# Physical methods of examining cultural property 

NMR for Cultural Heritage

## WATER-SURFACE INTERACTION

leonardo.brizi2@unibo.it

## What is a POROUS MATERIAL? (high Surface-to-Volume ratio: S/V)

Porous materials are materials with pores (cavities, channels or interstices).
The characteristics of a porous material depend on the porosity (the ratio of the total pore volume relative to the apparent volume of the material), on pore size distribution, shape and connection of the pores, as well as on the composition of the material.



In the figure: -top: the pore-size distributions of two stones obtained by Mercury Injection porosimetry (MIP);

- bottom: the corresponding NMR relaxation time distributions (as we will see, NMR Relaxometry provides this kind of distributions, as we will discuss later)

Pore size distribution can cover a wide range of values, from a few nanometers to the size of visible pores.
The determination of the $\mathrm{S} / \mathrm{V}$ is not an easy job.
Typically, simple assumptions are made on the shape of the pores.
Simple geometries are cubic or spherical, or cylindrical.

$$
S=6 \times \mathrm{L}^{2} \quad \text { and } \quad \mathrm{V}=\mathrm{L}^{3}
$$

Where:
$S=$ surface area (in units squared)
$V=$ volume (in units cubed)
$L=$ the length of one side of the cube.


It result, thus, that the surface-to-volume ratio is:

$$
\begin{equation*}
\frac{S}{V}=\frac{6 L^{2}}{L^{3}}=\frac{6}{L} \tag{2}
\end{equation*}
$$

In the case of a sphere, whose radius is $r$, the formulae for surface and volume become:

$$
\begin{equation*}
S=4 \pi r^{2} \quad \text { and } \quad V=\frac{4}{3} \pi r^{3} \tag{3}
\end{equation*}
$$

where $\pi=3.14$.
The surface-to-volume-ratio is

$$
\begin{equation*}
\frac{S}{V}=\frac{4 \pi r^{2}}{\frac{4}{3} \pi r^{3}}=\frac{3}{r} \tag{4}
\end{equation*}
$$

To define a "pore" is not an easy job. Where does the "pore" start and where does it end? And how can we define its size?
Assumptions are needed on the pore shape (cylindrical, spherical, cubic..).

In any case the "pore-size" is strictly bound to the concept of Surface-to-Volume ratio (S/V).

In a porous material, the internal $\mathbf{S} / \mathrm{V}$ can be of the order of $10^{\mathbf{2}} \mathbf{m}^{2} / \mathrm{cm}^{3}$ of material.

## Water-surface interactions

The high value of $S / V$ and the surface characteristics made the material permeable to water, the major cause of decay in materials exposed to rain water and/or to capillary absorption.

| Water normally present in materials (g/g \%) |  |
| :--- | :---: |
| wool | $\mathbf{1 6}$ |
| cotton fiber | $\mathbf{8}$ |
| silk | $\mathbf{1 0 - 1 5}$ |
| biological tissues | $\mathbf{7 0 - 9 0}$ |
| yolk | $\mathbf{5 0 - 6 0}$ |
| seasoned wood | $\mathbf{1 0 - 1 5}$ |
| stone materials | $\mathbf{0 . x}-\mathbf{5 0}$ |

## "kinds" of water

Essential water: as in gypsum $\mathrm{CaSO}_{4} \cdot 2 \mathrm{H}_{2} \mathrm{O}$, water molecules are essential part of the structure and are in stoichiometric proportion.
Not essential water: water not chemically bound, not in stoichiometric proportion.

- Adsorption water: water molecules interacting with surfaces by Van der Waals forces. It can go away by drying at temperatures even less than $100^{\circ} \mathrm{C}$.
- Absorption water: is the water condensed in interstices of the porous structure. It does not go away by drying at temperatures less than $100^{\circ} \mathrm{C}$.
- Sorption water: is water trapped in closed cavities.
- Solution water: is liquid water saturating the pore space, in different amounts.


## Introduction to surface phenomena

Why some insects can float on water surface, instead of sinking? Here an example of a needle floating on the water surface
Why when you spray water on a glass plate, the water in some cases forms drops and in other cases it forms a thin film?


Why water can go up along a glass capillary tube?


Igura 11 - Risalita di acqua colorata tango del menisco.


