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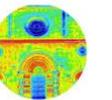
Proton NMR relaxation times allow to study molecular correlations within water-methanol solutions: the Hydrophobic interaction.

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L'Aquila, dal 23 al 27 settembre 2019

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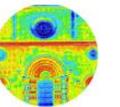


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- **Hydrophobic interaction, of basic importance in many research fields – including life sciences - is nowadays an open question in contrast to the well described hydrophilicity.**
- **As said by Ben Widom (one of the father of the modern thermodynamics): on despite of the many MD simulation studies there are only few experimental datum points (e.g., we don't have an analytical description of the hydrophobic intermolecular potential).**
- **Our aim here is to study, by using the NMR spectroscopy, the competitions between hydrophilicity and hydrophobicity in water-methanol solutions as a function of temperature and concentration.**
- **We take profit of a recent study that shows a dramatic change, at 8 °C, from hydrophilic to hydrophobic of pure water confined inside single wall hydrophobic nanotubes**

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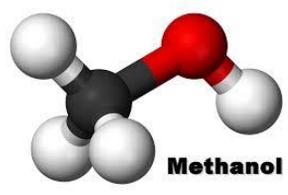
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Why methanol?

- ***Methanol is the smallest amphiphilic molecule allowing an easier investigation of the competition between hydrophobic and hydrophilic interactions.***

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- ***Water-methanol solutions are highly non-ideal (non linear thermodynamic behaviours in composition).***

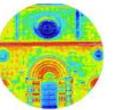


- ***As early as 1935, Gibson noticed the non-ideality of such solutions from studies on excluded volume, assuming that methanol favored the association between water molecules.***

- ***Frank and Evans later supported the still-debated hypothesis that methanol favors "iceberg-like" structures for water.***

- ***Then, Schott made fluidity measurements and argued that the water-methanol association is favored by an increase in temperature.***

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Temperature-Induced Hydrophobic-Hydrophilic Transition Observed by Water Adsorption

Hai-Jing Wang, Xue-Kui Xi, Alfred Kleinhammes, Yue Wu*

This Science paper reports a water hydrophobic-hydrophilic transition upon cooling at 8 °C via the observation of water adsorption isotherms in hydrophobic nanotubes measured by nuclear magnetic resonance.

This is ascribed to a considerable slowdown in molecular reorientation of such adsorbed water.

The observed transition demonstrates that the structure of interfacial water could depend sensitively on temperature, which could lead to intriguing temperature dependences involving interfacial water on hydrophobic surfaces

