Characterizing Distilled Water in Silica and Carbon Porus Matrices

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Abstract

The main objective of this work is to observe phase transitions of distilled water inside porous matrices of Carbon (M1R4FPC800°C) and Silica (CPG00075B). Atomic force microscopy is performed to characterize the roughness of plane samples (Glass, Graphite, and Al_2O_3). Then, we apply the drop shape method to measure the surface tension and the contact angle with plane samples. The capillary method is applied to measure the contact angle inside the pore. We observe a great increase in the contact angle inside the pore in contrast with plane samples. Finally, we apply the dielectric method to measure the capacitance of the sample and, by analyzing peaks in the imaginary capacitance, we obtain the relaxation time of water molecules, comparing the results obtained from bulk water with water inside the porous matrices. We observe a displacement, to lower temperatures, on the melting point of water inside porous matrices in contrast with bulk water. This result suggest that water is at high preasure inside of the pores.

1 Introduction

Understanding the behavior of liquids inside porous matrices, such as carbon and silica, is crucial for various applications, including catalysis, filtration, and energy storage. One key parameter in characterizing this behavior is the contact angle, which provides insight into the wettability and interaction between the liquid and the solid surface. The contact angle influences processes like wetting, adhesion, and fluid transport within these porous materials.

The capillary method is a reliable and widely used technique to measure the contact angle within these porous structures. It allows for precise determination of how water interactions with the surfaces of carbon and silica matrices. This method provides valuable data on the surface chemistry and porosity effects on wetting behavior.

Furthermore, the dielectric method offers another approach to study water dynamics within porous matrices. By measuring the capacitance of water, it becomes possible to calculate the relaxation time of water molecules and observe phase transitions. This technique is particularly useful for understanding the mobility and intermolecular interactions of water confined in nanoporous environments.

In this study, we utilize both the capillary and dielectric methods to investigate the contact angle and capacitance of water inside carbon and silica matrices. This dual approach aims to provide a comprehensive understanding of water's behavior in these important materials, contributing to advancements in various fields of science and technology.

2 Materials

We prepare the carbon $M1R4FPC$ powder in the lab. It has the next characteristics:

- Micropore Diam. (nm): 1
- Pore Vol. (cm^3/g): 0.191
- Surface Area (m^2/g) 452
- Interlayer distance (Å): 3.95

The silica $CPG00075B$ was obtained from an official distributor, the especificatios are:
CPG

- Mean Pore Dia. (Å): 74.3
- Pore Dist. ($\pm\%$): 7
- Pore Vol.(cm^3/g): .47
- Surface Area (m^2/g): 1027
- Particle Size: 120/200

3 Data Adquirition

We have masured the rougthness of plane surfices samples by AFM. Viscosity and Density of water is measured with ultra-high resolution. Surfice tension and contact angle in plane surfaces has been measured by image tecnics. Contact angle inside of porus matrices has been measured by the capilar method. Complex capacitance has been measured by dielectric method.

3.1 Density and Viscosity of Water

A Stabinger viscosimeter, applying the SVM standard method, was used to obtain density (ρ) and dynamic viscosity (η_d). Several measurements were performed to achieve ultra-precision in density.

$$\eta = 0.8775 \pm 0.02, \mathrm{m \cdot Pa \cdot s} \tag{1}$$

$$\rho = 0.99755 \pm 0.000001, \mathrm{g \cdot cm^{-3}} \tag{2}$$

These values correspond to distilled water at room temperature ($T \approx 25°C$).

3.2 Atomic Force Microscopy for Plane Samples

With micrometer resolution, we have scanned four plane surfaces of:

- Graphite (clean)
- Graphite (not-so-clean)
- Glass (silica)
- Porous surface of non-polarized Al_2O_3

