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Multi-scale model for time-dependent degradation of historic paper artifacts

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Abstract: The degradation of paper is due to complex physical and chemical processes that occur as the paper ages, and is enhanced by environmental factors, such as the temperature and relative humidity, and by intrinsic parameters, such as the acidity of the paper. The literature reports that a large percentage of historic documents, manuscripts, and paper objects in museums, libraries and collections is susceptible to degradation phenomena, which may ultimately affect their integrity and longevity. This contribution presents a novel computational model to predict the degradation and lifetime of historic paper. The approach is based on: i) a multi-physics modelling framework, which considers the relevant chemical and mechanical degradation processes and the influence by the ambient environmental conditions, and ii) a multi-scale description, which includes the effect of the intrinsic hierarchical structure of paper, from the fibre- and fibrous network levels to the effective macro-scale, paper sheet level. The paper fibres constructing the fibrous network are characterized by an age-dependent, chemo-mechanical constitutive behaviour. In particular, an evolution equation describes the reduction of the degree of polymerization of cellulose as a function of time and the specific environmental conditions, which in turn is used for determining the fibre tensile strength. The fibre stresses induced by hygro-expansion and hygro-contraction under a change in relative humidity are computed using a coupled hygro-mechanical model, and lead to brittle damage once the fibre tensile strength is reached. Accordingly, the chemical degradation of individual fibres affects the local damage development and stress distribution in the fibrous network, and thereby governs the material response at the paper sheet scale. Asymptotic homogenization is used to calculate the effective hygro-mechanical properties of the fibrous network. A set of numerical simulations is performed to predict the time-dependent degradation of historic paper under a range of temperature, relative humidity and acidity conditions. From these results, isochrone degradation maps are constructed that illustrate the expected lifetime of historic paper as a function of the ambient climate conditions and the acidity of the paper. Further, a practical, analytical degradation function is derived that can be used for a fast estimation of the time-dependent stiffness degradation of paper. The outcome of this work may help conservators to determine the optimal indoor climate conditions in museums, archives and libraries for limiting or delaying time-dependent degradation of historic paper artifacts.

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1. Introduction

The degradation of historic paper artifacts is one of the main concerns for cultural heritage curators. It has been estimated that up to 70-80% of paper documents located in western heritage institutions and librarian collections is possibly acidic [1], and therefore prone to acid-catalysed hydrolysis reactions that lead to rapid chemical and mechanical degradation [2]. While deacidification conservation interventions are certainly a potential solution to the problem [3], it may be cumbersome to intervene on a high number of paper objects in a critical state. As an alternative, better strategy, historic paper degradation can be mitigated or delayed through preventive conservation policies, by prescribing indoor climate ranges for which the deterioration of paper artifacts remains limited. In order to identify and optimize these specifications, however, a mechanistic understanding of the phenomena responsible for degradation of historical paper and the prediction of the expected end-life of the paper artifacts are of crucial importance.

In the literature, various efforts have been made to uncover the different chemical and mechanical processes governing paper degradation, which, in principle, may take place at multiple length scales. Paper is a composite material characterized by an intrinsic hierarchical structure, which involves length scales ranging from the molecular level of cellulose to the macroscopic, sheet level, see Figure 1. Cellulose is the major structural component of paper, and consists of a linear chain of several monomer units that are linked together by means of glycosidic bonds. Paper degradation initiates as a result of cleavage of cellulose molecular chains induced by breakage of the glycosidic bonds. This mechanism leads to a gradual reduction of the average molecular length, and thus of the molecular weight [2, 4]. The main processes causing chain cleavage in cellulose materials are hydrolysis reactions, possibly acid-catalyzed, and non-hydrolytic reactions, such as oxidation [5, 6, 7]. The rate and extent of these chemical reactions are typically controlled by several internal and external parameters, including the acidity of the paper, the metal ions present in the ink, and the environmental storage or display conditions, such as the temperature, relative humidity, light exposure, and the presence of air pollutants [8, 9, 10].

The chain scissions occurring at the molecular level have important consequences for the integrity of the paper, since the reduction of the molecular weight is directly related to a decrease of the effective mechanical properties (tensile strength, stiffness) of cellulose [11, 12, 13, 14, 15, 16, 17]. The interacting chemical and mechanical phenomena may finally lead to an embrittlement and loss of fragments in paper artifacts, clearly limiting their physical usability, readability and, more generally, their visual appearance. The kinetics of cellulose degradation is commonly modelled via an evolution equation that is formulated in terms of the degree of polymerization, which reflects the average number of monomeric units in the cellulose
molecules. Departing from the pioneering work of Ekenstam [18, 19], models have been proposed that describe the process of cellulose degradation at various degrees of complexity, by including relevant factors of influence such as the type of aging, the acidity of the paper, and the initial oxidation of cellulose, see e.g., [20, 21, 22, 23] and the comprehensive reviews [2, 3]. By taking these kinetic models as a basis, dose-response functions have been derived that predict the time-evolution of the degree of polymerization as a function of ambient degradation factors, i.e., the temperature, relative humidity, air pollutants and acidity of the paper [24, 25]. The dependency on a specific degradation factor is hereby calibrated from results of dedicated experiments or experimental data available in the literature. The damage functions constructed with this approach can be used to estimate the lifetime expectancy of individual paper artifacts in a collection, by comparing the predicted damage against a critical threshold value beyond which a paper object becomes unfit for use or display [26, 27]. Despite the great practical value of such studies, it should be mentioned that these methodologies are solely based on the description of the chemical degradation process, thus neglecting the modelling of the mechanical problem and the chemo-mechanical couplings. In addition, the dose-response functions are formulated at the macroscopic, paper sheet scale, without accounting for the interactions following from the different scales of observation defining the intrinsically multi-scale nature of paper.

In the present communication, a computational modelling framework is proposed that predicts the time-dependent degradation of historic paper based on i) a multi-physics approach, which considers the chemical and mechanical degradation processes of paper and the influence by the ambient environmental conditions, ii) a multi-scale description, which allows to consistently transfer effects from the fibrous network scale to the effective, macroscopic scale of paper. These two distinctive features make the proposed methodology novel for the study of time-dependent degradation of historical paper artifacts. The multi-scale formulation is developed within the frame of asymptotic homogenization [32, 33], which enables the calculation of the effective response of heterogeneous materials with a periodic micro-structure. Recent scientific works have proposed asymptotic homogenization models for the prediction of effective material properties for different applications, including thermo-mechanical [34, 35, 36], thermo-diffusive [37] thermo-piezoelectric [38, 39], hygro-mechanical [40, 41, 42], and chemo-diffusive-mechanical [43] problems. The displacement field is expressed as an asymptotic expansion in terms of microscopic and macroscopic length scales, and inserted into the mechanical equilibrium equation, which in turns is solved under the application of hygral, thermal, chemical and/or electrical loading conditions. This leads to the definition of boundary value problems at the micro-scale - the so-called “cell problems” -, which refer to a specific micro-structural geometry and are solved numerically by means of the finite element method. From the solution of the cell problems, the effective macro-scale material properties are computed, together with the local displacement, strain and stress fields in the micro-structure.

