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## A model for the prediction of stone deterioration in historical buildings

TESI DI LAUREA

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## Abstract

In questo lavoro di tesi si è focalizzata l'attenzione sulle principali cause di degrado dei materiali porosi.

L'umidità relativa e le variazioni di temperatura, connesse con i cicli stagionali e giornalieri, concorrono, insieme all'aggressione dovuta agli agenti inquinanti, all'indebolimento strutturale e all'alterazione fisico-chimica del materiale. Questi effetti sono comunemente noti, e nel presente lavoro si è proposto un modello fisico-matematico basato su un approccio diffusivo, con il quale si cerca di descrivere la compartecipazione di tali effetti.

L'accento è stato posto sui principali meccanismi di trasporto dell'acqua, in forma di flusso di vapore e di flusso capillare. Anche gli effetti termici sono stati descritti in termini diffusivi, tenendo in conto anche il calore associato alle transizioni di fase che l'acqua, all'interno dei pori, può subire. Effetto, quest'ultimo di natura locale. Gli effetti di bordo come l'irraggiamento solare e l'acqua piovana sono stati trattati come condizioni al contorno. Infine, un'impostazione diffusiva è stata utilizzata anche per descrivere l'aggressione del diossido di zolfo sul carbonato di calcio: equazioni differenziali sono state impiegate per descrivere la variazione della concentrazione del solfato e del carbonato i quali, reagendo, danno luogo a croste di gesso. Queste, oltre che a creare anti-estetiche patine, possono portare a catastrofiche conseguenze come il distacco di parti del materiale.

La tesi propone una, primordiale in questa fase, base teorica per un futuro approccio numerico, con il quale combinare i modelli iterativi già esistenti sul trasporto di umidità-calore e l'approccio diffusivo per il trasporto delle sostanze inquinanti. L'obbiettivo futuro è quello di avere un modello teorico il più completo e dettagliato possibile, sul quale strutturare un modello numerico che servirà a simulare su lunghe scale temporali, gli effetti di deterioramento veicolati da umidità relativa, effetti di calore e agenti inquinanti, ed eventualmente da altre cause che potrebbero essere individuate.

L'interesse rivolto a questo tipo di analisi risiede nel fatto che i materiali porosi sono stati ampiamente utilizzati nel campo dei beni storico-culturali, come palazzi nobiliari e chiese, così come monumenti e statue. E' evidente quindi l'iportanza di avere un modello che consenta di simulare e prevedere i meccanismi di deterioramento di tali beni, il quale potrebbe quindi, diventare una importante arma in mano a restauratori e storici.

A Mamma e Papà..

A zia Susy...

...non c'è montagna più alta di quella che non scalerò, non c'è scommessa più persa di quella che non giocherò.. (Lorenzo "Jovanotti" Cherubini, *Ora*, 2011)

Il traguardo alla fine di una carriera non è diverso dal traguardo alla fine di un match. L'obiettivo è non perderlo di vista, perchè ha una forza magnetica. Quando ci sei vicino puoi sentire quella forza che ti attira e servirtene per tagliarlo. Ma subito prima di entrare nel suo campo di attrazione ne avverti una seconda, altrettanto forte, che ti respinge. E' una faccenda inspiegabile, mistica, quella di queste forze gemelle, di queste energie contrastanti, ma è reale. Lo so, perchè ho passato gran parte della mia vita a cercare l'una e a combattere l'altra, e talvolta sono rimasto bloccato, sospeso, a rimbalzare tra le due come una palla da tennis. (Andre Agassi, *Open*, 2011)

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## Introduction

The study of the deterioration of porous materials has an important application into cultural heritage field. This is true, in particular, for two reasons: first of all, because the original materials used in buildings and in monuments with historical value, e.g. stone, brick, mortar, concrete, and so on, may have a porous structure, and then because the materials used for past restorations may be even of this type of materials. Thus, it is clear the importance of the knowledge of how these buildings' components undergo the effect of time. In parallel with the researchers of umanities and art historians, a principal role is played by scientists which work in the experimental field as well as in the theoretical one, to provide the best analysis of the sample and design the most suitable restauration plan for it.

In this work, three main mechanisms of deterioration are pointed out and analyzed: moisture transport, heat transport and air pollution aggression. These damage mechanisms are dangerous in general for all buildings or monuments which are exposed to the external environment, but they are obviously much more dangerous in the case of *historical buildings* or *historical monuments* because they have been exposed to the atmospheric surrounding for a long time.

In this thesis, those damage sources are described as transport mechanisms, which are described by means of physical diffusion equations.

In **chapter 1**, there is a definition of porous materials and a simple presentation of two important experimental techniques which are usually employed in the study of porous materials, namely Nuclear Magnetic Resonance, NMR, and IR - infrared - thermography. First of all, there is a description of the porosity of the material and a brief classification of the materials according to their pores' size. Furthermore, there is a description of the porosity on the physical-mechanical properties of the material and some recent experimental results about it are then summarized. It is also, qualitatively described the main mechanisms of degradation, which are classified as mechanical, physical and chemical processes. Finally, as mentioned above, there are a general description of NMR technique, and a brief presentation of its application on the porous material with an example of experimental measurements, performed in Bologna on historical buildings. So, in sake of completeness, there is a simple, divulgative description of the infrared thermography technique and a schematic presentation of its employ in historical heritage field.

In chapter 2, mechanisms of water transport are presented. First of all, there it is explained how

the moisture storage into porous materials depends on the relative humidity of the surrounding environment and there is a schematic presentation of the main mechanisms of transport which are present in standard conditions. These mechanisms are described into detail in the following sections: water vapour diffusion that is described as a flux due to a pressure gradient, and the water liquid transport, which can be divided into surface diffusion mechanism and capillary water mechanism, both considered as a flux of liquid water driven by the gradient of water content. Finally, there is some hint on the redistribution process which is a mechanism of water propagation when an hypothetical water source is cut off (as rainwater, e.g.) and there is a description of the liquid and vapour transport together.

In **chapter 3**, there is a description of heat transport. In the first section of this chapter, there is a brief summary of the basic thermodynamical concepts, with the introduction of the enthalpy one. It is the function of state that has been selected to describe the heat storage into a building component, because it can be interpreted as an open thermodynamic system. Furthermore, there is a presentation of the three mechanisms of heat transport: conduction, convection, and radiation. Conduction transport is described by the Fourier's law and so, the heat transport is formally described by means of a diffusion equation, where one may introduce a source/sink term which can be connected to the phase transitions or to chemical reactions.

**Chapter 4** point out the connection between moisture and heat transport with the definition of the main equations of transport. There is a formal approach to the thermodynamical problem in a open system, which starts from the Gouy-Stodola Theorem that was formulated in entropy terms and that it will adapted to the present work. Furthermore, there is a description of the phase transitions which are interesting in the building physics, evaporation-condensation and freezing-thawing, and a brief hint to the heat arising from a chemical reaction. Finally, there is a generical presentation of the boundary conditions which are described into detail in the subsequent chapter.

In **chapter 5**, the outdoor conditions are presented. There is a description of the precipitating water in rainy conditions with an empirical evaluation of the rain water amount on the surface, which depends on the weather conditions, first of all, if it is windy situation. The impact of the solar radiation is also analyzed, in particular there is a distinction between the short-wave and long-wave radiations and their effects on the building surface. Finnaly, there is a formal description of these effects which must be taken into account in the general model equations as boundary conditions.

Finally, in **chapter 6**, a formal description of the chemical air pollutant aggression is described. Sulphur dioxide is deposited on the building surface and reacts and corrodes the building material, as limestones, marble, mortar and so on. So in the first section there is a presentation of the damage process. In the following parts the mathematical formulation of the problem is presented, pointing out the evolution of the sulfation front, which is described in terms of sulphur dioxide flux, and the role of the water content. Finally, there is a description of the process from a concentration point of view, which means that the Fick's law is applied to the concentration of sulphur dioxide and to the concentration of calcium carbonate of the eroded stone and, at the end, some results are referred provided from literature numerical simulation. In **chapter 7**, there are reported conclusions at this work.

### Chapter 1

# Porous materials and experimental techniques

#### 1.1 Porous materials

#### 1.1.1 Porosity

The term *"porous material"* is related to a medium with a solid matrix, which is either rigid or undergoes to a very small deformation, and a system of void spaces which are indicated as *pores*. The pores allow the flow of one or more fluids (water and/or gaseous mixture), in one or more phases (tipically in liquid or in gaseous phase) [8] [16].

*Porosity*  $\phi$  is a scalar property of porous medium which is defined by

$$\phi = \frac{V_{void}}{V},$$

where

φ: porosity of the material [-],
V<sub>void</sub>: total volume of the medium which is occupied by void space,
V: total volume.

Note that  $1 - \phi$  is the volume fraction which is occupied by the solid skeleton. In particular, in this definition one takes into account only the void spaces which are interconnected. Strictly speaking, the void space into building material can be distinguished in true cavities, the pores, and in very small empty channels, the capillaries. Therefore, in literature, there are references to absolute porosity, which means total porosity that takes into account all void volumes, from the effective porosity, which quantifies all empty comunicating volumes. Note, at the end, that high porosity not necessarily implies that the material has high permeability, in fact pores can be closed.

It is interesting to perform a brief differentiation between different kind of pores, which one may see in a porous material: open pores, which are connected one to another or with the external surface of the material; they can be divided in two kinds: blind pores, which are open in only one side, or through pores, which are comunicating one to another. From the opposite side, there are closed pores, which are isolated from the neighbors ones and they can be assumed as inactivies from a transport point of view.

In building materials, pores are distribuited in an irregular manner and the typical pores-scale is at microscopical length. It is worth taking into mind that the quantities of interest are evaluated over areas large enough to cross many pores and, in the end, the space-averaged quantities have a macroscopical behaviour which provides a theoretical approch, that was not possible in a microscopical environment (see below).

#### 1.1.2 Pores classification

Another classification of pores is based on their sizes, ref. [34]. The term "pore size" is referred to the diametral dimension of the pore itself. But it is not completely clear what this means, infact if the pore is spheric or, obviously, it has some other regular geometrical form, the dimension of pore is radius, or in other words, is the distance between two pore walls. But, if the pore does not have a regular form, it is not possible to provide an accurate value of its dimension. In this complicated situation, one must define the "pore size distribution", which indicates the relative abundance of each pore size.

Pore size distribution can be represented as a function of the radius r, f(r), which quantifies how many pores have a radius value within an infinitesimal range centered on r. This function can be obtained by means of several experimental techniques (which are largely reported in literature) which provide an histogram result of data, that represents the frequency with which every size range is present in the analyzed material. Another useful representation of this function is the Gaussian distribution, which provides the probability density of all possible values of pore size around the most probable one, which can be assumed as the arithmetic average of all diameter values of pores in the sample.

It must be stressed that the situation is more complicated than what is presented above, due to the greater variability of the pores dimension and due to the irregularity of their geometrical form. IUPAC provides a classification which is generally assumed and which allows a relatively precise differentiation. It is reported in tab 1.1.

Porous material	Diameter of porous
micropores	< 2 nm
mesopores	2 nm < pore size < 50 nm
macropores	> 50 nm

Table 1.1: IUPAC classification of pores dimension

#### **1.1.3** The role of porosity

In a recent work [32] the influence is measured of the porosity of a certain material on its deterioration. The experimental measures have been performed on samples of one marble and four limestones which are all carbonate stones, widely used in historical architecture in the Mediterranean area (Italy and Malta).

The samples were selected with comparable calcite amounts, but very different porosity. The experimental protocol involved heating of the stone samples at high temperatures. This heating was performed twice during the experiment, in order to evaluate the additional effects on already altered samples. Stress and micro-cracks appear and porosity and water absorption increase, but mechanical properties decrease of importance.

In addition to the numerical results, one of the most important conclusions is the following. The initial porosity and pore size distribution are fundamental characteristics of the material which define the effects of the heating and, consequently, of the deteriorations of building stones. In particular, if the initial porosity increases, alterations in microstructural, physical and mechanical properties of materials decrease (as compressive and tensile strength or resistance to abrasion). This is explained taking into account that, if the material presents many void spaces (it means that the material is more porous), the calcite crystals have more space to deform themselves under heating and second re-heating, without causing stress, cracks and dangerous deformations inside the stone.

This behaviour is confirmed by the second reheating. After the first heating, several microcracks are opened and it means that the number of void spaces increases. For the same reason explained just above, the effects of the second heating are very limited because the initial empty (total) volume is enough big to avoid unpleasant changes in the micro-structure of the building material.

In ref. [32] the effects are reported on open porosity and on average radius of pores from the heating of samples; this latter represents the modifications of microstructural characteristics of the stones. But also physical-mechanical conseguences of the heating, are important and depend on the initial porosity.

In reference to the fig. 1.1.1, the main results are the following<sup>1</sup>:

- open porosity and average radius of pores increase due to the heating of the sample,
- the absorption coefficient, which is related to the rate of water sorption by capillary, increases with the heating: for marble, which is the sample with the lower open porosity (0.5%), this rise is more important, with respect to the rise of absorption coefficient of limestone stones, in particular of "pietra di Vicenza" sample or Globigerina sample, which have the greatest open porosity (L3: 24.9% and L4: 40.8%),
- obviously, the water content absorbed in 24 hours increases with the heating of the sample: this is a consequence of the rises of open porosity.

<sup>&</sup>lt;sup>1</sup>Several concepts and quantities which are mentioned in the following summary, will be defined and will be described in the thesis work.



Figure 1.1.1: M1: Carrara marble, L1: Pietra di Trani, L2: Crema Luna, L3: Pietra di Vicenza, L4: Globigerina (from Malta).

In the graphs, pore size distribution can be seen of the five samples analyzed in [32] in the natural condition (black lines), after the first (red lines, indicated with I) and second (yellow lines, indicated with II) heating.

In the relevant table the main characteristics of the samples are summarized: in the first column there are reported calcium carbonate contents in percent, in the second column there are the open porosity values (in percent) and in the last column, there are listed the average pore radii.

#### **1.2** Deterioration of porous building material

Deterioration of porous materials, specifically those with interest in building physics as stone, marble, concrete and so on, is caused by different mechanisms. The most important of these

have machanical, physical and chemical origins, and they are briefly presented in the following sections, with ref. [15].

#### 1.2.1 Mechanical degradation

Main mechanisms of mechanical damage of porous building materials are tensile stress, which provides an elongation of the material itself (proportional to the applicated force), and compressive stress, which provides a shortening of the sample. One of the most known example of mechanical stress is that caused by static loads which affect all horizontal building components; it depends on its locations on the buildings. Lintels must bear all the weight of the upper part of construction: this provides a deformation of lintels themselves. The upper surface is under compression while the lower one is under tension. It may produce a dangerous situations which can even lead to breaking of the lintel.

As for the present work, the main mechanical degradation source is the thermal expansion. As is well known, a building material absorbs energy during the day which arises from the solar radiation, and consequently it is warming and can expand; viceversa, during the night, the building sample release energy as radiation (infrared radiation), and so it is cooling and contracting (see fig. 1.2.1). If a bad-heat-conductor material is considered, e.g. stone, this subsequenth expansion and contraction, due to diurnal (day-night) and annual (summer-winter) thermal cycles, can provide a periodic deformation of the material and it is increasingly dangerous, as the time goes by.



Figure 1.2.1: Effect of the day-night cycle: during the day, stone block absorbs the solar radiation which determines its expantion; during the night, the block can contract due to the release of energy.

In connection to what is described above, thermal cycles can be dangerous even for some marbles, which have an important crystal structure. In this situation, as is just mentioned, thermal cycles can result in cyclic and anomalous expansions of the crystals, which are followed by a weakening of the structure of the material<sup>2</sup>.

<sup>&</sup>lt;sup>2</sup>As reported in [15], Carrara marble presents a total porosity about 0.2% when it is extracted, but this value can rise up to several percents after some centuries of exposition to the thermal cycles.

#### 1.2.2 Physical degradation

Most of the building materials are porous and hygroscopic (see par. 2.1). Water is absorbed and propagates into the building structure travelling in capillaries and pores. It is one of the principal causes of deterioration of building components because it produces weakening of the structure or anti-aesthetic damages. In the particular case of historical buildings (which have suffered wetting for long time), this fact means that the humidity absorbed during many years, may result in the destruction of the plaster or the damage of the stucco, for example on the facade of the building. Even worse the case is of a building facade which may be frescoed: in addition to the damage of the structural building, it can be possible the corruption of the frescoes.

Connected to the moisture damage, the problem arises of the freezing of the water content in capillaries or pores. The response of the material to the freezing is the formation of ice crystals into capillaries and this process is different for material with different pore size distribution. From one hand, the materials with large pores, in general, do not present serious damage: ice crystal starts its growth, when the temperature is below  $0^{\circ}$ , crystallizing the water available into the pore. When this water is sold out, the cristal sucks the water in the surrounding capillaries. If those are few, at a certain point, the water reserve exhaustes before than the ice crystal fills the whole volume of the pore (see fig. 1.2.2A). From the other hand, the materials with small pores may be seriously damaged by the freezing process. The ice crystal uses all the water disponible into the pore and can start to suck what is contained into surrounding many capillaries. In this case, the ice crystal can grow until it fills the whole available volume of the pore and, at the end, it can push against the pore wall providing a stress to the material (see fig. 1.2.2B). The damage due to the freezing of water is strictly connected to the stress which is exercised by the ice crystal during its growth. When it happens in a pore near the surface of the material the pressure exerted by the crystal, looks like a tensile stress and it is very likely that involve a serious damage.



Figure 1.2.2: Ice cristal growth in large pore (A) and in small pore (B)

#### 1.2.3 Chemical degradation

Large part of building materials can be classified as calcareous samples, which means that the main component is calcium carbonate. Principal building calcareous stones are marble, travertine, limestone and others. Carbonate component suffers the aggression of acids, as carbonic acid ( $H_2CO_3$ ), sulfuric acid ( $H_2SO_4$ ) and oxalic acid ( $H_2C_2O_4$ ), which are present in atmospheric water, as rain or dew.

Effects of acid rains on calcareous stones depend on the position of the sample with respect to the environment around the sample itself. It is demonstrated that, if the stone sample is directly exposed to rain action, the reaction products are washed away from the surface, which crumbles and gradually recedes; viceversa, if the stone is located in a more repaired position, reaction products remain on the surface and, with the time goes, a dense black crust may appear on the surface of the sample itself. It must be stressed that some of the reaction products are soluble in water and they washed away by the rain; from the other side, if the reaction products are insoluble, as calcium oxalate, they remain on the building surface and form unaesthetic patinas on the surface itself.

As mentioned above, the deposition of chemical substance present in atmospheric air is via atmospheric water. In literature this process can be divided into two different kinds: wet deposition and dry deposition. They are briefly described in the following.

#### A) Wet deposition

Wet deposition means chemical deposition on the material surface, which occurs through via the rainfall. Air pollutants deposited on the surface, react to the calcium carbonate of the stones and produce soluble calcium bicarbonate and calcium sulfate which are drained away by the rain. During this process, water may evaporate and the soluble products solidify in gypsum crystals which form incrustations or may be drained away producing erosion of the surface.

#### **B)** Dry deposition

This kind of chemical deposition occurs mainly during the night, when the external surfaces emit radiations and so they cool. Subsequently, if the temperature of the surface is below the dew point, the water vapour in the air may condensate, forming a veil of water on the cold surface. Since the water deposition is not so much great, water is not drained away but remains on the surface with all chemical impurities which are entrapped in water molecules themselves. By this way, chemical pullutants can penetrate in the material via cracks or pores for a millimeter depth range.

It can be stressed that, in urban environment, where the carbon level reaches high values, there is above all a formation of black crust; viceversa, in country environment there are higher levels of dust which provide thin layers of lighter patinas.

It is worth noting that "dry" does not mean that water is not involved, but this term indicates a lower level of liquid water with respect to water content during rainfall.

Wet and dry depositions are schematically presented in fig. 1.2.3.



Figure 1.2.3: Left: wet deposition due to rainfall which provides gypsum crystal formation. It is followed by the erosion of the surface or by the formation of incrustation due to the rainwater drained away. Right: dry deposition due to the formation of a thin dew layer during the night.

#### **1.3 NMR: measurement of material properties**

Nuclear Magnetic Resonance, NMR, is an experimental technique which allows to study the properties of the molecular nuclei which undergo to a fixed magnetic field and, subsequently, to a radiofrequency pulse. In the detail, NMR is known as a resonance technique because a radiofrequency pulse is imposed with a given frequency, and it provides some characteristic effects. In the building field, NMR is used to quantify the water (or, in general, some other fluid) present into the porous structure of a porous building component submitted to analysis. In the following, a brief description of this technique is provided with a basic overview of the key concepts of the nuclear properties of matter, refs. [33] [34].

#### 1.3.1 Introduction to NMR

As known from the nuclear physics, the atomic nucleus is composed by nucleons of two species: neutrons, which can are free of charge, and protons which are featured by a positive charge, equal but with opposite sign to the elementary charge of electron. Those nucleons are not at rest, but they are in continuous movement into nuclear volume. In other words, the atomic nucleus can be assumed as a charge sphere in movement, specifically in rotation respect to its symmetry axis which can be assumed as a current. From the theory of electromagnetism, this means that the charge nucleus provides a magnetic field around itself and the magnetic nuclear momentum can be introduced, which is connected to the quantum properties of the nucleus (angular momentum, spin momentum).

If the nucleus is dipped into an external magnetic field, it will try to align its magnetic momentum with the lines of external magnetic field, resulting in a polarization process. In a sample with a certain number of nuclei with a given magnetic momentum, if the intensity of external magnetic field rises also the number of polarized nuclei increases too.

NMR is based on the response of the nuclear magnetic momentum to an external field and it

implies that this measurement can be performed on nuclei with an odd number of nucleons. Typical nuclei which are observed are  ${}^{1}H$  or  ${}^{13}C$ , but hydrogen is mostly used because it is composed by only one proton and thus there are only two directions of spin (up and down); it is also characterized by the greater gyromagnetic factor<sup>3</sup> among all stable nuclei, and since it is almost 100% isotopic abundance, it is called also H-NMR.

