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MULTI-SCALE MOISTURE TRANSPORT IN PAPER: IMPACT OF PORE AND FIBRE TORTUOSITY & ANISOTROPY

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ABSTRACT

The diffusion of moisture in paper is a complex phenomenon with pore diffusion dominating at low moisture contents and diffusion through fibres dominating at high moisture contents. Vapor diffusion through the pore space depends on the topology of the pore connections. Recently available three dimensional digital reconstructions of the pore space using X Ray Micro computed tomography (XμCT) enable us to determine the impact of the pore and fibre tortuosities and connectivity to moisture diffusion in an explicit manner.

In this study, moisture diffusion was simulated through XμCT reconstructions of paper structures using a hybrid random walk algorithm that was developed to allow simultaneous diffusion in both the pore and fibre spaces with differential 'intrinsic diffusivities'. The algorithm is specifically applied to simulate simultaneous diffusion under low and high relative humidity conditions where diffusion occurs predominantly through one medium i.e. pore space and high humidity conditions where both media (i.e. fibre and pore spaces) are highly conductive. The 'intrinsic diffusivity' of moisture through fibres was determined by using numerical simulation and experimental results. This intrinsic diffusivity a fundamental fibre characteristics is found to be independent of refining level but depends only the fibre moisture content under the conditions studied.

The algorithm also allowed the determination of the anisotropy in diffusivity. One interesting result is that the anisotropy in diffusion is most significant at low moisture contents when diffusion through the pore space dominates. At high relative humidities (i.e. at high moisture contents), fibre conduction provides an alternative diffusion path, homogenizing diffusion to a large extent. As a result, diffusion becomes more isotropic with increased moisture contents in paper.

1 INTRODUCTION

Paper materials are complex three dimensional porous structures in which the transport of liquids and gases are strongly determined by the pore geometries. Paper is made of cellulosic fibres having significantly hygroscopic properties. Water is absorbed into the cell walls and can be transported through it in both liquid and vapor forms. Understanding the diffusivity and its relationship to the structure of pore space is necessary to estimate moisture absorption behaviour of the paper sheets and their performance under changing humidity conditions.

Moisture diffusion in paper occurs by two important mechanisms: as water vapor transported through the pore space in vapor form and as condensed moisture through the cell wall. The former is thought to be dominant at low moisture content whereas the latter is significant at higher moisture contents [1]. The net transport coefficient known as the effective diffusivity for moisture in paper is therefore composed of the contributions of both these mechanisms. The diffusion of water vapor through the pore space is determined primarily by the porosity and the tortuosity. Diffusion through the cell wall occurs due to chemical potential gradient of the condensed moisture. One can generally expect the diffusivity in this case to be strongly dependent on moisture activity in the cell wall although the connectivity i.e. tortuosity of the path through the fibres may contribute to this diffusivity. Since only macroscopic quantities such as the total moisture fluxes are accessible through experimental measurements, it is quite difficult to determine the contribution of the tortuosity of the pore space, the connectivity and topology of the fibre network on the effective diffusivity.

Recent developments in reconstructing the pore space structure of porous materials including paper allow us to study the contribution of the porous structure to effective moisture transport properties. Thus, by subtracting the contribution of the diffusion through the pore space from the net transport, the diffusivity through the cell walls can be determined. Since the intrinsic fibre diffusivities are generally unknown, the algorithm used the ratio of intrinsic diffusivities for the fibre and pore spaces as a parameter to determine the overall effective diffusivity of the structure. Using the experimentally determined effective diffusivity data under varying relative humidities of known sample structures, it is possible to estimate the intrinsic fibre diffusivities and how they change with mechanical treatment or fibre type. This might be very useful for future product engineering tailored for specific end-use applications.

2 3D STRUCTURE OF PAPER

X-ray micro computed tomography ((XμCT)) has recently emerged as a powerful tool to visualize and characterize the three dimensional structure of the pore space in paper and similar fibrous materials [2–8]. The resulting digitally reconstructed pore structure was analyzed and a number of structural parameters such as porosity, interfacial area, pore size distribution were determined. Structural variation in paper samples obtained by number of process treatments as well as using different types of fibres were compared with experimental data from conventional techniques such as mercury intrusion porosimetry (MIP) [4,8,9]. The image analysis results compared favorably well with other techniques and showed decreasing porosity with increasing fibre refining. The results showed interesting differences between the high resolution and low resolution images as well as the different fibre treatment and sources [6,10]. Comparison of the structural features in 3D using a sphere growing method and in 2D using a hydraulic radius concept show that the 3D characterization method correctly show a lower pore size distribution due to the contribution of the third dimension [11,12]. Interestingly, the 2D method does confirm the anisotropic nature of the structures by having different pore size distributions between the in-plane and transverse directions. The in-plane directions with a majority of fibres oriented in the plane of the sheet have smaller pores than in the perpendicular transverse direction. Structural anisotropy may lead to anisotropic behavior in material properties including transport properties, one of the key fundamental questions addressed in this work.