By departing from the formulation proposed in [40, 41], in the present work the historic paper is modelled as a two-dimensional, periodic repetition of a fibrous network unit-cell, whereby the individual paper fibres are characterized by an age-dependent, chemo-mechanical constitutive behaviour. The chemical constitutive formulation accounts for a time-dependent degree
Figure 1: Multi-scale structure of paper. (a) Molecular structure of cellulose. (b) Individual cellulose micro-fibril and (c) cellulose micro-fibril bundle. (d) A macro-fibril embedded into a hemicellulose and lignin matrix, forming a primary cell wall. (e) Paper pulp fibre. (f) In-plane view of paper fibrous network. (g) Cross-sectional view of a paper fibrous network. (h) Paper at the macroscopic, sheet scale. Images (a), (d) are reproduced from [28]; images (b), (c) are reproduced from [29]; image (f) is reproduced from [30]; image (g) is reproduced from [31].

of polymerization, which is calculated by means of Ekenstam’s equation [18], and depends on the ambient temperature, relative humidity, and the acidity of the paper. At each time increment the fibre stresses generated by hygro-expansions/contractions under a change in relative humidity are determined through a coupled hygro-mechanical model. The fibre behaviour is
simulated as transversely isotropic elastic, up to the level at which the stress in the fibre reaches the age-dependent tensile strength. The tensile strength is a function of the degree of polymerization, and thus varies when time develops. When the stress in a material point (i.e., finite element) reaches the fibre tensile strength, this material point is considered to fail in an ideally brittle fashion by removing the corresponding finite element from the fibrous network geometry. Subsequently, the finite element discretization of the unit-cell is consistently updated. The homogenized properties of the fibrous network are finally computed based on the damaged, micro-structural geometry. This procedure is repeated at successive, discrete time steps, which allows to characterize the time-dependent degradation of the effective material properties as a function of the chemical degradation of cellulose and the micro-scale defects generated at the fibre level. Since the loss of the effective mechanical stiffness is an appropriate indicator for the degradation level of a paper sheet, the developed model provides a practical analysis tool for determining the susceptibility to time-dependent degradation and the expected lifetime of historical paper under indoor climate conditions typical for museums, archives and libraries. A set of numerical simulations is performed that predicts the chemo-mechanical degradation process as a function of the environmental specifications and acidity of paper. From the simulation results, isochrone degradation maps are constructed and an analytical degradation function is derived, which enables a straightforward estimation of the expected lifetime of paper artifacts under specific acidity, temperature and relative humidity conditions.

This article is organized as follows. The modelling of time-dependent degradation of paper fibres is described in Section 2. Section 3 presents the multi-scale asymptotic homogenization framework that is used to upscale the degradation response of paper from the fibrous network level to the macroscopic sheet level. The numerical solution procedure and the material parameters used in the simulations are described in Section 4. Section 5 illustrates the numerical results of a reference model, and presents a variation study that considers the influence of the relative humidity, temperature and acidity conditions on the degradation process of the paper artifact. In Section 6, isochrone degradation maps are constructed and an analytical degradation function is presented, which can be used for a fast estimation of the expected lifetime of the paper artifact. Finally, Section 7 summarizes the main conclusions of the study.

The following notations for Cartesian tensors and tensor products are used: \( a, \mathbf{a}, \mathbf{A}, \) and \( ^n\mathbf{A} \) denote, respectively, a scalar, a vector, a second-order tensor, and an \( n \)th-order tensor. By employing Einstein’s summation convention, vector and tensor operations are defined as follows: the dyadic product is given by \( \mathbf{a} \otimes \mathbf{b} = a_i b_j \mathbf{e}_i \otimes \mathbf{e}_j \), and the inner products read \( \mathbf{A} \cdot \mathbf{b} = A_{ij} b_j \mathbf{e}_i, \quad \mathbf{A} \cdot \mathbf{B} = A_{ij} B_{jk} \mathbf{e}_i \otimes \mathbf{e}_k, \quad \mathbf{A} : \mathbf{B} = A_{ij} B_{jk} \), with \( \mathbf{e}_i \) (\( i = x; y; z \)) the unit vectors of a Cartesian vector basis. The symbols \( \nabla \) and \( \nabla \cdot \) indicate the gradient and divergence operators, respectively.
2. Time-dependent degradation of paper fibres

2.1. Chemical degradation

Degradation of paper is governed by a complex combination of chemical and mechanical processes interacting across multiple length scales. Paper fibers consist of cellulose macro-fibrils that are embedded in a hemicellulose and lignin matrix, as illustrated in Figure 1(d). Cellulose is the major structural component of paper fibres, while hemicellulose and lignin are typically present in smaller percentages, with the actual values depending on the type of pulping process adopted during manufacturing [44]. In this work, it is assumed that the chemo-mechanical degradation response of paper fibres is entirely controlled by the degradation of cellulose, and that the influence of the other phases may be neglected. This assumption is supported by recent studies in the literature, in which the lignin content was observed to have no influence on the aging rate of paper produced at a neutral pH value [45, 46]. Further, the chemical degradation process is considered to occur uniformly across the various length scales, as a result of which the molecular scale, the fibre scale, the fibrous network scale and the macroscopic, paper sheet scale are characterized by the same extent of chemical degradation. In view of these two assumptions, the process of chemical degradation at the level of individual paper fibres can be modelled by adopting the well-known reference model proposed in [11, 18] that describes the degradation of cellulose at the molecular scale. The degradation of cellulose molecules is caused by the cleavage of the long cellulose molecular chains, as governed by the breakage of glycosidic bonds. Cleavage results in a gradual reduction of the average molecular length, and thus in a decrease in molecular weight [2, 4]. The main processes causing chain cleavage in cellulose materials are hydrolysis reactions, possibly acid-catalyzed, and non-hydrolytic reactions, such as oxidation [5, 6]. Acid-catalyzed hydrolysis is particularly relevant for papers characterized by high acidity levels, while in neutral and alkaline conditions paper degradation is mostly governed by oxidation mechanisms [2]. In this contribution, reference is made to paper produced in the 19th century, which is acidic with pH values commonly ranging between 4 and 7 [1]. The expected dominating degradation process thus is acid-catalyzed hydrolysis. For this process, the moisture content of the paper plays an essential role [14, 47, 48, 49]. The reference model selected for simulating cellulose degradation is based on the well-known Ekenstam equation [11, 18], in which cellulose degradation is described through a first-order kinetic equation expressed in terms of the number of cleavages that occurs within the cellulose molecule. The model assumes that all glycosidic bonds are equal, and that chain cleavage may occur at random locations in the molecule. This process can be conveniently formulated in terms of the degree of polymerization that represents the number of monomer units in the polymer, i.e.,

$$\frac{1}{DP} - \frac{1}{DP_0} = kt$$

where $DP_0$ and $DP$ are the degrees of polymerization of cellulose at the initial time $t_0$ and the actual time $t$ (year), respectively. The coefficient $k$ (year$^{-1}$) describes the reaction rate of polymer cleavage, and may depend on both extrinsic (temperature, relative humidity, light...
exposure and pollution) and intrinsic (acidity, presence of additives or ink) parameters [8, 9, 10]. Following [24], it is assumed that the three most relevant factors controlling the rate of paper degradation are the temperature, moisture content, and acidity of the paper. Note that the presence of air pollutants, such as SO$_2$, NO$_x$ and partially O$_3$, and volatile organic compounds, as for instance acetic acid, may also affect paper degradation [2]. However, the concentrations of these compounds in typical library and museum environments are generally low [50], so that these contributions are left out of consideration in the present work.

The reaction rate $k$ in expression (1) may be defined in accordance with the Arrhenius equation:

$$k = A \exp \left( -\frac{E_a}{RT} \right),$$

(2)

in which $A$ is the frequency factor (year$^{-1}$), $E_a$ is the activation energy (J mol$^{-1}$), $R$ is the universal gas constant (J mol$^{-1}$ K$^{-1}$) and $T$ is the temperature (K). According to [17], for historic paper the frequency factor $A$ may be decomposed into three components, which describe the contributions to cellulose degradation of non-hydrolytic reactions, hydrolytic reactions, and acid-catalyzed hydrolysis, as

$$A = A_0 + A_1 m + A_2 m \left( 10^{-\text{pH}} \right).$$

(3)

Here, $A_0$, $A_1$, $A_2$ are the frequency factors related to non-hydrolytic reactions, hydrolytic reactions, and acid-catalyzed hydrolysis, respectively. Further, $m$ indicates the moisture content in the paper sheet, and pH denotes the acidity. Obviously, the values of the frequency factors $A_0$, $A_1$ and $A_2$ and the activation energy $E_a$ are dependent on the specific material characteristics, and need to be calibrated from experiments. Based on the data collected from 121 degradation experiments on historic paper subjected to a range of environmental conditions (temperature, relative humidity) and pH levels, for obtaining an accurate calibration, Strlić et al. [24] proposed to adapt the exponential form given by equations (2) and (3) to

$$k = \exp \left( \frac{1}{36.981 + 36.72 \left( \frac{\ln (1 - \text{RH})}{1.67T - 285.655} \right)^{2.491 - 0.012T} + 2.44 \ln (10^{-\text{pH}}) - \frac{14300}{T + 273.15}} \right),$$

(4)

where $T$ is the temperature in $^\circ$C and RH is the relative humidity (here defined as a ratio instead of a percentage). Although equation (4) has been calibrated from measurements performed at the macroscopic, sheet level, the pH level and the ambient temperature and relative humidity in this study are assumed to be uniform across the scales, which allows to use expression (4) for describing the reaction rate of an individual paper fibre. Note further that, different from expression (3), in (4) the reaction rate $k$ is defined in terms of the relative humidity RH instead of the moisture content $m$. The relation between the relative humidity and the moisture content of paper can be determined from moisture sorption experiments at constant temperature, whereby the expression proposed in [51] is used:

$$m = \left( \frac{\ln (1 - \text{RH})}{1.67T - 285.655} \right)^{2.491 - 0.012T}.$$
It is noted that the specific form of equation (5) has been obtained from experiments performed on *fine papers*, which are mostly composed of chemical pulps. In the case of other types of historic paper [52], for which different pulping processes or fillers have been used, alternative expressions for the moisture sorption isotherm may be more suitable.