The energy of a nucleus with magnetic momentum  $\mu$  in an external magnetic field  $B_0$  is

$$E = -\boldsymbol{\mu} \cdot \boldsymbol{B}_0 = -\boldsymbol{\mu}_z \cdot \boldsymbol{B}_0,$$

where  $\mu_z$  is the magnetic momentum component along the magnetic field direction z. If  $\gamma$  is the gyromagnetic factor, the magnetic momentum is  $\mu_z = \gamma I_z \hbar$  where  $I_z = \pm 1/2$  in the particular case of the hydrogen nucleus which has spin I = 1/2. For the <sup>1</sup>*H* nucleus there are only two energy levels which are splitted as in fig. 1.3.1. The energy difference associated to this configuration is

$$\triangle E = E(I_z^- - I_z^+) = \gamma \hbar B_0$$

and, in order to obtained the resonance of the system, namely the transition between different energy levels, it is necessary to supply to (or extract from) nuclei this energy,  $\triangle E$  by means of electromagnetic waves with the resonance frequency  $\nu = \frac{\triangle E}{h} = \frac{\gamma B_0}{2\pi}$ . It is clear that the transition between the two states involves the inversion of the spins.



Figure 1.3.1: Left: energy levels splitting due to the superimposed external magnetic field  $B_0$  and consequent alignment of spins. Right: linear dependence between magnetic field and energy; if  $B_0$  increases, the energy difference which must be supplied for exciting the nuclei rises too.

With no external magnetic field, nuclei are aligned, casually, in every possible direction. Superimposing an external field, the spins of nuclei follow its direction and the energy level that was previously degenerate, is splitted into two levels as mentioned above (fig. 1.3.1). In particular,

<sup>&</sup>lt;sup>3</sup>It is the proportional factor between the magnetic momentum and the spin angular momentum, which is an intrinsic property of every nucleus and must be evaluated by experimental way. For example:  $\gamma(^{1}H) = 2.68 \times 10^{8} rad \cdot T^{-1}s^{-1}$ ,  $\gamma(^{13}C) = 6.73 \times 10^{7} rad \cdot T^{-1}s^{-1}$ .

nuclei occupy the lower level ( $I_z^+ = +1/2$ ) according to the Pauli Principle. It may be demonstrated that the number of nuclei into the lower level raises with the external field intensity because the NMR signal amplitude is proportional to the nuclei density in the lower energy level. In other words, NMR signal depends on the excess of protons in the lower level, so providing a given magnetization which is the sum of all magnetic momenta of odd protons in the level +1/2. At the end, without any external perturbation but with only an external magnetic field aligned to the z axis, there is only the z component of magnetization, without components on the x-y plane.

If a radiofrequency pulse, with the correct resonance frequency, is superimposed to the system, the magnetization undergoes a deflection from the z axis and appears a trasversal component in the x-y plane. Magnetization starts to precede around z axis and the trasversal magnetization start a cyrcular motion on x-y plane.

When the pulse shuts off, the nuclear system tends to return to the equilibrium: the system relaxes to the initial condition and, respectively two different time constants can be introduced which characterize the relaxation process in z direction and on the x-y plane. In fig. 1.3.2 magnetization is shown in both equilibrium state and after several radiofrequency pulses.



Figure 1.3.2: In a) magnetization is in equilibrium, aligned to the magnetic field. In b), c), d), e) there is the magnetization flipped by a certain angle, depending on the radiofrequency pulse. Trasversal magnetization  $M_{xy}$  appears and generates the NMR signal.

#### 1.3.2 Relaxation times

Relaxation times are two different parameters,  $T_1$  and  $T_2$ , which indicate the time necessary to the system to return in equilibrium situation, after a perturbation. The relaxation process is, typically, an exponential process which is characterized by the time constant T. In other words, the inverse of this value represents how fast the system returns in the equilibrium state.

#### Longitudinal relaxation time

Longitudinal relaxation time, or spin-lattice relaxation time, is the time required for the magnetization to return at its maximum value along z axis (which is the direction of the external magnetic field). Or, in other words, it measures how much time the system remains in the state with higher energy, before dropping to the lower energy level.

Spin-lattice relaxation is due to the energy exchange between the nuclear spin (of hydrogen, referring to the water molecules) and the surrounding nuclei of lattice atoms. The hydrogen nucleus interacts not only with the external field  $B_0$ , but with the surrounding nuclei which provide small magnetic fields interacting with  $B_0$ . For example, the spontaneous emission of a photon caused by drop from the higher level (-1/2) to the lower one (+1/2) in an hydrogen nucleus, is ruled by a characteristic time ~  $10^{19}$  years. So only the stimulated emission must be taken into account, which is due to the interaction between fluctuating local magnetic fields with the original external field which tends to restore the equilibrium after the perturbation shuts off.

When the original magnetic field  $B_0$  is turned on, the magnetization along the z axis will be  $M_0$ , which is the magnetization of the equilibrium state and is proportional to the excess of nuclei in the lower energy level. When the perturbative field is superimposed, a trasversal magnetization appears but the z component disappears. After that, the perturbative pulse is shut off and the system tends to the equilibrium restoration. This relaxation process requires the time  $T_1$  which characterizes the temporal variation of the z component of magnetization in the following way:

$$\frac{dM_z(t)}{dt} = \frac{M_0 - M(t)}{T_1}$$

Solving this last equation, one can obtain the exponential trend of magnetization:

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}})$$

and it provides another lecture of the longitudinal relaxation time: it is the time which is necessary for reaching 63% of its final value ( $M_0$ ). See fig. 1.3.3 (left).

#### Trasversal relaxation time

Trasversal relaxation time  $T_2$ , or spin-spin relaxation time, is the time required by the system to abort the trasversal component of the magnetization, which appears in the x-y plane after the action of the radiofrequency pulse signal. The trasversal component of the magnetization is the coherent sum of the precession motion of the nuclear spins in the x-y plane:  $M_{xy}$  rotates about the z axis. When the pulse signal is shut off, the rotational motion of involved nuclei undergoes a loss of coherence and the total trasversal magnetization  $M_{xy}$  decreases gradually. This relaxation process is following by an energy release which is exchange between spins (not with the surrounding lattice). In other words, this relaxation is due to the phase displacement between the nuclear spins with each other. Precessing motion of every spin is characterized by a particular frequency determined by the total magnetic field,  $B_0 + B_{local}$ , where  $B_{local}$  is due to the interaction between spins around a certain position. In this complicate situation, is useful to define the FID (Free Induction Decay) which is the sum of all the oscillations, each characterized by a certain frequency. Also in the x-y plane an exponential law is assumed:

$$\frac{dM_{xy}(t)}{dt} = -\frac{M_{xy}(t)}{T_2}$$

with solution

$$M_{xy}(t) = M_{xy}(0)e^{-\frac{t}{T_2}}$$

where  $M_{xy}(0)$  is the maximum magnetization on the x-y plane at the instant time when the radiofrequency pulse is shut off. See fig. 1.3.3 (right).

Another interesting aspect is the following. In a porous material, the phase shift is due, not only to the magnetic fields, but also due to the interaction between the spins of fluid nuclei (e.g. water) and the spins of the porous solid matrix.



Figure 1.3.3: Left: longitudinal time evolution. After the application of a 90° pulse,  $M_z$  is reduced to zero but it starts to increase as soon as the pulse is shut off and tends to the equilibrium state.  $T_1$  is the time corresponding to 63% of total original magnetization value. Right: trasversal time evolution. After the application of a 90° pulse,  $M_{xy}$  reaches a maximum amplitude because all spins are rotate in the same phase. When the pulse is shut off, this amplitute starts to reduce because spins start to rotate out of phase (black arrows in the top of this pannel). This decay process, which is shown in grey lines (bottom of this pannel), is due to the spin-spin interaction. The real signal is represented with red line, which is characterized by the decay time  $T_2^*$ , taking into account both  $T_2$  standard decay and effects of local inhomogeneities of the magnetic field.

#### **1.3.3** NMR in porous material

NMR can be used to characterize a porous material, in particular to evaluate how much water is contained into pores or capillaries or the porosity of the material itself. When an external magnetic field is imposed on the material, hydrogen nuclei of moisture water are polarized by it. After that, a radiofrequency pulse is superimposed and when it shut off, the system of hydrogen nuclei tends to return to equilibrium with two characteristic times. Analyzing  $T_1$  and  $T_2$ , one may be obtain information about the material without damaging or destroying the sample itself, circumstance very important when one deals with monuments or historical buildings.

From an experimental point of view, the relaxation times of fluid nuclei into a porous material are shorter than for the same nuclei in a free fluid. This is due to several factors:

- relaxation process of the fluid itself: it has influence on both times and is dominant in a situation with larger capillaries or pores where nuclei have low probability of interacting with the walls;
- relaxation process due to surface effects: it follows from the interaction between the fluid and the porous material surface, it has influence on both times;
- relaxation process due to diffusion molecular effects: it has influence on trasversal relaxation time alone.

It must be stressed that the effects of surface diffusion on the relaxation process have some important consequences. The inverse values of two characteristic times can be connected to the pore Surface-Volume ratio and it is interesting because larger pores have smaller S/V (frequency of collision between nucleus and wall, is low) and, consequently, have long relaxation times; viceversa, in smaller pores there S/V ratios are higher, they have short relaxation time. Its clear that there is a connection between the relaxation time and the pores or capillaries sizes. Finally, exists a relationship between the inverse of the trasversal relaxation time and the diffusion coefficient of a certain fluid. It is useful since, if the diffusion coefficient is higher, the relaxation time is smaller and viceversa, and therefore if the relaxation time is measured by NMR, the evaluation of the diffusion coefficient becomes possible.

A rigorous description of the experimental method of measurement and the fine arrangements or precautions which should be adopted in the experimental phase, can be found in the literature. What it must be stressed here is that, the NMR signal is the relaxation data, and consists in the trend of the magnetization amplitude respect to the time, with tipically exponential dependence. It has to be transformed in the distribution of the relaxation time, using specific mathematical methods like Inverse Laplace Trasformation or other techniques.

In the following are presented, for completeness, some experimental results from refs. [35] [36].

#### 1.3.3.1 Experimental measurements

Some H-NMR experimental measurements were carried out, for instance, on samples from some historical buildings in Bologna and Ravenna (Italy). This kind of measurement provides

several characteristics of the stone samples, as porosity, pore size distribution, as well the as impact of air pollution and their changes due to the degradation. This technique also allows to determinate the origin of the stone sample.

As reported in [36], the signal of NMR provides:

- the number of hydrogen nuclei, which is proportional to the amplitude of the signal,
- relaxation times (of the hydrogen nuclei of water molecules), which depend on the pores surface-volume ratio.

From this last point, one can assume that, if the relaxation time is short, also the characteristic size of the pores is small, and viceversa. Obviously, it must be assumed a fixed form of the pores.

As mentioned above, mathematical inversion of the NMR signal provides the relaxation time distributions, which are reported below.



Figure 1.3.4: Longitudinal and trasversal distributions of relaxation time from the experimental NMR measurements on Orsi-Marconi building, in Bologna.

In fig. 1.3.4 there are two distributions of time relaxation,  $T_1$  and  $T_2$ , for four samples: two are taken from Orsi-Marconi building<sup>4</sup>, and the other two samples are from two different quarries in Bologna<sup>5</sup>. The samples from Orsi-Marconi building provide values of  $T_1$  between 80 to 900 ms, which correspond to a pores size in the range<sup>6</sup>  $10^{-2}$  to  $10^0 \mu m$ ; in the same manner, values of  $T_2$  are about 50 to 600 ms, which corrispond to the previous range of pores dimension values. Another observation concerns the dimensions of pores of two quarries: Montorio sample is characterized by a typical size of pores which is not compatible with Orsi-Marconi samples; in fact, the peak of the distribution of trasversal time relaxation is far from that of the

<sup>&</sup>lt;sup>4</sup>Orsi-Marconi building: via San Vitale, 28, Bologna, about 500 meters from Piazza Maggiore, in the center of the city.

<sup>&</sup>lt;sup>5</sup>Varignana quarry: in the south-est of Bologna, about 24 km far away the center of the city (Piazza Maggiore). Montorio quarry: in the soth-west of Bologna, about 40 km far away the center of the city.

<sup>&</sup>lt;sup>6</sup>General relation between time of relaxation and surface-volume ratio is  $\frac{1}{T} = \xi \frac{S}{V}$  and, if one assumes a spherical pore (numerical constant can be neglected) it becomes  $\frac{1}{T} = \xi \frac{1}{r}$  where r is the pore radius and  $\xi$  is the surface relaxivity  $[\mu m/s]$ .

historical building; Varignana pores size is more compatible, but presents the  $T_2$  peak at shorter relaxation time so suggesting the typical size of the pore of a stone which is not underwent to environmental injury.

In ref. [35], NMR can be used to obtain some information about the historical or cultural side. The study was conducted on the medieval Civic Tower of Ravenna, where three samples were taken at three different heights. The two samples from the lower part of the tower present smaller pores (corresponding to small relaxation time  $T_2$ ) than that presented by the sample from the higher part. It may be explained taking into account that the sample from the higher part of the tower is more exposed to the weather injury: wind and infiltration cause a reduction of pore space, due to recrystallization. Viceversa, the samples with larger pores are more interested by sulfation or black crust aggression.

#### 1.4 Thermography measurements

IR thermography is an experimental technique which allows to analyze large surfaces without damage or physical injury and allows to get information in short time: it is widely employed in the cultural heritage conservation.

In this paragraph a brief description of this technique is presented, with refs. [37] [38].

Thermography produce thermal maps of the surface area that is being analyzed and, for the historical material, that means:

- humidity: individuation and definition of the spatial distribution of anomalous level of moisture in the facades of the buildings or in other building components, as well as in sculputural heritages an so on;
- detachment: in order to study of the conservation of pictorial heritage, in particular frescoes and their detachment problem of the plaster, and analyze the status of mosaics;
- masonry: it allows to study the composition of the masonry, which is important for structural analysis or restoration plans, or simply for historical studies.

The physical basis of thermography is the emission of electromagnetic radiations by every objects which have a temperature above absolute zero. For the typical temperatures of buildings or historical materials, following the physical law of the emission by a black body and the resulting Wien's law, one can obtain the typical wave lenghts values which corresponds really to the infrared range. As known, a certain temperature corresponds to a heat flux emitted by irradiation. Thermography is based on the detection of this heat flux, which is exchanged between the inspected surface and the surrounding, and in turn it depends on several parameters as the geometry of the volume under analysis or its material thermal properties.

Thermography may be of two kinds, passive and active, depending on the emission conditions. In the former situation, the measurement is carried out in natural condition when the inspected surface undergoes to the solar radiation, but in the latter case the sample is subjected to an artificial reheating to amplify the thermal response. It can be stressed that for analyzing heritage buildings or great samples, passive thermography is preferred than active one.

Passive thermography is an experimental measurement with a natural heat source like solar radiation. It is a real-time monitoring of the evolution of temperature on the surface during the natural solar radiation. It is important because it allows to measure sample of big size, but on the other side it is very sensible to the environmental conditions. Viceversa, in active thermography measurements, an external non-contact heat source is applied to the surface, as lamps, air guns or devices which push the sample under analysis in vibrational conditions and the heating and cooling processes are analyzed.

It must be taken in mind that, if one wants to get a good measurement, the boundary conditions are also very important:  $CO_2$  concentration, relative humidity of the environment, temperature and speed of air, are some of environment parameters which must be defined during the measurements.

Thermal camera records temperatures of all the points on the surface and provides the thermal image, which shows the surface temperature distribution. Thermal IR radiation recorded by the thermal camera, is composed by three components: emitted radiation, trasmitted radiation and, finally, reflected radiation. Each of these radiation components is quantified by heat transported in each previous physical mechanism, and each heat flux is proportional to a specific coefficient which depends on several factors, like the kind of material, some surface properties of the building component, its temperature and so on. It can be noticed, in real building material the transmitted coefficient can be neglected and the radiation which is important in the thermographic measurement is composed by reflected and emitted components only. Finally, it is worth stressing that thermography is a useful technique because of its rapidly response and its almost friendly use, but must be regarded as qualitative, infact it can provide wrong or incomplete results. For this reason, it must be implemented with other techniques. At the end of this brief description, here some interesting applications of thermography on the historical buildings are here described.

#### Detachment

Thermography can be employed for the study of frescoes detachment or, in general, of plaster detachment. In the first case, the measurement must be performed inside the church or other historical buildings and it is possible to exploit the external solar radiation as uniform heat source. In this situation, heat flux from the outside to the inside is stopped by a local defect which is carachterized by a low heat conducibility, as air buildup which caused the detachment of the fresco plaster. For that local buildup, heat is stored on the reheated side of wall and on the other side of the wall (the inside one, where the measurement is performed) there is a corrispondent area with lower temperature. Viceversa, if plaster detachment of a wall is studied, the measurements are carried out on the same side of the solar heating and, in this case, buildups of moisture are detected in the warmer areas, because the moisture buildups prevent



the heat trasmission to the layers below.

Figure 1.4.1: Schematic view of the detachment process. On the left, there is a representation of normal condition: red arrows indicate the heat source, orange ones the propagation of heat in the material and green lines are temperature profile ( $T_1 < T_2 < T_3 < T_4$ ) along the material thickness. On the right, there is a defect, which means detachment, that deforms lines of temperature and the direction of heat propagation. Reflection side means that the measurement is performed on the same side of irradiation (tipically the extenal side of a wall) and the defect provide an heat storage in front of itself (red cyrcle), viceversa if the measurement is performed on the opposite side than radiation, the area appear colder because the defect obstructs heat flux (blu cyrcle).

#### Diagnostic moisture in a building wall

When a liquid evaporates, it become colder. In coloured thermographic diagnosis, moisture areas appear dark, for example blue or green, because they are colder than dry areas, which appear light, as yellow or red. This experimental analysis is used to detect a surface region with no just visible damage due to humidity, because moisture is not yet to the surface, but it still in the underlying layers. But it is less dangerous. Obviously, this kind of information is very important for the restoration planning.

In the same manner, thermographic analysis can be provided on a facade with visible alteration due to the capillary raises. With use of this technique, it is possible to determine, for example, the stopped of the capillary risies bacause zones undergo evident moisture damage results, everywhere, warmer than it should be, if there was still water<sup>7</sup>.

#### Material analysis

Thermographic measurements provide some information on the material composition of the building. This information may be obtained by analyzing the temperature evolution (in time) after external thermal stress, fig. 1.4.2. It is interesting to know if there have been past restorations or if there are unvisible structures.

<sup>&</sup>lt;sup>7</sup>For example, SS. Egidio and Omobono Church, in Cremona.



Figure 1.4.2: Response of a composite wall (plaster, stone, bricks) to a temperature stress. In top left panel there is a schematic view of the wall, and in the top right one there is the same wall under solar radiation. In the bottom there are the responses of the wall during the heating (left) and during the cooling (right): stone, which is characterized by higher thermal conductivity but lower specific heat, reaches high temperature during heating and it will cool quickly, and viceversa, for bricks.

### Chapter 2

# Mechanisms of water transport in porous material

#### 2.1 Moisture storage

A building material can be classified in two different ways, depending on its response to moist air contact. If a building material not absorb moisture, it is defined *non-hygroscopic*, while if it pick up water molecules it is know like *hygroscopic material*.

The former kind of material, e.g. glass, metal and some plastic foams, not absorb moisture unless the temperature falls below the dew point and if  $\varphi < 100\%$  they remain dry ( $\varphi$  is defined below). The latter kind of material is divided in *hydrophilic*, which absorbs water by capillary suction, otherwise is regarded as *hydrophobic*.

In particular, a hydrophilic material is able to attract water molecules infact the water spreads on its surface and wetting this. In other words, if a material is hydrophilic a water drop, form with the surface of the material, a small contact angle (see fig. 2.1.1A). Viceversa, if the material is unable to attract water molecules, it is defined like hydrophobic and it form a large contact angle (larger than 90°) with the surface of water drop (see fig. 2.1.1B) [15].





The maximum water content reached in natural condition is know like *free water saturation*, but higher amount can only be reached with an external superimposed forced [6].

The most common building materials are hygroscopic and capillary-active, which means that they absorb water until balance with the humidity of external air, or the free water saturation level, by capillary suction.

The water in the porous materials can occurs in different phase: gaseous, liquid and solid, which are difficult to quantify and, in general, it is not possible to differentiate from one physical state to another. For this reason the *water total content w* (also know like *water storage function*) shall be deemed as the only important parameter, and it is defined as the total moisture content in the material regardless of the different aggregate state. The function *w* depend on the relative humidity  $\varphi$ , which is the ratio between the water vapour concentration and the water vapour concentration at the saturation (in percent) [10]:

$$\varphi = \frac{\rho_v}{\rho_{v,sat}} = \frac{Pv}{P_{sat}}$$
(2.1.1)

where  $\rho_v$ : water vapour concentration [kg/m<sup>3</sup>],  $\rho_{v,sat}$ : water vapour concentration at saturation [kg/m<sup>3</sup>],  $P_v$ : water vapour pressure [Pa],  $P_{sat}$ : water vapour pressure at saturation [Pa].

In building materials can be distinguished several regimes of storage function w depending on  $\varphi$ . Earlier is present fig. 2.1.2 that shows this regimes and subsequently is performe a classification of such ones for a hygroscopic, capillary-active material, like a building stone.



🖚 Relative humidity (0–100 %)

Figure 2.1.2: Typical trend of water storage function for different values of relative humidity. The sorption moisture region (or hygroscopic region) is characterized by a relative humidity up to 95%, for  $\varphi$  above 95% up to free water saturation there is the capillary moisture region (or super-hygroscopic region) and finally, the supersaturated region is defined by relative humidity of 100% for any value of moist content.

#### The sorption moisture region (or hygroscopic region)

The water sorption from the surrounding moist air proceeds until the equilibrium with the humidity of the ambient is reached. Experimental measurements have shown that the influence of the temperature is negligible and for this reason, the water sorption is defined *isotherm sorption*. This region is defined by relative humidity from dry-state up to 95% and it is named A in fig. 2.1.2. The most important mechanism of moisture transport are water vapour diffusion and effusion (see par. 2.2). As the relative humidity increase (up to 15%), the water vapuor can condensate in a monomolecular coating layer. Rising values of  $\varphi$ , until about 50%, this layer became thicker (multimolecular coating) and, at the ending, with a progressive increase of relative humidity occur the real capillary condensation (surface diffusion, see par. 2.3.1) [6] [7].