3 MOISTURE DIFFUSIVITY IN PAPER & THE DUAL PHASE RANDOM WALK ALGORITHM

3.1 Effective diffusivity in paper

In porous media, transport can occur in the pore or open space and also simultaneously in the dual phase i.e. the solid component. This has been experimentally observed in paper with an increase in overall diffusivity at higher relative humidities. The effective diffusivity for moisture in paper, D_{eff}, can be given as two fundamental diffusivities, as shown in equation (1). One is the diffusivity of moisture in vapor form through the pore space (D_p) and second the diffusivity of condensed moisture through the fibre space (D_q) [1]. The diffusivity of the pore space (D_p) is related to the diffusivity of moisture in air (open space diffusivity at a given temperature, (D_a)) and the characteristics of the structure, namely porosity (ε) and diffusional tortuosity (τ_p). We can hypothesize that similarly, the diffusivity of the fibre space is related to the intrinsic diffusivity of the fibre cell walls (D_f) and the solidity of the fibre space ($(1 - \varepsilon)$) and fibre space diffusional tortuosity (τ_f) [13].

$$D_{eff} = D_p + \int_{q_1}^{q_2} D_q \, dq = D_a \frac{\varepsilon}{\tau_p} + D_f \frac{(1-\varepsilon)}{\tau_f} \tag{1}$$

Unlike the open space normal diffusivities (D_a), the fibre space intrinsic diffusivities are difficult to estimate and or determine experimentally. The fibre diffusivity D_f should be a function of moisture content, q (see e.g. [1, 13]). The tortuosities for the pore and fibre spaces represent the net increase in the diffusion path length separately through each of these phases. Thus, if one can measure these tortuosities individually, say from detailed information on the 3D structure of the pore space, the intrinsic diffusivities can be estimated. Another approach is to simulate the diffusion of a tracer molecule (walker) through the entire structure, allowing for conduction through both the phases but at differently tuned rates. In the following section, a dual phase random walk simulation method is described to predict the effective diffusivity of porous materials such as paper considering both pore and fibre space diffusion as well as a method to estimate the intrinsic fibre diffusivity, for the first time.

3.2 Diffusion simulations – random walk method

Goel [10] and Gupta [14] developed a random walk simulation method to predict the effective diffusivities of paper structures using X-ray tomography images. The random walk method is based on the Green's function solution to the transient diffusion equation. The simple random walk algorithm is to move the walker to a new position, incremented by a normally distributed random vector whose mean is zero and whose variance is proportional to the diffusivity. The following equation describes the incremental change in position for the walker,

$$x(t_{i+1}) = x(t_i) + \sqrt{2D\Delta t}\; w(t_i) \tag{2}$$

In this equation D is the free space diffusivity of the walker and w is a normal random number with mean 0 and unit variance. An accelerated version of the random walk algorithm was originally developed by Siegel and Langer [15] and Zheng and Chiew [16]. In this modified random walk, when a tracer is sufficiently far away from any interface, it is possible to use a larger step size and take it into account as if it were the result of many small steps. The first passage time obtained by solving the appropriate stochastic differential equation yields the time taken for a walker to reach the edge of a sphere which intersects the void space tangentially at a single location. The random walker is now placed on the surface of this sphere and the walk is continued. The time step is incremented by sampling from the first passage time distribution. The total displacement and the total time taken yield the diffusivity of the walker as constricted to move within the pore space alone. Goel [10] used an hybrid technique combining true random walk and first passage time principle to predict effective diffusivities of porous structures using an actual 3D image. In the case of paper, it is necessary to further modify the random walk algorithm on account of the hygroscopicity or conductivity of the fibres and the significant structure anisotropy.

The present method modifies the earlier method in two important ways. First, the size of the samples, particularly in the thickness direction was too small to achieve reasonable ensemble and time averaged walker displacement data. So, reflection boundary conditions in the thickness direction were implemented in the random walk algorithm. The second modification was to allow for the fibre phase to be open for random walk but with important boundary conditions. This is described in section 3.4. For a more detailed description of the random walk technique reference to [9] may be made.

3.3 Random walk method – model validation

The random walk algorithm was validated by conducting simulations of simple structures such as cubic arrays of spheres. It is theoretically expected that the displacement squared scales linearly as the distance travelled or the time elapsed for molecular travel. While conducting simulations, it is necessary to ensure that this criterion is being met and also the whole sample volume is traversed to more accurately characterize the properties of the material. Some of the earlier work did not give enough attention to this point either limiting the displacement to only smaller distances from the starting point, thus not traversing the entire structure or not verifying the linear relationship for the entire molecular travel.

In order to validate the method and verify its accuracy, an isotropic structure of uniform samples of known geometry, i.e. a bed of spheres of varying porosities were analyzed, and compared to results from known theoretical results. Figure 1 shows the close agreement between the random walk simulations and the theoretical results for a wide range of porosities, providing validation for random walk simulations.

3.4 Simultaneous pore-fibre diffusion – dual phase random walk algorithm

In a true random walk mode, a tracer can therefore land into a voxel of the other phase. Although most simulations do consider the solid phase to be completely impermeable, in paper samples one could expect this to be only the case at very lower humidities; while at higher humidity levels, fibres would become more conductive and can absorb water molecules as well. The approach below is based on that described by Laso [19].

Defining the ratio of intrinsic diffusivities in fibre and pore (open space) as,

$$R_D = \frac{D_f}{D_a} \tag{3}$$

The modified location for the random walker when entering the fibre space (lower diffusivity) will be given as Equation 4

$$x_2 = x_i + \sqrt{R_D}\,(x_1 - x_i) \tag{4}$$

with x_i the interface coordinate, x_1 the point where the tracer would have landed had it not crossed an interface, and x_2 the modified point where the walker lands after considering the difference in diffusivity.