### 2.2. Hygro-mechanical coupling

The paper fibres are assumed to be characterized by a hygro-elastic, brittle material behaviour, whereby the fibre stresses are limited by a fracture strength that depends on the extent of chemical degradation. Due to the hydrophilic nature of cellulose, the deformation behaviour of paper fibres is rather sensitive to moisture content variations [53, 54]. The constrained moisture-induced deformations of individual fibres in the bonding regions result in a built-up of internal stresses in the fibrous network. In the elastic regime, the development of fibre stresses occurs in accordance with a hygro-mechanical model of which the properties are transversely isotropic with respect to the longitudinal fibre axis, as characterized by the fourth-order compliance tensor $4\mathbf{S}^f$ and the second-order hygro-expansion tensor $\mathbf{\beta}^f$ [55, 56, 57]. Since the fibres are mainly oriented in the in-plane direction of a paper sheet, a two-dimensional plane-stress model is assumed, for which the tensors $4\mathbf{S}^f$ and $\mathbf{\beta}^f$ read

$$
4\mathbf{S}^f = \frac{1}{E_t} \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t - \frac{\nu_{tt}}{E_t} \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t - \frac{1}{E_t} \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t + \frac{1}{G_{tt}} \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t \otimes \mathbf{e}_t ,
$$

$$
\mathbf{\beta}^f = \beta_{\ell} \mathbf{e}_\ell \otimes \mathbf{e}_\ell + \beta_{t} \mathbf{e}_t \otimes \mathbf{e}_t .
$$

Here, $E_\ell$ and $E_t$ respectively are the longitudinal and transverse stiffness moduli, $G_{tt}$ is the in-plane shear modulus and $\nu_{tt}$ is the in-plane Poisson’s ratio, with $\ell$ and $t$ the longitudinal and transverse material axes of the fibre, respectively. The compliance tensor $4\mathbf{S}^f$ can be calculated from the stiffness tensor $4\mathbf{C}^f$ via the usual relation $4\mathbf{S}^f = (4\mathbf{C}^f)^{-1}$. In addition, the hygroscopic response is described through the longitudinal and transverse hygro-expansion coefficients of the fibres, $\beta_{\ell}$ and $\beta_{t}$, respectively. Note that in the constitutive properties (6) the effect by thermal expansions/contractions is ignored, since for paper fibres this contribution typically is considerably smaller than the effect by hygral expansions/contractions [53]. Furthermore, the elastic properties of paper fibres in principle may depend on the moisture content [58, 59]. This aspect, however, is omitted here for simplicity reasons. Instead, in the analyses presented in Sections 4 and 5 the elastic properties are selected in relation to a representative moisture content value experienced during the specific loading process.

The fracture response of paper fibres is considered as brittle, whereby the integrity of the fibre material is lost abruptly once the stress in the material point reaches the fracture strength. It is assumed that the fibre failure criterion describing this effect is isotropic, and that the fracture strength $\sigma_u$ of the fibres depends on the chemical degradation process through the
degree of polymerization (DP) of cellulose, i.e.,

\[ \sigma_u = \sigma_{u,0} \left( 1 - \gamma \left( \frac{\text{DP}_0}{\text{DP}} - 1 \right) \right). \]  

(7)

In this expression, \( \sigma_{u,0} \) represents the initial fracture strength corresponding to the initial degree of polymerization \( \text{DP}_0 \). Note that the strength \( \sigma_u \) vanishes for a specific, minimal value of the degree of polymerization equal to \( \text{DP} = \text{DP}_{\text{min}} = \gamma/(\gamma + 1)\text{DP}_0 \); this expression can be used to calibrate the value of \( \gamma \) from experiments. Relation (7) is formulated in analogy with the experimental relationship established in [14], which refers to the breaking length of paper as a function of DP, as measured from a zero-span tensile test. This analogy is reasonable, since the zero-span breaking length is commonly considered as a measure for the tensile strength of individual paper fibres [16]. It is emphasised that in the present model the fracture criterion at the network scale is solely determined by the time-dependent tensile strength of individual fibres, see equation (7). In other words, the specific strength of the inter-fibre bonds is not considered, since several studies presented in the literature have shown that the loss of the macroscopic tensile strength of paper during aging is controlled by a decrease in fibre tensile strength rather than a decrease in bond strength [12, 16, 17, 60]. Nevertheless, failure in the network typically will occur at inter-fibre bond locations, which is where the constrained moisture-induced deformations of individual fibres lead to the highest values of internal stress.

3. Multi-scale model

3.1. Geometry and modelling assumptions

The multi-scale degradation behaviour of paper can be analysed by determining the time decay of the effective material properties. For this purpose, two length scales are identified, as illustrated in Figure 2. At the macro-scale, which is associated to the characteristic length \( L \), paper is assumed to be a two-dimensional homogeneous domain \( \Omega \) characterized by its effective material properties, see Figure 2(a). At the micro-scale, it is idealized as a fibrous network unit-cell \( Q \) with a characteristic length scale \( L = \eta L \), see Figure 2(b). The macroscopic domain \( \Omega \) is hereby considered as a periodic repetition of fibrous network unit-cells \( Q \). Under the condition of a strong separation of the microscopic and macroscopic length scales, \( \eta \ll 1 \), the field quantities governing the mechanical response of paper (e.g., displacement, strain, stress) can be assumed to vary smoothly at the macro-scale, and may vary rapidly at the micro-scale. The micro-scale field fluctuations are considered to be periodic across the fibrous network unit-cell. In correspondence with these assumptions, the field quantities are dependent on two variables: a slow variable \( \mathbf{X}(X,Y) \) at the macro-scale level and a fast variable \( \mathbf{x}(x,y) \) at the micro-scale level, with \( \mathbf{x} = \mathbf{X}/\eta \).
Figure 2: Multi-scale model of paper. (a) Macroscopic domain $\Omega$ representing a paper sheet, which consists of the periodic repetition of a (b) micro-scale domain $Q$ reflecting a fibrous network.

### 3.1.1. Fibrous network model

The micro-scale unit-cell is based on the network model proposed in [41, 40]. The network unit-cell $Q$ is modelled as a square domain with edges of length $L$. The fibres in the network have a rectangular shape with length $l$ and width $w$, and a rectangular cross-section $wh$, with $h$ the fibre thickness. The network is generated by depositing each individual fibre in the region $Q$, and considering i) a uniform random point field to define the location of the geometrical centre $x_c$ of the fibre, and ii) a uniform orientation distribution function to define the angle $\theta$ between the horizontal, $x-$axis and the longitudinal fibre axis. This approach results in an isotropic distribution of the fibre orientations across the network\(^1\). In order to guarantee periodicity, the fibre parts that at a specific boundary fall outside the square domain $Q$ are placed inside the domain at the opposite boundary. The number of fibres across the paper sheet thickness and their orientations are defined at each material point in the fibre network. The fibres that overlap in a given material point of the network are assumed to be perfectly bonded. The average thickness of the network is quantified via the areal coverage $\bar{c}$, which represents the average number of fibre layers characterizing the fibre network. The coverage $\bar{c}

\(^1\)Note that the proposed network model in principle can incorporate the effect of an anisotropic fibre distribution, for which a wrapped Cauchy probability density function may be used to represent the fibre orientations, see equation (10) in [61]. Since it is expected that the analysis of an isotropic network generally captures the key mechanisms controlling the time-dependent chemo-mechanical degradation of paper, the specific effect of an anisotropic fibre orientation distribution will not be considered in this contribution, and thus remains a topic of future research.
is computed as the ratio between the total area of the fibres and the area of the unit-cell:

$$\bar{c} = \frac{n_f w l}{Q},$$

(8)

where \(n_f\) is the number of fibres in the network.