#### The capillary moisture region (or superhygroscopic region)

When in the porous material above 95% relative humidity is reached, the water content increases steeply until the limit of water saturation (region named B in fig. 2.1.2). In this situation, liquid transport becames more important than the vapuor diffusion but the maximum values of water content not corrisponde to the whole empty porous volume available. Infact, some air is still remained entrapped and the only way to fill this air bubbles is the application of an external forcing (e.g. external high pressure or temperature gradient).

Capillary condensation depends on the suction capillary pressure and the entire mechanism can be understand by the simple model of cylindrical capillary.



Figure 2.1.3: Cylindrical capillary model. Balance of forces on the separation surface and the pressure condition along the vertical direction.

The balance condition of the forces, in assumption of spherical meniscus, with reference to fig. 2.1.3, is described by:

$$P\pi r_c^2 = P_w \pi r_c^2 + 2\sigma \pi r_c \cos \vartheta \tag{2.1.2}$$

and subsequently:

$$p_c = P - P_w = \frac{2\sigma\cos\vartheta}{r_c} \tag{2.1.3}$$

where  $p_c$ , P,  $P_w$ : capillary pressure [Pa], air (total) pressure [Pa], water pressure [Pa],  $\sigma$ : water surface tension [N/m],  $r_c$ : capillary radius [m],  $\vartheta$ : contact angle between the meniscus and the capillary wall [-].

The relation between the capillary pressure and the relative humidity over a curved meniscus is know as Kelvin's law:

$$\varphi = \exp\left(-\frac{p_c}{\rho_w R_v T}\right) \tag{2.1.4}$$

where

 $\rho_w$ : density of water [kg/m<sup>3</sup>],  $R_v$ : gas constant for water vapour (=462) [J/kg·K], T: absolute temperature [K].

As in the sorption moisture region, also in the capillary one, the storage function is driven by capillary pressure and shows a hysteresis between wetting and drying; but several studies with sample of natural stone show that is no more pronounced than in the moisture region [6] [7]. In ref. [6] is described the last part of storage function w in the superhygroscopic region. The plot of water content over the relative humidity shows a rises steeply above 99% of the relative humidity, corresponding to a pore radii of  $10^{-7}$ m. This rise, that is several magnitudes higher than in the sorption region, is taken as evidence of the non-linear relation between the pore radius and the relative humidity.

#### The supersaturated region

In this region (named C in fig. 2.1.2), the relative humidity is always 100% or higher, or in other words, the content of water is higher than the water saturation limit. It is possible only if an external forcing is applied. In this region there is not a unique relation between the capillary pressure and water content since the removal mechanism of air bubble can change w but not  $p_c[7]$ .

Because this particular condition is extremely rare in standard natural condition: in general this third regione is ignored.

In summary, fig. 2.1.2 shows an example of a complete storage function: in A it can be possible assumed a sorption isotherm process up to 95% of relative humidity, B is the capillary moisture range in which there is a well defined relationship between the suction stress and the relative humidity and, at the end, the supersaturated region C where, in general, the water function has a vertical trend at 100% of relative humidity values.

In sake of completeness, one must differentiate between wetting (absorption) and drying (desorption) processes but as has been shown in [6], [7] and [11] this *hysteresis effect*, in most isothermal cases with temperature between 5 °C to 15 °C, is negligible for moist transport description and the absorption curve is enought to describe the moisture storage, see fig. 2.1.4.



Figure 2.1.4: Hysteresis effect between absorption and desorption processes. Generally, the absorption isotherm is enough to characterize the moisture storage.

In the following, there is an explanation of the principal mechanisms of moist transport in a porous material: vapour diffusion and liquid transport. These processes are independent of each other, infact the former is the typical phenomenon that occurs in large porous whereas the latter is distinctive effect of small capillaries, pore surface and crevices. Also, the driving force for vapour diffusion seems to be the partial vapour pressure, while for the liquid transport is capillary suction, or in other words the relative humidity (see 2.1.4) [11].

May be useful to summarize the most important mechanisms of transport which occur in the capillaries. Tab 2.1 is provide for this scope, refs. [7] and [10].

Phase	Transport mechanism	Driving potential
	water vapour diffusion	water vapour concentration or vapour pressure
Gaseous	effusion	vapour pressure and temperature
Gaseous	thermal diffusion	temperature
	gas flow	total pressure
	capillary conductivity	suction capillary pressure
Liquid	surface diffusion	water content or relative humidity
Liquid	hydraulic flow	total pressure
	electro kinesis	electrical voltage

Table 2.1: Transport forms of moisture transport in porous building materials.

Some of this transport phenomena are, however, negligible in the practical conditions. Hydraulic flow and gas flow<sup>1</sup> are due to convective phenomena which caused by a difference of overall pressure, but in normal conditions (wind pressure) the possibilities for natural convection are minimal. The electrokinesis<sup>2</sup> effect is not entirely clear on moisture transport. Thermal diffusion is trascurable if compared to other transport mechanisms, infact only about 0.05% of overall transport is seems to be due to a temperature gradient [7].

<sup>&</sup>lt;sup>1</sup>The first is a flux of liquid water and the second in a flux of water vapour gas due to the convection mechanisms which provide a material transport thanks to the pressure difference which exist between indoor and outdoor side of a building component.

<sup>&</sup>lt;sup>2</sup>Hydrophilic building material attracts the water molecules or, in other words, its surface can establish hydrogen bonds which polarize the surface itself. This polarization provides a weak electrical field which can move the water molecules. This motion is know as *electrokinesis*.

#### 2.2 Water vapour diffusion

"*Moist air*" means a mixture of two ideal gases: dry air and water vapour [8]. The first one is a compound of O<sub>2</sub>, N<sub>2</sub>, Ar, CO<sub>2</sub>, SO<sub>2</sub>, ..., which is non-condensable costituent, and the second one is a condensable gas. The partial pressure of each component is given by the ideal gaseous law:

$$P_v = \rho_v R_v T \tag{2.2.1}$$

$$P_a = \rho_a R_a T \tag{2.2.2}$$

where  $P_a$ : dry air pressure [Pa],  $\rho_a$ : dry air concentration [kg/m<sup>3</sup>],  $R_a$ : gas constant for dry air (=287.1) [J/kg·K]<sup>3</sup>,

clearly, the total gas pressure is the sum of 2.2.1 and 2.2.2:  $P = P_a + P_v$ . The humidity ratio represents the mass of water vapour content with respect to the mass of dry gas in the mixture and it can be quantified by the adimensional ratio

$$x_{hr} = \frac{\rho_v}{\rho_a} = \frac{P_v/R_vT}{P_a/R_aT} = 0.622 \frac{P_v}{P - P_v}.$$
(2.2.3)

The density of moisture air is

$$\rho_{ma} = \rho_a + \rho_v = \rho_a (1 + x_{hr})$$

If gas is completely dry,  $x_{rh} = 0$  and the density  $\rho_{ma}$  is equal to the density of dry air. If  $\gamma$  (=1.293 kg/m<sup>3</sup>) is the density of dry air in normal condition, i. e. at temperature of 273 K and at pressure of 1 atm, the density of dry air in the moisture become

$$\rho_a = \gamma \frac{P_a}{P} \frac{273}{T}.$$

Note that, using the standard expression of ideal gas law<sup>4</sup> instead 2.2.1 and 2.2.2, it can be possible ri-define the expression of humidity ratio in terms of molar weights of water vapour and dry air and, at the end, one can obtain the following relation

$$\rho_{ma} = \gamma \frac{P_a}{P} \frac{273}{T} (1 + x_{rh}) = \gamma \frac{273}{T} \left[ 1 - \left( 1 - \frac{M_v}{M_a} \right) \frac{P_v}{P} \right].$$
(2.2.4)

One can distinguish between two situations:

• if  $M_v < M_a$ , at fixed temperature *T* and pressure *P*, the density of moisture air increases with the rising of partial vapour pressure, in line with the gas law;

<sup>&</sup>lt;sup>3</sup>Following [21], here is summarized the two costant gas:  $R_a = 287.1 \text{ J/Kg} \cdot \text{K}$  for dry air and  $R_v = 462 \text{ J/Kg} \cdot \text{K}$  for water vapour.

 $<sup>{}^{4}</sup>P = \frac{\rho RT}{M}$  where R is the universal gas constant (= 8.314 J/mol·K) and M is the molar weight of a generic species (Kg/mol).

• if  $M_v > M_a$ , the contrary is true: with the increasing of partial pressure than the density of moisture air decreasing.

In both cases, if temperature rising, the density of moisture air decreases [30].

In reference to the kinetic gas theory, it is possible to decribe the diffusion of the molecules in a mixed gas by means of an equation in which take into account all driving potentials: the mass (or concentration) fraction, the temperature and the total pressure. In the specific application of this arguments to describe the water vapour diffusion in air in the building materials, this equation looks like:

$$g_v = D_m \nabla m + D_T \nabla T + D_P \nabla P \tag{2.2.5}$$

where  $g_v$ : water vapour diffusion flux [kg/m<sup>2</sup>s],  $D_m$ : mass diffusion coefficient [kg/m·s],  $D_T$ : thermal diffusion coefficient [kg/m·s·K],  $D_P$ : pressure diffusion coefficient [kg/m·s·Pa], m: mass fraction of water vapuor (respect to the total mass of moisture gas) [-].

The third term is negligible in building physics (see above). The second term describes thermal diffusion, or Soret effect, which is the vapour transport due to a temperature gradient. It is based on the density difference between the molecules of dry air and vapour air: the latter, which is lighter than the former, move from cold to warm regions. This effect is minimal for temperature below 50°C and for this reason the second term of 2.2.5 can be forgotten in the following discussion [10]. The first term represent the mass diffusion which is driven by a gradient of mass fraction. It is also note as *Fick's law*.

As there exists an relationship between mass (or concentration) and pressure in an ideal gas, instead of the gradient of mass it may be use the gradient of vapour (partial) pressure (using the eq. 2.2.1). In detail, one must takes into account a mixture of two gasses, dry air and water vapour. When there are temperature and pressure which are constant, one kind of gas moves towards the second one, and at the same time the second type of gas moves to the first one and, at the end, they are mixed each other, resulting in molecular diffusion.

In building physics, the situation is simplified, infact the partial pressure of water vapour is smaller than the partial pressure of dry air. In this case, only the diffusion of water vapour can be considered, and it means that the diffusion of dry air can be neglected. In the end, one can assumed a motion of water vapour molecules from a location of high (partial) pressure to another location of lower vapour pressure [21].

In the building material an additional resistance to the diffusion must be take into account, which is due to the porosity and tortuosity of the porous material, as well as pore obstruction by water capillary condensation. All these phenomena are take into account with the introduction of vapour diffusion resistance coefficient  $\mu$  (adimensional) which is specific to each porous material. In other words, the coefficient  $\mu$  can be defined as the diffusion resistance in a porous
material layer, compared to the diffusion in a layer with the same thickness of air.

Values of the coefficient  $\mu$  range from 1, in stagnant air, to infinite for a material without pores or with only closed pores. The actual value of  $\mu$  depends on the pore system and should be stressed some foundamental factors, with refs. [21] and [28]:

- the size of pores open sections: a pore with larger open area per unit of surface of material, has smaller vapour resistance factor than a pore with a lower open area, which has higher vapour resistance. The limit case is a pore with open area tending to zero: the resistance factor goes to infinite and the water vapour diffusion cannot take place;
- path length: the vapour resistance factor depends on the ratio between the path length travelled by the vapour molecules and the thickness of the layer. If this ratio increases, more the vapour resistance factor will be great;
- tortuosity: more complicated and tangled are pores and capillaries, the greater the resistance to the diffusion.

These situations are shown schematically in the following fig. 2.2.1.



Figure 2.2.1: A) the vapour resistance coefficient increases if the open area per unit of surface decreases:  $A_{o,1} > A_{o,2} \Longrightarrow \mu_1 < \mu_2$ .

B) the vapour resistance coefficient increases with the path length of the vapour molecules  $l_0$ , in fact  $\mu \propto \frac{l_0}{d_0}$  where  $d_0$  is the layer thickness.

C) the vapour resistance coefficient is higher if the tortuosity of capillaries or pores is higher too.

Finally, two clarifications are necessary. First, the water vapour diffusion resistance coefficient  $\mu$ , is independent from the temperature, but depend on the water content in capillaries. In the sorption moisture region,  $\mu$  can be regarded as constant because in this region, liquid and

vapour transport occur independently each other. Infact there is a relatively low water liquid content and thus, if there are some localized liquid spots, these not affect the water vapour diffusion. In the superhygroscopic region, water filled capillaries and the diffusion transport can be obstructed by the presence of water in liquid phase which form water islets (theory by Philiph and de Vries). These water islands reduce the diffusive path length, as shown in fig. 2.2.2. These effects are very difficult to estimate but it is clear that depend on water content which must be sufficiently large.



Figure 2.2.2: With increasing the relative humidity, the limit of capillary condensation can be reached. In this situation, several water islets can be formed and this involves the shortening of the diffusion path length of the water molecules.

In other words, this is the situation of the supremacy of the capillary conduction respect to the vapour diffusion, and thus, it is possible believe in the vapour diffusion indipendence from the amount of water in capillary tubes [6].

Second, the relation between the mean relative humidity in the sample and the water vapour permeability is non linear. When the former increases, the latter change also very steeply [7].

Water vapour pressure leads to another important phenomenon in gasseous transport: the *ef*-*fusion*.

Vapour effusion, or Knudsen effect, occurs when the pore radii are smaller than the free path length<sup>5</sup> of the gas molecules and therefore the collision between vapour molecules and the pore wall are more frequent than the collisions between themselves. With the purpose of take into account this effect, it can be introduced the *Knudsen factor*, which describes the ratio between the mean free path of vapour melecules and the twice pore radius (diameter):

$$K_n=\frac{L}{2r}$$

where *K*<sub>n</sub>: Knudsen factor [-], *L*: mean free path [m], *r*: pore radius [m].

<sup>&</sup>lt;sup>5</sup>The (mean) free path length is the (average) distance travelled by a water molecule between two subsequently collisions.

The Knudsen factor allows to distinguish between different regimes:

• if  $K_n > 1 \rightarrow L > 2r$ : this is the case of very narrow capillaries ( $r < 5 \times 10^{-9}$ m) where the pure effusion is preferred. The diffusion, in this situation, is described by the following equation, valid for cylindrical capillaries:

$$g_{eff} = -\frac{8}{3}r_c\sqrt{\frac{M}{2\pi RT}}\nabla P_v \tag{2.2.6}$$

where  $g_{eff}$  is effusion flux density [kg/m<sup>2</sup>s], and *M* is the molecular weight [kg/mol].

• if  $K_n \ll 1 \rightarrow L \ll r$ : in this case the radius of the capillaries is larger ( $r > 10^{-6}$ m) and therefore the Fick's diffusion is dominant. The diffusion is described by:

$$g_{diff} = -\frac{2\sqrt{2}}{3} \frac{\sqrt{\frac{1}{M_a} + \frac{1}{M_w}}}{N_L \sigma_{aw}^2 P} \left(\frac{RT}{\pi}\right)^{3/2} \nabla P_v$$
(2.2.7)

where  $g_{diff}$  is diffusion flux density [kg/m<sup>2</sup>s],  $M_a$  and  $M_w$  are molecular weight of air and water [kg/mol], and  $N_L$  is know like Loschmidt number [mol<sup>-1</sup>],  $\sigma_{aw}$  is the average gas-kinetic impact diameter [m].

• In the intermediate range both two transport mechanism take place.

In real contest is not possible distiguish one from the other mechanism.

However, it can be observe that in every case the driving potential is partial vapour pressure gradient. So, from now on, it will be used a common relation with a unique diffusion coefficient for describe every vapour transport mechanism:

$$g_v = -\frac{D_v}{\mu R_v T} \nabla P_v \tag{2.2.8}$$

where  $D_{v}$ : vapour diffusion coefficient in air [m<sup>2</sup>/s],  $\mu$ : water vapour diffusion resistance factor [-].

The coefficient  $D_v$  is determined in empirical way:

$$D_v = 2,3 \times 10^{-5} \frac{P_0}{P} \left(\frac{T}{273}\right)^{1,81}$$
(2.2.9)

where *P*<sub>0</sub>: atmospheric standard pressure [Pa].

It is possible to define a more compact factor named *vapour permeability*  $\delta$ , and finally, the most popular formula of the water vapour diffusion is:

$$g_v = -\frac{\delta}{\mu} \nabla P_v$$

where  $\delta$ : water vapour diffusion permeability [kg/m·s·Pa].

This equation applies until the partial vapour pressure reaches 10% of the total pressure. Beyond this value can not possible continue to ignore the convective motions [6], [7] and [10].

### 2.3 Water liquid transport

"*Liquid water*" consist of adsorbed water or bound water, which is present in the whole range of water contents, and of capillary water or free water, which is present if the water content is higher than the solid saturation poit [12].

Mechanism of transport of water in liquid phase, must be separated in two regimes. Refering to tab. 2.1, liquid water can undergo *surface diffusion* in the sorption moisture region and *water capillary conductivity* in capillary moisture region (third region can be forgotten).

### 2.3.1 Surface diffusion

It consist in a mechanism of moisture transport in molecular layer of water adsorbed at the pores walls (in hygroscopic material). At the same time, adsorption process can be separated in two steps:

- *mono-molecular adsorption:* there is a monomolecular layer of water on the surface of the pore and it thickness increases with the rising of water content, but it remains very small however, in fact it carachterized the lower relative humidity range (φ ~ 25%),
- *multi-molecular adsorption:* if water content rises, the thick of adsorbed layer increases also.

In other words, if water content increases above the critical moisture value, capillary conductivity becomes favourite with respect to the surface diffusion (see fig. 2.3.1). Although the real separation between one regime to the other one, is strongly dependent on the pores structure of different materials. For example, the surface diffusion for paper products start at  $\varphi \sim 30\%$ and for sandstone at about  $\varphi \sim 60\%$ , as reported in [6] and [10].



Figure 2.3.1: Two steps of water adsorption process: as the relative humidity increases, the thickness of water adsorbed also rises untill the limit of capillary condensation value.

In detail, on the inner capillary wall, there is a molecular layer of adsorbed water which form a thin film. Depending on its thickness, also the mobility of water molecules varies as well. If exista a relative humidity gradient, the mass flow in the liquid film can start.

This mass transport, in surface diffusion, is proportional to the gradient of the water content thickness, and it is represented with an equation like Fick's law:

$$g_{w,s} = D_{w,s} \frac{dw}{dx} \tag{2.3.1}$$

where  $g_{w,s}$ : surface diffusion flux density [kg/m<sup>2</sup>s],  $D_{w,s}$ : surface diffusion coefficient [m<sup>2</sup>/s].

It should be stressed that the surface diffusion depends on the temperature, via the coefficient  $D_{w,s}$ , in fact it can be see that if T rises, also the surface diffusion flow increases too, because if temperature became high, consequently the viscosity of the fluid decreases.

At this point, could rises a doubt: might one consider the partial pressure as driving potential of surface diffusion? The answer is no. In [6] is presented a study of moisture fluxes through a paper membrane (shown fig. 2.2.1).





In the top pannel, one can see the dependence of moisture flux with respect to the vapour pressure difference for various values of temperature: if T increases, the diffusion flow related to the partial pressure highly rising, unlike what happens in the vapuor diffusion (where the driving potential is truly a pressure gradient) where the vapour flow became high at higher T (see eq. 2.2.9).

In the bottom pannel, there is the trend of moisture flux respect to the relative humidity at different temperature: the diffusion transport became more important as T rising, as one would expect.

In other words, a pressure gradient is the driving potential of vapour diffusion; a relative humidity gradient is the driving potential of surface diffusion, which must be considered as a type of liquid transport.

## 2.3.2 Capillary conduction

Capillary condensation occours when the water molecules re-arrange in a more stable configuration due to surface tension. A liquid molecule is surrounding by other molecules, which interacts one to the others by forces known as cohesion. A meniscus between liquid and gaseous phase appears, and it can be concave or convex: in the first case there are adhesion forces, which are forces carried out by the wall surface molecules on the water liquid molecules, and they exceed cohesion forces and the fluid seems to be attracted on the wall; in the second case, viceversa, the adhesion forces are lower than the cohesive ones and wall seems to reject the fluid.

If the fluid is in equilibrium with the surrounding environment, there is not transport of water thus there are neither condensation nor evaporation, and the thermodynamic equilibrium at the meniscus is described with the Kelvin's law (2.1.4) which links the relative humidity to the liquid water density and to the capillary pressure.

Capillary conduction is a mechanism of water transport due to the concentration gradient, which is zero everywhere but not in the site where the meniscus is located. By the way, this position is not fixed in time, infact, for example, in a cylindrical capillary, the Hagen-Poiseuille's law provides depth in water penetration as function of square root of time. For capillary with a generic form, this  $\sqrt{t}$  relationship also appears.

This argument is used for understand that water content does not remain constant and, at the end, one can think the flow of liquid water in the same fashion of other fluxes:

$$g_w = -D_w(w)\frac{dw}{dx} \tag{2.3.2}$$

where  $g_w$ : liquid transport flux density [kg/m<sup>2</sup>s],  $D_w(w)$ : liquid transport coefficient [m<sup>2</sup>/s].

Equation 2.3.2 formally defined water content as driving potential.

The liquid transport coefficient depends strongly on the water content itself and on the temperature via the temperature dependence of surface tension  $\sigma$  and (trascurable respect to) viscosity of water. For example, the surface tension coefficient for pure water is expressed by

$$\sigma = (75.9 - 0.17T^{\circ}) \cdot 10^{-3},$$

where  $T^{\circ}$  indicates the temperature in Celsius degrees and the coefficient  $\sigma$  is measured by N/m. Note that, if temperature increases the surface tension decreasing and, at the end, note that if there are salts dissolved in the water, the coefficient  $\sigma$  increases.

It can be stressed that the description of capillary conduction is more difficult to analyze because the porous structure is highly complex, in fact there are capillary diameters which are variables, and for this reason is not easy get a formal description.

In the specific case of building material is necessary takes into account that the water gradient exists also because there are variable cross-section capillaries, consequently there are differently capillary pressure (2.1.3) and differently tractive force (which is proportional to the inverse value of capillary radius). The liquid into pore is accelerated by this tractive capillary tension until the equilibrium with flow resistance is reached. This latter resistance is proportional to the inverse the inverse value of the square of the radius.