The pictures shown in Figure 1 represent the 3D plot of around $10 \times 10\mu m$ of the surface. As can be observed, there are several differences in the roughness of the four materials. We want to highlight the roughness of the porous surface in Figure 1d. This material is particularly interesting, showing notorious roughness, while the others show mostly plane surfaces. The peaks observed in carbon and glass are explained as dust electrically attached to the surface.
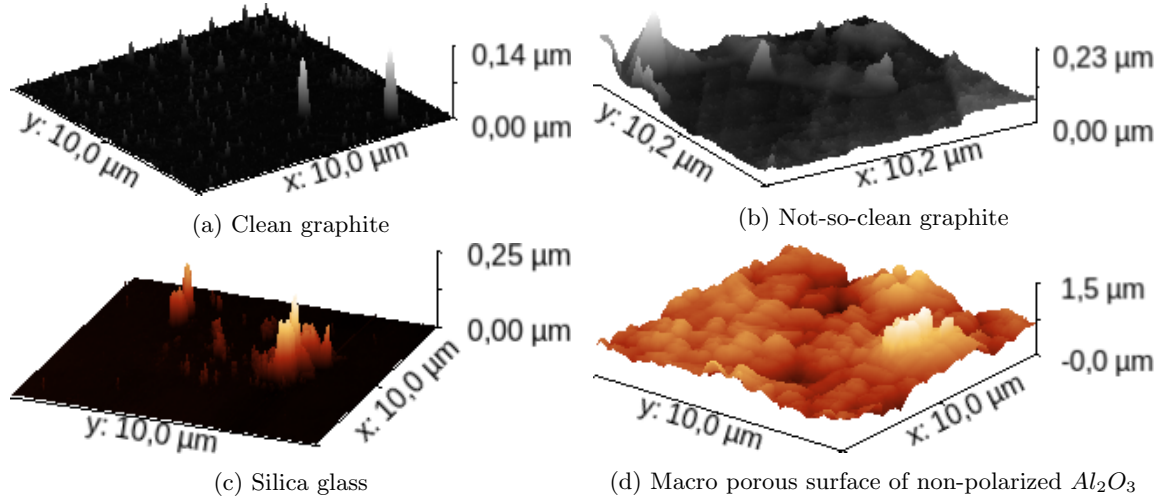
(a) Clean graphite

(b) Not-so-clean graphite

(c) Silica glass

(d) Macro porous surface of non-polarized Al_2O_3

Figure 1: AFM 3D maping of diferent plane samples

3.3 Surface Tension and Contact Angle for Water

Drop shape analysis (DSA) has been developed to obtain the surface tension (γ) of water and the contact angle on clean carbon (graphite) and silica (glass) samples.

$$\gamma_{water} = 65 \pm 1\,\text{mN/m} \tag{3}$$

$$\theta_{\text{Graphite}} = 76.3 \pm 0.4° \tag{4}$$

$$\theta_{\text{Glass}} = 52.5 \pm 0.1° \tag{5}$$

Water Inside the Porous

3.4 Contact Angle by Capillary Method

The capillary method involves the observation of liquid absorption in a capillary tube or porous matrices to determine the contact angle. This method leverages the balance of capillary forces and gravitational forces acting on the liquid.

3.4.1 Procedure

1. **Preparation of Samples:**

   - The sample (carbon or silica) was grained in order to obtain homogeneus powder.
   - Then, we placed the sample into a pipette tip, it was spined for 5-10 minutes.

2. **Capillary Rise Experiment:**

   - A container was filled with liquid and placed inside of the chamber where high-precision scale measure the weight of the porous matrices.
   - The tip of the porous matrices was immersed vertically into the liquid and allow the liquid to rise by capillary action.
   - Record the weight Δm of the the porous matrices wile the liquid rise up.

3. **Calculation of Capillary Constant C:**

- Hexane was used as test liquid, known for its well-characterized properties and low contact angle with many materials.
- The weight Δm of the absorbed liquid is related to the capillary constant C by the slope S:

$$S_0 = \frac{\Delta m^2}{\Delta t} \tag{6}$$

and the model for capillarity shows:

$$S_0 = CL_0 \cos \theta \tag{7}$$

where

$$L_0 = \frac{\rho^2 \gamma}{\eta} \tag{8}$$

where ρ is density, γ is surface tension and η is viscosity.
- Since hexane is used, its surface tension and density and viscosity are known, simplifying the calculation of C with the next identity:

$$C = \frac{S_0}{L_0} \tag{9}$$

4. **Determination of Contact Angle θ:**

- With the constant C obtained from the hexane experiment, repeat the capillary rise experiment using water.
- Measuring the new weight Δm_{water} of the absorbed water we obtain S_{water}.
- Rearrange the capillary rise equation to solve for the contact angle θ_{water}:

$$\cos \theta_{\text{water}} = \frac{S_{water}}{CL_{water}} \tag{10}$$

- Use the previously determined C value and the known properties of water to compute the contact angle.