The constitutive properties of the fibre network model are calculated by departing from the elastic stiffness and hygro-expansion tensors \(4C^f\) and \(\beta^f\) given by equation (6), which provide the material properties of an individual fibre \(i\) oriented along a certain direction \(\theta\) with respect to its local reference system \((\ell, t)\). First, for each fibre \(i\) the tensors \(4C^f\) and \(\beta^f\) are expressed with respect to the global reference system \((x, y)\) by applying a standard coordinate transformation. The transformed tensors are indicated as \(4C^{f(i)}\) and \(\beta^{f(i)}\). Subsequently, for all material points \(x\) within the network the local values of the elasticity tensor \(4C(x)\) and the hygro-expansion tensor \(\beta(x)\) are calculated by identifying the \(n\) fibres passing through a given location \(x\), followed by adding up their individual stiffness contributions and their hygro-expansive contributions, and dividing the result by the local thickness \(nh\), i.e.,

$$4C(x) = \frac{1}{nh} \sum_{i=1}^{n} h \left(4C^{f(i)}\right); \quad \beta(x) = \frac{1}{nh} \left(4C(x)\right)^{-1} : \sum_{i=1}^{n} h \left(4C^{f(i)} : \beta^{f(i)}\right).$$

(9)

The constitutive properties above can be used for computing the stress distribution in the fibrous network, as explained in Section 3.2. Note that, due to the adopted two-dimensional description and the perfect bonding assumed at all fibre contacts, the number of inter-fibre bonds, and thus the level of constraint that the bonds offer to the network, will be somewhat overestimated.

3.2. Asymptotic homogenization and effective hygro-elastic properties

The local displacement, strain and stress fields in the fibrous network and the effective hygro-mechanical properties of paper are computed by following a multi-scale approach that is based on asymptotic homogenization [32]. In case of a strong separation of the macroscopic and the microscopic length scales, asymptotic homogenization enables to describe a heterogeneous medium characterized by rapidly oscillating material properties - i.e., the stiffness and hygro-expansion tensors \(4C(x)\) and \(\beta(x)\) - via the properties of an equivalent homogeneous solid. This is done in accordance with the homogenization strategy presented in [41, 40], as summarized below.

In the absence of body forces, the mechanical equilibrium equation reads

$$\nabla \cdot \sigma = 0,$$

(10)

with \(\sigma\) the Cauchy stress tensor, which is defined by the usual hygro-mechanical constitutive relation

$$\sigma(X) = 4C(x) : (\nabla u - \beta(x) \Delta m(X))$$

(11)
in which the stiffness and hygro-expansion tensors $^4C(x)$ and $\beta(x)$ are given by expression (9), $\nabla u$ is the gradient of the displacement field, and $\Delta m(X)$ is the macroscopic moisture content variation, which is determined from the difference between the current moisture content $m$ and the initial, reference moisture content $m_0$, i.e., $\Delta m = m - m_0$. In the present study, the macroscopic moisture content variation is taken as uniform across the fibrous network unit-cell $Q$. Further, the displacement field $u$ in equation (11) is expressed through an asymptotic expansion in terms of $\eta$, i.e.,

$$ u(X) = u^0(X) + \eta u^1(X, X/\eta) + \eta^2 u^2(X, X/\eta) + \ldots \quad (12) $$

in which $u^0$ represents the global, macro-scale displacement field and the terms $u^1, u^2, \ldots$ characterize the local, micro-scale displacement field.

The effective material response of the equivalent homogeneous medium is retrieved at the fibrous network level through an averaging procedure that departs from inserting the constitutive law (11) in the equilibrium equation (10), followed by substituting the asymptotic expansion of the displacement field (12) in the resulting expression. This leads to the formulation of two sets of mathematical problems, one defined at the micro-scale and one at the macro-scale.

- **Micro-scale problem.** The mathematical problem at the micro-scale focuses on the calculation of the influence functions $^3N^1(x)$ and $b^1(x)$. The influence functions $^3N^1(x)$ and $b^1(x)$ describe the periodic micro-fluctuations of the displacement field of the network in response to variations of the average macroscopic strain and moisture content, respectively. The functions can be calculated as the solutions of so-called cell-problems, which are represented by two boundary value problems for the unit-cell $Q$. The cell-problems only depend on the micro-structural constitutive properties $^4C(x)$ and $\beta(x)$ given by equation (9), and have the form

$$ \nabla \cdot (^4C(x) : (\nabla (^3N^1(x)) + ^4I^S)) = ^30, $$

$$ \nabla \cdot (^4C(x) : (\nabla b^1(x) - \beta(x))) = 0. \quad (13) $$

Here, $^4I^S$ is the fourth-order symmetric identity tensor, with components $I^S_{ijkl} = (\delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})/2$, where $\delta_{ij}$ is the Kronecker delta symbol. Equations (13) are completed by periodic boundary conditions on the (unknown) influence functions $^3N^1(x)$ and $b^1(x)$, which require that the values assumed by each influence function at corresponding points on opposite boundaries (left and right, top and bottom) remain constant during the simulation. Further, for the uniqueness of the solution, the influence functions are prescribed to vanish on average across the unit-cell.

The cell-problems in equation (13) are solved for a given network geometry by means of a finite element simulation. Subsequently, the computed influence functions $^3N^1(x)$ and $b^1(x)$ are used to construct the local stress and strain fields in the fibrous network. For this purpose, the local displacement field $u^1$ in expression (12) is written as a superposition of a macroscopic contribution $u^0$, defined in relation (12), and a microscopic $v^1(x)$
contribution, i.e.,
\[
\mathbf{u}^1(\mathbf{x}) = \mathbf{u}^0 + \mathbf{v}^1(\mathbf{x}) = \mathbf{u}^0 + 3\mathbf{N}^1(\mathbf{x}) : \nabla \mathbf{u}^0 + \mathbf{b}^1(\mathbf{x}) \Delta m ,
\] (14)
where, for notational convenience, the explicit dependency of \( \mathbf{u}^0 \) and \( \Delta m \) on the slow variable \( \mathbf{X} \) has been dropped. Note from expression (14) that the microscopic displacement \( \mathbf{v}^1 \) is obtained as the sum of two contributions, which are related to the mechanical influence function \( 3\mathbf{N}^1(\mathbf{x}) \) and the hygroscopic influence function \( \mathbf{b}^1(\mathbf{x}) \).