These two different dependences on the radius are the reason why the water in the larger capillaries pushes on ahead than in the closer ones. In other words, there is a continuos decrease of the water content along the absorption direction. This process is know as *redistribution* which is more important if suction process is interrupted. In the end of this paragraph there is a brief description of this phenomenon.

Capillary transport can be described also with Darcy's equation:

$$g_w = k_l \frac{dp_c}{dx},$$

where  $k_l$ : permeability coefficient [kg/m·s·Pa].

The permeability coefficient is constant if the porous material is water saturated, but it is strongly dependent on moisture content if the level of saturation is not reached. Capillary pressure  $p_c$  can be obtained from Kelvin's law and it can be inserted in the last relation, by the ridefining of the coefficient, it can be possible to obtain the capillary flow equation:

$$g_w = -k_c \frac{d}{dx} (T \ln \varphi),$$

where  $k_c$ : capillary coefficient [kg/m·s·K],

whence

$$g_w = -k_c \frac{dT}{dx} \cdot \ln \varphi - k_c \frac{T}{\varphi} \frac{d\varphi}{dx}$$

Now, if temperature gradient is negligible as in the real condition, it can be takes into account only the second term, where defined the liquid conduction coefficient  $D_{\varphi}$  ([kg/m·s]) and reformulated last equation as:

$$g_w = -D_\varphi \frac{d\varphi}{dx}.$$
(2.3.3)

The liquid conduction coefficient is a function of the relative humidity and increases with the temperature.

The advantage of this reformulation is that the equation 2.3.3 describes the liquid capillary diffusion regardless of the parameters of porous material.

At the end, by comparing equations 2.3.2 and 2.3.3 is got

$$D_{\varphi} = -D_w \frac{dw}{d\varphi} \tag{2.3.4}$$

where  $\frac{dw}{d\omega}$ : variation of moisture storage function [kg/m<sup>3</sup>].

From equation 2.3.4 it can be possible describe the liquid capillary conduction (at least in moisture capillary region  $\varphi > 95\%$ ) forgetting the distinction between capillary suction process and redistribution, and the hysteresis effects [6], [7] and [10]. In particular case of capillary transport in the supersaturated region, it can not be happend in general because the driving potential (suction stress or relative humidity) remaines constant.

### Redistribution

In a building material, as already mentioned in par. 2.3.2, a water gradient is always present since pores and capillaries are of different sizes. Thus, water content into these variable capillaries experience different tractive capillary tension and flow resistance, which have the following trends respect to the capillary radius r:

• tractive capillary force  $\sim \frac{1}{r}$ 

• flow resistance  $\sim \frac{1}{r^2} \Rightarrow$  (Hagen-Poiseuille law).

Following the model of the interconnected cylindrical capillaries explain in [7], it can be possible know the water content profile. As shown in fig. 2.3.3, one can think about a system of capillary in contact one with another and with variable radius.

If this apparatus is in contact with a water source, the water in larger porous is propagated to longer distance despite the lower tractive tension, due to the lower flow resistance. In this case, there is a continuos profile of moisture content in the same direction of sunction motion (fig. 2.3.3, left). Viceversa, if the water supply is removed, the fluid motion ongoing. This is due to smaller porous, that are not completely filled, which dry the larger ones: the former have small radii and thus, greater traction, respect to the latter ones (fig. 2.3.3, right) [7].



Figure 2.3.3: Left: normal sunction. Right: redistribution.

Redistribution is, in other words, a water propagation into the complex system of capillaries and porous, when the contanct of building materials and a water source is cut off. This fluid transport is due to the competition between tractive capillary suction and the flow capillary resistance, which intensity depending on the capillary radius.

The liquid conduction coefficient increases with the water content but some experimental results have demostrated the difference between the absorption and redistribution trends. As has been explained previously, in the absorption phase the larger capillaries driving the sunction process but in the redistribution phase they are almost inactive, and in this situation only the smaller pores act. Redistribution is comparatively slow and it provide the difference between the liquid transport coefficient during these two processes, as it can be possible see in fig. 2.3.4, ref. [11].



Figure 2.3.4: Liquid transport coefficient for the absorption and redistribution diffusivities. Both coefficients increase with water content ( $w_f$  here means the capillary saturation water content), but in a different manner.

## 2.4 Superimposed liquid and vapour transport in building component

The superimposed liquid and vapour transport has different behaviours depending on the thermal conditions.

In isothermal situation the vapour pressure gradient and the relative humidity gradient ranging in the same direction. Thus, the pressure gradient drives a vapour diffusion transport mechanism and, at the same time, the adsorption moisture gradient drives the liquid transport in the adsorption layer and these two mechanisms of transport proceed along the same direction. In the following figure, there is represented also the sorption moisture equilibrium which would develops without liquid transport in the sorption phase (dashed line) and the equilibrium with liquid transport (solid line). It can be possible see that the sorption moisture drops below the equilibrium moisture content in the higer relative humidity side, and viceversa it rises above equilibrium level on the opposite side, ref. [7].



Figure 2.4.1: Liquid and vapour transport in isothermal condition:  $T_1$ , in the left side (or indoor-side) coincides with  $T_2$ , in the right side (or outdoor-side).

In non-isothermal situation there is a gradient of temperature (e.g. in winter condition there is an higher temperature in the indoor-side than the outdoor-side) and the behaviour changes in the following manner. The relative humidity is always higher in the lower-temperature side and in the higher-side temperature there is the higher pressure value. In other words, if there is a temperature gradient, it provide a pressure gradient from high-T side to low-T side and a relative humidity gradient from low-T side to high-T side. This means that in non-isothermal condition both gradients are opposed to each other and, likewise, vapuor diffusion and liquid transport are opposed to each other (dashed line and solid line have the same meaning which these had in the previous figure) [11].



Figure 2.4.2: Liquid and vapuor transport in non-isothermal condition:  $T_1$ , the indoor temperature is higher than  $T_2$ , the outdoor temperature. In this situation, which is typical of the winter season, the two mechanisms of transport are developed in opposite direction.

In the sake of completeness, it must be stressed that this last non-isothermal situation also changes, depending on the moisture content in the building component, as can be see in the fig. 2.4.3. If the building sample is dry (or the moisture content is lowest) the vapour diffusion is the unique mechanism of water transport can occur, because the adsorbed water remains immoble due to the higher adhesive forces values. As the water content rises, there develop a sorbate film of liquid water which is thicker on the outside (where relative humidity is higher) than the inside and if the water content rises so, the mobility of water molecules increased too. This leads to the surface diffusion, which is part of liquid transport driving by the relative humidity gradient. In the limit case, the humidity content is so high that the main mechanism



of transport is capillary conduction, with refs. [6] and [11].

Figure 2.4.3: Representation of moisture transport in porous hygroscopic material depend on the humidy content, in non-isothermal condition e.g. in winter season.

## **Chapter 3**

# Heat transport

## 3.1 Review on thermodynamic concepts

In this paragraph, some concepts of thermodynamic are reported, which can be useful in the following discussion. Here are remembered the most important definitions and variables, with refs. [20] and [21].

• Internal energy U ([J]) = microscopic kinetic energies of particles + microscopic potential energies of particles

where microscopic kinetic energies are due to motions of particles:

- traslation,
- rotation,
- vibration;

microscopic potential energies are due to composition of:

- chemical bonds,
- intermolecular forces;
- Heat Q ([J]) : energy of the system exchanged between the system and the environmet, subsequently to a temperature variation,
- Work W ([J]) : mechanical energy spent by the system, it comes to "work performed" by it.

In thermodinamic field, a phisical system can be defined as closed or open. In the first case, the system can exchange energy but not matter with the external environment, in the second case the system can exchange both energy and matter with the surrounding. If the system does not exchange energy nor matter with the surrounding, it is defined as isolated system [31].

If the system is closed, the First Law of Thermodinamics (in differential form) defines the equivalence between heat and mechanical energy of the system. Without transfer of matter, it prescribes the change of energy of a system, which is energy supplied by the exterior environment, as an exchange of heat summed to the mechanical work, performed at the boundaries of the system:

$$dU = dQ - dW.$$

In the last expression, it is interesting note the signs: heat is preceded by a positive sign which represent heat received by the system from the exterior, viceversa the minus sign before work term, indicates that is the system which does work against the environment. In literature, it refers to internal energy as a function of state: it can be described as a function of indipendent variables, which describes the thermodynamical state of the system (V, T, or others). From these observations, follows that the internal energy is an exact differential, which means that the integral is independent to the path following during the thermodinamical trasformation, but depends only by the starting point and ending point, or states, of the system.

Another important concept is enthalpy, which is strectly connect to internal energy. Under the assumption of isobaric transformation, it means that the transformation occurs at costant pressure, which is assumed normal to the surface of the system, the work term in the last equation becomes  $dW = P \cdot dV$ , and so one obtained:

$$dU = dQ - P \cdot dV.$$

Following [31], one can introduce enthalpy which is a function of state: H = U + PV. Now, the first law of thermodinamycs can be reformulated in the following manner

$$dH = d(U + PV) = dU + dP \cdot V + P \cdot dV = dQ + V \cdot dP$$

It is interesting do two considerations. First, in isobaric transformation there is not any variation of pressure and thus, an infinitesimal change of enthalpy of the system corresponds to an infinitesimal change of heat; second, if the system is in isobaric condition and it is also isolated from the surrounding, it can not exchange heat with the surrounding and, in other words, the entrophy of the system remains costant.

If the system (supposing, in sake of simplicity, homogenous system) is open, it exchange energy and mass with the surrounding (e.g. evaporation process), so in the expression of the energy conservation, a term which explicit the mass variation has to be added

$$dU = dQ + hdm - P \cdot dV$$

where dm identifies the matter exchanged between the system and its surrounding, and h is the specific enthalpy<sup>1</sup>.

It can be useful to introduce the flow connected to the heat transport:

• Heat flow rate  $\Psi = \frac{Q}{t}$ : amount of heat flowing per unit time through a well defined area

<sup>&</sup>lt;sup>1</sup>It is a state variable which is defined as  $h = \frac{U+PV}{M}$ 

[J/s],

• Density of heat flow  $q = \frac{\Psi}{A}$ : heat flow rate per unit of area [J/m<sup>2</sup>s].

## 3.2 Time-dependent physical processes

A thermodinamical system can be considered in *thermodinamical equilibrium* if there occur three conditions, simultaneously:

- Thermal equilibrium: system and the external environment are at the same temperature and there is an equilibium condition with respect to heat exchange,
- Mechanical equilibrium: there are no forces which might change the thermodinamic coordinates of the system, or in other words, this means that the system and the surrounding are at the same pressure value,
- Chemical equilibrium: there is equilibrium respect to chemical reactions and to the microscopical transport of matter. This means that the system and the environment present the same chemical potential value.

A system which is in a thermodinamic equilibrium state could proceed to another equilibrium state in different ways: it is defined quasi-static process if the intermediate states do not deviate significantly from an ordered succession of equilibrium states. In a quasi-static evolution from an equilibrium state to another one, there are not informations on time variations of the variables. If there is at least an intermediate state of non-equilibrium, the system is defined as real process.

From another point of view, the boundary conditions might change and, in this situation, the process could be defined as reversible or irreversible. In the first case it is considered a physical system which is describe by time-dependent equations which are invariant respect to the inversion of the time variable sign. It is the tipical case of a system without dissipative effects. Viceversa, if the equations which describe the evolution of the system depend on the sign of t, the process is called time-irreversible process.

## 3.3 Mechanisms of heat transport

There are three principal mechanisms of *heat transport*. In the following they are presented briefly, with refs. [20] and [21].

### Conduction

Thermal conduction is, from a macroscopic point of view, the exchange of heat inside solids, liquid or gaseous sample, without material movement. It is due to the transfer of kinetic energy

by atoms or molecules which are present in a zone at a higher temperature, to other atoms or molecules in adjacent areas at lower temperature.

#### Convection

The thermal convection is a kind of heat transport which occurs in the presence of macroscopic relative motion of fluid elements compared to a surface. This surface is supposed, for example, at a temperature above that of the surrounding fluid. The convective heat transfer occurs in several stages: first the heat passes by conduction from the surface to elements of fluid adjacent, increasing their temperature. Then, the elements of the fluid, which are heated, move towards parts of fluid at a lower temperature, where it ceding part of their energy. Briefly, convection is an energy transport mechanism which is characterized by a bulk motion: the heat is pick up in a certain warmer points of space into material and it is released to a different colder location. Convection needs a medium.

### Radiation

This heat transport mechanism is characterized by the emission or by absorption of electromagnetic waves by the material and therefore in this process is no medium needed for the propagation of heat. In the temperature range which is interested for the building physics (from -20°C to +40°C), the radiation is know as heat radiation or thermal radiation, and it follows the same trend of the Stefan-Boltzmann law.

The concept of heat transport is directly connected to the problem of *phase change*. As is well note, a variation of the temperature can produces a phase change, like melting, solidification or evaporation processes. In a porous building material, the pores are filled with water in one or more phases and it is clear that the description of this situation is far from simple situation. In fact, if one considers the substance that fills pores (tipically water) is pure, there is a particular single temperature in which this substance solidifies, while if the substance is a mixture or presents some impurities, there is a range of temperatures in which the solidification can occur and thus appears in two coesistance phases, solid and liquid [18]. In the same manner, there is a similar complication in the case of the pores are filled with liquid water and gaseous mixture of dry air and water vapour [19]. In fig. 3.3.1 is reported a qualitative phase transition between liquid-gas phase in a mixture.



Figure 3.3.1: Qualitative representation of a phase transition in a mixture: units are arbitrary. In the mixture there are two component, A and B, but the diagram represent the temperature trend respect B concentration

 $T_B$  and  $T_A$  are the boiling point of component B and A respectly. The lower line, from  $T_A$  to  $T_B$  represent the B fraction in liquid phase, at various T, viceversa the upper one represent the B fraction in gaseous phase. In  $T_B$  there is the maximum concentration of B, and in  $T_A$  there is the minimum concentration of B; in  $T_A$  there is the opposit situation for A. For example, for a fixed concentration of B,  $x_{B1}$ , there is a range of temperatures over liquid and gaseous are in equilibrium: gas is more A rich and liquid are more B rich.

The heat transport mechanism is not simple to describe infact it can be cataloged as a *free boundary problem*. Free boundary problem is a particular case of mathematical analysis which describes a physical process without fixed boundary condition. In the specific case of phase change, the two-phase boundary moves with the same speed of lost or absorption heat and at the end, is not possible to localize the position of this boundary which become part of the problem [18].

## 3.4 Heat storage

*Enthalpy* is defined as the heat content which is stored into a material in homogeneous conditions. In the present study, is studied the enthalpy (and not entropy, as is usually done) because here are analized open systems, which exchange energy and matter with the exterior beside the fact that the system undergoes some phase transitions.

In the temperature range of the building physics is almost true a linear relationship between enthalpy and temperature. To quantify the amount of enthalpy (read "heat") stored into material, one must distinguish between two situations, with ref. [6]:

• dry material: the only heat stored is that of the material itself

$$H_d = \rho_d c_d T$$

where  $H_d$ : enthalpy of the dry building material [J/m<sup>3</sup>],  $\rho_d$ : mass density of the dry building material [kg/m<sup>3</sup>],  $c_d$ : specific heat capacity of dry building material [J/kg·K], • moisture: heat storage of the water content into building material must be added to the enthalpy of dry material

$$H_w = \left[ (w - w_f)c_w + w_f c_f - h_f \frac{dw_f}{dT} \right] T$$

where  $H_w$ : enthalpy of the moisture content into building material [J/m<sup>3</sup>],  $c_w$ : specific heat capacity of liquid water [J/kg·K],  $c_f$ : specific heat capacity of ice [J/kg·K],  $h_f$ : specific melting heat (enthalpy) [J/kg],  $w_f$ : frozen water content [kg/m<sup>3</sup>].

If the building material is dry, one must take into account only  $H_d$  while, if it is moist, one must use  $H_d + H_w$ .

Remark that *specific heat capacity c*, means the heat needed to increase the temperature of 1 kg of certain material by 1°C (without phase change). If one assume a 1 m<sup>3</sup> of material which has density  $\rho$ , the volumetric specific heat capacity is defined as  $c\rho$  and it is measured as  $[J/m^3K]$ ; it represents the change in heat stored in unit volume of material and for unit change of temperature. In sake of completeness, one must takes into account that the specific heat capacity is strictly dependent on the particular trasformation during heating. In particular in building physics, the trasformation tipically occurs with constant pressure and because solids and liquids have about the same value of specific heat capacity in isobaric conditions, it is possible use the same notation *c*, as in [21] and [28].

In particular, the enthalpy of the water depends on the physical state in which it exists, but it is not simple to defined, and it is required to take into account the latent heats which characterized the phase changes.

## 3.5 Thermal conduction

In accordance with what has been done previously for the moisture transport, one can define a driving potential also for the heat transport, which is the temperature. As is known in literature, the heat flow (density) rate is defined by the first Fourier's law, which quantifies the heat flow via temperature gradient and thermal conductivity:

$$q = -\lambda \frac{dT}{dx},$$

where

λ: thermal conductivity [W/m·K],  $\frac{dT}{dr}$ : temperature gradient [K/m].

The minus sign indicates the heat flow rate and temperature grandient are opposite one each other. The heat flux is always direct along to normal vector of the isothermal surface, which is a surface of fixed temperature.

This last equation describes the heat flow under the assumption of only one dimensional transport occurs. In the real case, the true expression of heat transport is described by

$$\bar{q} = -\lambda \nabla T \tag{3.5.1}$$

where

 $\bar{q} = (q_x, q_y, q_z)$ : heat flow vector,  $\nabla = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right)$ : gradient vector, T = T(x, y, z): tridimensional scalar temperature field.

The Fourier's law has the following properties. First, it is a fenomenological law, or it is not derivable by first principles, and so it defines the concept of thermal conductivity; second, it is a vectorial relation and so it defines the direction of heat flux and finally, it applies for all matter in any state (solid, liquid, gaseous).

In isotropic material, <sup>2</sup>  $\lambda$  is the same in each of the three directions and, if one consider a tridimensional problem it is need define three equations analogous to the last one, one for every cartesian directions. While in an anisotropic material, as a porous building material, the thermal conductivity can be different in each of the three directions [21].

Connected to the volumetric specific heat capacity, it can be introduced the *stored heat density*, which is defined by the ratio between the heat Q and the volume of sample V. It is indicated by e and measured by [J/m<sup>3</sup>]. Connected to a temperature difference, there is a variation of stored heat density

$$\triangle e = c \rho \triangle T.$$

From the previous considerations performed about the First Law of Thermodynamics, this stored heat density may be identified as the enthalpy variation due to  $\Delta T$ , which depends on the heat of a phase transition through the specific heat capacity c of the substance which undergoes to the transition. In the specific case of a porous material, water undergoes to some phase transition: condensation-evaporation and freezing-thawing (see par. 4.2).

Starting from the balance equation of the heat transport one can obtain the *heat diffusion equation,* which provides the temperature distribution T(x, y, z) as a function of time (in other words, it is a re-formulation of the energy conservation):

$$-\nabla \cdot \bar{q} + S_e = \frac{\partial e}{\partial t} \tag{3.5.2}$$

where  $S_e$ : source or sink (density) of heat [W/m<sup>3</sup>].

The balance equation describes the conservation of heat into a volume of reference:  $S_e$  is positive if represents a source, negative if sink.

Using the equation for *e* and the first Fourier's law into eq. 3.5.2 one get the following relation:

$$-\nabla \cdot (-\lambda \nabla T) + S_e = \rho c \frac{\partial T}{\partial t}.$$
(3.5.3)

<sup>&</sup>lt;sup>2</sup>namely a material which has properties are indipendent from the directions.

If the material is isotropic and so the thermal conductivity is the same in each of the three coordinates, the eq. 3.5.3 become

$$\nabla^2 T = \frac{\rho c}{\lambda} \frac{\partial T}{\partial t} - \frac{S_e}{\lambda}$$
(3.5.4)

where  $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ : Laplace operator.

Eq. 3.5.4 is known as the second Fourier's law (in isotropic condition). The Fourier equation describe the heat equilibrium in terms of temperature and it is a clear example of irreversible approach to the thermal equilibrium, in fact it is not invariant with respect to the substitution of  $t \rightarrow -t$ .

**Remark** It is usefull note that this formulation of heat transport is correct in a sufficiently long time scale. If the heat propagation happens in time scale  $\triangle t$  such as

$$\frac{l_{mfp}}{v_m \triangle t} \ll 1$$

(where  $l_{mfp}$ : mean free path of particle which conducts heat,  $v_m$ : mean molecular velocity), the finite velocity of propagation of thermal information can be neglected. Viceversa, if time scale not satisfies this last condition, the Fourier's description of heat transport is not valid for finite speed heat propagation and other nanoscale theories must be used [29].

In porous building materials, heat transport is closely related to the water content *w*. In general, *thermal conductivity* depends on the temperature (which may be different depending on the spatial location) and, which is more interesting, explicitly depends on the water content in the following fashion

$$\lambda(w) = \lambda_0 \left( 1 + b \frac{w}{\rho_d} \right) \tag{3.5.5}$$

where  $\lambda(w)$ : thermal conductivity of moist building material [W/m·K],  $\lambda_0$ : thermal conductivity of dry building material [W/m·K], *b*: thermal conductivity addition [-].

The coefficient *b* is an additional term which counts how many percent the thermal conductivity increases for every percent of moisture mass. This coefficient is characteristics of the material but there are many known values for hygroscopic building materials [6].

It must be underline that a porous material, as it just be define, is a solid matrix with several pores and capillaries wich can be considered filled by water in liquid or vapuor phase and, possibly, by dry air. In the void volumes, some phase change can happen, like condensation of a certain ammount of water vapour on the solid matrix surface. In this situation it must take into account the enthalpy of vaporization, or in other words the heat released during the phase change. In total counting of heat in porous cavities one must to consider heat of water liquid,

water vapour gas, dry air and heat of change phase.

Might be useful clarify the difference between two concepts used up to now: (specific) heat capacity and thermal conductivity. The former describes the ability of the material to store heat as energy: it is not a truly transport property but is a thermodynamic property of the considered material. The second one, is a really transport property in fact describes the ability of the material to transport heat with conduction mechanism [20].