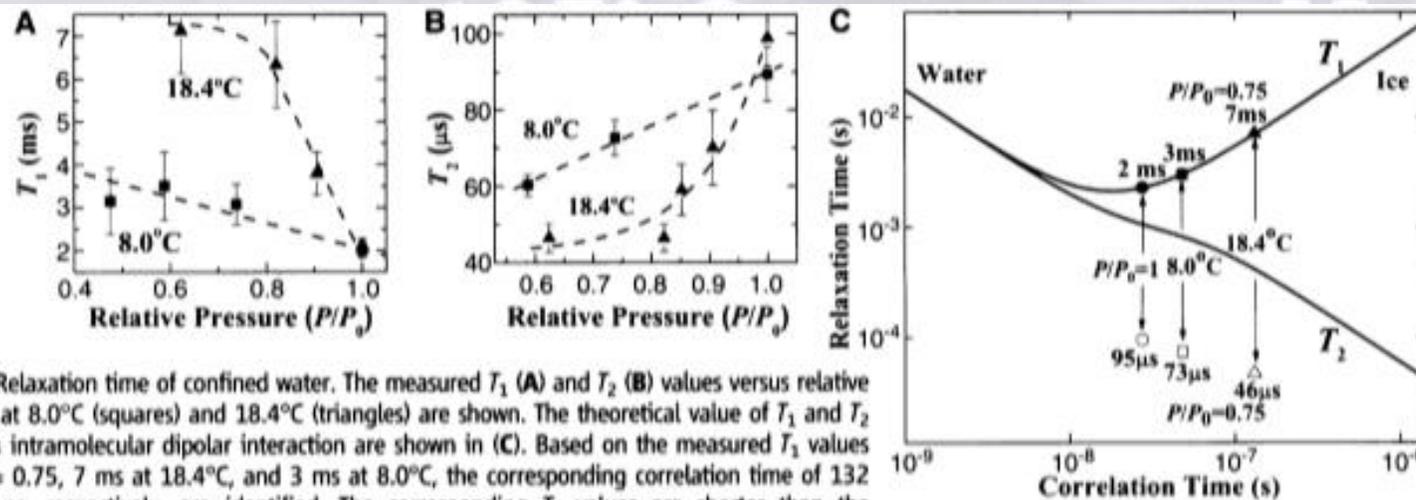


Fig. 2. Relaxation time of confined water. The measured T_1 (A) and T_2 (B) values versus relative pressure at 8.0°C (squares) and 18.4°C (triangles) are shown. The theoretical value of T_1 and T_2 based on intramolecular dipolar interaction are shown in (C). Based on the measured T_1 values at $P/P_0 = 0.75$, 7 ms at 18.4°C, and 3 ms at 8.0°C, the corresponding correlation time of 132 and 46 ns, respectively, are identified. The corresponding T_2 values are shorter than the theoretically expected values. The correlation time at these two temperatures becomes the same at $P/P_0 = 1$ (26 ns).

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Outline

- *The dynamic behavior of water-methanol solutions has been studied by means of NMR spectroscopy as a function of concentration and temperature, including the supercooling regime. In particular, the thermal evolution of the longitudinal or spin-lattice and the transverse or spin-spin relaxation times, T_1 and T_2 respectively, has been investigated at different methanol molar fractions.*
- *In such a way, the reciprocal influences of hydrophobicity on the solvent and of hydrophilicity (through hydrogen bond interactions) on the solute have been pointed out by means of a single characteristic correlation time τ_c that reflects all local structural configurations and characterizes the corresponding dynamics.*
- *The data show that the temperature increase progressively reduces the lifetime of the hydrogen bond interactions with consequent decoupling in the dynamic modes of the system. Specifically, at temperatures above about 265 K, hydrophobicity becomes progressively stronger and governs the physical properties of the solutions.*
- *We find that at low temperature both relaxation times are strongly correlated when the HB lifetime is long; instead at high temperature the HB lifetime decreases: hydrophilicity prevails destroying the water clusters and decoupling the dynamic modes of the system.*



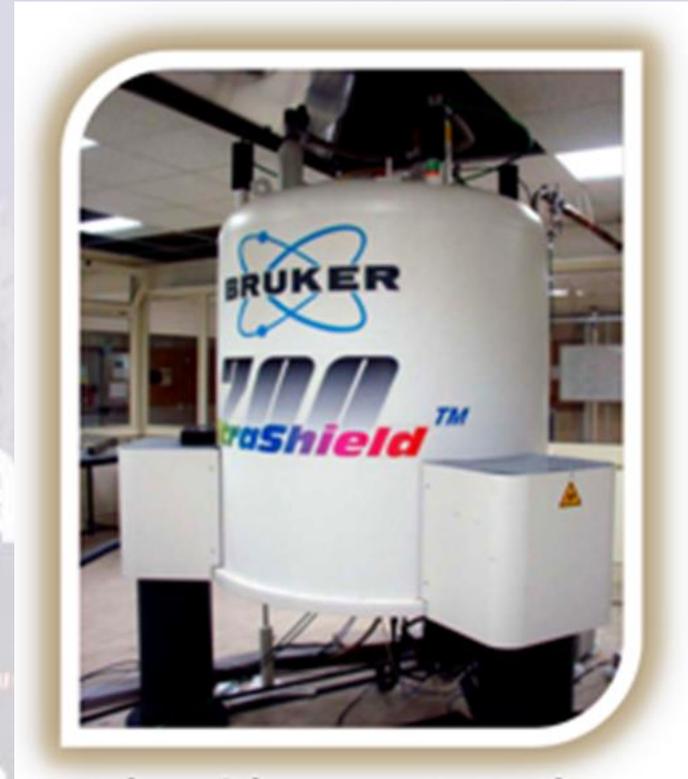
NMR

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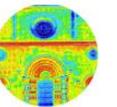
- ^1H NMR is a unique probe able to follow contemporary but individually the dynamics of the different chemical groups present within the system.