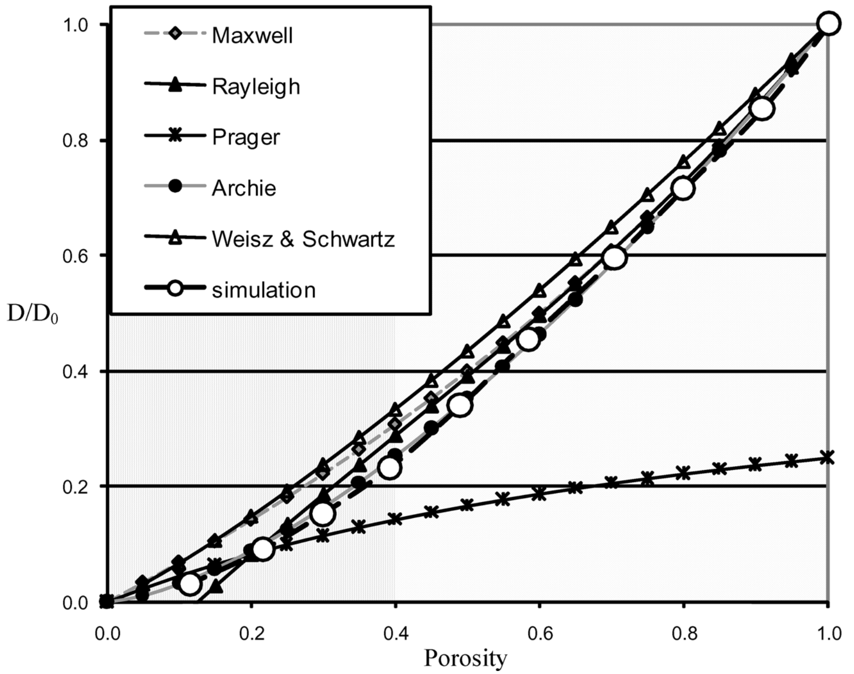


Figure 1. Comparison of the effect of porosity on the effective diffusivity ratio (D/Do) for a bed of uniform (Maxwell) spheres by random walk simulations with theoretically derived relations from the literature [9,18].

The difference in diffusivity between the pore and fibre space not only affects the walk length but also decides the likelihood that a tracer does indeed enters a fibre. Laso [19] showed that a tracer will enter the fibre with the probability $R_D^{0.5}$.

So every time a tracer should land into a fibre, a random number r is generated such as $r \in U(0, 1)$ and compared to $R_D^{0.5}$ so as to determine whether it will enter the fibre or not.

If the tracer does not enter, it then bounces back (reflection case). While considering the reverse, a walker entering from a less conductive fibre to a more conductive pore, it is always allowed to enter the pore space due to the higher intrinsic diffusivity (normal diffusivity for open space) of the pore space.

The modified location for the walker entering the pore space from the fibre space is given as,

$$x_2 = x_i + \frac{1}{\sqrt{R_D}}(x_1 - x_i) \tag{5}$$

x_i, x_1, x_2 follow the same notation as earlier. And since R_D is < 1, the walk length will always be longer as it enters the pores, in the case of paper samples.

In order to consider additional possibilities, for example fibres with larger diffusivities than the pore space, following Tomadakis and Sotirchos [20], a probability criterion similar to what was used in the pore-fibre case was introduced. Here a tracer coming from a fibre will enter the pore with the probability $R_D^{-0.5}$.

So every time a tracer should land into a pore, a random number r is generated such as $r \in U(0, 1)$ and compared to $R_D^{-0.5}$ so as to determine whether it will enter the pore space or not.

4 EXPERIMENTAL METHOD FOR PREDICTING INTRINSIC FIBRE DIFFUSIVITY

Massoquete *et al.* [21, 22, 1] reported effective moisture diffusivities for refined pulp hand sheets, same sheets analyzed three dimensional structure using X-ray computed tomography. Moisture was allowed to diffuse through paper samples which were subjected to different humidity conditions on each side [22], and the steady state moisture flux was measured. Their experiments included transport in the transverse i.e. *z* direction as well as the in-plane or x-y direction of paper. The effective diffusivity (as obtained above) is in itself insufficient to predict transient moisture transport for two reasons. First, the effective diffusivity is generally a function of moisture content of the sheet. Therefore the relationship with moisture content must be established. Second, transient moisture sorption can occur in sequential steps where pore and fibre diffusion interact with each other and lead to non-Fickian transport as was shown recently by Massoquete [22]. Therefore, it is necessary to analyze the diffusivity data to identify the contributions of the pore and fibre phases individually. The effective diffusivity can be related to the intrinsic or 'individual phase diffusivities', using eq. (1) shown by Radhakrishnan *et al.* [1].

300 gsm hand sheets of bleached softwood of varying refining levels were first prepared. Samples cut from these sheets were then examined using the ESRF's X-Ray facility in Grenoble, France (beamline ID19 which was highly parallel and monochromatic). The choice of energy was decided from past experiences at the ESRF, at 20 keV. The pixel size was chosen at 0.7µm, to ensure a large enough field of view, while still retaining a balance of high

resolution in the scanned sample and imaged using X-μCT [23, 24, 25]. Experimental in-plane and transverse vapor diffusivity characteristics of these paper samples at varying RH have been determined using the diffusion cup technique [21, 22].

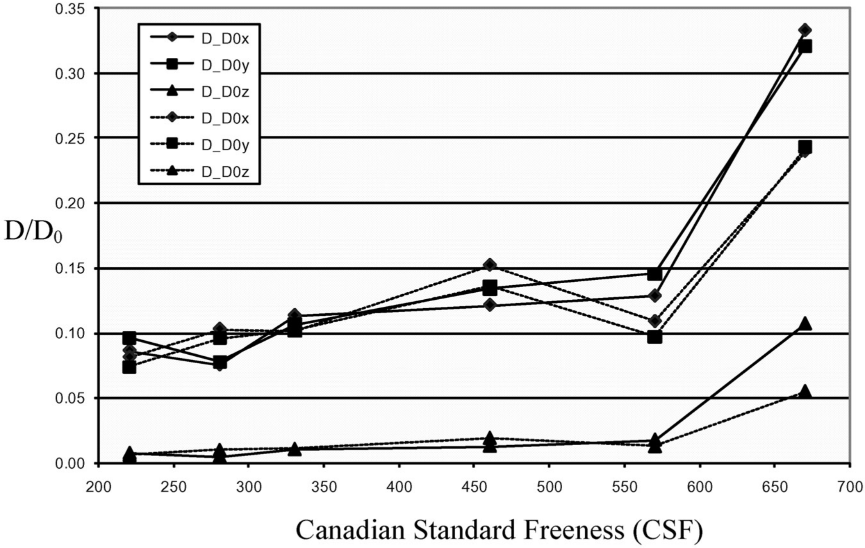
5 RESULTS AND DISCUSSION

Since diffusion coefficient of water vapor inside the fibre (i.e. intrinsic fibre diffusivity) and the internal structure of fibre is not known a priori, several ratios of intrinsic diffusivities of fibre and pore space (R_D) were considered. This enables covering the entire range of intrinsic diffusivities from impermeable to highly permeable corresponding to range of RH conditions from 0% to 100%.