## Chapter 4

# Heat and moisture transport

This chapter has the purpose to point out the mechanisms presented previously, but with the aim to show the connection from one transport mechanism to another, because in this way, become clear the complexity and the heterogeneity of the problem.

## 4.1 Moisture and heat transport equations

The driving principle for defines what are the equations which describe the transport problem is, obviously, the law of continuity [6]. It means that the time variation of moisture content in a reference volume element is due to the divergence of moisture flow through the surface of this element plus a source or a sink term. This continuity equation can be define as well as for the heat transport referred to this volume element. The model of heat-moisture transport can be summarized with the following formulation:

$$\begin{cases} \frac{\partial w}{\partial t} = -\nabla (g_w + g_v) + S_w \\ \frac{\partial H}{\partial t} = -\nabla q + S_e \end{cases}$$
(4.1.1)

where w: water content in the building material [kg/m<sup>3</sup>],  $g_w$ : liquid transport flux density [kg/m<sup>2</sup>s],  $g_v$ : water vapour transport flux density [kg/m<sup>2</sup>s],  $S_w$ :moisture source or moisture sink [kg/m<sup>3</sup>s],

> *H*: total enthalpy  $[J/m^3]$ , *q*: heat flux density  $[W/m^2]$ , *S<sub>e</sub>*: heat source or heat sink  $[W/m^3]$ .

The first equation of the previous system represents the conservation of water content in a volume element. g represents the flux of water which can be divided into two contributions: water liquid flux,  $g_w$ , and water vapour flux,  $g_v$ .

Water liquid flux could be expressed, for example, in terms of water content grandient and with the distinction between the liquid transport coefficient or with the surface diffusion coefficient, one can distinguish the two mechanisms: capillary conduction or surface diffusion. As is shown in the par. 2.3.2, the most useful expression of the liquid flux is in term of relative humidity, in fact it is a parameter that is relative simple to control. Concretely, the liquid transport flux can be express as:

$$g_w = -D_\varphi \nabla \varphi. \tag{4.1.2}$$

Water vapour flux is determinated by the vapou pressure gradient:

$$g_v = -\frac{\delta}{\mu} \nabla P_v \tag{4.1.3}$$

where, note that the ratio between the water vapour permeability  $\delta$  and the vapour diffusion resistance factor  $\mu$ , is known as water vapour permeability of building material (units kg/m·s·Pa). Finally, remember that the real expression of  $g_v$  should be distinguished in two machanisms: Fick's diffusion and effusion.

The second equation of the system represent the balance of the heat exchange in terms of the total enthalpy of the system which consists of the of the enthalpy of the solid dry building material plus the enthalpy contribution due to the water:  $H = H_d + H_w$  (units J/m<sup>3</sup>). The heat flux density can be expressed as the Fourier's law of the heat conduction due to a temperature gradient:

$$q = -\lambda \nabla T \tag{4.1.4}$$

where, remember that the thermal conductivity of the moist building material may be explicitly dependent on the water content.

Inserting eqs. 4.1.2, 4.1.3, and 4.1.4 in the system 4.1.1 one obtained:

$$\begin{cases} \frac{\partial w}{\partial \varphi} \frac{\partial \varphi}{\partial t} = -\nabla (-D_{\varphi} \nabla \varphi - \frac{\delta}{\mu} \nabla P_{v}) + S_{w} \\ \frac{\partial H}{\partial T} \frac{\partial T}{\partial t} = -\nabla (-\lambda \nabla T) + S_{e} \end{cases}$$
(4.1.5)

where are highlighted the moisture storage  $\partial w / \partial \varphi$  and the heat storage  $\partial H / \partial T$ .

In building physics, moisture source terms can be neglected in standard condition, as which considered in the present work, but viceversa it cannot neglected in special conditions as in case of a ruptured water pipe [6] and in analogous way moisture sinks are not taken into account in first approximation. Finally, the enthalpy flows due to phase transitions as evaporation-condensation transition and freezing-thawing transition or a chemical reaction, can be defined as source terms which will be explain in par. 4.2.3 and 4.3. So the term  $S_e$  will be specialized in every situations.

#### **4.1.1** Formal approach to the heat problem

Following [45] one can try to approach the thermodinamic behaviour of a natural process with a lagrangian point of view. Infact the lagragian formalism can be an usefull analytical key in order to describe the thermodinamical transformations that can be performed by an open irreversible system [35] as is any natural process.

The statement of the thermodinamic second law, by Lord Kelvin, says that it is impossible obtain a system which is *only* able to transform heat absorbed by the system itself into work. From this statement, follows that [45] in an irreversible natural process part of work,  $W_{\lambda}$ , is lost and it can be connect to the entropy generated by the irreversibility from, for the open system, the Gouy-Stodola Theorem<sup>1</sup>.

As defined in [45], the work lost by a natural system due to an irreversible process is:

$$W_{\lambda} = \int_{0}^{\tau} dt \dot{W}_{\lambda} \tag{4.1.6}$$

where  $\dot{W}_{\lambda}$  is the difference between the maximum power transferred, which is the maximum work transfer rate between the system and the environment in the limit case of ideal reversible process, and  $\dot{W}$  is the effective power transferred. So, concretely:  $\dot{W}_{\lambda} = \dot{W}_{max} - \dot{W}$ .

In thermodynamic field, one of the most important state function is *entropy* which defines the heat exchange during certain process. In this contest, the system is open and the process is irreversible, so the entropy of the whole system, whichs take into account the open system and the surrounding environment, is defined as:

$$S := \int \left(\frac{\delta Q}{T}\right)_{rev} = \triangle S_{rev} + S_g \tag{4.1.7}$$

where  $\triangle S_{rev}$  is the entropy variation that would be obtained exchanging the same heat flux in reversible conditions, and the term  $S_g$  is the entropy generation because the irreversibility of the process<sup>2</sup> and it is defined as:

$$S_g = \int_0^\tau dt \dot{S}_g \tag{4.1.8}$$

where, with the same notation used above,  $S_g$  is the entropy generation rate during the irreversible process, which has lifetime  $\tau$ .

As explained in the introduction and in refs. [35] and [45], the entropy generation, which is the term due to irreversibility, measures how much is the system far from the reversibility condition, when this term should be dropped.

For the evaluation of the entropy generation one may use the Gouy-Stodola Theorem:

<sup>&</sup>lt;sup>1</sup>Original references:

G. Gouy, Sur l'énergie utilisable, Journal de Physique, 8, (1889), pp. 501-518;

A. Stodola, (1898), Die kreisprozesse der dampfmaschine.

<sup>&</sup>lt;sup>2</sup>As in [35] note that is a formal term which is introduced to avoid inequalities of heat or energy transfer.

**Theorem:** In any open system, the work lost for irreversibility  $W_{\lambda}$  and the entropy generation  $S_g$  are related each another as:

$$W_{\lambda} = T_a S_g$$

where  $T_a$  is the surrounding environment (ambient) temperature.

So, this theorem supports the connection between the work lost in a irreversible process to the enetropy generation and it is expressed in a global way.

At this point, one can use a lagrangian approach in order to describe the most probable path followed by the system for goes from the initial to final state in the lifetime  $\tau$ . In accordance to [45], the thermodynamic Lagrangian is:

$$\mathcal{L} = W_{\lambda} \tag{4.1.9}$$

and, at the stationary state, the work lost for irreversibility is an extremum. In fact, one can introduce the action in the following manner:

$$\mathcal{A} = \int_0^\tau dt \mathcal{L} = \int_0^\tau dt W_\lambda \tag{4.1.10}$$

and for the least action principle one obtain:

$$\delta \mathcal{A} \le 0 \Longrightarrow \delta W_{\lambda} \le 0 \tag{4.1.11}$$

which means, for the entropy generation inside the system  $\delta S_g \leq 0$ , and viceversa, for the entropy generation inside the environment  $\delta S_g \geq 0$ .

But, in the present work, what does it mean? Entropy and enthalpy of a system are connected by the Gibbs free energy [31]:

$$G = H - TS \tag{4.1.12}$$

and in conditions of constant pressure, which means that the mechanical work can be neglected, and of contact to a termal bath, which means that the temperature remains constant, a variation of *G* means  $\triangle G = \triangle H - T \triangle S$ . A natural spontaneous process tends to the minimum of the variation energy, which means:

$$\triangle G = \triangle H - T \triangle S \le 0. \tag{4.1.13}$$

In the limit situation, the equality holds, and so  $\triangle H = T \triangle S$ . In this last expression  $\triangle S$  must be interpreted as the sum in 4.1.7 and so it must be splitting in a term of the entropy variation in reversible process plus the entropy generation for irreversibility. In the same manner  $\triangle H$  is splitted:

$$\triangle H = \triangle H_{rev} + H_{irr}$$

with the same significance of the term.  $H_{irr}$  represents how much the variation of enthalpy of the real process is far from the variation enthalpy in the ideal reversible situation. Proposing an extension of the Gouy-Stodola theorem to the enthalpy generation due to irreversibility, in the limit condition of the eq. 4.1.13:

$$H_{irr} = T_a S_g = W_\lambda \tag{4.1.14}$$

and in the general situation:

$$H_{irr} < T_a S_g = W_\lambda. \tag{4.1.15}$$

So, from the limit condition 4.1.14 one can try reformulate the variational principle presented above for the entropy and apply it to the enthalpy, which is the function of state under analysis in the present work. Using eqs. 4.1.9 and 4.1.14, one obtains:

$$\mathcal{L} = W_{\lambda} = H_{irr} \tag{4.1.16}$$

and proceeding with the definition of the action:  $\mathcal{A} = \int_0^{\tau} dt \mathcal{L} = \int_0^{\tau} dt H_{irr}$ , and finally with the least action principle:

$$\delta \mathcal{A} \le 0 \Longrightarrow \delta H_{irr} \le 0. \tag{4.1.17}$$

For the real situation of the present work, the enthalpy of the system is streactly connect to the water content in pores and capillary. In the simple case of standard situation, which means that the option of supersaturated regime condition is neglected, there is a maximum value of the water content in the material and it is the water saturation value  $w_{sat}$ . So, at the end, the least action principle it must be applied taken into accout this constraint of the maximum water content:

$$\begin{cases} \delta H_{irr} \le 0\\ \int_V (w_{sat} - w) dt = 0 \end{cases}$$
(4.1.18)

### 4.2 Phase transition

### 4.2.1 Condensation - Evaporation

In the physics of buildings, and in particular in building restoration science, condensationevaporation cycles must be taken into account. Those cycles occur several times and from one hand, they influence the local variation of the liquid water, and from other hand, they play an important role in the transport of chemical pollutant. In the former situation, locally condensated water is as a water supply which may cause dissolution of the solid material in the stones, may reduce the mechanical resistance of the material in rocks or mortars and it may alter the crystal structure (as expansion, stress and fractures) in some kind of limestone [41]. In the latter situation, condensation-evaporation cycles cause weakening of material due to some mechanisms as efflorescence of salts, which is largely reported in literature and will not be described in the following. Furthermore, adsorption-evaporation cycles can cause irreversible dilatation damage which may be of the order of 1mm/m.

As in refs. [40] and [41], it is interesting to describe how water condenses into pores. This process is mainly linked to the pores geometry, spatial connection between pores, pore geometry, as well as the surrounding atmospheric relative humidity.

First, one can assume an hemispheric cavity with radius  $r_p$  (it can be associated to the capillary radius  $r_c$  according to the Kelvin's law), which is located, typically on the surface of the body, in interaction with the external environment. This cavity remains almost empty, until the relative humidity reaches the critical value  $\varphi(r_p)$ , which depends on the pore radius minus the thickness of monolayer of adsorbed water. If the relative humidity increases, the pore cavity starts to fill with condensed water and then by the meniscus radius increases. When relative humidity reaches the maximum value, as 100%, so meniscus radius theoretically goes to infinity and the cavity is filled, that means the water meniscus is flat and the contact angle between the meniscus and the surface is zero. Since during all steps of the cavity filling there is equilibrium with the external humidity, this condense process is reversible, namely when the external relative humidity decreases, also the meniscus radius decreases (from the ideal infinity value), until the initial condition is restored, when the meniscus radius is equal to the pore radius and the cavity is empty. See fig. 4.2.1A.

Second, if an internal pore is considered, condensation process becomes irreversible. Internal pore means that it is linked to the external environment with an aperture radius smaller than the pore radius. This kind of pore is, generally, located inside the material. Just as the previous situation, condensation starts when the relative humidity reaches the critical value relevant to the pore radius,  $\varphi(r)$ . As the relative humidity starts to increase, on the internal pore surface some layers of condensate water appear. In this situation, however, the free space into the pore decreases, and the meniscus radius decreases too. Following that, also the relative humidity related to the actual meniscus radius becomes smaller, as a consequence of the Kelvin's law. In this complicate situation, the initial relative humidity results greater than the actual relative humidity,  $\varphi(r_m) < \varphi(r_v)$ , and the process is accelerated because the initial value of relative humidity appears as a non-equilibrium value, and at the end, the filling of the cavity occurs. The evaporation process starts when the relative humidity becomes smaller than the critical value  $\varphi(r_0)$ , which is related to the pore aperture radius  $r_0$ . In this situation, water can leave the pore and the meniscus radius starts to increase as the corrispondent relative humidity value,  $\varphi(r_m)$ , but on the contrary, the external humidity remains lower than the critical value,  $\varphi < \varphi(r_0)$ . Determined by this gradient of relative humidity, evaporation is accelerated until the pore returns to is initial void condition. See fig. 4.2.1B.



Figure 4.2.1: A) Condensation in an hemispheric open cavity: subscripts 1 and 2 mean two different condition of relative humidity, where  $\varphi(r_{m,1}) < \varphi(r_{m,2})$ , means when the external humidity increases, the meniscus radius increases too, and viceversa for evaporation. B) Condensation in an inner pore: when the process starts, the meniscus radius decreases as the cavity is filled by water  $\varphi(r_{m,1}) > \varphi(r_{m,2}) > \varphi(r_{m,3})$ , and viceversa for evaporation.

### 4.2.1.1 Dew deposition

In this paragraph a short study of dew deposition is presented. This process, which is part of the surface water deposition problem with, for example, the rain water deposition, is very important during the night radiative cooling and it appears in the form of a liquid water layer or droplets. The former is characteristic of a hydrophilic material, like most of building materials (without any kind of insulation treatments) which immediatly absorb the water in their inside, the latter is the typical dew formation of hydrophobic materials.

This problem, as it has often been pointed out, is directly connected to the damage of historical buildings or historical heritages and it plays a main role in the chemical aggression of them, which is strongly driven by the water presence on the object surface. Ref. [42] presents some experimental simulations of the water deposition on samples surfaces, distinguishing between vertical and horizontal exposition, with respect to the sky, of them.

From the Lambert law, intensity of the radiation emitted by the surface, when it cools, depends on the angle between the normal to the surface and the emission direction. This means that samples in the same atmospheric condition emit in different way depending on the location and this fact is followed by a different temperature condition of samples themselves. One of the most important results is that, in all the material samples, the ammount of water deposited on the horizontal surface is much more than that on the vertical surface, and this effect is increases with less porosity of material. The measurements have been performed in different climatic conditions, and the results are summarized below:

- humidity ratio<sup>3</sup>: the amount of dew water deposited on the surface depends linearly on the ratio between mass of water vapour (moisture component) and mass of dry air;
- wind (light ventilation): in laboratory, it is found a linear relationship between the amount of dew water and the wind speed, which is assumed to run from 0 m/s to 4 m/s, holding all other climatic variables fixed;

<sup>&</sup>lt;sup>3</sup>It ranges from nearly 0 in cold continental air masses up to about  $20 \cdot 10^{-3}$  kg kg<sup>-1</sup> in the tropics.

• transparence of the atmosphere: in fully clear night, as soon as the environment temperature drops below the dew point, the condensation is heavy and it is more important on the horizontal surface than on the vertical one; in not fully clear night (cloudy night, e.g.) on the horizontal surface appears a moderate water condensate even if the temperature slightly drops below the dew point, viceversa on the vertical surface there is neither condensation nor evaporation because the temperature remains close to dew one.

Dew night formation depends on the climatic condition and on the seasonal conditions, which are related one to another. Briefly, in winter the nights are longer than in the summer time and the humidity mixing ratio is lower than in the summer time. This means that in winter-autumn there is the maximum amount of water condensate during one clear night, at least to the same latitude of Italy.

### 4.2.2 Freezing - Thawing

As just mentioned in the first chapter, near the condensation-evaporation cycles, also the freezingthawing cycle is dangerous. In fact, when the temperature drops below zero, water content into pores or capillaries can freeze with a consequent increase of volume about 10%, and this ice crystal formation can produce a pressure force on the inner surface of the pores, which may have distruptive consequences for the material itself. As in the condensation-evaporation process, also in freezing-thawing, one the geometry of the pores, the pore size distribution and the presence of water can play an important role.

First of all, it can be stressed that, in contrast with what one may expect, smaller pores suffer the most important damage. Small pores have sizes between 0.1 to 1  $\mu m$ . Another useful consideration is that the freezing process can occur at temperature below 0°C: if the radius is smaller of the meniscus of water content into pores, smaller is the freezing temperature too. For the qualitative description of the freezing process, one refer to sec. 1.2.2; whereas in ref. [41] the variation of the freezing point in spherical pore geometry is described.

Eperimentally it can be shown that the freezing point depression, namely the difference between 0°C and the temperature at which the real porous material freezes, increases as the pore radius decreases, infact there is an inverse proportional dependance.

In ref. [27] is underlined the importance of the moisture content and the quality of the material, which define the critical moisture content for frost  $w_{c,f}$  which is the critical value of ice moisture. This parameter is linked to the water saturation level  $w_{sat}$  in the material:  $w_{c,f} \le 0.9w_{sat}$ . In fact frost is dangerous when the moisture saturation reaches 90% of the pore volume, due to 10% of expansion of ice. If  $w_{c,f} < w$  the frost damage is inevitable.

Finally, when the ice formation starts to melt, this may cause the erosion of the stone of the, just mentioned, salt deposition on the material surface.

#### 4.2.3 Heat exchange during a phase transition

In the overall description of the heat transport, a term appears of heat source or heat sink  $S_e$  which takes into account the local production of heat due to a phase transition like condensantionevaporation cycle or freezing-thawing cycle, which are previously described.

As in ref. [6], the heat source or sink term is described as a gradient of the water vapour diffusion flux taking into account the latent heat of evaporation-condensation phase change. So, if  $g_v$  describes the water vapour diffusion flux density produced by the evaporation of condensated water, one can describe the related source term as the following expression:

$$S_{e,v} = -h_v \nabla g_v \tag{4.2.1}$$

where  $S_{e,v}$ : heat source or sink due to condensation-evaporation [J/m<sup>3</sup>s],  $h_v$ : specific evaporation enthalpy [J/kg].

Note that the specific evaporation enthalpy of pure water is about 2260 kJ/kg and it has positive sign if the process is the evaporation one, so liquid  $\rightarrow$  vapour and it represents the heat which must be absorbed by the system (namely one mole of vaporized substance, in standard conditions). From the opposite side, the specific evaporation enthalpy has the minus sign if the process is condensation, so vapour  $\rightarrow$  liquid, and it represents the heat which must be supplied to the system.

In the same manner, one can try to estimate the heat source due to freezing-melting cycle:

$$S_{e,f} = -h_f \nabla g_f \tag{4.2.2}$$

where  $S_{e,f}$ : heat source or sink due to freezing-thawing [J/m<sup>3</sup>s],  $g_f$ : melted water liquid flux density [kg/m<sup>2</sup>s].

Specific melting enthalpy of (ice) water is about 334 kJ/kg, and it is positive if the melting process, solid $\rightarrow$ liquid, takes place, conversely it is negative if the freezing process, liquid $\rightarrow$ solid, occurs. Melted water liquid flux density may be evaluated generalizing the liquid water conduction in eq. 2.3.1:

$$g_f = -D(w)\nabla w_f$$

where the minus sign appears for accounting the melting of the ice water content, which is upper limitated by  $w_{c,f}$ . The diffusion coefficient is the same that appears in chap. 2 and it describes the liquid water diffusion and it empirically depends on the temperature.

## 4.3 Chemical reactions

In the sake of completeness, one must take in mind that also a chemical reaction can produce a certain amount of heat, which must be added in the overall computation of the heat balance.

Followed the approach adopted in this work and in ref. [47] one can try to define a source term which is connect to the enthalpy variation due to a chemical reaction. If a reaction with N chemical species is take into account, each species is connected to a precise heat of formation  $h_i^0$ , which is evaluated at standard temperature. If the temperature goes from the standard value to the actual temperature *T*, the enthalpy connected to the i-specimen in the reaction becomes:

$$h_i = h_i^0 + \int_{T_0}^T C_{p_i}(s) ds$$
(4.3.1)

where  $C_{p_i}$  are specific heats at constant pressure.

For evaluated a source term connected to the heat provide from the reaction, one can observe that as the reaction proceeds, the density  $\rho_i$  of the chemical specimen i, varies. At the end, for every i-specimen, in the reaction one can assume that the heat produced is:

$$q_{r,i} = -h_i D \nabla \rho_i$$

where  $h_i$ : enthalpy produced by the reaction of the i-speciem, D: diffusion coefficient,  $\rho_i$ : density of the i-speciem.

Finally, the total heat provide from the reaction of all species, one can get:

$$q_r = \sum_{i=1}^{N} q_{r,i} = -D \sum_{i=1}^{N} h_i \nabla \rho_i.$$
(4.3.2)

Following the previous approach, one can define an heat source connected to the reaction:  $S_r = -\nabla q_r = \nabla \left( D \sum_{i=1}^N h_i \nabla \rho_i \right).$ 

## 4.4 **Buondary conditions**

Equations introduced in the present work are differential fashion and in the aim of to close the formal description, it is necessary to define the initial and the boundary conditions. Following refs. [6], [12] and [29], it is possible to catalogue these boundary conditions in three categories:

- First kind, or *Dirichlet's boundary conditions*: occur when the surface conditions are the same as the ambient surrounding. Temperature and humidity are fixed. Mechanisms of transport which can happen are:
  - heat transport and vapour transport \implies building component is in contact with water or ground
  - liquid transport  $\iff$  component surface is totaly wetted from rain

- Second kind, or *Neumann's boundary conditions*: occur when the surface is not completely wetted and/or heat transport is subjected to solar radiation. Moisture flux and heat flux are fixed and constant. In the adiabatic condition the flows, in particular the heat flow, are zero at the boundary.
- Third kind, or *Cauchy's (mixed) boundary conditions*: occur when the flux to/from the surface depends on the difference between the reference variable (temperature for heat and water content for moisture) at the surface and at the environment value. This means that, for example, the gradient of a certain magnitude is proportional to the magnitude itself. It is the simplest case of non-linearity which can be considerated, but it can clarify the complexity of this kind of boundary condition.