- In particular by means of ^1H NMR experiments we quantify the molecular properties of the system across a very large temperature range and measure both the proton spin-lattice relaxation time (longitudinal - T_1) and the proton spin-spin relaxation time (transverse - T_2) and hence the time required for a molecule to interact with its surrounding or with the homologous molecules.

- For the NMR experiments we used a Bruker Avance spectrometer operating at 700 MHz.

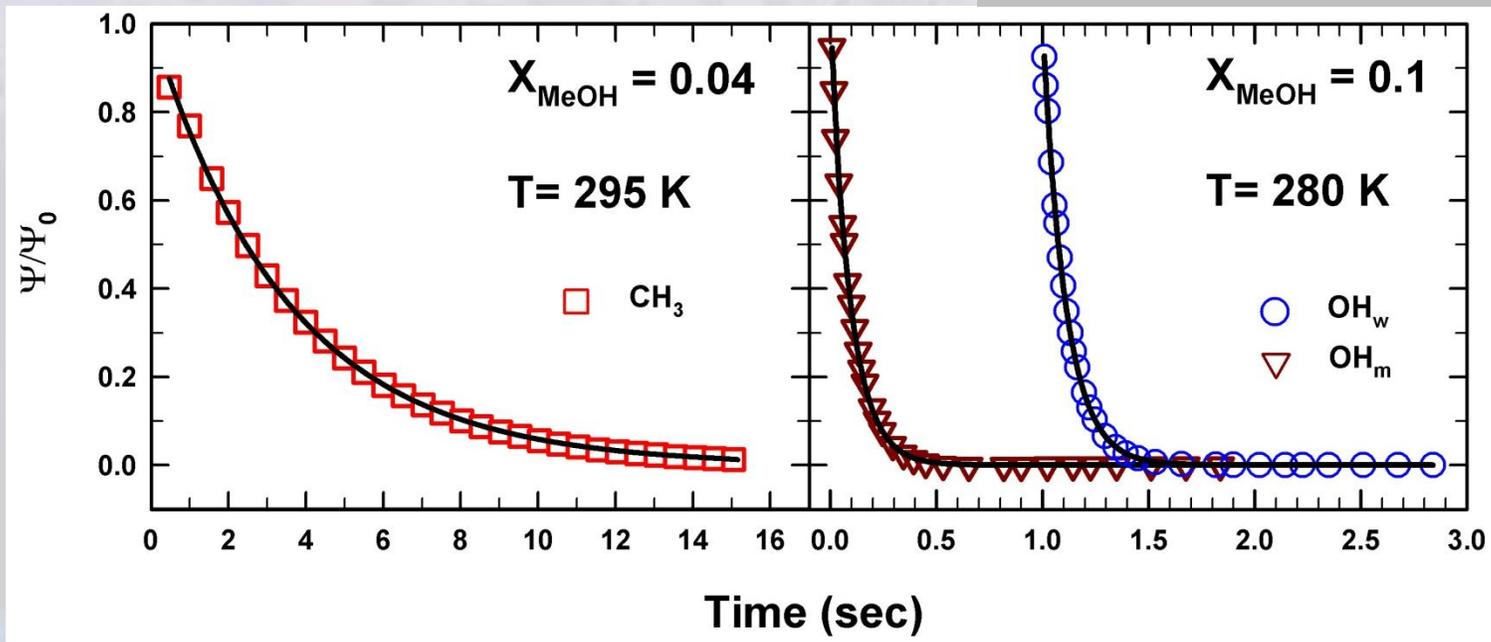
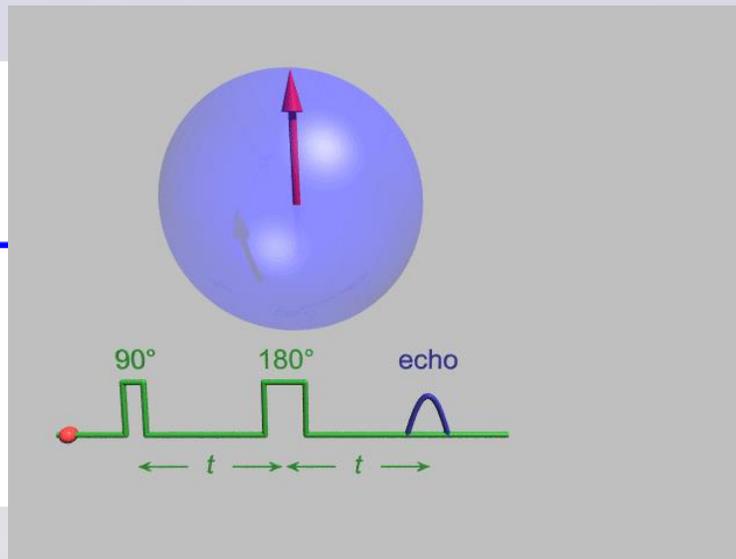
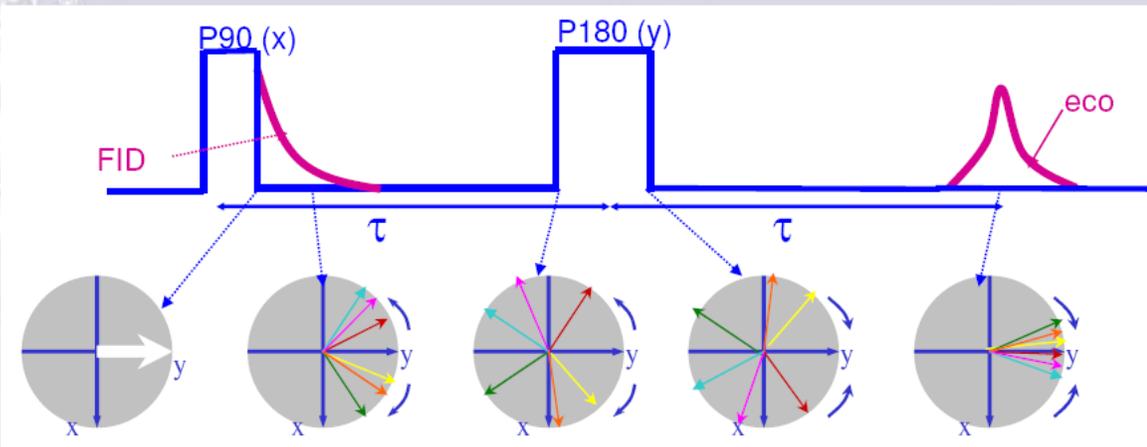