Consider now the loading case that is relevant for historical paper, whereby a fibrous network with zero average stress can freely expand and is subjected to a macroscopic moisture content variation \( \Delta m \). The macroscopic strain generated under this hygroscopic condition equals \( \bar{\varepsilon}^0 = \nabla \mathbf{u}^0 = \bar{\beta} \Delta m \), where \( \bar{\beta} \) is the effective hygro-expansion coefficient that is computed from the influence function \( \mathbf{b}^1(\mathbf{x}) \), as will be explained in more detail below when treating the Macro-scale problem. The local, microscopic strain \( \varepsilon(\mathbf{x}) \) can be obtained by taking the gradient of relation (14), and combining the result with the expression for the macroscopic strain \( \bar{\varepsilon}^0 \) given above, which leads to
\[
\varepsilon(\mathbf{x}) = \nabla \left[ \mathbf{u}^0 + \mathbf{v}^1(\mathbf{x}) \right] = \left( \bar{\beta} + \nabla(3\mathbf{N}^1(\mathbf{x})) : \bar{\beta} + \nabla \mathbf{b}^1(\mathbf{x}) \right) \Delta m .
\] (15)

The stress field \( \mathbf{\sigma}(\mathbf{x}) \) in the fibrous network can now be calculated by inserting equation (15) in the hygro-mechanical constitutive relation
\[
\mathbf{\sigma}(\mathbf{x}) = \mathbf{4C}(\mathbf{x}) : (\varepsilon(\mathbf{x}) - \beta(\mathbf{x}) \Delta m) ,
\] (16)
with the elastic stiffness tensor \( \mathbf{4C}(\mathbf{x}) \) and the hygro-expansion tensor \( \beta(\mathbf{x}) \) following from equation (9). The stress \( \mathbf{\sigma}(\mathbf{x}) \) can be interpreted as a moisture-induced self-stress, which depends on the moisture difference \( \Delta m \) between the actual moisture content \( m \) during display/storage and the initial, reference moisture content \( m_0 \). In accordance with the local stiffness and hygro-expansion tensors given in equation (9), \( \mathbf{\sigma}(\mathbf{x}) \) reflects the average stress across the thickness \( nh \) at location \( \mathbf{x} \) of the fibrous network. The local, maximum principal stress computed from \( \mathbf{\sigma}(\mathbf{x}) \) will be compared against the time-dependent tensile strength \( \sigma_u \) of the fibres, as defined by equation (7), in order to determine whether brittle fracture occurs or not.

- **Macro-scale problem.** The second mathematical problem describes the average response of the fibrous network via the effective properties representative of an equivalent homogeneous domain at the macro-scale. The effective properties are specified via the effective stiffness tensor \( \bar{\mathbf{4C}} \) and hygro-expansion tensor \( \bar{\beta} \), in accordance with the expressions
\[
\bar{\mathbf{4C}} = \frac{1}{|Q|} \int_Q \mathbf{4C}(\mathbf{x}) : (\nabla(\mathbf{3N}^1(\mathbf{x}))) + \mathbf{4I}^3 dQ ,
\]
\[
\bar{\beta} = \frac{1}{|Q|} \mathbf{4C}^{-1} : \int_Q \mathbf{4C}(\mathbf{x}) : (\beta(\mathbf{x}) - \nabla \mathbf{b}^1(\mathbf{x})) dQ ,
\] (17)
where the influence functions \( \mathbf{3N}^1(\mathbf{x}) \) and \( \mathbf{b}^1(\mathbf{x}) \) follow from the solutions of the two cell-problems in equation (13). The effective properties \( \bar{\mathbf{4C}} \) and \( \bar{\beta} \) are evaluated at subsequent
time increments in order to predict the time-dependent degradation response of paper, as described in Section 4.1 below.

4. Numerical simulations

4.1. Incremental solution procedure of the multi-scale and multi-physics problem

The combined multi-scale and multi-physics model for the simulation of degradation of historical paper has been implemented in an in-house software program formulated within a finite element method framework and developed in MATLAB. The key elements of the modelling approach are the chemo-mechanical degradation response of individual paper fibres presented in Section 2 and the multi-scale approach described in Section 3. In the numerical solution procedure, the chemical problem is one-way coupled with the mechanical analysis. That is, the time course of the degree of polymerization is computed first, which depends on the specific temperature, relative humidity and acidity conditions (uniformly) imposed on the fibrous network. Subsequently, from the degree of polymerization, the evolution of the fibre tensile strength is calculated, which is used as input for the mechanical analysis. The incremental update scheme is schematically presented in Table 1.

The solution procedure presented in Table 1 departs from the generation of the fibrous network unit-cell, whereby each fibre is modelled as a two-dimensional, rectangular object. The generation of an adequate finite element mesh for a fibrous network geometry is a challenging task, especially at the inter-fibre bonding regions where two or more fibres with different orientations have an overlap that needs to be consistently transferred to the local mesh densities of the individual fibres. For this purpose, a relatively simple but robust meshing strategy is adopted, which is based on discretizing the domain by a regular grid of \( n_e \) square finite elements with an edge length \( l_e = w/\zeta \), where \( \zeta \geq 1 \) is an integer. In accordance with equation (9), the stiffness of a specific finite element is determined from the contributions of all the fibres that pass through the geometrical centre of that finite element. Figure 3(a) presents an example of a fibrous network with a coverage \( \bar{c} = 1 \), whereby the fibres have an aspect ratio \( l/w = 50 \). The choice of \( \bar{c} = 1 \) has been made here for clarity reasons, as it allows to explicitly indicate how individual fibres within a layer are distributed and oriented across the fibrous network. Note that this choice is not representative for a real, thicker paper micro-structure composed of multiple fibre layers, e.g., the historic paper with \( \bar{c} = 5 \) analysed in Section 5. A representative detail of the finite element mesh is shown in Figure 3(b). The average number of finite elements across the width of a fibre is hereby selected in accordance with \( \zeta = 5 \), for which it is observed that the irregularities from the serrated fibre boundaries resulting from the regular mesh remain acceptably small.

At the onset of the simulation, the input parameters necessary for performing the numerical analysis are assigned to the network model, which are the initial chemical properties (the
initial degree of polymerization DP₀, and the acidity pH) and the mechanical properties of the paper fibres (elastic moduli Eᵋ, Eᵋ, shear modulus Gᵋᵋ, Poisson’s ratio νᵋᵋ, hygro-expansion coefficients βᵋ, βᵋ, initial fracture strength σᵋ₀, fracture strength coefficient γ). The mechanical model is completed through the application of periodic boundary conditions on the micro-scale fibrous network. Next, the environmental conditions experienced by the paper sheet during the time of display (or storage) are prescribed in terms of the temperature T and the relative humidity RH, and their initial, reference values T₀ and RH₀, which, via equation (5), provide the actual moisture content m in the fibrous network and its initial value m₀. The environmental conditions define the reaction rate k of the chemical degradation process of paper via relation (4), which allows to compute the time-dependent degree of polymerization of the fibrous network through equation (1), and the corresponding degradation of the tensile strength via relation (7).

Adopting an incremental time-stepping procedure for the mechanical analysis, at each specific time increment t_j the influence functions ³N¹(x) and b¹(x) of the fibrous network geometry are calculated from relations (13)₁ and (13)₂, respectively. Subsequently, the effective mechanical stiffness ⁴C and the hygro-expansion coefficient asurer are computed via, respectively, expressions (17)₁ and (17)₂. The strain field ε(x) and stress field σ(x) in the fibrous network are successively obtained from expressions (15) and (16), respectively. From the stress σ computed in the integration points of a finite element, the corresponding maximum principal stress values σ_I are calculated, and subsequently averaged over the element. The element-averaged maximum principal stress eration is compared with the current value of the fibre tensile strength σ_u(t_j). If this maximum principal stress has reached or (slightly) exceeded the fibre strength, ervation ≥ σ_u(t_j), the corresponding finite element is considered to be fully damaged and

Figure 3: Example of a micro-scale unit-cell. (a) Fibrous network configuration with a coverage ̄c = 1, characterized by fibres with an aspect ratio l/w = 50. The red box designates the part presented in detail in Figure 3(b). (b) Detail of the finite element discretization, whereby an average of 5 finite elements along the fibre width has been applied.
1. **Initialization procedure.**
   1.1. Generate the discretized fibrous network unit-cell.
   1.2. Assign the initial chemical properties of the paper fibres (DP₀, pH).
   1.3. Assign the mechanical material parameters of the paper fibres (Eₜ, Eₜ, Gₜ, νₜ, βₜ, βₜ, σᵤ₀, γ).
   1.4. Prescribe the environmental conditions (RH, T) during display/storage of the paper, together with the reference values (RH₀, T₀). Calculate the value of the moisture content \( m \) and the reference moisture content \( m₀ \) in the fibrous network as a function of RH and T by using relation (5). Obtain \( Δm = m - m₀ \).
   1.5. Prescribe mechanical periodic boundary conditions for the unit-cell.

2. **Chemical analysis.**
   2.1. Compute the value of the reaction rate \( k \) as a function of the environmental conditions (RH, T) and the pH of the paper, by using relation (4).
   2.2. Use equation (1) to compute the time-dependent degree of polymerization DP.
   2.3. Calculate the time evolution of the fibre tensile strength \( σᵤ(t) \) by means of expression (7), and transfer the result to the mechanical analysis.