This kind of boundary condition is also known as convection regime.

In the following, it is analyze in detail the boundary conditions of heat transport at the surface. In the general case there is two surface, which bounding the building component, and it may be defined the condition of the temperature on each ones. The coordinate x = 0 indicates the surface of the wall and, for example, the positive x direction is assumed along the material with the temperature distribution.



Figure 4.4.1: Summary of boundary conditions in heat transport: on the left there is a first kind, in the middle there is the second kind, and on the right there is the third kind of boundary conditions.

In the left hand side, there is the representation of the first kind of boundary condition, where the temperature of the surface is maintained at fixed value ( $T_s$ ) which is the same of the surrounding environment. It is the condition, for example, of a melting solid or a boiling liquid in contact with the surface. In the middle figure, there is a schematic view of the second kind, or Neumann's, conditions where there is a fixed, constant heat flux dependent on a temperature gradient by the Fourier's law (one dimensional). It is the case of, for example, a heat source like a heater. In this second kind there is a particular case, known as adiabatic condition, in which the heat flux is set to zero and it correspond to a case of insulated surface. In the right hand side there is a reprensetation of the third, convective, boundary condition which happen when there is a convection heating or cooling flux at the surface. It describes an heat flux which is proportional to the difference between the temperature surface and the ambient temperature, indicated by  $T_{\infty}$  in the figure [29].

In the follow chapter there are analyzed the most important external conditions.

# **Chapter 5**

# **Outdoor conditions**

## 5.1 Rain-fall problem

The precipitating water is very dangerous for the health of a building in general, and for historical buildingS in particular. The water rain is one of the most important sources of damage for facade of building; in fact it can be driven into joints of stone and penetrate into the building structure, so providing a several and serious problems [23], [25] such as:

- it amplifies injuries due to the freezing problem,
- it introduces moisture controlled salt migration<sup>1</sup>,
- it causes discoloring efflorescence,
- erosion and changing appearance of the soiled facade,
- biological degradation of building component (mould growth),
- structural cracking.

The problem connected to the rain-fall is not related only to the amount of water fall during downpour, but in reference to what described at the end of par. 2.3, it is also related to the redistribution process. In other words, one must take into account the moisture transport also when the water supply has been removed, for example during the sunny weather after the rain, starting a humidity sorption due to the redistribution which can lead to the condensation in some spatial points [24].

<sup>&</sup>lt;sup>1</sup>Salts, which are trasported by moisture water, are deposed onto the surface of stone sample when the water is evaporated. This salt deposition is dangerous for the surface because it provides chemical corrosion of the plaster or the original stone.

### 5.1.1 Wind-driven rain effect

In rainy weather there are two situations: in windless case, rain falls vertically, while in windy weather the raindrop trajectory is oblique. In the latter case, the vertical component is named as precipitation and the horizontal one is called wind-driven rain. The water precipitation wets horizontal and sloped surfaces, while the wind-driven rain affects also the vertical surface [24]. In other words, the wind-driven rain is given by the horizontal component of wind velocity. Wind-driven rain is one of the most important moisture source for building materials and consequently, it is a fundamental boundary condition that must be taken into account in the description of the behaviour of a building component. The wind-driven rain intensity is very difficult to evaluate, infact it depends on several parameters as the building geometry, the position of the building component which is analyzed, the location of the building in the environment, as well as speed wind, wind direction, horizontal rainfall intensity and the raindropssize distribution. In the same manner, it is not simple to measure it because measurements are time-consuming, expensive and often impractical, and especially, are specific of the particular building which is investigated. Therefore, the data relating to a particular building facade at a particular site, can be applicable in a very limited way to other facades in other locations [26]. In practice, if an approximately horizontal surface is subject of study, it is sufficient to know the rain data provided by the nearest weather station, viceversa if the driven rain impacts on a vertical wall or sloped surface, it is covenient to perform an in situ measurement. In real situation, the in situ measurement of water rainfall is not simple, in fact a part the com-

plications presented above, it can vary depending on the height of the building, on the position of the point under analysis and on the orientation of the sample building. Thus, it can be useful to define a relation between this variable and the precipitation, which is simpler to be measured [6].

From theoretical point of view, it is assumed that all the raindrops are of the same size and that the wind speed does not increase with the height of building (velocity is uniform), and it is steady and horizontal. The wind direction is also supposed to be perpendicular to the building wall at every time and no deflection of wind is admited. The intensity of wind-driven rain can be expressed as:

$$R_{WDR} = R_P \frac{v_W}{V_t},\tag{5.1.1}$$

where  $R_{WDR}$ : wind-driving rain intensity [kg/m<sup>2</sup>s],  $R_P$ : precipitation rain intensity [kg/m<sup>2</sup>s],  $V_t$ : raindrop terminal velocity [m/s],  $v_W$ : wind speed (normal to the wall) [m/s].

The wind speed is determined, in metereology, by measuring amplitude and direction in open field at 10 meters hight with respect to the ground level and by averanging over three seconds, in order to obtain the "istantaneous wind value", and over 10 minutes to obtain the "average wind value".

The raindrop terminal velocity depends on the size of the drops and, in sake of simplicity, one can assume a uniform size distribution. Subsequently, it is introduced the "wind-driven rain coefficient" as the inverse value of raindrop terminal velocity and it is defined in s/m units. This coefficient is a property of the site under analysis, but for example, some on-site measurements<sup>2</sup> performed at different locations, provide values which ranged from 0.130 s/m to 0.221 s/m. In later works<sup>3</sup>, it was found an empirical relationship between the average drop radius and  $R_P$  and  $V_t$ .

The final result provides the following empirical expression

$$R_{WDR} = r_s v_W R_P^{0.88},$$

where  $r_s$ : wind-driven coefficient, or site-specific driving-rain coefficient [s/m].

The typical value of the site-specific driving-rain coefficient is 0.222 s/m and it is referred to the measurement of a surface about 2 meters above the ground and in calm condition (without flow). This coefficient must be considered an average value because the empirical expression which defines the raindrop size is assumed averaged also. More precise determination of this coefficient is carried out with an experimental estimate of  $r_s$ . A simplified version of this last equation is obtained omitting the exponent 0.88:

$$R_{WDR} = r_s v_W R_P. \tag{5.1.2}$$

[6] [24] [26].

In ref. [6] is presented an example of this measurement procedure, which is reported is fig. 5.1.1. There is the result of a measurement performed on the middle of the facade at 4 m hight, while precipitation rain and the wind speed which are assumed perpendicular to the facade, are measured at 10 m high. The points in the figure represent the experimental values, recorded hourly during 4 years time. The straight line indicated the linear regression theoretically expected by the 5.1.2.

<sup>&</sup>lt;sup>2</sup>In the earliest works, those measurements were performed in Norway.

<sup>&</sup>lt;sup>3</sup>R.E. Lacy (1951) performed measurements on facades in Thorntonhall (Scotland) and Garstone (England).


Figure 5.1.1: Ratio of wind-driving rain and normal rain (precipitation) with respect to the wind velocity normal to the facade. The site-specific driving-rain used is abount 0.2 s/m.

For completeness, it must be note that in the build environment, eq. 5.1.2 cannot be simply applied. Buildings in an open field may catch more (up to forty) times wind-driven rain than buildings in a dense neighbourhood, which can be evaluated with a suitable coefficient. Finally, wind-driven rain density impinging locally on the building wall is quantified by

$$R_{WDR} = 0.2C_{WDR}\cos\theta v_W R_P, \tag{5.1.3}$$

where  $C_{WDR}$ : wind-driven rain factor [s/m],  $\theta$ : angle between wind direction and the normal to the building wall [-].

The wind-driven factor depends on the environment surrounding, the facade details, and it is a function of the type of precipitation which depends on the raindrop size [27].

#### 5.1.2 Effects of raindrops on the surface

Raindrops strike on the building surface can be absorbed or run-off down the facade. Indeed, the situation is more complicated since, part of the raindrops hits the surface and can be absorbed in the inner layers of the material, but other parts can be lost by splashing, bouncing, evaporation or can spread on the surface (see fig. 5.2.1). In this last case, in particular, several drops can coalesce forming a water liquid film. If the film thickness increases until a critical value, the gravity force becomes more intense respect to the surface tension force. Finally, the film can flow down along the wall of the building: this is the *run-off* mechanism [25].



Figure 5.1.2: (a) Representation of the strike of raindrop in wind-driven rain situation, immediately before the impact on the wall. (b) schematic illustration of the several mechanisms which can happen when the raindrop hits on the wall surface.

When a raindrop hits on the surface it can be absorbed through a capillary tube and one can assume a one-dimensional flow, which starts on the surface, and propagates inside the material, following a perpendicular direction respect the surface itself.

Absorption depth into wetting porous material can be determinated by:

$$x = \frac{A_c^2 w_{cr}}{R_{WDR}(w_c^2 - w_{cr}^2)} \left( \sqrt{1 + \frac{2R_{WDR}^2(w_c^2 - w_{cr}^2)t}{A_c^2 w_{cr}^2}} - 1 \right),$$
(5.1.4)

where  $w_{cr}$ : critical moisture content in the material [kg/m<sup>3</sup>],  $w_c$ : capillary moisture content [kg/m<sup>3</sup>],  $A_c$ : capillary water absorption coefficient [kg/m<sup>2</sup>s<sup>1/2</sup>], t: time [s].

The two variables,  $A_c$  and  $w_c$ , are capillary properties of the building material. Critical moisture content,  $w_{cr}$ , is the lowest moisture content value at which it can hypothized that the capillaries are still filled by water. If the moisture content in the material is greater than  $w_{cr}$ , capillary flow regime is dominant; viceversa, if the moisture content is less than  $w_{cr}$  the vapour diffusion develops.

Linked to the absorption depth is the moisture content at the exterior surface, which is defined by:

$$w_{sur} = w_{cr} + \frac{R_{WDR}(w_c^2 - w_{cr}^2)x}{A_c^2},$$
(5.1.5)

where  $w_{sur}$ : exterior surface moisture content [kg/m<sup>3</sup>].

 $R_{WDR}$ ,  $A_c$  and  $w_c$  fix the maximum of the absorbed water content before the run-off starts. When the surface is completely wet and the run-off is dominant with respect to the absorbtion because the building component is totally saturated and cannot take up more water-rain, the boundary conditions change. It must be taken into account the boundary condition of the first type instead of the second one, and the relative humidity of the building component must be set equal to 1, [6], [24].

#### 5.2 Solar radiation

All forms of matter emit or absorb electromagnetic waves, if they are at warmer temperature than zero kelvin degree. This thermal wave is due to the thermal agitation of atoms and molecules of the substance. In building physics, this is typically a surface phenomenon which interests only atoms in the most external layer of building component. Infact, in most of solids or liquids, the radiation emited by the internal layers is auto-absorbed by the material itself and in the same way, the radiation coming from the external surrounding is absorbed by the external layer of matter before this will able to achieve the inner part of matter object. In general, in building material, it can be possible to assume that the radiation emitted by an atom or molecule that is within 1  $\mu m$  of distance to the surface, is able to leave the material itself [29]. Another important property of thermal radiation is that no medium is required for propagation of the electromagnetic wave.

#### But, what is thermal radiation?

In the fig. 5.2.1 is presented the complete electromagnetic spectrum. The term "thermal" is referred to the intermediate portion of the spectrum which ranges from about 0.1 to 100  $\mu$ m: it includes part of the ultraviolet (UV) radiation and all of visible and infrared (IR) radiation.



Figure 5.2.1: The complete electromagnetic spectrum. Thermal radiation includes: part of UV radiation (0.1 <  $\lambda$  < 0.38  $\mu$ m), visible radiation (0.38 <  $\lambda$  < 0.78  $\mu$ m) and IR radiation (0.78 <  $\lambda$  < 10<sup>3</sup>  $\mu$ m).

This electromagnetic radiation is strictly related to the thermal state of the emitting object or, in other words, with the temperature of the matter.

As will known, if the radiation is composed by one wavelength only, it is called as monochromatic radiation, viceversa, as it is usual in a realistic situation, an electromagnetic radiation composed by different wavelengths and provides a spectrum of the radiation. In the particular case of the thermal radiation, it is composed by several wavelengths and so, it is not monocromatic, but it is characterized by a spectral distribution, as the solar radiation is.

In building physics, is useful to distinguish two ranges of the radiation which can be affect a building component: long-wave radiation and short-wave radiation.

Long-wave radiation, or *environmental radiation*, includes several contributions: radiation from the Earth's surface, from urban environment or from the ri-emitted radiation from the surface

itself. It is characteristic of objects with temperature surface from 250 to 320 K, and which corrisponds to a wavelength about (from Wien's law):

$$\lambda_{max} = 2.8976 \cdot 10^{-3} \frac{1}{T},$$

thus  $\lambda$  is about 10  $\mu m$  (typically  $\lambda > 4 \mu m$ ).

Short-wave radiation, or *solar radiation*, is characterized by the emission from the sun, with temperature about 6000 K, which corresponds to a wavelength about 0.5  $\mu m$  (typically  $\lambda < 4 \mu m$ ). Contributions of these two components are shown in the following figure.



Figure 5.2.2: Schematic spectral distributions of short (solar) radiation and long (terrestrial) radiation

As in ref. [39], long-wave radiation is often neglected or treated in a simplified way, defining a heat transfer coefficient. So, only the short-wave radiation is usually taken into account for the description of a surface heating during the day solar irradiation. It is clear that, from one hand the daily heating of the building surface is relatively well described, conversely the night-time cooling of the exterior surface is described in an approximate manner, when this is done, or even not at all.

#### 5.2.1 Long-wave radiation

As mentioned above, long-wave radiation is formed by the emission radiation from the surface and by the radiation which is emitted by surrounding objects, as neighboring buildings walls or ground.

In building physics, a facade or a building component is described as a grey body, which emits radiation with intensity defined by the Stefan-Boltzamann law. The long-wave intensity depends on the fourth power of the surface temperature, as the black body law, but a corrective factor must be introduced: the body emissivity (or emittance).

It can be demonstrated that the emissivity depends on the temperature, so the correct expression becomes  $\varepsilon(T)$ . As in ref. [21], the temperature range in building physics is in the interval from -20 °C to 50 °C, and as the temperature is not varying very much, also the emissivity can be assumed as constant. If the emissivity is equal to 1, the body is a black body, viceversa if

Material surface	Emissivity $\varepsilon(-)$	Absorptance $\alpha(-)$
plaster	0.91	0.30 - 0.50
cement mortar	0.93	0.73
brick light	0.85 - 0.95	0.36 - 0.62
brick dark	0.85 - 0.95	0.63 - 0.89
marble	0.90 - 0.93	0.44 - 0.592
limestone	0.90 - 0.93	0.33 - 0.53
sandstone	0.90 - 0.93	0.54 - 0.76
concrete	0.85 - 0.95	0.65 -0.80

 $\varepsilon$  < 1 the body is named as grey. For non metallic surfaces and for typical building material surface 0.85 <  $\varepsilon$  < 1. Some values as listed in tab. 5.1.

Table 5.1: Some values of emissivity and absorptance

A building component can also absorb part of the long-wave radiation by the sourronding terrestrial object and by the sky, which can be indicated in overall manner as  $I_{l,a}$ , where subscripts l means long-wave, and a means absorbed.

The terrestrial contribution is defined by a mixture of Plank's blackbody radiations emitted by the surrounding terrestrial surface, whose temperature is close to air temperature. The atmospheric contribution is due to the radiation emitted by clouds, fog or gaseous components of the atmosphere, as water vapour or carbon dioxide. In order to quantify this effect, one can introduce the ratio between the absorbed energy flux to the total incident energy flux, a factor known as absorptance,  $\alpha$ (-). In tab. 5.1 some values are reported. In the detail, absorptance depends on the temperature, the incident wavelength, the direction of the incident radiation and on the material properties. Kirchhoff's law says that, for any surface, the absorptance is the same function of wavelength and temperature as emissivity (if one assumes only the long-wave contribution). Following the previous considerations, if the emissivity of the surface is assumed as constant, then also its absorptance is a constant. Finally, it must be stressed that the radiation emitted is only long-wave, but the absorbed radiation can be long-wave or short-wave, which is briefly described in the following.

#### 5.2.2 Short-wave radiation

As mentioned above, the short-wave radiation is the radiation which comes from the sun, and it corresponds to the wavelength in a range from the longer wavelength of the ultraviolet region, to about the shorter of the infrared region. Typical solar spectrum is shown in fig. 5.2.3.



Figure 5.2.3: Spectral distribution of solar radiation.

The solar radiation can be described by a blackbody emission, as prescribed by Stefan-Boltzmann law, whose spectrum is presented in dashed line in the previous figure, the peak occurring at approximatively 0.5  $\mu m$  (or 500 nm in the figure).

This radiation traverses the space between the sun surface and the top of the Earth atmosphere and, for this reason, the form of the solar spectrum is slightly modified from the blackbody trend (indicated in the figure with "extraterrestrial"). After that, the solar radiation so obtained, passes throught the atmosphere and interacts with atmospheric costituents. In this path length, radiation can undergo absorption and scattering on various particles and molecules of water vapour, aerosols, pollutants and so on, and thus, some other portion of solar energy is lost. The solar radiation that reaches the Earth surface is reported in the previous figure. Note that, solar radiation is mainly absorbed by the ozone component of the atmosphere ( $O_3$ ), which mainly affects the UV radiation component, by water vapour molecules which dominate the absorption of the IR component, and by  $O_2$  and  $CO_2$ . The solar radiation can be also scattered by very small gas molecules (Rayleigh's scattering) or by larger particles of dust or aereosol (Mie's scattering). In both cases the solar radiation suffers a deviation, or redirection, from its original path [21] [29].

The solar energy transported by the short-wave radiation provides to the building surface a certain amount of energy in form of heat (and light). At the buildings surface the direct component of the solar radiation arrives plus the diffuse ones and plus the component of the solar radiation which is reflected by the ground. Overall, the total short wave radiation is  $I_s = I_{s,dir} + I_{s,diff} + I_{s,refl}$ .

#### 5.2.3 Radiation balance

As in ref. [39], the formal radiation balance can be quantified by taking into account the longwave and the short-wave contributions. The intensity of the long-wave radiation emits by the analyzed building component is defined by

$$I_{l,e}=\sigma\varepsilon_eT_e^4,$$

where  $I_{l,e}$ : emitted long-wave energy flux [W/m<sup>2</sup>],  $\sigma = 5.67 \cdot 10^{-8}$ : Stefan-Boltzmann constant [W/m<sup>2</sup>K],  $\varepsilon_e$ : body emissivity [-],  $T_e$ : temperature of the surface [K].

The intensity of the long-wave radiation emitted by the surrounding environment and absorbed by the analyzed building surface  $I_{l,a}$ , is not simple to be defined. The component of the radiation from the urban environment may be assumed yet as the blackbody radiation, just taking into account the temperature and the emissivity of the particular neightboring building surfaces. But the complicate situation refers to the long-wave radiation component which comes from sky or from the ground. It can be stressed that the atmosphere is quite opaque to its thermal emission and it can be shown that the radiation reaching the ground level is originated at 200 meters from this level at most. Consequence of this fact is that ground has about the same temperature of the sky. Some authors treat this component also as a black body, describing the atmospheric components, as clouds, like blackbody emitters whose intensity depends on their size, thickness and hight.

Finally, the solar short-wave radiation presents the direct component, which is the radiation coming from the sun (and it is defined as "solar constant" which is about 1390  $W/m^2$ ) and attenuated by passing through the extraterrestrial and terrestrial atmosphere, the diffusive and reflected components which describe the incoming solar radiation after the interactions with clouds, water vapour molecules, and so on. Short-wave radiation also depends on the time during the day, and on the zenith angle of the surface analyzed.

Overall, the total radiation which hints on the buildings component surface is

$$I = \alpha \cdot (I_s + I_{l,a}) - I_{l,e},$$

where  $I_s$  and  $I_{l,a}$  have positive signs because they are incoming radiation components, viceversa  $I_{l,e}$  is preceded by minus sign because it is the energy component emitted by the surface, or in other words, energy which is lost by the surface.



Figure 5.2.4: Radiation balance on the exterior building surface

#### 5.3 Solar radiation and rain

Concretely, as in ref. [6], the external solar radiation and the rain effect on the external surface can be taken into account as terms of boundary conditions. In the detail, one can assume a second kind of boundary conditions.

Connected to the total solar radiation *I*, one can assumed that the heat flow on the building surface is q = I, but several authors, as e.g. [6], take into account only the heat transport due to the short-wave solar radiation and the boundary term of heat flux become:

$$q = \alpha I_s$$

where q: heat flow from short-wave radiation [W/m<sup>2</sup>],  $\alpha$ : absorptivity of the material (for short-wave) [-],  $I_s$ : solar short-wave radiation normal to the surface [W/m<sup>2</sup>].

In the same manner, one can view the wind-driven rain  $R_{WDR}$  on the building surface as water flux term:

$$g_w = \alpha_r R_{WDR}$$

where  $g_w$ : surface liquid flux density [kg/m<sup>2</sup>s],  $R_{WDR}$ : rainwater load normal to the surface [kg/m<sup>2</sup>s],  $\alpha_r$ : precipitation absorptivity [-].

Precipitation absorptivity is a coefficient which take into account the ability to absorb rainwater of the surface and depends on the characteristics of the surface and of the type of precipitation. As in [6], if hail or snow, this coefficient tends to zero, and in the case of fla surface it is about 1, infact the splashing water however impact on the surface itself.

When the ammount of rainwater reaches a level over those the building surface is not be able to take up more rain, that is the surface is completely wetted, the boundary condition change: from those of second kind to ones of the first kind. If the external condition vary another time, which means that the intensity of the rain decreases, for example, the boundary conditions can change again.