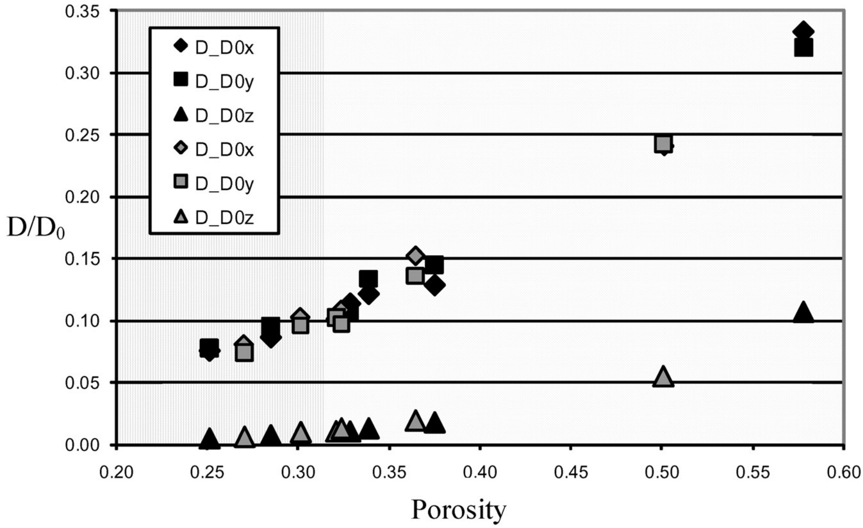
Using the case of the $R_D = 0$, the pore space diffusivity simulations using the combined stochastic dynamic model and hybrid technique were conducted for paper samples of varying structure and compared with experimental results reported by Massoquete *et al.* [21, 22] (see simulation results in figures 2a and b and comparison with experiments in figure 4). Both the simulation results and experimental data indicate a gradual increase in pore space diffusivity with increasing porosity of the structure. The in-plane (lateral) diffusivity (x,y) is much higher than the transverse diffusivity for all the samples considered, indicating the increased tortuosity in the z-dimension. Fig. 3a and 3b show sample random walks through the pore space; clearly, the tortuosity of the pore space is high.

Both the experimental data and simulation results were compared in Figure 4 below, where D/D_{0x} and D/D_{0y} were averaged for the simulation data with two repetitions per sample at each CSF, to offset any skewness from sample tilting. Error analysis showed that due to sample heterogeneity, variability from one sample to another, and the small sample volumes, the variabilities in diffusivities can be of the order of +/− 10–25%. Both computer simulations and experimental data show that the diffusion coefficient is higher in the in-plane direction compared to the transverse direction. A power fit was used for the simulation data. The experimental data show several outlying data points. However, measuring diffusivity coefficients with experimental setup is a very challenging task. The other difference comes from the size of the sample: the tomography samples were about 1mm × 1mm, and the samples used for the experimental measurements are about 30mm × 30mm.

During X-ray imaging, the relative humidity of the sample is most definitely close to 0% (heat from the X-ray beam contributing to near dryness condition). The lowest humidity condition in the experimental setup was 30%

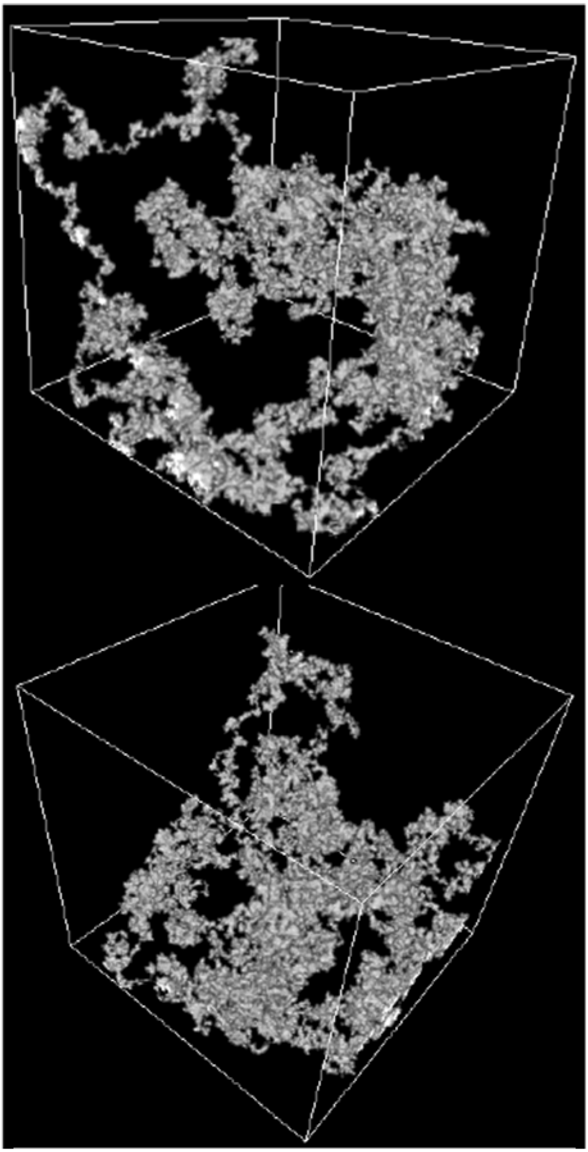


(a)



(b)

Figure 2. (a) Diffusivity in pore space, D_p as a function of refining level of pulps (denoted by CSF, ml) and (b) diffusivity in pore space, D_p as a function of sheet porosity.