## The intermolecular forces

The surface of materials and substances have particular properties. The phenomena described above are due to surface properties. These properties are due to intermolecular forces.
Matter is made of molecules in thermal agitation, that interact by means of forces.
When two molecules come closer together, electrical charges redistribute in such a way that the average distance between opposite charges is slightly less than the average distance between charges of the same sign.
The resultant is an ATTRACTIVE FORCE at low range ( $\mathrm{r}<1 \mathrm{~nm}$ ).
But, if they come too close the negative charges start to overlap and that produce a REPULSIVE FORCE.

## Surface Tension

Inside a liquid, the distribution of the intermolecular forces is isotropic and the resultant R of all the forces acting on the molecules is zero: $\quad \mathrm{R}=0$.

At the surface, for example at the interface between water and air, in a layer (thickness about 2 nm ) the molecules are in different conditions.

## BUT, the resultant force on each molecule is still zero!!!!! <br> R = 0 !!!!!!!!!!!!!!!!!



This is due to the most distant molecules, and tends to push the molecule inside the water

This is due to the closest molecules, and tends to push the molecule outside the water

## $\mathbf{R}=\mathrm{Fa}+\mathrm{Fr}=\mathbf{0}$

The balance of these forces is obtained by a redistributions of the molecules at the interface (water-air), and the interface acquires special properties: the surface behaves as an elastic

## membrane.

If a molecule for some reasons tends to enter into the fluid, Fr becomes larger than Fa . This prevents the molecules to move closer. Viceversa, if one molecule tends to go away, Fr becomes smaller than Fa. This prevents the


Image from: http://labman.phys.utk.edu/phys221core/modules/m7/surface_tension.html molecules to go away.
The surface behaves as an elastic membrane, that, for example, makes the surface able to carry the weight of an insect. The physical property is called SURFACE TENSION

## Definition of surface tension

An operational definition of surface tension is needed. Operational definition of a property is the procedure used to measure that property.

In order to give an operational definition of surface tension, let us take a metallic wire folded in the shape of $U$, as in the figure, with a mobile side. If we dip it in soapy water, a water membrane is formed.



## surface tension

 $\mathbf{F}=\tau \mathbf{2} \mathbf{b}$If we pull the mobile side of the wire with a force $\mathbf{F}$, we can pull it until the soapy membrane breaks. The value of the force F that one applies just before the membrane breaks depends on the surface tension. Experimentally, it is found that this force, that opposes the extension of the membrane, lays on the surface, is perpendicular to the mobile side, and is proportional to the length of the mobile side $\mathbf{b}$. The constant of proportionality $\tau$ is the surface tension. So it is a force / length unit ( $\mathrm{N} / \mathrm{m}, \mathrm{N}$ is the unit Newton and $m$ is the unit meter). ( 2 times because we have 2 surfaces of the membrane)

We can compute the work made by the force $\mathbf{F}$ to extend the membranes (the work is given by the product of the force by the displacement in the direction of the force).


The work to extend the membrane is:

$$
\begin{aligned}
& \Delta L=\mathbf{F} \Delta I=\mathbf{F}\left(I_{2}-\mathrm{I}_{1}\right) \\
& =\tau \mathbf{2} \mathbf{b}\left(\mathrm{I}_{2}-\mathrm{I}_{1}\right)=\tau \Delta \mathbf{A}
\end{aligned}
$$

Therefore, one can state that $\tau$ is the work (or energy) per surface unit ( $\mathrm{J} / \mathrm{m}^{2}$ ) (Joule (J) is the unit for work and energy). That is the reason why liquids tend to acquire a curvature.
The curvature produces the minimum surface per unit of volume, that corresponds to the minimum surface potential energy.
A water drop is a sphere because the sphere is the solid with the minimum surface / volume unit.

## Wettability - Contact angle

Let us consider, at the air-material interface, a drop of liquid on a flat surface. The drop can take the shape of a sphere or the shape of a thin film.

In the first case one speaks of low wettability of that surface respect to water, in the second one of high wettability.


Low wettability if contact angle is larger than $90^{\circ}$ High wettability if the contact angle is smaller than $90^{\circ}$
The two conditions are described by means of the contact angle, the angle formed between the tangent to the surface formed between liquid and gas and the tangent formed between solid and liquid, in the point where the three phases coexist.