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Hahn Echo:



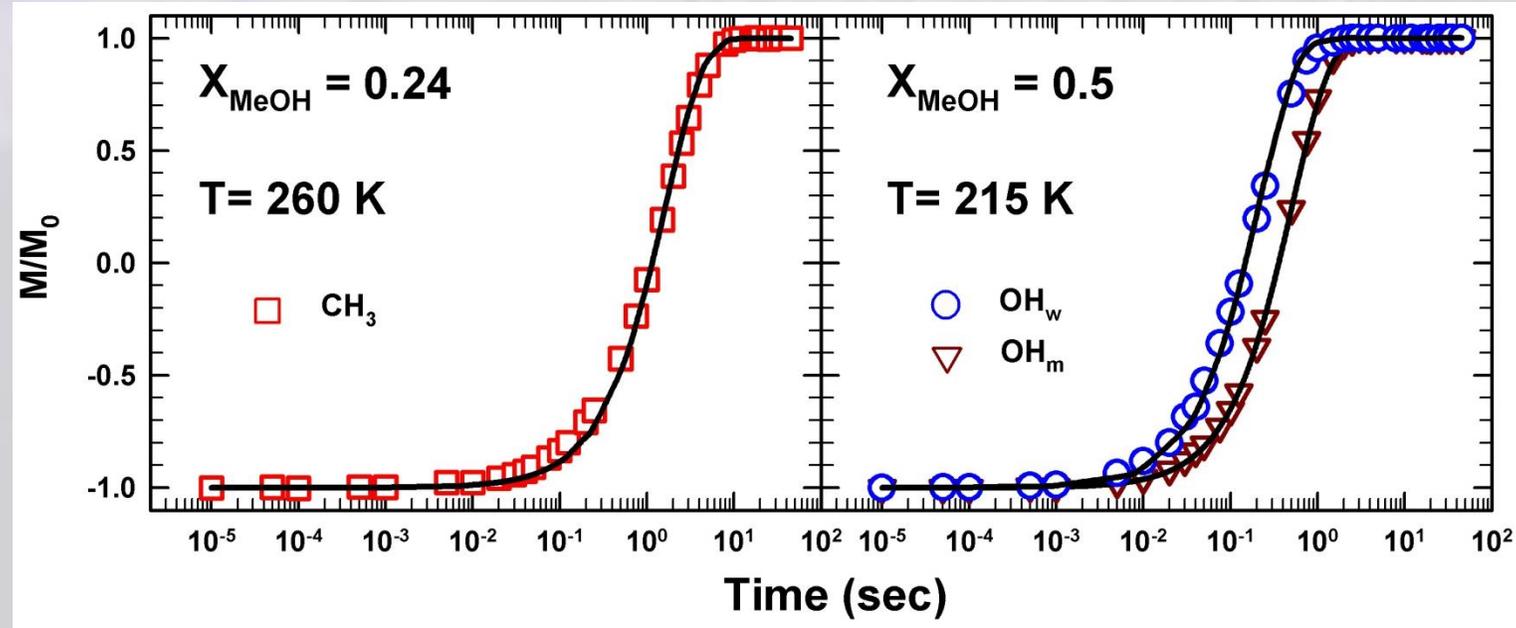
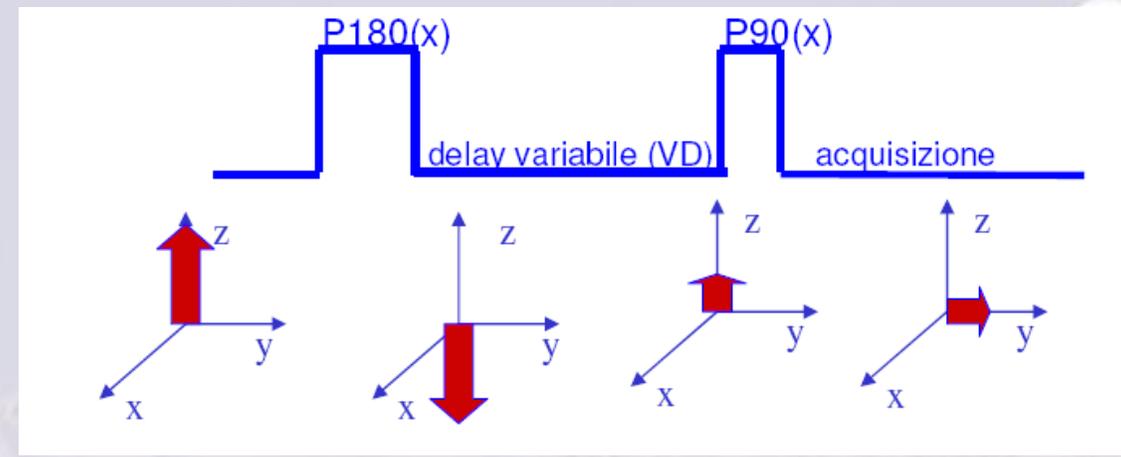
$$\Psi / \Psi_0 = \exp(-t / T_2)$$



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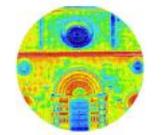
Inversion Recovery & Spin-Lattice relaxation

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$$M / M_0 = 1 - 2 \exp(-t / T_1)$$