(a) (b)

Figure 3. (a) and (b) are sample random walks within the pore space.

RH, which, even though it is still a low, can influence the structure and the diffusivity. Fibres can swell at higher humidities during the experiments thus influencing the structure and the intrinsic fibre diffusivity and the effective diffusivity of the structure.

Figure 5 below shows the effect of porosity on the effective diffusivity ratio comparing laboratory made hand sheets, commercially made paper samples and the isotropic bed of spheres. In Figure 5, refining refers to bleached softwood Kraft pulp refined to varying degrees as indicated earlier and hand sheets made in the laboratory. Furnish refers to handsheets made from various commercial fibre furnishes including Oak, Maple, Eucalyptus, Birch and Blend (mixture) in the laboratory. BKP REM and MK (calendared and non-calendared) are paper samples made in the pilot paper machine. Similar to the relationship between porosity and diffusivity for samples of varying refining levels, machine made samples also exhibit a non-liner relationship with porosity. The machine made papers have a higher diffusivity at the same porosities compared to more uniform, laboratory made hand sheets, probably owing to more open structures and local non-uniformities. The difference between in-plane and transverse diffusivities is less pronounced for machine made structures than laboratory made structures. Interestingly,

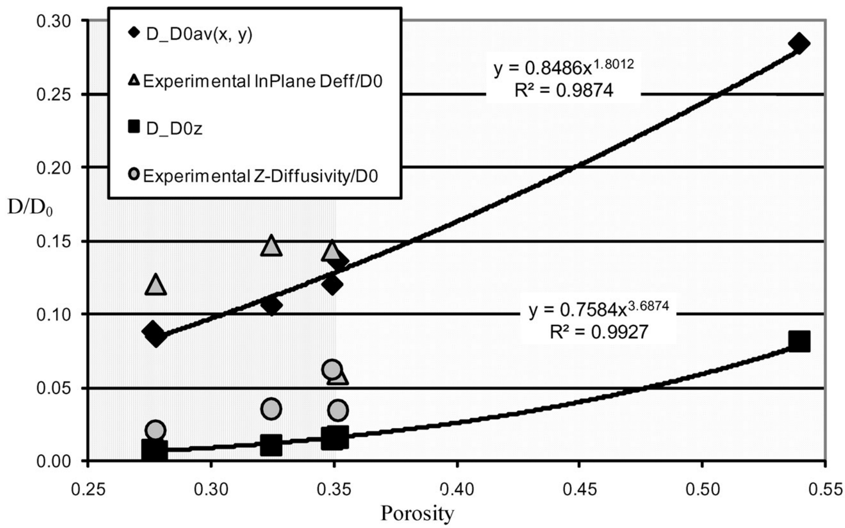


Figure 4. Comparing experimentally measured in-plane and transverse diffusivities with random walk simulations for samples of varying refining levels.

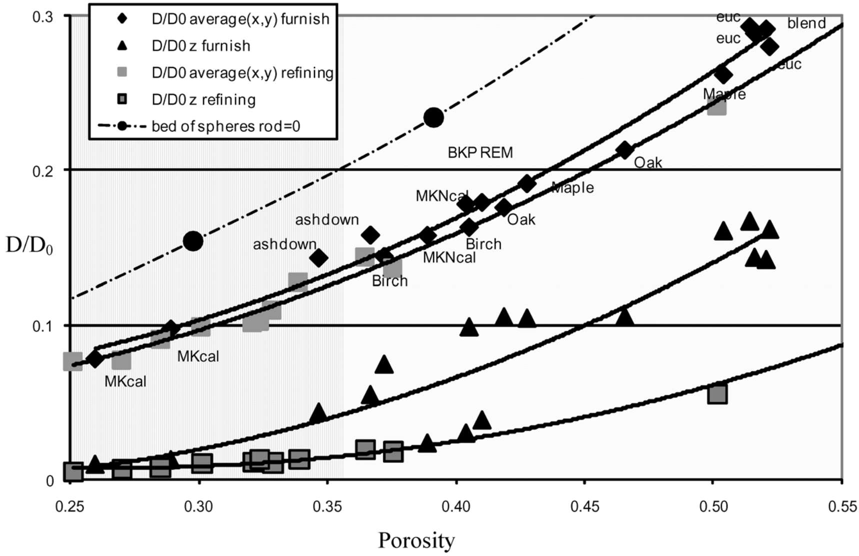


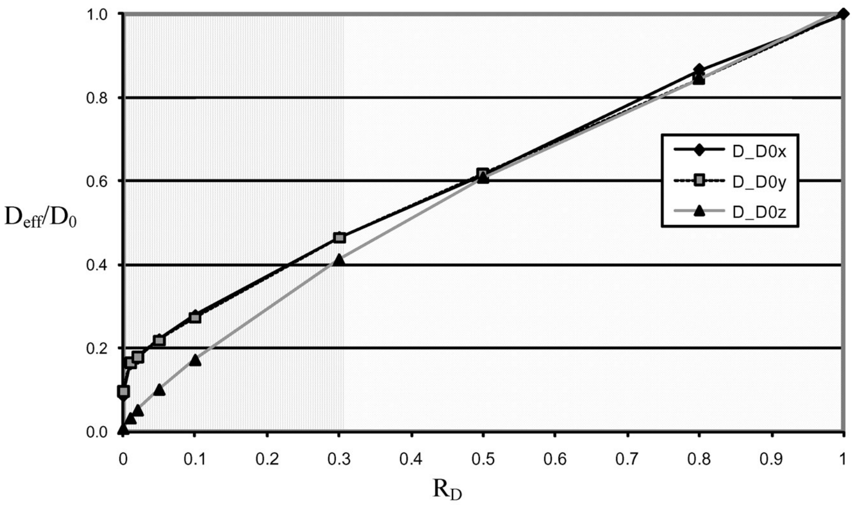
Figure 5. Comparison of the effect of porosity on diffusivity for laboratory made, machine made paper structures; a reference bed of spheres is also shown.

the reference isotropic structure of a bed of spheres is still more diffusive than paper structures.

