is porous. Its hygroscopicity is attributed to the adsorption of water vapour on to the cell wall constituents. Concrete also belongs to group B, but it is generally thought that it owes its hygroscopicity to surface and capillary condensation on its very large internal area.

When there is no free water in wood (say below 95% RH), its porous structure is expected to transport water vapour, much like a material in group A. Part of the transport may be as surface flow. The cell wall, however, is expected to transport and sorb moisture, like a thin specimen of group C.

A model of vapour transport and sorption in wood must describe both the transport and the sorption. Therefore, a model should have two parts: one describing the flow through the material and one describing the sorption in the cell walls. The models of NFB in polymers discussed in the following section only describe the sorption in non-porous polymers like the cell wall, not sorption in a porous material like whole wood.

To be of any practical use, a model of NFB in the cell wall must be able to handle both rapid and slow changes in partial vapour pressure, p . Most work on sorption in polymers has been done by studying the weight change following a step change in p . In wood, however, most cell walls will not feel a rapid change on the surface of the wood specimen, because it takes some time for the transport to raise p inside the wood. Therefore, a model of cell-wall sorption must be able to handle both rapid and slow changes in p . This is also necessary for the model to be of any practical use, as normal changes in p are not like steps.

From results of measurements reported by Hunt [15] one may expect the sorption to have many different time scales. Figs 1 and 3 also give evidence of such a behaviour, as it is seen that one fraction of the weight increase is very fast, while others are much slower.

The following criteria are judged as important for a model to successfully predict NFB in wood cell walls.

1. The model should not only be applicable to steps in p .
2. It should be able to predict simultaneously sorption with widely different time scales as a result of a step in p [6, 15].
3. The sorption rate should not be dependent on cell-wall thickness, i.e. the sorption should not be governed by diffusion [7].
4. Small rapid changes in p should give slower fractional sorption than large rapid changes [6].

It should preferably also be a physical model, i.e. it should not be a numerical or quasi-physical model with many fitting parameters.

4. Models of NFB in synthetic polymers

A large number of models of NFB in polymers has been proposed (see e.g. the review by Frisch [17]). Some are discussed here, and their ability to model NFB in a wood cell wall is assessed. The criteria discussed above are referred to as C1–C4.

Crank and Park [18], Long and Richman [2] and Kishimoto and co-workers [3, 19] modelled NFB as a result of a lag in attaining equilibrium on the surface after a step in p . This does not satisfy any of the criteria above. Frisch [20] used irreversible thermodynamics to show that these three models follow from a more general description of internal variables. His model does, however, seem to be rather hard to use and is more of theoretical interest.

Crank and Park [18] proposed a diffusivity which only slowly attained its equilibrium value, D_{eq}

$$\frac{\partial D}{\partial t} = a(D_{eq} - D) \quad (4)$$

where a is a constant and D is the diffusivity at time t . This model does not fulfil C2–C4. Crank [21] extended this theory by letting the diffusivity have one rapidly changing part and one part as in Equation 4. This model does not meet C3 and C4.

Newns [22] outlined a model for water-vapour sorption on regenerated cellulose by proposing that the first sorption swelled the polymer to such an extent that no more sorption could take place until relaxation had decreased the stresses. The sorption will then be independent of thickness, if the diffusion is rapid compared to the relaxation. These ideas could probably be developed into a model which could fulfil some of the criteria above.

Crank [21] proposed a simple model of strain-dependent diffusion. The sample is modelled as partly swollen and partly dry. The diffusivities are related to the strain. The assumptions made are not realistic for vapour sorption in wood. Petropoulos and Roussis [23, 24] extended this theory by assuming the polymer to have linear visco-elastic properties characterized by instantaneous and long-term elastic moduli and a stress relaxation frequency, which were all exponential functions of c . Diffusivity was assumed to be a function of stress. The large number of parameters (seven

relaxation frequencies and other parameters in [24]) makes it difficult to judge if the model is suitable for wood cell walls. The model does, however, probably fulfill C1–C3, but not C4.

Joshi and Astarita [25] used the deviation from equilibrium concentration as a measure of the polymer state. This is further developed by Astarita and Meldon [26] and Kalospiros *et al.* [27], who have developed interesting models by rewriting both Equations 1 and 2 as

$$F = -D_p(h) \frac{\partial p}{\partial x} - \phi \frac{\partial F}{\partial t} \quad (5a)$$

$$\text{and} \quad \frac{\partial h}{\partial t} = f(h, p) \quad (5b)$$

here $h = c/p$ (the solubility), ϕ is a relaxation parameter and f is a function describing the attainment of the equilibrium sorption isotherm ("the kinetics of swelling"). The physical interpretation of an extra term to Equation 1 is not clear, but the model is interesting as it is developed from equations governing the transport and sorption only. In the articles it is tested under the simplest possible conditions and shown to be able to predict many non-Fickian effects. It does probably meet C1–C3, but it is not known if it also fulfils C4.

Vieth and Sladek [28] proposed a dual sorption model of NFB. The sorption isotherm is modelled as the sum of a linear part (Henry's law) and a non-linear one (a Langmuir isotherm). The second part was called "hole filling" as these molecules are not taking part in the transport. Vieth and Amini [29] extended the theory by also considering deviations from Henry's law. These models could be modified to incorporate the sorption behaviour of wood, but they will probably never meet C3 or C4.

Ottino and co-workers [30–33] have developed an effective medium model for binary polymer blends by using the theory of equivalent networks. The polymer is modelled as having two randomly dispersed phases, each of which has its own transport behaviour. It has only been tested with Case II kinetics (see below) in each domain. It is expected to give NFB even if each domain shows Fickian sorption. It is probably not useful for wood cell walls.