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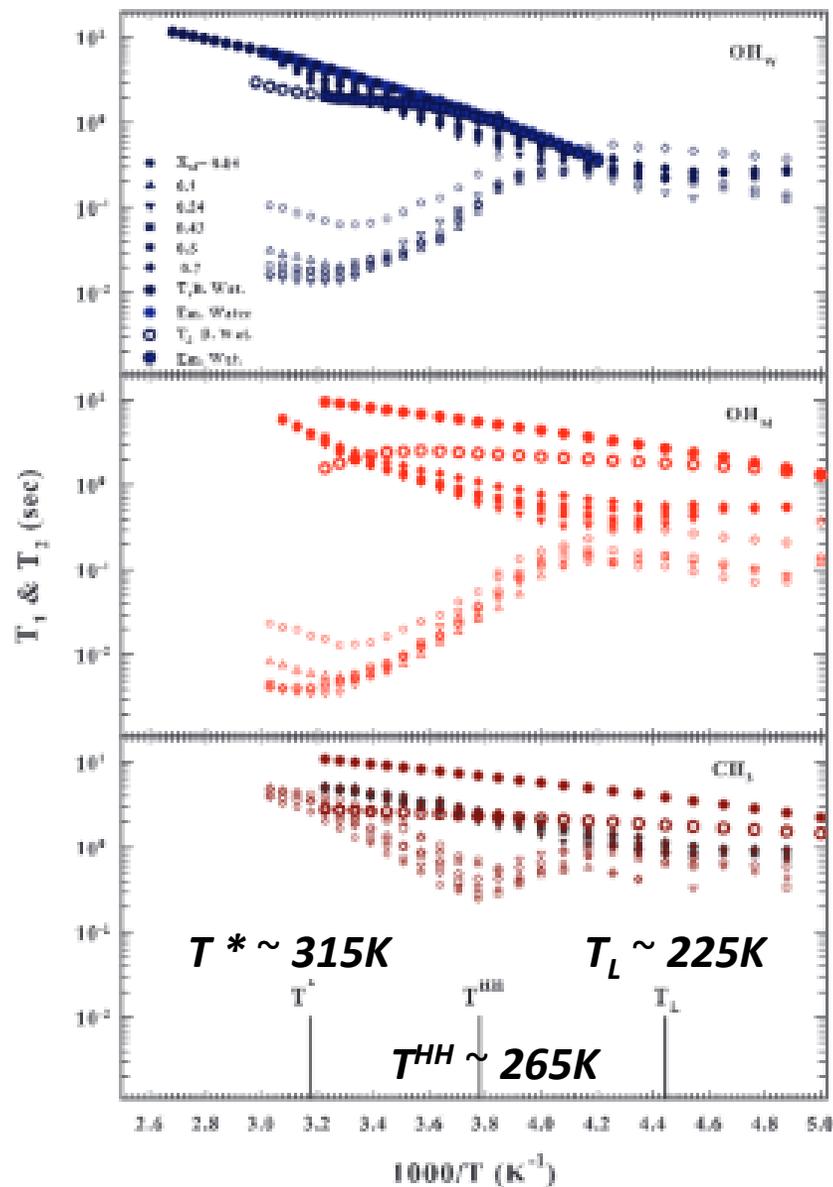
NMR relaxation times vs. T

This figure shows the trends of T_1 and T_2 both for pure liquids (solid symbols) and at several concentrations for the different molecular groups (open symbols).

It is important to note that the T_2 of the hydroxyls in the solution is two orders of magnitude lower than that in pure liquids, indicating the presence of strong interactions between the hydrophilic groups of water and methanol and that it has a maximum of about 225K.

Instead, the T_2 of methyls shows a minimum at about 265K, which can be ascribed to the onset of the hydrophobic effect.

Finally, we note how the temperature of about 315K can be associated with the "end" of the preponderance of the hydrophilic effect. Above it, water begins to behave as a simple liquid.