The different behaviour is due to the different values of cohesion forces (between molecules in the liquid) and adhesion forces (between liquid and solid). When the cohesion forces are lager than the adhesion forces, there is low wettability, viceversa there is high wettability.
To change wettability, surface are treated with hydrophobic compounds. That reduces the amount of water absorbed.

## MRI images of internal slices of Lecce stone treated with PB72. Water uptake kinetics through the untreated face

Untreated stone


20 min


3 h


1 h


24 h


2 h


7 days

Treated stone


## Capillary Pressure

The presence of the surface tension determines a pressure difference between two fluids separated by an interface, as in the case of a vapor bubble in a liquid (it happens also in the case of a condensed liquid inside a capillary tube).


Let's consider a bubble of radius r ;
the external pressure is $\mathrm{P}_{\mathrm{e}}$ and the internal pressure is $\mathrm{P}_{\mathrm{i}}$.

In order the bubble to exist, at the equilibrium $P_{i}>P_{e}$, because $P_{1}$ must balance the external pressure, plus the pressure due to the surface tension.

It is possible to demonstrate that:

$$
\left(\mathbf{P}_{\mathrm{i}}-\mathbf{P}_{\mathrm{e}}\right)=2 \tau / \mathbf{r} \quad \text { Laplace equation }
$$

## $\left(\mathbf{P}_{\mathbf{i}}-\mathbf{P}_{\mathrm{e}}\right)=2 \tau / \mathbf{r} \quad$ Laplace equation

The pressure difference

- is proportional to $\tau$, therefore a fluid with high $\tau$ produces a lager pressure difference, if the radius is the same,
- is inversely proportional to r , therefore, the smaller the bubble, the higher the pressure difference.

Example: In the case of a soap bubble, that means air in air, with a liquid membrane in between, there are two surfaces, so the equation reads: $\quad\left(\boldsymbol{P}_{1}-\boldsymbol{P}\right)=4 \tau / r$
by assuming $r=2 \mathrm{~mm}, \tau=710^{-2} \mathrm{~N} / \mathrm{m}$, one gets $P_{1}-P=1.410^{2} \mathrm{~Pa}$, ( Pa is the unit of the pressure (Pascal))
but, if $r=2 \mu \mathrm{~m}, P_{1}-P=1.410^{5} \mathrm{~Pa}=0.110^{6} \mathrm{~Pa}$, that means of the order of one atmosphere.

## Capillarity

Let's suppose to have water inside a clean glass tube immersed in a container with water. Water wets the surface of the tube and tends to form a concavity (meniscus) inside the clean glass tube. On the contrary, a liquid that doesn't wet the glass makes convex surfaces. In the first case (water in a glass tube) the liquid goes up if the tube is very narrow (capillary tube). The phenomenon is called capillary rise. That happens because clean glass has high wettability.

The level of water rise in the capillary tube increases until the forces that bring it up balance the weight of the water column, that push the water down

## Capillary rise



Capillary water flow in a brick that is in contact with water at the bottom. The time elapsed after first contact with water is indicated. The brick height is 225 mm .

## ... Venice



## Jurin's Law

Jurin's Law: quantifies the rise (h) of a fluid with density $\rho$ into a capillary tube with a radius $r$

$r$ is the radius of the capillary
$\rho$ is the density of water
$\alpha$ is the contact angle
$\mathrm{P}(\mathrm{H})>\mathrm{P}(\mathrm{K})$
$\mathrm{P}(\mathrm{H})-\mathrm{P}(\mathrm{K})=\mathrm{Pc}=2 \tau \cos \alpha / \mathrm{r}$
(Laplace equation)
$P a=P(A)=P(H)=P(D)=P(K)+\rho g h$ (hydrostatic low)

$$
P(H)-P(K)=\rho g h
$$

$$
P(H)-P(K)=P c=2 \tau \cos \alpha / r=\rho g h
$$

$$
\rho g h=2 \tau \cos \alpha / r
$$

$$
\begin{aligned}
& h=\frac{2 \tau \cos (\alpha)}{\rho g r} \\
& \text { Jurin's Law }
\end{aligned}
$$



If the liquid doesn't wet the surface, the liquid goes down following the same law. In this case the contact angle is $\alpha>9 \mathbf{0}^{\circ}$, that means $\cos \alpha$ is negative. Therefore the height $h$ becomes negative.