Berens and Hopfenberger [34, 35] modelled the result of sorption measurements as the sum of a number of uncoupled processes

$$\frac{\Delta M_t}{\Delta M_\infty} = a f(t) + \sum_{n=1}^m b_n (1 - e^{-k_n t}) \quad (6a)$$

where

$$a + \sum_{n=1}^m b_n = 1 \quad (6b)$$

and $\Delta M_t/\Delta M_\infty$ is the fractional weight change at time t , $f(t)$ is a Fickian fractional weight change, and a , b_n and k_n are constants. Using a Fickian part, and one or two exponential terms, Berens and Hopfenberger could reproduce all their sorption curves. The main use of this model is to find the number of time scales of a sorption process. It should, however, be noted that it

is sometimes difficult to find a single best solution even if only one exponential term is added to the Fickian term (three unknowns).

Wang and co-workers [36–38] and Peterlin [39–42] have modelled NFB by adding a term to Equation 1

$$F = -D_c \frac{\partial c}{\partial x} - ac \quad (7)$$

where a is a constant. The position in a sample with a certain concentration will be

$$x = b_1 t^{1/2} + b_2 t \quad (8)$$

where b_1 and b_2 are constants. This is a mixture of normal Fickian sorption and Case II (see below). This does not seem to be relevant for wood cell walls.

There is a large number of other models more or less confined to Case II behaviour [43–49]. Case II (Fickian diffusion is Case I) is an extremely relaxation-dependent sorption which gives a weight increase that is proportional to time [50]. It is governed by the swelling processes between dry and swollen material and it is mostly seen for liquid sorption. It is of no interest in connection with vapour sorption in wood cell walls.

5. Models of NFB in wood

A few simple numerical models have been used to describe NFB in wood [9, 51, 52]. Christensen and Kelsey [6] have also proposed that the time to half sorption depends on the initial, p_i , and final, p_f , vapour pressures of a step change by

$$t_h^{1/2} = \frac{a}{\log(p_f/p_i)} \quad (9)$$

where t_h is the time to half sorption (Table I) and a is a constant. This partly empirical relation is based on arguments of the swelling pressure in the cell wall and shows a resemblance to the model by Newns [22].

In a very simple model of NFB [53] the sorption in the cell wall was modelled as being caused by the slow transport in the cell wall. This, however, is probably not the mechanism responsible for the low sorption rates.

It should be noted that the Fickian models that have been made for wood [54, 55] cannot describe the non-Fickian behaviour seen in unsteady-state experiments.

6. Discussion

It has been shown that there is at present no usable model for the non-Fickian behaviour (NFB) of wood. The prospects for developing such a model are, however, good. The experimental evidence of NFB in wood and the work done on NFB in synthetic polymers, provide a good basis for such a task. It should also be noted that criteria C3 (the sorption is not dependent on cell-wall thickness) simplifies such a model. The same is true for the fact that sorption is independent of direction (transport is not).

Purely numerical modelling may be made for specific cases with Equation 6 [34, 35]. The only use of this, however, is to show that sorption curves are non-Fickian and to find the number of time scales involved.

The coupling of a model of NFB in the cell wall to a purely Fickian diffusivity in whole wood (Equation 1) is probably the best way to construct a model. Such a model has been made for paper by Lescanne *et al.* [56], who, however, modelled the transport both through the paper and into the individual fibres with Fick's law. As seen above, the models of NFB in polymers can probably not be used for the cell-wall part of such a model. Some of them [22, 24, 27] could, however, be tested and modified if necessary.

It has been shown that the sorption isotherm of wood may be constructed from the sorption isotherms of the wood polymers [57]. The viscoelastic properties of wood cells may also be calculated from a knowledge of the properties of the wood polymers and how they are arranged in the cell wall [58]. It is probable that a similar modelling could be done to increase our understanding of sorption in wood.

Christensen and Kelsey's [5–7] measurements on single cell walls in the absence of air could be redone, using not only step changes in p , but also ramps and sinusoidal variations. The aim would be to obtain a more complete description of the response of c in the cell wall to variations in p .

It would be best to also check Equation 1 experimentally. As the flow is probably governed by many mechanisms (vapour diffusion, surface flow, bound water flow), and there is no local equilibrium between p and c , Equation 1 could be rewritten, for example, as

$$F = -D_c(c, p) \frac{\partial c}{\partial x} - D_p(p, c) \frac{\partial p}{\partial x} \quad (10)$$

Such an equation is probably not easy to verify experimentally. It could, however, perhaps be done by having quite thin wood specimens fixed between two flow-through chambers. In these one should be able both to vary p in the entering air and to measure p very accurately in the air leaving the chambers. The system should work under atmospheric pressure, so the mass transfer coefficient at the wood surface must also be investigated very carefully.

It does seem that one should take measurements rather than perform modelling at the present stage, as data on NFB in wood are very incomplete. It is also important to know if other factors may influence the NFB. Can variations in temperature and moisture conditions speed up sorption processes? Is there a limiting temperature for NFB? Are the very rapid changes in p during sorption measurements partly responsible for the NFB?

7. Conclusions

There is no useful model of non-Fickian behaviour (NFB) in wood. From measurements of vapour sorption, some characteristics of NFB may be constructed, but there does not seem to be any model of NFB in

synthetic polymers that can reproduce these. Therefore, it is thought that new models should be developed for wood. These must be based on a more complete experimental description of the sorption behaviour of the cell wall.

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