$$\theta = \arccos(\cos \theta) \tag{11}$$

3.4.2 Analysis and Interpretation

The error in angle can be propagate from the other cuanqities measured before:

$$\Delta L = \frac{\rho^2 \gamma}{\eta} \sqrt{\frac{2s^2 \Delta \gamma - \Delta \eta}{\rho^2}} \tag{12}$$

$$\Delta \cos \theta = \frac{L_0}{L} \frac{S}{S_0} \sqrt{\frac{\Delta L_0^2}{L_0^2} + \frac{\Delta L^2}{L^2} + \frac{\Delta S_0^2}{S_0^2} + \frac{\Delta S^2}{S^2}} \tag{13}$$

$$\Delta \theta = \sqrt{\frac{\Delta \cos \theta^2}{1 - \cos \theta^2}} \tag{14}$$

By carefully conducting the capillary method and analyzing the results, we can obtain precise measurements of the contact angle and thus gain a better understanding of the interaction between water and the porous matrices of carbon and silica. This information is vital for optimizing the performance of these materials in their respective applications.

The results obtained for carbon and silica porous matrices are show in table 1. We can notice a increase in contac angle in comparition with plane samples, equations 4 5.

Porous Sample	C-constant	Contact Angle θ
Carbon (M1R4FP)	0.0005	$89.8 \pm 0.2°$
Silica (CPG00075B)	0.00029	$81 \pm 1°$

Table 1: Constant C and contact angle for carbon and silica by capilar method. Error calculated from standar deviation of 3 mesurments.

3.5 Capacitance by Dielectric Method

We prepared a sample with pores filled with water. To achieve this, the sample was left in a vacuum chamber for 24 hours to remove any air from the pores. After this period, water was added to the powder to fill the pores completely.

By applying the dielectric method to the resulting sample, we measured the real and imaginary components of the capacitance of water at different frequencies and temperatures.
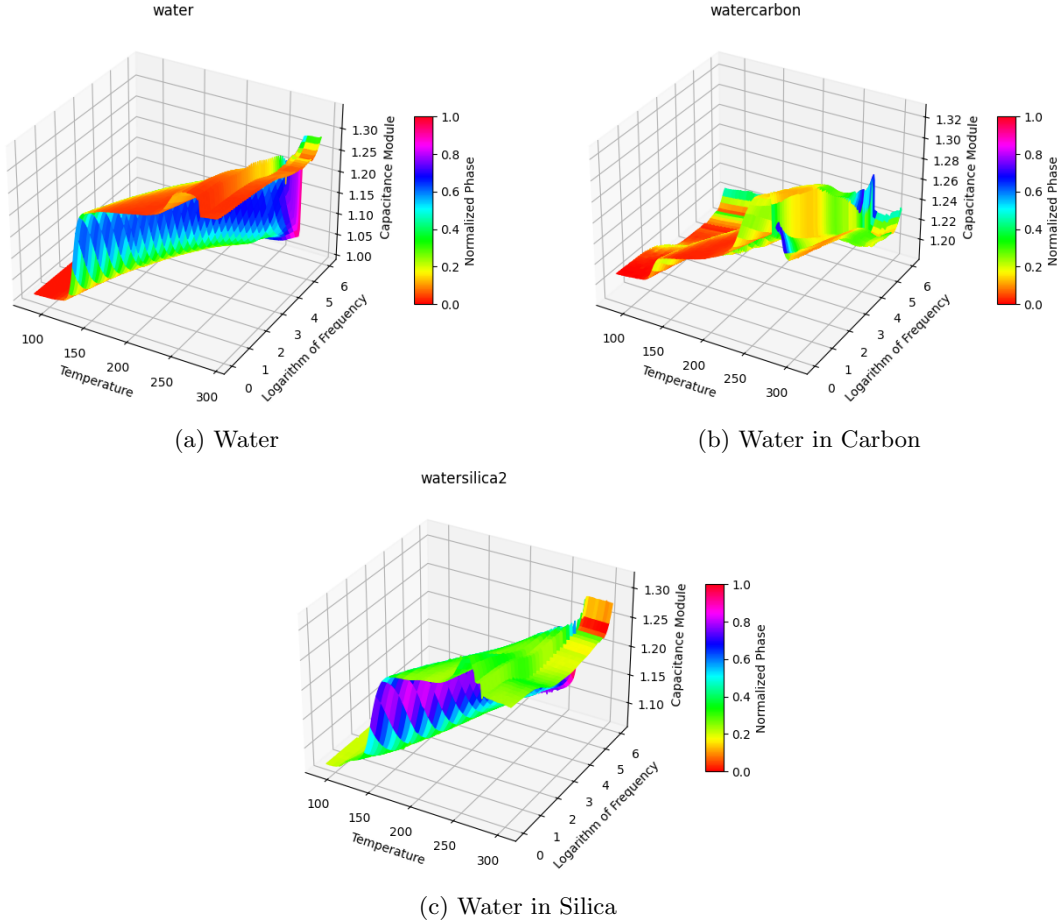