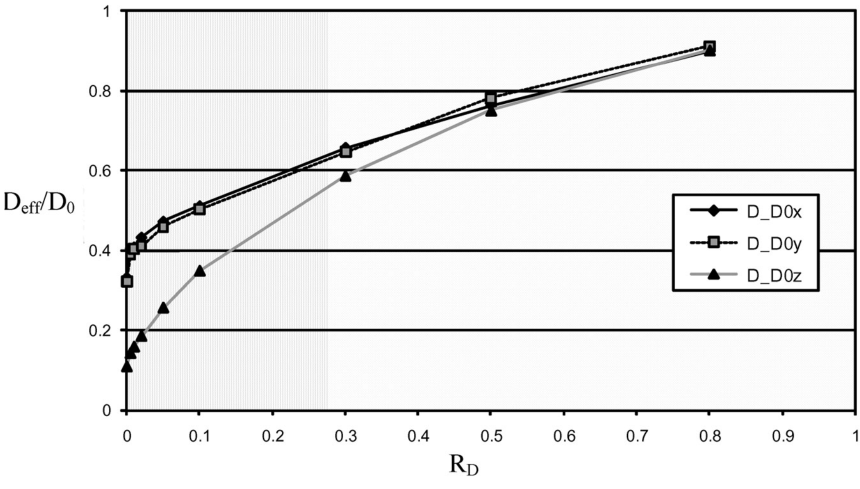
In Fig. 6a and b, the effective diffusivity scaled by open space diffusivity D_a (D_{eff}/D_a) is shown as a function of intrinsic diffusivity ratio R_D for two different paper samples (220 ml CSF and 670 ml CSF). Note that when $R_D = 0$, diffusion through the fibre space is prohibited simulating the case when the sheet is dry (i.e. RH = 0), whereas when $R_D = 1$, the fibres are just as conductive as the pore space. In the latter case, there is no tortuosity effect of the pore space and the fibres and pores behave as one uniformly conducting phase and the random walk occurs as if it was through free open space. As expected, the scaled effective diffusivity approaches unity. It is also possible to conduct simulations at $R_D > 1.0$, reflecting case when the fibre phase is more conductive than the pore space. One observation was that the diffusivity in the transverse dimension is lower than the in-plane direction but the difference between the two decreases as the conduction through the fibres becomes more dominant. This shows that as the fibre conductivity increases, diffusion becomes more isotropic, even in structurally anisotropic materials such as paper samples. First of all, the diffusivities in the two in-plane directions are almost identical; this is expected as in a uniformly made laboratory hand sheets the paper structure in the two in-plane directions should be very similar. The transverse pores in paper tend to be much more tortuous than the in-plane and therefore the tortuosity of the diffusion paths in the transverse dimension is much larger than that in the in-plane dimensions. Interestingly, as the fibres become more conductive, i.e. R_D is increased from 0 to a higher value, both the in-plane and transverse effective diffusivities of the whole structure increase and also the difference between transverse and in-plane directions becomes smaller.

This is an interesting result indicating that the anisotropy in transport property inherent in layered porous structures such as paper slowly decreases as both the phases become conductive, i.e. the structure start to behave more like an isotropic material. For this particular sample, beyond a R_D of ~0.5, the diffusivities in all three directions become almost identical behaving more like an isotropic material. The effective diffusivity ratio becomes 1.0 at $R_D = 1.0$ simulating an open volume and confirming that the overall simulations are indeed working well. The above effect of R_D influencing the structures to behave more like an isotropic structure at higher values has been observed in many other sample structures as well. Simulations using both 670 ml CSF sample and 220 ml CSF sample showed similar behavior of decreasing anisotropy with increasing R_D. Differences between in-plane and transverse diffusivities disappeared for $R_D \sim 0.5$. The effective diffusivities in general for the less refined 670 CSF's are greater than that for the highly refined 220 ml CSF samples. The larger gap between the two orthogonal directions slowly converge as seen in the 220 ml CSF. Even after convergence, 670 ml CSF sample is more diffusive than the 220 ml CSF sample, confirming that refining does consolidate the structure making them more resistive for transport. The rather rapid increase in diffusivity for the highly refined case (220 ml CSF) as compared to the less refined pulp (670 ml CSF) is quite interesting. It appears that increased refining can decrease the fibre space tortuosity probably because of increased densification of the structure and increased relative bonded area in the refined sheets thus providing additional diffusional pathways through the fibres. This points out the dominance of fibre phase conduction, at high humidities/moisture contents. Also, these results indicate that in denser, less open structures increasing fibre phase conductivity may accelerate decreasing the anisotropy of the overall structure.

Based on the experimentally measured effective diffusivities at a given relative humidity and pore space diffusivities obtained at $R_D = 0$, the intrinsic diffusivities of the fibres as a function of relative humidities for the various refining levels were then calculated and shown in Figure 7. The fibre phase intrinsic diffusivity, a fundamental characteristic of the fibre cell wall structure is thus estimated for the first time using a combination of theoretical



(a)



(b)

Figure 6. (a) Ratio of effective diffusivity to normal diffusivity (D_{eff}/D_0) as a function of intrinsic fibre diffusivity ratio (R_D) for (a) hand sheet made with pulp of 220 ml CSF and (b) hand sheet made with pulp of 670 ml CSF.