3. **Mechanical analysis.** Incremental time-stepping procedure at time increment \( t = t_j \).
   3.1. Solve the unit-cell problems (13)₁ and (13)₂ to obtain the influence functions \( ³N₁(x) \) and \( ³b₁(x) \).
   3.2. Calculate the effective properties \( ⁴C \) and \( ³B \) of the fibrous network geometry by means of expressions (17)₁ and (17)₂.
   3.3. Calculate the strain \( ε(x) \) at each integration point of the fibrous network using relation (15). Use the computed strain to determine the corresponding stress \( σ(x) \) in accordance with expression (16).
   3.4. Use \( σ(x) \) to compute the maximum principal stress \( σ_I(x) \). Calculate the element-averaged maximum principal stress \( ³σ_I \). Compare this stress value with the value of the tensile strength \( σ_u(t) \) evaluated at the actual time step \( t_j \). If \( ³σ_I ≥ σ_u(t_j) \), then remove the corresponding finite element from the discretized fibrous network model.
   3.5. Update the discretized network geometry by accounting for the removed, damaged elements, and use the result in the next time increment of the mechanical analysis. Go to 3., and repeat the mechanical analysis for the next time increment \( t_{j+1} \), until the simulated degradation process has finished.

Table 1: Schematic representation of the one-way coupled, incremental time-stepping procedure used for modelling the time-dependent degradation of paper.

thus removed from the fibrous network geometry. Subsequently, the finite element mesh of the fibrous network is consistently updated, after which the mechanical analysis is repeated for the next time increment \( t_{j+1} \). The incremental time-stepping procedure continues until the fibrous network has lost its structural integrity and the degradation of the paper sheet is complete.
4.2. Input parameters

The geometrical parameters and chemical and mechanical properties adopted for the fibrous network model have been taken from the literature, and are summarised in Table 2. A network of pure cellulose fibres with a uniform fibre orientation distribution has been considered, for which the geometry of the fibres is defined by the width \( w \) and the average length \( l \). The width \( w \) has been selected as \( w = 35 \mu m \) [62], from which the average fibre length \( l \) has been calculated by adopting a representative aspect ratio \( l/w = 50 \) [53], leading to \( l = 1.75 \text{ mm} \). Since the local constitutive properties in the fibrous network depend on the ratio between the fibre thickness \( h \) and the local fibrous network thickness \( n_h \), see relations (9), the fibre thickness \( h \) does not influence the computational result and therefore does not need to be defined. The coverage has been taken as \( \bar{\kappa} = 5 \), which is a representative value for paper sheets [53]. The size \( L \) of the micro-scale unit-cell has been determined from a convergence study of the effective material properties computed as the statistical average of 5 different micro-structural realizations. In this way, it can be assured that the unit-cell incorporates sufficient micro-structural information in order to be considered as statistically representative of a real, arbitrary micro-scale domain [41, 63]. The minimum size of a representative cell hereby corresponds to the ratio between the size of the unit-cell \( L \) and the fibre length \( l \) at which the effective hygro-mechanical properties have reached constant values within a certain tolerance, which, from a previous study, appears to be the case for \( L = 2l = 3.5 \text{ mm} \) [40].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometrical parameters</td>
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<tr>
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<td>( \mu m )</td>
</tr>
<tr>
<td>Average fibre length</td>
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<td>( \text{mm} )</td>
</tr>
<tr>
<td>Unit-cell edge ( L )</td>
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<td>( \text{mm} )</td>
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<td>Coverage ( \bar{\kappa} )</td>
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<td>-</td>
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<tr>
<td>Chemical parameters</td>
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<td></td>
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<td>-</td>
</tr>
<tr>
<td>Acidity pH</td>
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<td>-</td>
</tr>
<tr>
<td>Mechanical parameters</td>
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<td></td>
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<td>GPa</td>
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<td>Transverse elastic modulus ( E_t )</td>
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<tr>
<td>Shear modulus ( G_{\ell t} )</td>
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<tr>
<td>Poisson’s ratio ( \nu_{\ell t} )</td>
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<tr>
<td>Longitudinal hygro-expansive coefficient ( \beta_\ell )</td>
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<td>-</td>
</tr>
<tr>
<td>Transverse hygro-expansive coefficient ( \beta_t )</td>
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<td>-</td>
</tr>
<tr>
<td>Initial fibre tensile strength ( \sigma_{u,0} )</td>
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<td>GPa</td>
</tr>
<tr>
<td>Tensile strength coefficient ( \gamma )</td>
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<td>-</td>
</tr>
</tbody>
</table>

Table 2: Geometrical and material parameters used in the reference simulation of historic paper.
The finite elements used for meshing the unit-cell are square-shaped bilinear quadrilaterals equipped with a four-point Gauss quadrature. The element size equals $l_e = w/\zeta = w/5 = 7 \ \mu m$, resulting in a regular grid of $500 \times 500$ elements. Further, the total time of the simulated degradation process is discretized into 50 equal time increments. Additional simulations not presented here have confirmed that these spatial and time discretizations are sufficiently fine for reaching mesh- and time step size-independent computational results within a small, predefined tolerance.

The initial degree of polymerization of cellulose has been selected as $DP_0 = 2366$ [14]. The acidity of the paper has been set equal to $pH=6$, which is a typical value for acidic paper dated from the 19th century [1, 64]. The longitudinal elastic modulus has been chosen as $E_\ell = 35 \ GPa$ [65] and the transverse elastic modulus and the shear modulus are chosen in correspondence with the ratios $E_\ell/E_t = 6$ and $E_\ell/G_{\ell t} = 10$ [66, 55], leading to $E_\ell = 5.8 \ GPa$ and $G_{\ell t} = 3.5 \ GPa$. The Poisson’s ratio of the fibre is $\nu_{\ell t} = 0.3$. [66]. The hygro-expansive coefficients in the longitudinal and transverse directions are equal to $\beta_\ell = 0.013$ and $\beta_t = 20 \beta_\ell = 0.26$ [53]. Finally, from tensile experiments on cellulose fibres as reported in [67], the initial fibre tensile strength is determined as $\sigma_{\ell 0} = 0.8 \ GPa$. The evolution of the fibre tensile strength with the degree of polymerization is calibrated with equation (7) from the experimental results reported in [14], leading to a tensile strength coefficient of $\gamma = 0.0524$.

The values of the environmental boundary conditions at which the paper artifacts are displayed/stored have been chosen according to common climate specifications in museums, libraries and collections as $T = 20^\circ C$ and RH = 50% [68, 69]. The initial, reference value of the relative humidity $RH_0$, with respect to which the self-stresses are built up, relates to a water content that is characteristic for a production process of paper, whereby dry pulp is dispersed into water to form a slush [70]. Accordingly, it may be assumed that $RH_0 = 100\%$. As already mentioned, the thermal strains in paper typically are negligible compared to the hygral strains [53]; hence, the reference value of the temperature $T_0$ only enters the model for determining the reference value of the moisture content $m_0$ with equation (5), and for simplicity is set equal to the temperature at storage/display conditions, $T_0 = T = 20^\circ C$. Section 5.1 below starts with considering the results of a *reference simulation* that is based on the set of parameters listed in Table 2 and the climate boundary conditions mentioned above. Subsequently, the influence of the temperature, relative humidity and acidity of the paper on the degradation process is investigated through a parameter variation study as presented in Section 5.2.

5. Numerical results

5.1. Reference simulation

The numerical results of the *reference simulation* illustrate the effect of chemical degradation on the effective hygro-mechanical properties of paper characterized by the geometrical and material parameter values listed in Table 2, and stored under controlled climate conditions with a relative humidity $RH = 50\%$ and a temperature $T = 20^\circ$. The corresponding value of
Figure 4: Time-dependent degradation of paper with a pH = 6, displayed/stored at a temperature T = 20°C and a relative humidity RH = 50%. (a) Evolution of the degree of polymerization DP as a function of time $t$ (years). (b) Evolution of the fibre tensile strength $\sigma_u$ (GPa) as a function of degree of polymerization DP.

the reaction rate $k$ of the depolymerization process follows from relation (4), and is equal to $3.74 \cdot 10^{-6}$ year$^{-1}$.