(a) Water

(b) Water in Carbon

(c) Water in Silica

Figure 2: 3D maping of real capacitance vs temperature and logarithm of frequency, imaginary capacitance in colors.

In figure 2, we can observe the presence of different phase transitions when water is confined within the pores.
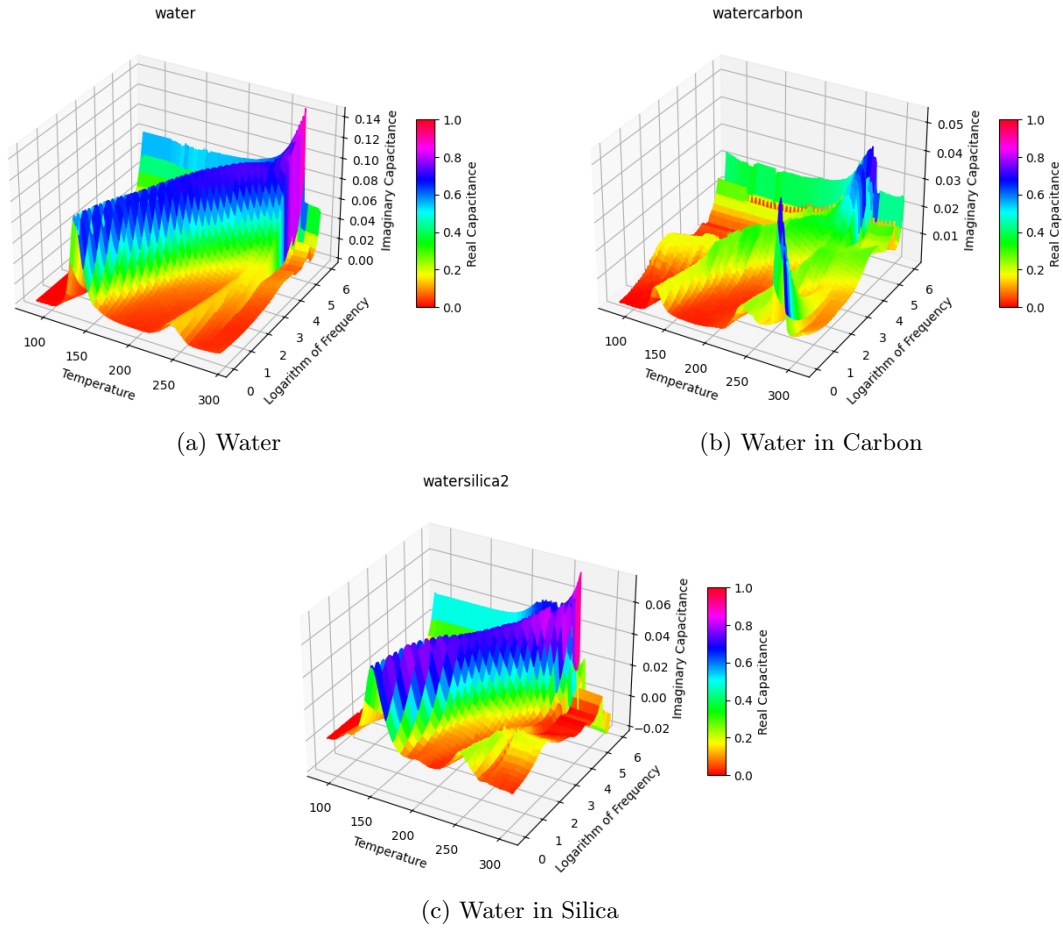
(a) Water

(b) Water in Carbon

(c) Water in Silica

Figure 3: 3D maping of imaginary capacitance vs temperature and logarithm of frequency, real capacitance in colors.