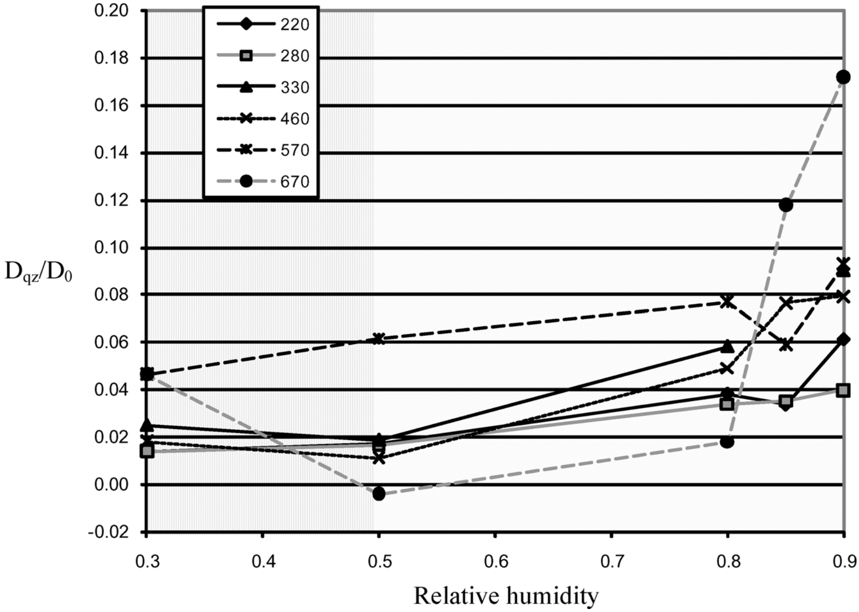


Figure 7. Intrinsic fibre diffusivity ratio (R_D) as a function of relative humidity for samples of varying refining levels.

simulation and experimental data. For all of the samples of varying structures studied, the ratio of intrinsic fibre diffusivity to normal diffusivity (R_D) decreases with decreasing RH, reaffirming that fibre phase conductivities decrease as the paper samples become less moist. In almost all of the samples for the entire range there is a slow, gradual drop in R_D with decreasing RH. However, interestingly, the intrinsic fibre diffusivity ratio decreases only from about 0.08 to 0.01 as the humidities decrease from high to low for almost all of the samples. Intrinsic fibre diffusivities are estimated to be about 8% to 1% of the normal open space diffusivity of moisture in air. Even though the absolute intrinsic fibre diffusivities appear to be small, it is an order of magnitude change from higher humidity to lower humidity.

6 CONCLUSIONS

One of the important benefits of non-intrusively imaged 3D structures of porous materials is their potential applicability for predicting the mechanical, transport and optical properties in addition to quantifying the 3D structural characteristics. Structural anisotropies inherent in paper structures have been clearly shown by the differences in diffusivities and diffusional tortuosities in the three orthogonal directions. In the in-plane direction, diffusivities were always higher than in the perpendicular transverse direction for all samples studied. This is also confirmed by experimental data for samples of varying structures. This is interesting indeed given that the pore sizes and their distributions have been shown to be more open in the transverse direction. The results presented in this work indicate that even though the pores in the in-plane direction may be smaller owing to the directional orientation and layering of the fibres in the plane, the diffusional paths are shown to be actually less tortuous in the in-plane direction resulting in higher diffusivities. The diffusional tortuosity is at least an order of magnitude higher in the transverse direction than in the in-plane direction. The tortuosities in complex, anisotropic paper structures are significantly higher than in the isotropic, symmetric array of periodic spheres. In general, the porosity-tortuosity relationship does appear to be non-linear as was the case for bed of spheres. The resolution of the images does contribute to a difference in their estimations of diffusivities with higher resolution images yielding lower diffusivities than lower resolution images.

Unlike the open space normal diffusivities, the fibre space intrinsic diffusivities are difficult to estimate and or experimentally determine. The fibre phase intrinsic diffusivity, a fundamental characteristic of the fibre cell wall structure is estimated for the first time using a combination of theoretical simulation and experimental data. For all of the samples of varying structures studied, the ratio of intrinsic fibre diffusivity to normal diffusivity (R_D) decreases with decreasing RH, reaffirming that fibre phase conductivities decrease as the paper samples become less moist. Since the intrinsic fibre diffusivities are unknown, the ratio of intrinsic diffusivities for the fibre and pore space (R_D) were used to predict its effect on the overall effective diffusivity of the structure. At an (R_D) of 0, the effective diffusivity represents the diffusivity through the pore space and at an (R_D) of 1 it represents a free open space simulation. It is interesting that (R_D) shows a non-linear relationship to effective diffusivity for all the structures studied. Paper samples generally anisotropic with clearly different transport properties in the in-plane and transverse directions tend to become more isotropic with similar transport properties in all three directions as the fibres become more conductive. Beyond an approximate (R_D) of ~0.5–0.6, the transport properties in all three directions converge, asymptotically approaching 1.0 at an (R_D) of 1.0. Intrinsic fibre diffusivities are estimated to be about 8% to 1% of the normal open space diffusivity of moisture in air. Even though the absolute intrinsic fibre diffusivities appear to be small, it is an order of magnitude change from higher humidity to lower humidity. Using the effective diffusivity data under varying relative humidities of known sample structures, it is possible to estimate the intrinsic fibre diffusivities and how they change with mechanical treatment or fibre type. This might be very useful for future product engineering tailored for specific end-use applications.

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Transcription of Discussion

MULTI-SCALE MOISTURE TRANSPORT IN PAPER: IMPACT OF PORE AND FIBRE TORTUOSITY & ANISOTROPY

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Ilya Vadeiko FPInnovations

You made a very important comment that you measured the structure in the dry state, but you showed results for different relative humidity levels, how you did that?