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NMR Correlation Time τ_c

$$A = 3\gamma^4 \hbar^2 / 10$$

r = Interatomic distance

ω_0 = Larmor Frequency

$$R_1 = \frac{1}{T_1} = \frac{A}{r^6} \left(\frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right)$$

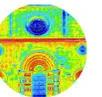
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$$R_2 = \frac{1}{T_2} = \frac{A}{2r^6} \left(3\tau_c + \frac{5\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{2\tau_c}{1 + 4\omega_0^2 \tau_c^2} \right)$$

$$12B (\omega_0 \tau_c)^4 + (37B - 8) (\omega_0 \tau_c)^2 + 10B - 5 = 0$$

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$$B = T_2 / (2T_1)$$



Correlation Time τ_c

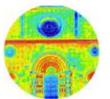
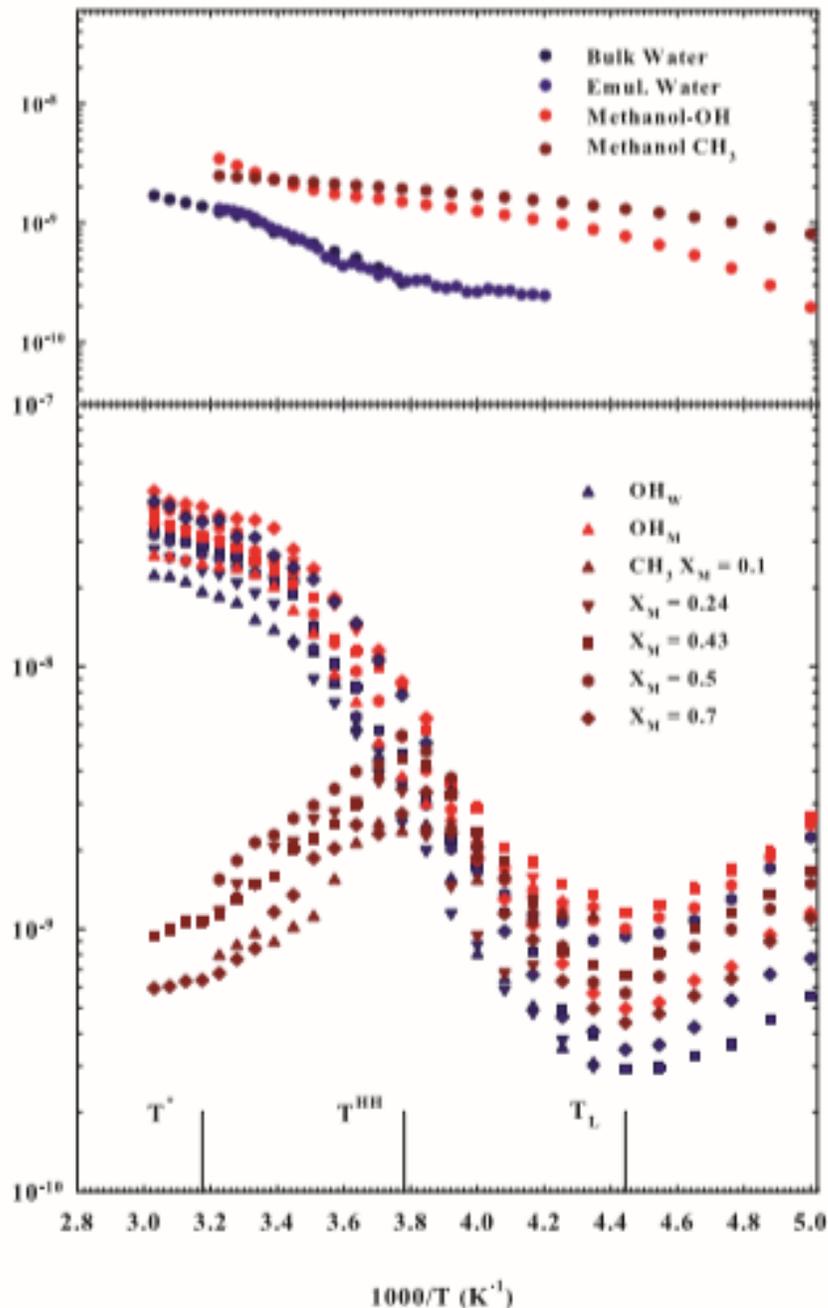
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This figure shows the τ_c trend as a function of temperature for pure liquids (top) and for the different concentrations (bottom).