In figure 3, several peaks can be noticed when water is confined within the pores, indicating different relaxation processes.
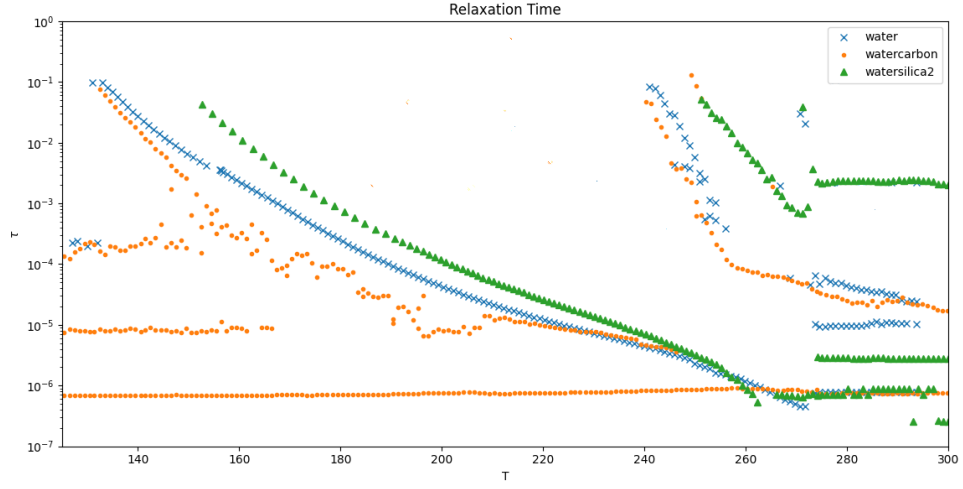
Figure 4: Relaxation times for water.

From the peaks in the imaginary capacitance versus frequency for each temperature, we can determine the relaxation times. Figure 4 shows the shift in the melting point when water is confined within the pores, illustrating how confinement affects the relaxation dynamics of water.

4   Results

We observe a significant increase in the contact angle of water inside the porous matrices. Additionally, we observe a displacement in the melting point, indicating high pressure inside the pores. The melting point of bulk water is observed between temperatures $T_- = 271.7\,\mathrm{K}$ and $T_+ = 273.6\,\mathrm{K}$. The melting point of water inside silica pores is observed between temperatures $T_- = 262.2\,\mathrm{K}$ and $T_+ = 266.1\,\mathrm{K}$. The melting point of water inside carbon pores is observed between temperatures $T_- = 246.2\,\mathrm{K}$ and $T_+ = 250.2\,\mathrm{K}$. The distinction between the lower limit T_- and upper limit T_+ for the melting point temperatures illustrates the range between the onset of melting and the point where all the water has melted.

Above $T = 273\,\mathrm{K}$, we observe several straight lines. This behavior can be explained by Maxwell-Wagner interfacial polarization.

In summary:

1. **Contact Angle Increase**: The significant increase in the contact angle suggests that the wetting properties of water are altered when confined within porous matrices. This phenomenon could be due to changes in surface energy and interaction forces at the solid-liquid interface.

2. **Melting Point Displacement**: The shift in the melting point for water inside porous matrices compared to bulk water is a critical observation. This shift indicates that confinement within the pores induces high pressure, which in turn affects the phase transition temperature. The difference in melting points between silica and carbon pores also suggests that the material of the porous matrix influences the extent of pressure-induced melting point changes.

3. **Pressure Effects**: The high pressure within the pores can be attributed to the capillary forces and confinement effects. These forces create a unique thermodynamic environment that alters the physical properties of water, including its melting point.

4. **Maxwell-Wagner Interfacial Polarization**: The presence of straight lines above $T = 273\,\mathrm{K}$ indicates a dielectric relaxation phenomenon known as Maxwell-Wagner interfacial polarization. This occurs in heterogeneous materials where charge carriers accumulate at the interfaces, leading to a polarization effect under an external electric field. This behavior is often observed in composite materials and systems with significant interfacial areas, such as porous matrices filled with water.

Additional Considerations

- **Pore Size and Distribution**: The size and distribution of the pores within the matrices could further influence the observed melting point shifts and contact angles. Smaller pores tend to induce higher pressures, leading to more significant melting point depression.
- **Surface Chemistry**: The chemical composition and surface functional groups of the porous matrices can affect water's interaction with the pore walls, thus influencing the contact angle and phase transition behavior.