As discussed in Section 4.1, the evolutions of the degree of polymerization and the tensile strength are considered to be equal for all the fibres in the network, and are computed from equations (1) and (7), respectively. Figure 4(a) shows the evolution of the degree of polymerization of the cellulose fibres, which departs from the initial value $DP_0 = 2366$ and progressively decreases as a function of time. Figure 4(b) illustrates that the process of depolymerization of cellulose causes a decrease in the fibre tensile strength, whereby at a minimum value of $DP_{min} = 118$ the tensile strength vanishes. Initially, the reduction in tensile strength under a decreasing degree of polymerization takes place at a relatively low rate, but becomes substantial when the degree of polymerization drops below a value of 600. This behaviour can be explained from the fact that the tensile strength of cellulose fibres is affected by both the degree of crystallinity and the reduction in molecular weight [4]. During the initial stage of degradation, the tensile strength is mostly governed by the degree of crystallinity of cellulose, which initially increases. Hence, despite that the molecular weight is reducing, the decrease in strength is only mild. Conversely, at a later stage of degradation the reduction of the molecular weight becomes the dominating factor in the process, as a result of which the tensile strength rapidly reduces to zero. This behaviour is supported by the experimental observations presented in [14], on which equation (7) is based. In accordance with the trends depicted in Figure 4 and equations (1) and (7), it follows that the tensile strength $\sigma_u$ of the fibres reduces linearly with time $t$.

The evolutions of DP and $\sigma_u$ depicted in Figure 4 are used as input for the incremental solution procedure of the mechanical problem, see Table 3. The mechanical analysis provides i) the
time-dependent stress and strain fields in the fibrous network, and ii) the time-dependent effective hygro-mechanical properties of the historic paper, as computed from the averaged response of 5 different realizations of the fibrous network. Figure 5 illustrates the degradation process of one of the 5 fibrous network realizations analysed, by considering the element-averaged maximum principal stress $\bar{\sigma}_I$ at 4 different time instants, namely $t = [0, 500, 1000, 1920]$ years. The initial stress distribution in the fibrous network at $t = 0$, as presented in Figure 5(a), results from the hygral strain profile induced by the difference between the moisture content $m$ under the actual display/storage conditions and the initial, reference moisture content $m_0$. Note that the fibrous network is considered to be undamaged at the onset of the simulation. The small white spots that are visible in Figure 5(a) result from the random network generation procedure. Specifically, the number of fibres that is locally superimposed across the thickness on average is equal to the coverage $\bar{c} (= 5)$; however, due to the randomness of the generation process, the fibers may not necessarily cover the entire area of the unit-cell. Further, the light green lines denote the stress trajectories for which the value lies relatively close to the initial fibre tensile strength of 800 MPa. The removal of damaged elements in which the element-averaged maximum principal stress at some stage has reached the decreasing fibre tensile strength modifies the structural geometry of the unit-cell, as illustrated by the increasing number of micro-scale defects (visible as small white spots) in the fibrous network, see Figures 5(b) and (c). The damage distribution develops more or less uniformly across the unit-cell, and leads to a redistribution of the local stresses. After approximately 2000 years the damage is maximal, and the integrity of the fibrous network is completely lost, see Figure 5(d).

The progressive degradation of the fibrous network can be quantified by the effective elastic stiffness tensor $\bar{\bm{C}}$ and the effective hygroscopic expansion tensor $\bar{\bm{\beta}}$, which are calculated in accordance with expressions (17)_1 and (17)_2. Figures 6(a) and (b) illustrate the effective stiffness component $\bar{C}_{xxxx}$ and the effective hygro-expansion coefficient $\bar{\beta}_{xx}$ in the $x-$direction as a function of time. Due to the isotropic fibre distribution, these effective properties are similar to those in the $y-$direction. Since the other components of the stiffness tensor and hygroscopic expansion tensor show the same time-dependent behaviour as $\bar{C}_{xxxx}$ and $\bar{\beta}_{xx}$, they are not depicted here. The symbols in Figure 6 designate the values computed for the 5 individual micro-structural realizations, and the continuous black line represents the best fit of the average trend calculated for these micro-structural realizations. It can be observed that the effective stiffness and the effective hygro-expansion of the paper artifact monotonically decrease as a function of time. Initially the stiffness degradation occurs at a relatively low rate, but grows substantially when the paper becomes older than 1000 years. Consequently, the stiffness of the paper is completely lost at about 1940 years. The hygro-expansion coefficient, which degrades at a lower rate, at this stage still has a finite value. This can be explained from the fact that the numerous damaged fibre parts that characterize the end of the lifetime of the fibrous network are no longer able to transfer stresses (i.e., the elastic deformation has become zero), but do experience some hygral deformation.

From the computational results of the individual network realizations it appears that abrupt jumps occur in the values of the effective material properties. These jumps reflect a situation...
Figure 5: Time-dependent degradation of paper with a pH = 6, displayed/stored at a temperature $T = 20^\circ C$ and a relative humidity $RH = 50\%$. The damage developing in the fibrous network is represented by the emergence of micro-scale defects (visible as small white spots), as determined from the reference simulation at 4 different time instants: (a) $t = 0$ years; (b) $t = 500$ years; (c) $t = 1000$ years; (d) $t = 1920$ years. The displayed contour plot variable is the element-averaged maximum principal stress $\bar{\sigma}_I^e$ (MPa).

in which in a large part of the micro-structural realization the local stresses reach the tensile strength more or less simultaneously, leading to the instantaneous removal of a substantial number of finite elements in accordance with the brittle damage assumption. The time instants at which such jumps occur are different for each of the micro-scale realizations, since these obviously depend on the individual geometrical and morphological features of the fibrous network. Nevertheless, the global trend and spread of the computed values turn out to be similar for the 5 unit-cells considered, which confirms that the micro-scale realizations are statistically comparable, and representative of a real, arbitrary fibrous micro-structure.
5.2. Variation study on display/storage conditions and acidity of paper

The influence of the display/storage conditions and the acidity of the paper on its time-dependent degradation behaviour is explored by means of a parameter variation study. For this purpose, the values of the temperature $T$ and relative humidity $RH$ are varied over specific ranges that are representative of the climate conditions in museums, libraries or archives. The influence of the acidity on the chemo-mechanical degradation process is explored by considering a range of pH values representative of historic paper. The remaining parameters are the same as those of the reference simulation as listed in Table 2. The computational results are presented by means of the average response calculated from 5 micro-structural realizations.

5.2.1. Effect of display/storage conditions on paper degradation

The influence of the relative humidity on the stiffness degradation of historic paper is analysed by selecting three different values of RH, namely $RH = [30\%, 50\%, 70\%]$, whereby $RH = 50\%$ relates to the reference simulation discussed in Section 5.1. From Figure 7(a) it is observed that the stiffness generally deteriorates faster for a larger value of the relative humidity. In particular, for the highest value of $RH = 70\%$ the lifetime of the paper is approximately 4 times shorter than for the lowest relative humidity of $RH = 30\%$. This trend is caused by the fact that a higher relative humidity results in a larger chemical reaction rate $k$, see equation...
The effect of temperature on the degradation of paper is investigated by considering three different values for the display/storage temperature, namely $T = [10^\circ C, 20^\circ C, 30^\circ C]$. Note that the reference simulation refers to a temperature of $T = 20^\circ C$. Figure 7(b) reveals that a higher temperature substantially accelerates the degradation of the stiffness. Specifically, a paper stored at a temperature $T = 30^\circ C$ looses its structural integrity in less than 500 years, whereas at lower temperatures of $T = 20^\circ C$ and $10^\circ C$ this happens after approximately 2000 years and 8300 years, respectively. Similar to the effect of RH, this behaviour is due to the dependency of the chemical reaction rate $k$ on the temperature, as described by equation (4). The results presented in Figure 7 show that the ambient temperature has a larger impact on the degradation of historical paper than the relative humidity, which is in agreement with findings from other studies [26, 27, 24].