### Chapter 6

## Transport of air pollutant

#### 6.1 Air pollution damage

Atmospheric pollution is one of the most important factor of damage on building heritage and monumental heritage. The two principal pollutants which can be considered are *nitrogen oxides*  $NO_x$ , which are producted by combustion engines, and *sulfur dioxide*  $SO_2$  from combustion of fossil fuels. This last chemical agent can be considered one of the most important factor of damage of stones.

Sulfur dioxide acts on any calcareous components in the stones, which is followed by the formation of a crust or by the production of a layer of gypsum which is soluble and so may be drained away by rain. These processes strongly depends on the relative humidity and on the nature of the stone. The main consequence of these effects is the loss of material due to solubilization, which can be up to 30-50% of material lost, and due to the detachment of the thick crust, refs. [5] and [13].

As mentioned in ref. [44], the main degradation of calcareous samples are known as white, grey and black crusts. White areas are tipical of the surfaces exposition to rainfall, which drains away the dry deposits and the eroded material. Grey areas are tipical of the monuments parts which are not wetted. These areas are mainly composed by gypsum and their colour is due to the dry deposition of carbon particles which are present in the air. From a damage point of view, these grey crusts represent the first step of the stone aggression and it is characterized by a duration time which is not enought to the complete damage reaction. At the end, black areas are mainly located on surface which are not directly exposed to the rainfall, infact the black colour is due to the deposition of atmospheric particles and polluting gases which are not washed away by the rain and so that remaine on the surface. Black crusts are composed mainly by crystals of gypsum which grow perpendicularly to the stone surface and they are very dangerous because, in long time, they can lead to the catastrophic events as their detachment and it means the loss of the stone material.

Gypsum crusts formed on the surface are greatly solubile and porous with respect to calcium carbonate, and it is the main cause of water infiltration, which drives the sulphation and corro-

sion process until the underlying layers. Obviously, chemical composition and physical characteristic of the crust are different with respect to the original stone sample ones, and this is why the crust formation is dangerous for the building stone. Infact, firstly, gypsum has a volume greater than calcium carbonate and it means that stress tension appears inside the stone structure. This allows to the decohesion and fragmentation of the stone sample itself. Secondly, gypsum and marble (or, in general, the original carbonatic stone) have different thermal expansion and it means that the response to the thermal solicitation, as the solar radiation, may be very different. This effect is more important for the black crusts because, due to their dark colour, the solar radiation is largely absorbed. At the end, also permeability and diffusivity may be very different, in particular may be reduced for the crust than the original stone, and it allows an unpleasant and dangerous water retention [44].

The formation of gypsum can be represented with two chain reactions: the starting point is the reaction of the sulfur dioxide on the calcium carbonate stones which produces calcium sulphite, subsequently the latter compound reacts with the water content and produces calcium solphate (gypsum). Formally:

$$CaCO_3 + SO_2 + \frac{1}{2}H_2O \rightarrow CaSO_3 \cdot \frac{1}{2}H_2O + CO_2$$
$$CaSO_3 \cdot \frac{1}{2}H_2O + \frac{1}{2}O_2 + \frac{3}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

This argument can be simplified taking in mind that the proportion of calcium sulphite and sulfate depend on the relative humidity and on the presence of some catalysts substances and one should be considered two last reactions in an independent way. In situ analysis show only the presence of calcium sulfate. Ultimately, can be considered the calcium sulfate formation in a simplified one-step reaction:

$$CaCO_3 + SO_2 + \frac{1}{2}O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$
 (6.1.1)

In other words, one can say that on the typical time scale of the sulphatation process (about one year) two main assumptions can be introduced: first, the distinction between the two previous reactions can be neglect; second, the simplified one-step reaction can be considered istantaneous.

Thus, a sharp free boundary between gypsum and the unreacted calcium carbonate can be assumed.

From the many observations submitted, it is obvious the complexity of all phenomena involved and their consequences. Studies in this field are aimed to know in detail the mechanisms of damage reactions but also to evaluate, as precisely as possible, the deterioration rate of exposed stones to the atmospheric aggression. As in ref. [43], this studies are aimed to the identification of "damage functions", which are mathematical functions proposed to describe the rate of stones loss which depends on the concentration of  $SO_2$  and on the amount of rainwater. Infact, for this last point, note the role of water in damage reaction, eq. 6.1.1.

Lipfert's equation is one of the first functions proposed and it is still used today. This empiric equation connects the mass lost of the building stone with the amount of rainfall, *SO*<sub>2</sub> concentration and its deposition rate, and the rain pH. This formula is reported in [43], but even though it is useful for a qualitative evaluation of the average mass stone loss due to the rainfall washing away, but it does not takes into account the characteristic of the material and the chemical alteration of it, which provides the formation of the black crusts and the subsequently detachment.

At the end of this pharagraph, it is emphatized the role of relative humidity with reference to eq. 6.1.1. Depending on the amount of  $\varphi$ , or in other words on the amount of water, three different regimes of  $SO_2$  reactivity can be identified :

- $\varphi < 45\%$ : sulfur dioxide slowly reacts, until the limit in which not reacts at all;
- 45% < φ < 75%: the reaction of SO<sub>2</sub> on the calcium carbonate proceeds more rapidly as *φ* increases;
- $\varphi > 75\%$ : *SO*<sub>2</sub> reacts completely.

What does it mean? The interpretation is as follows.  $SO_2$  reactivities depends on the amount of relative humidity or, in other words, on the water content into material. From one-step reaction, eq. 6.1.1,  $SO_2$  reacts on  $CaCO_3$  if enough water and  $O_2$  are available. It is the key point. If  $\varphi < 45\%$  there is not liquid water present and the reaction 6.1.1 stops. If  $\varphi$  is in the second previous range, the liquid water exists in some localized points where the one-step reaction may be happen. At last, in the third regime there is enough relative humidity to form a liquid film on the whole surface involved and, therefore, the reaction can occur wherever on it.

#### 6.2 Swelling and gypsum's motion

For the purpose to describe the swelling rate and the evolution of sulfation front (see par. 6.4) it can be stressed that molar ratio between  $CaCO_3$  and  $CaSO_4$  is 1:1. It means that the consumption rate of calcium carbonate is equal to the production rate of gypsum (see eq. 6.1.1). The previous molar ratio is described, during the time evolution, with the relation:

$$\mu_m \frac{d\sigma(t)}{dt} = \mu_s \left| \frac{d\sigma_0(t)}{dt} \right|$$
(6.2.1)

where  $\mu_m$ : molar density of  $CaCO_3$  in marble [#moles/cm<sup>3</sup>],  $\mu_s$ : molar density of  $CaSO_4$  in gypsum [#moles/cm<sup>3</sup>],  $\sigma(t) = x$ : sulfation front [cm],  $\sigma_0(t) = x$ : gypsum surface exposed to air [cm]. If the *swelling rate*  $\omega$  (adimentional) is introduced, as the molar density ratio between  $\mu_m$  and  $\mu_s$ , the equation 6.2.1 can be rewrite in a more compact manner:

$$\dot{\sigma}_0 = -\omega\sigma \tag{6.2.2}$$

which describes the gypsum layer velocity of propagation and where the minus sign means that the two fronts, one of sulfation and one of exposed to air, propagate in opposite direction due to swelling. The eq. 6.2.2 is defined in the frame of reference in which the marble is at rest, as one can see in fig. 6.2.1.



Figure 6.2.1: Growth of the internal (calcium carbonate) and external (air surface) free boundaries.

Relate to this last equation, one can introduce some assumptions:

1. molar densities  $\mu_m$  and  $\mu_s$  can be consider constants, infact [5]:

 $\mu_m$  is related to marble, which is believe homogeneous material,

 $\mu_s$  is related to gypsum, whose structure is standarly independent from the production rate;

- 2. along with equation 6.2.2 and referring to fig. 6.2.1, the following conditions are introduced:
  - (a) if  $\sigma(0) = \sigma_0(0) = 0$ , than  $\sigma_0(t) = -\omega\sigma(t)$ the thickness of gypsum layer, at a general time instant t, can be defined as  $h(t) = \sigma(t) - \sigma_0(t) = (1 + \omega)\sigma(t)$ ,
  - (b) if  $\sigma(0) > 0$  and  $\sigma_0(t) > 0$ , than  $\sigma_0(t) \sigma_0(0) = -\omega[\sigma(t) \sigma(0)]$

It can be stressed, therefore, that the swelling phenomenon is not small, and in particular, the motion of gypsum can influence the flows of air and other gaseous.

#### 6.3 Air motion

In this part, will be shortly described the motion of air through gypsum. This phenomenon is quite complicated because the air density is a function of air pressure which is different in the external air (reference pressure typically 1 Atm) respect to the pressure in the gypsum, and thus is estabilished a pressure drop. Consequently, a pressure gradient arises resulting in flow of air relative to gypsum, which can be described by Darcy's law: a flow of forced air exist through the gypsum to fill the volume made available.

In the same frame of reference introduced in the previous paragraph, it can be possible to consider air and gypsum in movement with the same speed, in the typical scales of length and time of the sulfation process.

This argument is useful for justify the following identification

$$v_a = \sigma_0 \tag{6.3.1}$$

where  $v_a$ : air (external) speed [cm/s],

or, in other words, lets say that there is not relative motion between air and gypsum, with refs. [5] and [14]. In appendix to ref. [5], there is the complete and formal treatment of this argument. What matters is that, in an appropriate rescaling variables, it can be assume the air density in gypsum layers to be almost uniform and constant and consequently it can be assume the costancy of the pressure too.

#### 6.4 SO<sub>2</sub>-front motion

In this section the two sulfation regimes, corresponding to the two last conditions on  $\varphi$ , described previously, are presented. Assuming temperature T and pressure P are known, it can be possible distinguish between the full and reduced speed regimes, which are described by the same governing differential equations but with different boundary conditions on the unreacted marble surface. This is the key point.

In ref. [14] is assumed that the sulfur dioxide flux is Fickian. This means that  $SO_2$  flux is driven by the gradient of its concentration, *s*. This gradient exist because there is a different ammount of  $SO_2$  molecules between a point on the sulfation front and a point in other location. In particular, on the sulfation front, the concentration of sulfur dioxide is minimun because on this points, sulphur dioxide reacts with calcium carbonate (marble) and desappear forming calcium sulfate.

Thus, the flow of SO<sub>2</sub> (relative to the air) is described by the following first Fick's law:

$$j_s = \phi_g(-d_s \frac{\partial s}{\partial x} + v_a s) \tag{6.4.1}$$

where  $j_s$ : flux intensity of  $SO_2$  [gr/cm<sup>2</sup>s],  $\phi_g$ : porosity of gypsum [-],  $d_s$ : diffusivity of  $SO_2$  in air [cm<sup>2</sup>/s].

The sulfur dioxide transport mechanism is defined by the (second Fick) equation:

 $\phi_g \frac{\partial s}{\partial t} + \frac{\partial j_s}{\partial x} = 0$ 

thus

$$\frac{\partial s}{\partial t} - d_s \frac{\partial^2 s}{\partial x^2} - \omega \sigma \frac{\partial s}{\partial x} = 0$$
(6.4.2)

where are used eqs. 6.3.1 and 6.2.2.

As justified in par. 6.3, pressure can be considerated constant through gypsum and air and, consequently, the  $SO_2$  concentration on the separation surface between air and gypsum can be assumed as a some know function of time:

$$s(\sigma_0(t), t) = s_a(t)$$
 (6.4.3)

To define the free boundary condition on the front of  $SO_2$  reaction on calcium carbonate, one must distinguish two regimes.

#### Full sulfation speed regime

This is the case in which relative humidity exceeds some treshold, about 75%, and so it is assumed that water must condense in a thin liquid film. In other words, there is water enough in order to occur the reaction everywhere. The sulfur dioxide concentration on the external surface is describe by eq. 6.4.3, while on the internal surface, in contact to marble, one can assume that  $SO_2$  completely react with  $CaCO_3$  and thus totally disappears:

$$s(\sigma(t),t) = 0.$$

In the gypsum layer  $\sigma_0(t) < x < \sigma(t)$  the mass balance is described by:

$$-\phi_g \frac{d_s}{M_s} \frac{\partial s}{\partial x}(\sigma(t), t) = \mu_m d$$

where  $M_s$ : molar weight of  $SO_2$  [gr/mol].

#### **Reduced sulphation speed regime**

In this situation the relative humidity is in the range 45% - 75% and there is not a water film coating everywhere, but rather there are some water localized points in which the sulphation

reaction can occur. Thus, the free boundary conditions are changed. Usually, is defined an efficiency value  $\alpha(w, T, P)^1$  which is a function of concentration of  $H_2O$  (in vapour phase), named w, temperature T and air pressure P.

The free boundary condition became:

$$rac{\dot{j}_s}{M_s} = rac{
ho_m}{M_m} \dot{\sigma} + \phi_g rac{s}{M_s} \dot{\sigma}$$

where  $\rho_m$ : density of marble [gr/cm<sup>3</sup>],  $M_m$ : molar weight of marble [gr/mol],

which expresses the molar balance of sulphur dioxide.

#### 6.5 Water vapour motion

As just mentioned at the beginning of chap. 6, water must be present on marble surface because the reaction can start. Marble is an hygroscopic material thus the creation of water film occurs by a sorption-desorption mechanism, which is influenced by temperature and relative humidity. Assuming that the rate constants of this sorption-desorption mechanism are much larger than the reciprocal time scale of sulfation process, one can consider the formation process of water film as independent of sulfation one.

The following equation describes the total flux of water vapour:

$$j_w = \phi_g(-d_w \frac{\partial w}{\partial x} + w \omega \dot{\sigma})$$
(6.5.1)

where  $j_w$ : flux intensity of water vapour [gr/cm<sup>2</sup>s],  $d_w$ : diffusivity of  $H_2O$  in air [cm<sup>2</sup>/s],

now, using the Fick's law one can formulate the  $H_2O$  mass balance:

$$\frac{\partial w}{\partial t} - d_w \frac{\partial^2 w}{\partial x^2} - \omega \sigma \frac{\partial w}{\partial x} = 0$$
(6.5.2)

and, at the end, one supposes the external boundary condition in the same manner of eq. 6.4.3:

$$w(\sigma_0(t),t) = w_a(t).$$

As shown in the  $SO_2$ -front motion, what changes between the two sulfation regime is the free boundary condition on the sulfation front.

<sup>&</sup>lt;sup>1</sup>Following [5] one can denote  $\alpha(w) = \frac{1}{w_0 - w} - \frac{1}{w_0 - w_1}$  where  $w_0 \in w_1$  are the two threshold: the former is full reaction threshold and the latter is no-reaction threshold.  $\alpha(w)$  varies from 0 when  $w = w_1$ , to  $\infty$  when  $w = w_0$ .

#### Full sulfation speed regime

The water vapuor concentration on the internal surface must satisfies the following prescription in every time:

$$w(\sigma(t),t) \ge w_0(T,P)$$

and the balance equation on the reaction front is:

$$-\phi_g \frac{d_w}{M_w} \frac{\partial w}{\partial x} = 2 \frac{\rho_m}{M_m} \dot{\sigma} + \phi_g (1+\omega) \frac{w}{M_w} \dot{\sigma}$$
(6.5.3)

In eq. 6.5.3 the film thickness and the water content are neglected in marble. The left-hand side of this last equation must be considered as the water supply of the moisture film and the first term of right-hand side can be interpreted as the water consumption rate on the sulfation surface. Into detail, the water film thickness can be supposed very small if it compare to the typical scale lenght of the reaction and, in the sake of completeness, if some water molecules are naturally present into marble one must take into account an extra term which evaluate the water concentration in marble.

#### **Reduced sulfation speed regime**

In this range, the water concentration is between the two thresholds just mentioned in par. 6.4:

$$w_1(T,P) \le w(\sigma(t),t) \le w_0(T,P)$$

and the reaction efficiency equation, which specifies the reaction speed, is

$$\frac{\rho_m}{M_m}\dot{\sigma} = \phi_g \alpha(w) \frac{s}{M_s}$$

one can distinguish between two trends:

$$\begin{cases} \alpha \to +\infty \quad s(\sigma(t), t) \to 0 \\ \alpha \to 0 \qquad \frac{\partial s}{\partial x} = 0 \end{cases}$$

or, in other words, the first case is the full sulfation speed regime while the second condition represents the front stop situation and the subsequent  $SO_2$  flux disappearance.

# 6.6 Air pollutant transport described from a concentration point of view

From another poin of view, it can be useful describe the chemical aggression process by outling the time evolution of the total  $SO_2$  concentration and the density of marble (in general, calcium

carbonate content of the stone under analysis) with respect to the time evolution of their front. This approach is based on physical relations as the balance laws of the chemical reactions and the diffusive Fick's laws.

Therefore, one can adopt some useful variable and defining new useful ones. *s* is the porous concentration of  $SO_2$  respect to the total volume of pores in gypsum and  $\rho_s$  is the total concentration of suphur dioxide, *c* is the density of  $CaCO_3$  (calcite), *g* is density of  $CaSO_4 \cdot 2H_2O$ , or gypsum. This last three variables,  $\rho_s$ , *c* and *g*, are evaluated with respect to the whole volume of the material, including both solid and gaseous components.  $\rho_a$  and  $\mathbf{V_a}$  are, respectively, density of air (including  $O_2$ ,  $CO_2$  and water vapour, but without taking into account  $SO_2$ ) and air velocity, while  $\mathbf{V_s}$  is sulphite velocity.

First, it is supposed the balance of concentrations of all components:

$$\partial_t \rho_s + \nabla \cdot (\rho_s \mathbf{V_s}) = \dot{r_s} \tag{6.6.1}$$

$$\partial_t \rho_a + \nabla \cdot (\rho_a \mathbf{V_a}) = \dot{r_a} \tag{6.6.2}$$

$$\partial_t c = r_c \tag{6.6.3}$$

$$\partial_t g = r_g \tag{6.6.4}$$

where  $r_s$ ,  $r_a$ ,  $r_c$  and  $r_g$  are rispectively the production or consumption rates of sulphite, air, calcium carbonate and gypsum. For the conservation of the matter, the following equation must hold:

$$\dot{r_s} + \dot{r_a} + \dot{r_c} + \dot{r_g} = 0.$$

If  $\omega$  is the reaction rate and  $m_s$ ,  $m_a$ ,  $m_c$  and  $m_g$  are the masses of a single molecules of sulphite, air, calcite and gypsum, the previous rates become:  $\dot{r}_s = -m_s \omega$ ,  $\dot{r}_a = m_a \omega$ ,  $\dot{r}_c = -m_c \omega$ ,  $\dot{r}_g = m_g \omega$ .

Note the opposite sign of sulphite and air rates, in accordance with the direction of the chemical reaction: if sulphite desappears,  $CO_2$  appears (it is counted as an air component). The same observation can applied to calcite and gypsum opposite rates.

Reaction rate  $\omega$  (which is known as swelling ratio) can be expressed also as:

$$\omega = k \left(\frac{\rho_s}{m_s}\right) \left(\frac{c}{m_c}\right) \tag{6.6.5}$$

where *k* is a proportional coefficient which depends on the temperature.

Replacing the esplicit formulation of calcium carbonate and gypsum production rates into eqs. 6.6.3 and 6.6.4 and summing them, one obtains the conservation expression of the total material density:

$$\partial_t \left( \frac{c}{m_c} + \frac{g}{m_g} \right) = 0$$

and assuming the initial concentration values as  $c_0$  and  $g_0$ , one gets the equation of the gypsum

density as a function of calcite density:

$$\frac{c}{m_c} + \frac{g}{m_g} = \frac{c_0}{m_c} + \frac{g_0}{m_g}$$

Now, it can be introduced a calcite porosity parameter,  $\phi$ , which is not fixed since during the chemical aggression the volume void of the calcareous stones is altered. For this reason, the generic material porosity is defined as a function of the calcium carbonate concentration:  $\phi = \phi(c)$ . In ref. [46] there is the esplicit derivation of the dependence of  $\phi$  on the calcite concentration. Here, it is worth remarking that this dependence is linear and that  $\phi$  is connected to the porosity of pure calcium carbonate stone and to the long-term porosity, when zero concentration of calcium carbonate can be assumed. With the definition of material porosity, a connection between the  $SO_2$  porous concentration and the total concentration holds:

$$\rho_s = \phi(c)s \tag{6.6.6}$$

and, in the same manner, the seepage velocity of sulphur dioxide is related to the fluid velocity by the Dupuit-Forchheimer relation:

$$\mathbf{v_s} = \phi(c) \mathbf{V_s} \tag{6.6.7}$$

and, similar consideration can be carried out for air:

$$\rho_a = \phi(c)C_a$$
 $\mathbf{v_a} = \phi(c)\mathbf{V_a}$ 

where  $C_a$  is the porous concentration of air (respect to the volume of gypsum pores) and  $\mathbf{v}_a$  is the seepage velocity of air.

Replacing these so-defined variables into eqs. 6.6.1 and 6.6.3 one obtains:

$$\partial_t(\phi s) + \nabla \cdot (s \mathbf{v_s}) = -k\phi s \frac{c}{m_c}$$
(6.6.8)

$$\partial_t c = -k\phi c \frac{s}{m_s} \tag{6.6.9}$$

and for air, eq. 6.6.2 becomes:

$$\partial_t(\phi C_a) + \nabla \cdot (C_a \mathbf{v_a}) = k\phi\left(\frac{m_a}{m_s m_c}\right) sc$$
(6.6.10)

In order to solve the system of eqs. 6.6.8 and 6.6.9 another equation is necessary, and in particular one needs the expression of sulphur seepage velocity. For this purpose, one introduces the total concentration *C*, which represents the concentration of polluted air into calcium carbonate stone and it takes into account sulphite contribution and the pure air (pure means all particles without  $SO_2$  ones), and the total seepage velocity **v**:

$$C = s + C_a,$$
$$C\mathbf{v} = s\mathbf{v_s} + C_a\mathbf{v_a}.$$

Finally, one introduces the sulphite diffusive velocity,  $\mathbf{u}_{s} = \mathbf{v}_{s} - \mathbf{v}$ . From a physical point of view, the seepage velocity is given by Darcy's law 6.6.11 and the diffusive velocity is given by the Fick's law 6.6.12:

$$\mathbf{v} = -\frac{\kappa}{\nu} \nabla p \tag{6.6.11}$$

$$s\mathbf{u}_{\mathbf{s}} = -D\nabla s \tag{6.6.12}$$

where  $\kappa$  is the permeability of the calcium carbonate stone,  $\nu$  is the viscosity of polluted air, p is the pressure of polluted air and D is the diffusive coefficient.