Shri Ramaswamy

The diffusivity experimental data is from different relative humidities. So the paper's structures are actually swollen when you do the diffusion experiment, but the X-ray tomography image was obtained only with a dry sample. So yes there is a discrepancy between the dry structure and numerical simulation and the swollen structure and experiments.

Ilya Vadeiko

So is it technically difficult to get X-ray tomography data from a swollen structure, from samples not in dry state?

Shri Ramaswamy

Perhaps Jean-Francis Bloch will speak more about it in his review tomorrow. I think the structure itself would dry during X-ray imaging, and you would have to have a controlled-humidity condition to maintain it during the experiments.

Ilya Vadeiko

I think it would be interesting to compare the structural changes as you change the relative humidity with your imaging technique, and then assess the amount of diffusivity due to the structural changes and due to the fibre component. Thank you.

Tetsu Uesaka FPInnovations

I am just trying to understand this whole picture. You defined, first of all, the ratio of the diffusivities between those in the air and those in a fibre, so called ROD. For the moment, it is not known *a priori*. You later on determined it?

Shri Ramaswamy

That is correct. It is not experimentally determined, so we do the simulation for the whole range of possible ratios from 0 to 1, and actually we have done work even with greater than 1 meaning fibres being more conductive than the open space. Yes.

Tetsu Uesaka

So according to your definition of ROD, it seems to be controlling the probability that vapour goes into the fibre phase or stays in the air. Right?

Shri Ramaswamy

Yes, that is one of the concerns.

Tetsu Uesaka

Yes. It means that this probability has to do with, so-called, equilibrium moisture content somehow?

Shri Ramaswamy

It has to do with conductivity differences between the two phases.

Tetsu Uesaka

Yes. I understand, but it eventually determines the equilibrium moisture content. So this means that from that data, you can accurately determine ROD without going through all the other procedures, no? From this data (the equilibrium moisture content) you can accurately determine this ratio, from some of the data you found?

Shri Ramaswamy

Yes! That is what we are doing. We take the experimental data where the effective conductivity is determined for the whole structure, but the intrinsic conductivity of the fibre phase is unknown. So, say for example, I have a 670 freeness refined sample and we do our simulation for the various RODs from 0 to 1 and then take the experimental data and determine which effective intrinsic diffusivity ratio matches with the experimental data. So that is how we tried to arrive at what I called the equivalent ROD. Referring to the figure, this is the actual data from experiment for one particular sample and you see about 0.25 and this is the ratio of diffusivities.

So based on this, the ROD is about 0.08; this is based on experimental data. So this now is the ratio of intrinsic diffusivities and from this you can find out what the intrinsic diffusivities in a fibre phase are. And this is what we then compare to see how it changes. So, this is the same value that you see as the equivalent ROD, and then we looked at that for all the samples and determined how it changes with the relative humidity. Knowing that the images are using dry structures and the actual experiment is with swollen structures.

Jukka Ketoja VTT

Here, you leave diffusivity in the fibre phase open and try to determine it but here are also experiments using NMR where the diffusivity as a function of moisture content can be determined. They indicate an exponential dependence. Also some indirect other experiments support this, even giving similar exponents. I cannot see that coming out from your analysis.

Shri Ramaswamy

Yes, actually, we have not done the MRI-based work on looking at the transport within the fibre. That would be an interesting way of comparing the effective diffusivity to the values obtained here, even if it is for some other fibres. We have not done that.

Jukka Ketoja

There seems to be a stronger behaviour indicated in this other type of experiments.

Shri Ramaswamy

Through using MRI?

Jukka Ketoja

Yes.

Lars Wågberg KTH

First of all I have a comment on the data. You showed pore volume distributions where mercury intrusion data was compared with your sphere-filling model. Your sphere-filling data fit very well to some earlier data published by us, where we used simple pore volume distribution equipment based on liquid extrusion and mercury porosimetry. We actually found the bimodal distributional with small pores from mercury porosimetry and larger pores from liquid extrusion. So your results were nice to see. Also, I wanted to ask you a question on your random walk simulations for the movement of moisture through the structure. What is the random walker, is it a single water molecule?

Shri Ramaswamy

This is self-diffusion, if you want to call it that. So essentially you are following the movement of a walker. It is not a molecular dynamic simulation where you have a number of molecules and you consider the impact or the interaction between the molecules. So this will be individual walkers, you know, which are essentially traversing through the structure following the physics.

Lars Wågberg

In this model, do you account for the heat of absorption when that is released, when the water molecules are interacting with the surface? How will that influence the conditions for the diffusion?

Shri Ramaswamy

Yes, it is assumed that we are considering only steady state conditions. So there is no sorption being considered as part of this model, so we assume that the flux at the interface between the pore and the fibre is equal, there is no accumulation.

Lars Wågberg

Okay, thank you. I guess that when you simulate the movement of water within the fibre, then the dimension of the walker starts to become important. In the pore this might not be so important.

Shri Ramaswamy

Yes, and that is considered. The conductivity being different is considered and also the probability of being able to enter the fibre versus being in the pore. So, for example, my starting point is in a pore and I could have landed here if there was no fibre, but am I able to go into the fibre? In fact the original landing point needs to be modified because of the difference in conductivity.

Lars Wågberg

Okay. Thank you.

Ramin Farnood University of Toronto

I would like to follow up an earlier comment regarding the ROD that you defined. It seems that this ratio has to be somewhat related to the partition coefficient equilibrium – the partition coefficient of water molecules in the gas phase and the fibre phase. So I was wondering if you had a chance to plot ROD versus the partition coefficient and see whether there is a correlation?

Shri Ramaswamy

Yes, it is an interesting point. We have not done that. The use of MRI was another suggestion where we have to go back and look at the comparison between ROD and experimentally determined values in cellulose structures. It will be interesting to look at that.