It is noted that for the effective hygroscopic expansion $\beta$ similar dependencies on the relative humidity and temperature are found as depicted in Figure 7 for the effective stiffness $\bar{C}_{xxxx}$. However, since the effective hygroscopic expansion from a practical viewpoint is less relevant for assessing the degradation behaviour of historic paper than the effective stiffness, these results are omitted here.

![Graphs showing the effect of temperature and RH on stiffness degradation](image)

Figure 7: Parameter variation study regarding the influence of the storage/display conditions on the time-dependent degradation behaviour of paper. Stiffness component $\bar{C}_{xxxx}$ (GPa) as a function of time $t$ (years) for: (a) three different values of the ambient relative humidity, RH = [30%, 50%, 70%], and (b) three different values of the ambient temperature, $T = [10^\circ C, 20^\circ C, 30^\circ C]$. The black line refers to the reference simulation.
5.2.2. Effect of acidity on paper degradation

The influence of the acidity of the paper on the degradation of its effective stiffness $\bar{C}_{xxxx}$ is illustrated in Figure 8 by selecting three different pH values, namely pH = [5, 6, 7], whereby a pH = 6 corresponds to the reference simulation presented in Section 5.1. The stiffness degradation takes place faster for a more acidic paper, i.e., for a lower pH value. This observation confirms that deacidification of paper, as, for example, discussed in [3], may be an effective technique for increasing the lifespan of paper artifacts.

6. Isochrone degradation maps and degradation function

6.1. Isochrone degradation maps

The model developed can be used as a tool for determining the lifetime of historical paper and its susceptibility to time-dependent degradation under indoor climate conditions typically maintained in museums, archives and libraries. The lifetime of historic paper can be defined as the expected time at which the artifact reaches a threshold state whereby it becomes unfit for use or display. There are several criteria to quantify this “fitness threshold”, which may be based on changes in mechanical, physical, chemical, and visual properties [1]. For example, it may correspond to the loss of a large piece of paper with text from a document [26]. The fitness threshold can be established either by specifying an absolute limit for a specific property, or by considering the change (typically, a reduction) relative to its value at the initial state. In the literature, the degree of polymerization regularly is identified as a representative measure of the fitness condition of paper [24]. A degree of polymerization in the range of 150-300 commonly
Figure 9: Isochrone degradation map illustrating the life-expectancy of a *low-quality acidic paper* characterized by a pH of 5 and an initial degree of polymerization DP$_0$ of 600, as obtained from (a) the multi-scale degradation model proposed in the present work, and (b) the damage function proposed in [24].

is associated to a significant loss of the mechanical strength of paper, such that it is considered to be no longer suitable for usage/display.

Since the interplay between the chemical and mechanical processes contributing to historic paper degradation are consistently accounted for in the present model, the fitness threshold can be based here on a mechanical property rather than a chemical property. In particular, the normal stiffness component $C_{xxxx}$ is selected for measuring the fitness condition of paper, whereby a stiffness loss of 20% compared to the initial value is taken as the threshold. For the numerical results presented in Section 5.1 this threshold is reached when the degree of polymerization is approximately equal to 300, which corresponds to the value of the chemical fitness threshold adopted in [1].

Figures 9, 10 and 11 illustrate the isochrone maps that have been constructed for three types of paper present in archives and libraries, namely low-quality acidic paper from the first half of the 19th century, rag paper, and contemporary printing paper using calcium carbonate filler [24]. For the low-quality acidic paper, a pH equal to 5 and an initial degree of polymerization DP$_0$ of 600 have been assumed. For rag paper, a pH of 7 and a DP$_0$ of 1500 have been selected. The contemporary printing paper is characterized by a pH of 8 and a DP$_0$ of 2000. For each paper type, a set of numerical analyses has been performed for different combinations of the display/storage environmental conditions (RH, T), whereby the relative humidity and the temperature have been selected within the ranges [20-80%] and [5-40°C], respectively. The times corresponding to the fitness threshold of the specific paper have been read off from the simulation results and depicted in an RH-T diagram, which, after connecting the points with the same time threshold, results in the isochrone degradation maps presented in Figures 9(a), 10(a)
and 11(a). It can be observed from these figures that the low-quality acidic paper appears to be most fragile and prone to deterioration, followed by the rag paper and the contemporary printing paper. For comparison, Figures 9(b), 10(b) and 11(b) illustrate the isochrone degradation maps constructed from the damage function for historic paper proposed in [24]. This damage function is based on a purely chemical model formulated at the macroscopic scale, which departs from similar modelling assumptions as those considered in the present work. In particular, in [24] the time evolution of the degree of polymerization is assumed to be governed by Ekenstam’s equation (1), with the chemical rate parameter $k$ defined by equation (4). Further, the fitness threshold is set to correspond to a degree of polymerization of 300, which, as mentioned above, is more or less comparable to the 20% stiffness reduction criterion adopted for the present numerical degradation model. Consequently, the isochrone maps constructed from the two methodologies are comparable for the three types of paper, and lead to a similar lifetime prediction.

6.2. Degradation function

In order to allow the results of the model to be used by conservators, librarians, and archivists, besides the isochrone maps presented in Figures 9, 10 and 11, a closed-form expression describing the age-dependent stiffness of paper is derived as a function of the temperature, relative humidity, and acidity. This expression is established using the results of 224 numerical simulations for papers with different acidity (pH = 4, 5, 7, 8) and displayed/stored at relative humidity and temperature values varying within the ranges [20-80\%] and [5-40°C], respectively.
The closed-form expression, which matches the numerical results with an accuracy $R^2 = 0.96$, has the following polynomial form

$$\bar{C}(t) = \bar{C}_0 \left( -1.688 \cdot 10^6 (kt)^3 - 5.6205 \cdot 10^3 (kt)^2 + 0.0269 kt + 1 \right), \quad (18)$$

where $\bar{C}_0$ is the initial effective stiffness at $t = 0$ and $k$ is the chemical reaction rate that depends on temperature, relative humidity and acidity via expression (4). Note that, in principle, $\bar{C}_0$ is unknown, and should be computed with the present multi-scale methodology. However, since the selected fitness threshold is based on the loss of stiffness relative to its initial value, the specific value of $\bar{C}_0$ is not needed to predict the lifetime of the paper artifact.

7. Conclusions

This work presents a novel multi-scale and multi-physics computational framework for the prediction of the time-dependent degradation of historic paper. The multi-scale description models paper as a periodic arrangement of fibrous network unit-cells that are generated by random deposition of cellulose-based fibres. The degradation of cellulose fibres is monitored via the time-dependent degree of polymerization, which is a function of the ambient climate conditions and the degree of acidity of the paper. The fibre stresses induced by hygro-expansion/contraction under a change in relative humidity are determined using a coupled hygro-mechanical model. The fracture response of the fibres is brittle, i.e., the integrity of the fibre material point is lost instantaneously once the local stress reaches the fracture strength.
The fracture strength of the fibres depends on the degree of polymerization and thus reduces in time, as a result of which the micro-scale defects induced in the fibrous network geometry continue to grow. Asymptotic homogenization is used to compute the consequent reduction in the effective properties of the fibrous network. A set of numerical simulations is performed that predicts the time-dependent degradation of historic paper under different temperature and relative humidity conditions, thereby revealing the influence of chemical degradation of cellulose and local fibre damage. In agreement with other studies presented in the literature, the temperature appears to be the most critical factor for paper degradation. Isochrone degradation maps are constructed from the numerical results, which illustrate the expected lifetime of paper artifacts of different acidity as a function of the ambient climate conditions. These maps turn out to be in good agreement with those obtained from a macroscopic damage model presented in the literature. Finally, a closed-form degradation function is derived from the numerical results, which provides the time-dependent decay of the mechanical stiffness of paper as a function of temperature, relative humidity and acidity. Together with the isochrone degradation maps, this expression may serve as a practical tool for conservators to predict the susceptibility to time-dependent degradation and the expected lifetime of historical paper artifacts under indoor climate conditions typically maintained in museums, archives and libraries.

In order to further reveal and quantify the multi-scale, time-dependent degradation behaviour of historical paper, future research will focus on the calibration and validation of the present multi-scale model, using detailed experimental results obtained at different scales of observation (individual fibre, fibrous network, paper sheet).

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References