Therefore, one can obtain the complete model (known as *nonlinear parabolic-elliptic model*):

$$\begin{cases} \partial_t(\phi s) + \nabla \cdot (-D\nabla s) = -k\phi sc \frac{c}{m_c} + \nabla \cdot \left(s\frac{\kappa}{\nu}\nabla p\right) \\ \partial_t c = -k\phi c\frac{s}{m_s} \\ \partial_t(\phi C) - \nabla \cdot \left(C\frac{\kappa}{\nu}\nabla p\right) = -\frac{k}{m_s} \left(\frac{m_g - m_c}{m_c}\right)\phi sc \end{cases}$$
(6.6.13)

where let us notice that  $m_g - m_c = m_s - m_a$ .

This complicate situation is simplified if it is assumed that polluted air is incompressible, so that the concentration *C* is constant, and with the approximation of neglecting permeability  $\kappa$ , in accordance to ref. [46]. Thus the Darcy velocity **v** is setted equal to zero, while only the Fick's diffusive contribution is kept into consideration. Eq. 6.6.12 provides the expression of sulphite seepage velocity, which is just mentioned in [4] and [5]:

$$s\mathbf{v_s} = -D \cdot \nabla s$$

where the Fick's diffusive coefficient is, now, a function of calcium carbonate density, D = D(c):

$$D(c) = d \cdot \phi(c)$$

where *d* is the scalar effective molecular diffusive coefficient. With this semplification, the complicate model 6.6.13 can be semplified in the *nonlinear degenerate parabolic differential model*:

$$\begin{cases} \partial_t(\phi s) = -k\phi sc\frac{c}{m_c} + d \cdot \nabla(\phi \cdot \nabla s) \\ \partial_t c = -k\phi c\frac{s}{m_s} \end{cases}$$
(6.6.14)

This equation system must be closed with the initial condition of sulphure concentration and calcite concentration, s and c at initial time t = 0, and with the boundary condition for s (tipically, Dirichlet or Neumann conditions).

#### 6.6.1 Resolutive approach and results

The model-system 6.6.14 is solved introducing the space and time rescaled variables, which provide the spatial adimensional system and thus the space (one-dimensional) coordinate  $x \in [0, 1]$ .

In this situation, the initial conditions are s(x, 0) = 0 and  $c(x, 0) = c_0$ , and the boundary conditions may be setted as  $s(0, t) = s_0$  and  $\frac{\partial s(1,t)}{\partial x} = 0$ .

From a mathematical point of view, this model can be solved by means of a numerical approach which is not described in the following but it can be found in literature [4], [5]. Here, it is interesting to describe the solutions of this model.

Numerical solutions for calcite density and dioxide sulphure concentration are presented in the following figure 6.6.1. Space adimensional range is used and the proportional coefficient k is setted to  $10^5$ . This last definition of the parameter k does not influence the curve shape: it only shifts the curve itself. Finally, the initial calcite density is setted on  $c_0 = 1.0$  and the initial concentration of  $SO_2$  is posed equal to  $s_0 = 0.1$ .



Figura 6.6.1: Space front. Left: calcite density profile. Right: SO<sub>2</sub> concentration profile.

Solutions have been obtained for three different values of time range. Note that, the calcite density increases if the depth into material increases and it means that the chemical aggressor does not penetrate in depth. Viceversa, the  $SO_2$  concentration decreases if the depth increases, in fact it reacts with the marble and so disappears.

Another important observation concerns the evolution of the crust thickness with time. It must be noted that no experimental measure is available, but only laboratory test results have been performed. In the following figure 6.6.2 the numerical simulation and the laboratory data are presented and it is clearly a similar linear trend which depends on square root of time. It is possible to note a qualitative good agreement.



Figura 6.6.2: Thickness of gypsum crust. Left: numerical simulation in fast reaction conditions with  $k = 10^{5}$  (adimentional variables). Right: laboratory test results (data reported in tab. 1)

For the laboratory test graph, the data are reported in tab. 1:

Time (hours)	Thickness ( $\mu m$ )
0	0
24	214
48	357
72	450
96	506
120	620
144	700
168	788

Tabella 6.1: Gypsum thickness measured in laboratory test.

Moreover, it can be interesting to report other two simulation results [5]. The simulation model has been applied to Villa Ada in Rome. Data relevant to  $SO_2$ , relative humidity, atmospheric condition as well as the temperature have been detected every hour during 2006. The model has been introduced to compute marble degradation and the growth of total gypsum expected thickness is reported in the following figure 6.6.3 (left). Finally, as previously discussed, the thickness crust growths with  $\sqrt{t}$  and so it can be observed 6.6.3 (right) and oscillation around a parabolic behavior of the gypsum front advancement after 9 years.



Figura 6.6.3: Gypsum front. Left:one year evolution of the gypsum front during 2006 at Villa Ada. Right: simulation of the gypsum front advancement in 9 years at Villa Ada.

Concluding this paragraph, in tab. 6.2 are present the typical values of principal magnitudes of air pollutant transport mechanism.

Label	Variable	Value	Dimension
$\phi_g$	gypsum porosity	0,3	-
$\phi_m$	marble porosity	0,005-0,015	-
$M_m$	molar weight marble	100,087	gr/mol
$M_s$	molar weight gypsum	172,166	gr/mol
$d_s$	$SO_2$ diffusivity in gypsum <sup>2</sup>	0,1	cm <sup>2</sup> /s
$d_w$	<i>H</i> <sub>2</sub> <i>O</i> diffusivity in gypsum	0,2178	cm <sup>2</sup> /s
$ ho_m$	mass density of marble	2,83	gr/cm <sup>3</sup>
$ ho_w$	mass density of water	1	gr/cm <sup>3</sup>
$ ho_g$	mass density of gypsum	1,6	gr/cm <sup>3</sup>
ω	molar density ratio	$\approx 2$	-
w	H <sub>2</sub> O reference density	$17, 3 \cdot 10^{-6}$	gr/cm <sup>3</sup>

Table 6.2: Important variables in pollutant aggression on building materials.

## Chapter 7

## Conclusions

In this thesis work, basic terms and concepts of the main mechanisms of transport in porous building materials are presented. Porous materials are widely used in historical architecture or historical monuments, as stones, bricks, marbles and so on. They are subjected to environmental injuries which are more evident, as the historical object is more ancient, because it has been esposed to the environmental conditions for a long time.

First of all, the water storage and transport mechanism is described. Moisture is present in the building component as liquid and/or vapour water or, under certain atmospheric conditions, as ice crystals. The mechanisms of water supply into the wall material is different depending on the humidity level: at lower humidity conditions, moisture is absorbed from the environment by the materials thanks to the surface condensation; at higher humidity content, the presence of water is due to the capillary transport into pores and capillaries. There are several mechanisms partecipating to the water transport: if gaseous phase is considered, water vapour diffusion and effusion transport are the two main effects which are described in this work, neglecting thermal diffusion and convective phenomena; viceversa, if the liquid phase is analyzed, capillary conductivity and surface diffusion are the main mechanisms which have to be taken into account.

One can divide the moisture storage in three regions, which define the hygroscopic conditions of the material: hygroscopic region represents the humidity balance condition between the material and the surrounding, superhygroscopic region, where the liquid transport becomes more important and the limit of water satuartion can be reached, supersaturated region is a region characterized by 100% of relative humidity and it is not reachable in natural conditions.

The formal description of the moisture transport is provided by means of a continuity equation which describes the time variation of the moisture content in terms of a gradient of fluxes due to water vapour flux and liquid water flux. These two fluxes are defined, respectively by a grandient of partial vapour pressure and a gradient of relative humidity. Vapour pressure and relative humidity are know as "driving potentials". Fluxes and gradient of driven potentials are connected by a coefficient which depends on the relative humidity in capillary transport and on the water vapour diffusion, which describe the diffusion of water vapour in air, and vapour resistance, taking into account that the diffusion happens into a porous material and not in air. In sake of completeness, in conservation equation of moisture content appears also a source (or sink) term which can be disregarded in first approximation, for natural, standard building components.

In similar manner heat storage and transport are described. From a thermodynamical point of view, one must describe a building component as an open system because it exchanges both matter and energy with the surrounding and for this reason enthalpy and, more generally, Gibbs function are taken into account, as the function of state of the system. In other words, the heat stored into material is described as a (density of) enthalpy which is assumed to have a linear dependance on the temperature, that is the driving potential of the heat transport. In detail, there are two terms of stored heat: one connects to the solid dry material matrix, and the other which takes into account the heat due to the presence of water.

Heat transport is described as a thermal conduction due to the presence of a temperature gradient which provides an heat flux, by the Fourier's law. As in water transport, also the heat transport can be described with a continuity equation, which provides a relation for the time variation of the stored heat (total enthalpy) and the gradient of heat flux, which is due to the variation of temperature, by adding a source/sink term. These source heat term is connected to the heat provided by a phase transition or a chemical reaction, which is important from a local point of view.

It is worth noticing that a formal lagrangian approach has been attempted. Gouy-Stodola Theorem is introduced to identify the lost work in an irreversible transformation with the entropy generation from the irreversibility, by the environment temperature. This lost work is the thermodynamic lagrangian of the system, that provides the action and, finally by the least action principle, the condition on the entropy generation: its variation is minus or equal to zero inside the system. It means that a natural, open system, which undergoes to an irreversible transformation, tends to a minimum of the generation entropy against the environment. In this thesis an extension of this theorem is proposed. By the Gibbs free energy function, one can connect the entropy to the enthalpy and the lost work becomes equal to an irreversible enthalpy term which takes into account the energy distance from the real system and the ideal reversible one. With this assumption, thermodynamic lagrangian becomes equal to this irreversible enthalpy, and from the least action principle one obtains a minimum condition of the variation of enthalpy. This minimization process in the building physics contest, must be performed taking into account the real constraint of the total liquid water content, which can be equal, in limit conditions, to the water saturation.

In order to close the model, one must take into account the outdoor conditions. First of all, the rain-fall problem has been described considering the wind-driven rain component which is given by the horizontal component of wind velocity and it is, in first approximation, normal to the surface. In literature there are some empirical expression to quantify the amount of rainwater, but all observed facts suggest a linear dependence on the wind-driven rain intensity and the wind velocity normal to the surface and the precipitation rain intensity. Another important condition on the external wall in a building physics is the irradiation. It must be divided into two contributions which are briefly described. Short-wave radiation, which rep-

resents the radiation coming from the sun and that is modelized by a black body radiation but taking into account the effects of the atmosphere components which absorb parts of the original spectrum. Long-wave radiation takes into account the radiation emitted by the surface itself and radiations produced by the surrounding environment. This last contribution, is described for completeness, but not more taken into account. Finally, short-wave solar radiation and the wind-driven rain are treated as boundary terms.

Another important damage source for the historical heritage exposed to the environment is, clearly, the chemical aggression due to air pollutants. Among all pollutants, sulphur dioxide is taken into account. This is deposited by rain, on the building surface and reacts and corrodes the building material, as limestones, marble, and so on. The dramatic consequence of this deposition is the formation of unaesthetic crusts on the surface and the loss of material due to solubilization of the gypsum product, or because the thickness of the crust becomes so thick that it drops under the action of the gravity force.

The main role in the sulphation process is played by the water which drives the reaction of the dioxide sulphur on the calcium carbonate and therefore three regimes can be identified: full sulphation speed regime when enough water is present in order to occur the reaction everywhere, reduced sulphation speed regime when the water is localized in some spots and only in these spots the reaction can take place, and if the relative humidity below a threshold, the reactios stops. Air pollutant transport is described by the conservation equations, which provide the production or consuption rates of concentration of  $SO_2$ , air, gypsum and the calcite. The complete approach provides a nonlinear parabolic-elliptic model, which is composed by three diffusive equations for dioxide sulphure, calcium carbonate and one that describes the gaseous mixture air plus dioxide sulphure. This model is obtained by means of the Darcy's law which describes the seepage velocity of  $SO_2$  and by the Fick's law which describes the diffusive velocity of dioxide sulphure. This situation it is possible to neglect the presence of the air. Finally, some numerical simulation results are provided from the literature.

This thesis tries to point out the complexity of the description of porous materials damage and it is more true in the historical buildings or historical monuments cases, where there is a relevant historical and cultural value. This work is a first description of the main damage mechanisms which can occur in a building component. Several iterative algorithms just exist for the coupled differential equation of moisture and heat transport, but one would be define a complete system which takes into account also the chemical aggression, as done in this work from a theoretical point of view. One of the future goals should be to obtained a powerful and exaustive algorithm which will provide a prevision on long temporal scale of the evolution of the building or monument deterioration, and some projects on this direction are being started in Europe (Italy, Spain and Russia, first of all) and this work is an attempt to the formulation of the complete theoretical structure.

# Appendix A: notes on preliminary simulation work

From numerical and simulation points of view, some preliminary work has been done in collaboration with researchers of the Keldysh Institute of Applied Mathematics of the Russia Acamy of Sciences in Moscow. New effective methods of solution of complex mathematical models, such as those object of this thesis, are today available by means of progressive numerical approaches on parallel computers. For instance, vacancy - gas pores and cracks into crystal lattices - problems discussed in previous chapters - can be modelled as phase transitions of first kind. Therefore, the investigation of initial state porosity due to fluctuation of thermodynamical parameters of the system "atmosphere – sample stone" was performed by using algorithms for numerical solution of the Kolmogorov equation describing non-equilibrium initial stage of the phase transition. Since nucleation of defects into crystal lattice, for instance, led to more easy penetration for pollutants as well as degradation of its qualities, these results are useful to define the initial and boundary conditions for our set of equations, previously introduced. In fact, these calculations, even preliminary, calculations provide the possibility to know mechanisms of nucleation into lattices and determine initial rates of degradation in buildings' materials. Analogous numerical approaches and algorithms will be used to solve the system of equation describing the time evolution of degradation on the surface and in the bulk of stones of historical buildings.

## **Appendix B: nomenclature**

#### **Greek letters**

α	absorptivity of material [-],
α <sub>r</sub>	precipitation absorptivity [-],
$\gamma$	density of the dry air in standard condition $[kg/m^3]$ ,
δ	water vapour diffusion permeability [kg/m·s·Pa],
ε	emittance (emissivity) of material [-],
θ	contact angle between the meniscus and the capillary wall [-],
θ	angle contact between wind direction and the normal to the building wall [-],
$\lambda_0$	thermal conductivity of dry building material [W/m·K],
$\lambda(w)$	thermal conductivity of moist building material [W/m·K],
μ	magnetic momentum vector [MeV/T],
μ	water vapour diffusion resistance factor [-],
$\mu_m$	molar density of $CaCO_3$ in marble [#moles/cm <sup>3</sup> ],
$\mu_s$	molar density of $CaSO_4$ in marble [#moles/cm <sup>3</sup> ],
ρ	mass density [kg/m <sup>3</sup> ],
$\rho_a$	dry air concentration [kg/m <sup>3</sup> ],
$ ho_d$	density of the dry material $[kg/m^3]$ ,
$ ho_m$	density of marble [gr/cm <sup>3</sup> ],
$ ho_{ma}$	density of moisture air [kg/m <sup>3</sup> ],
$ ho_s$	total concentration of dioxide sulphure $[kg/m^3]$ ,
$ ho_v$	water vapour density [kg/m <sup>3</sup> ],

$ ho_{v,sat}$	water vapour concentration at saturation [kg/m <sup>3</sup> ],
$ ho_w$	density of water [kg/m <sup>3</sup> ],
σ	water surface tension [N/m],
$\sigma_{aw}$	average gas-kinetic impact diameter [m],
$\sigma(t)$	sulfation front [cm],
$\sigma_0(t)$	gypsum surface exposed to air [cm],
φ	relative humidity [-],
φ	porosity of the material [-],
$\phi_g$	porosity of gypsum [-],
Ψ	heat flow rate [J/s],
ω	swelling rate [-].

#### Latin letters

а	thermal diffusivity of the material [m <sup>2</sup> /s],
$B_0$	external magnetic field [T],
С	density of $CaCO_3$ [gr/cm <sup>3</sup> ],
<i>C</i> <sub>d</sub>	specific heat capacity of dry material [J/kg·K],
C <sub>f</sub>	specific heat capacity of ice [J/kg·K],
Cw	specific heat capacity of liquid water [J/kg·K],
$C_{p_i}$	specific heats at constant pressure [J/mol·K],
$C_{WDR}$	wind-driven rain factor [s/m],
$d_s$	diffusivity of $SO_2$ in air $[cm^2/s]$ ,
$d_w$	diffusivity of $H_2O$ in air [cm <sup>2</sup> /s],
$D_{arphi}$	liquid conduction coefficient [kg/ms],
$D_m$	mass diffusion coefficient [kg/m·s],
$D_P$	pressure diffusion coefficient [kg/m·s·Pa],
$D_T$	thermal diffusion coefficient [kg/m·s·K],
$D_v$	vapour diffusion coefficient in air [m <sup>2</sup> /s],

$D_{w,s}$	surface diffusion coefficient [m <sup>2</sup> /s],
$D_w(w)$	liquid transport coefficient [m <sup>2</sup> /s],
е	stored heat density [J/m <sup>3</sup> ],
Е	energy of the nucleus [MeV],
8	density of gypsum [gr/cm <sup>3</sup> ],
8diff	diffusion flux density [kg/m <sup>2</sup> s],
<i>8eff</i>	effusion flux density [kg/m <sup>2</sup> s],
<i>8</i> f	melted water liquid flux density [kg/m <sup>2</sup> s],
$g_v$	vapour diffusion flux density [kg/m <sup>2</sup> s],
$g_w$	liquid transport flux density [kg/m <sup>2</sup> s],
$g_{w,s}$	surface diffusion flux density [kg/m <sup>2</sup> s],
$H_d$	enthalpy of dry material [J/m <sup>3</sup> ],
$h_f$	specific melting heat (enthalpy) [J/kg],
$h_i^0$	heat of formation [J/mol],
$h_v$	specific evaporation heat (enthalpy) [J/kg],
$H_w$	enthalpy of moisture content into building material [J/m <sup>3</sup> ],
I <sub>l,a</sub>	absorbed long-wave energy flux [W/m <sup>2</sup> ],
I <sub>l,e</sub>	emitted long-wave energy flux from the surface [W/m <sup>2</sup> ],
$I_S$	total short-wave energy flux [W/m <sup>2</sup> ],
I <sub>s,diff</sub>	diffuse short-wave energy flux [W/m <sup>2</sup> ],
I <sub>s,dir</sub>	direct short-wave energy flux [W/m <sup>2</sup> ],
I <sub>s,refl</sub>	reflected short-wave energy flux [W/m <sup>2</sup> ],
<i>js</i>	flux intensity of $SO_2$ [gr/cm <sup>2</sup> s],
<i>j</i> w	flux intensity of water vapour [gr/cm <sup>2</sup> s],
<i>k</i> <sub>c</sub>	capillary coefficient [kg/m·s·K],
$k_l$	permeability coefficient [kg/m·s·Pa],
$K_n$	Knudsen factor [-],

т	mass fraction of water vapour [-],
М	molecular weight [kg/mol],
Ma	molecular weight of air [kg/mol],
$M_m$	molecular weight of marble [gr/mol],
$M_s$	molecular weight of $SO_2$ [gr/mol],
$M_v$	molecular weight of water vapour [kg/mol],
$M_w$	molecular weight of water [kg/mol],
$N_L$	Loschmidt number $[mol^{-1}]$ ,
Р	air (total) pressure [Pa],
$P_0$	atmospheric standard pressure [Pa],
Pa	dry air pressure [Pa],
<i>p</i> <sub>c</sub>	capillary pressure [Pa],
P <sub>sat</sub>	water vapour pressure at saturation [Pa],
$P_v$	water vapour pressure [Pa],
$P_w$	water pressure [Pa],
9	density of heat flux $[J/m^2s]$ ,
Q	heat [J],
r <sub>c</sub>	capillary radius [m],
$r_s$	site-specific driving-rain coefficient [s/m],
$R_a$	gas constant for dry air [J/kg·K],
$R_v$	gas constant for water vapour [J/kg·K],
$R_p$	precipitation rain intensity [kg/m <sup>2</sup> s],
$R_{WDR}$	wind-driving rain intensity [kg/m <sup>2</sup> s],
S	porous concentration of $SO_2$ [gr/cm <sup>3</sup> ],
$s_a(t)$	$SO_2$ concentration in air [gr/cm <sup>3</sup> ],
Se	heat source or sink density of heat [W/m <sup>3</sup> ]
S <sub>e,f</sub>	heat source or sink due to freezing-thawing $[J/m^3s]$ ,

$S_{e,v}$	heat source or sink due to condensation-evaporation $[J/m^3s]$ ,
$S_w$	moisture source or moisture sink [kg/m <sup>3</sup> s],
t	time [s],
Т	absolute temperature [K],
$T_1, T_2$	longitudinal and trasversal time [s],
u <sub>s</sub>	Fick's velocity [cm/s],
v	Darcy's velocity [cm/s],
$v_a$	air external speed [cm/s],
$v_W$	wind speed (normal to the wall) [m/s],
Va	air velocity [cm/s],
$V_s$	sulphite velocity [cm/s],
$V_t$	raindrop terminal velocity [m/s],
w	water toral content (or water storage function) [kg/m <sup>3</sup> ],
$w_a(t)$	water concentration in air [gr/cm <sup>3</sup> ],
w <sub>c</sub>	capillary moisture content [kg/m <sup>3</sup> ],
w <sub>cr</sub>	critical moisture content in the material [kg/m <sup>3</sup> ],
$w_{c,f}$	critical moisture content for frost [kg/m <sup>3</sup> ],
$w_f$	frozen water content [kg/m <sup>3</sup> ],
w <sub>sat</sub>	water saturation content [kg/m <sup>3</sup> ],
w <sub>sur</sub>	exterior surface moisture content [kg/m <sup>3</sup> ],
W	work [J],
<i>x</i> <sub>hr</sub>	humidity ratio [-],
$\frac{dw}{d\varphi}$	variation of moisture storage function [kg/m <sup>3</sup> ],
<u>dH</u> dT	variation of heat storage function [J/m <sup>3</sup> K],

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