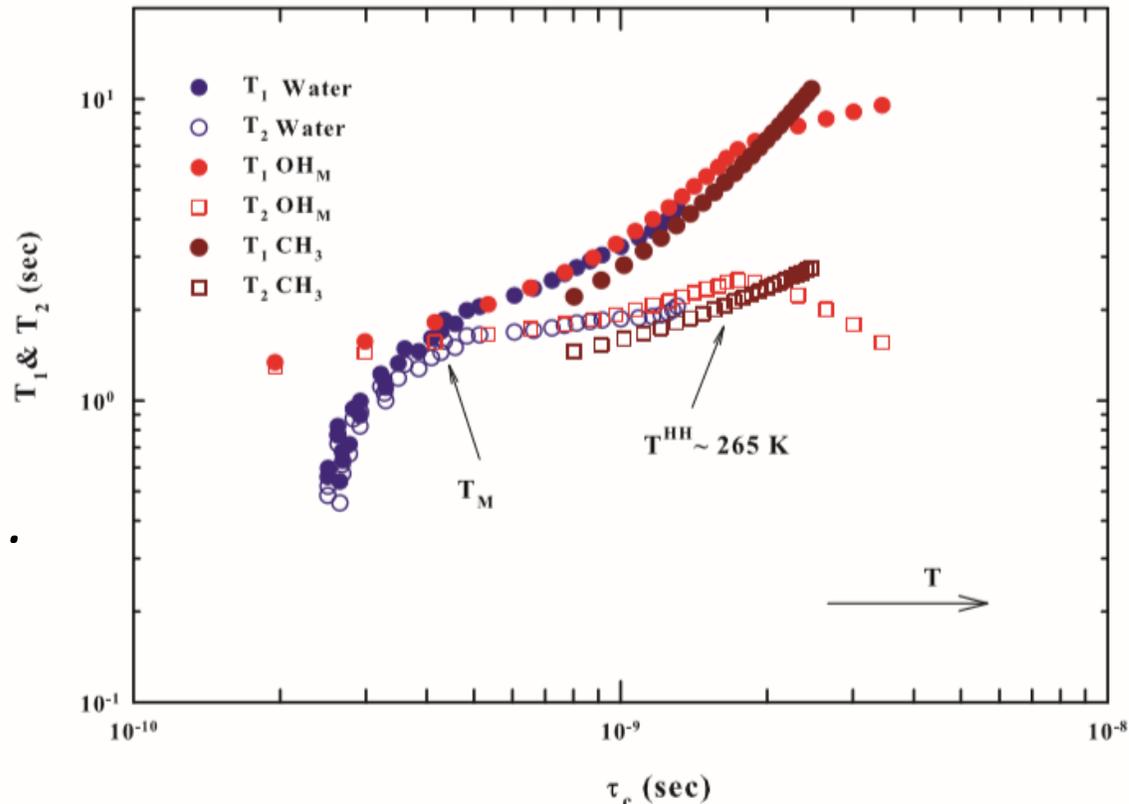
The temperatures above mentioned and associated to the competition between the different intermolecular correlations that occur within the system (hydrophilic between the OH groups and hydrophobic between the CH₃ groups) are here more evident. Note that the τ_c behaviour depends only on the temperature, whereas its amplitude is also a function of concentration.

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T_1 and T_2 Vs τ_c : pure liquids



The analysis of T_1 and T_2 as a function of the same τ_c is shown in the figure where one can note that the melting temperature T_M of water is a crossover temperature. Below it $T_2 \approx T_1$ whereas above it T_1 evolves with a marked increase and T_2 remains almost constant.

In detail, at around T^{HH} (265K) the methanol OH shows a maximum in the spin-spin relaxation time T_2 and a variation in the growth rate of the longitudinal T_1 whose values cross those of the T_1 of the methyl group.

This confirms the competition between the hydrophobic and hydrophilic effect in determining the local order of the pure alcohol.

This occurs at a relatively high T for liquid methanol and the lower lifetime of HBs causes the predominance of hydrophobicity.

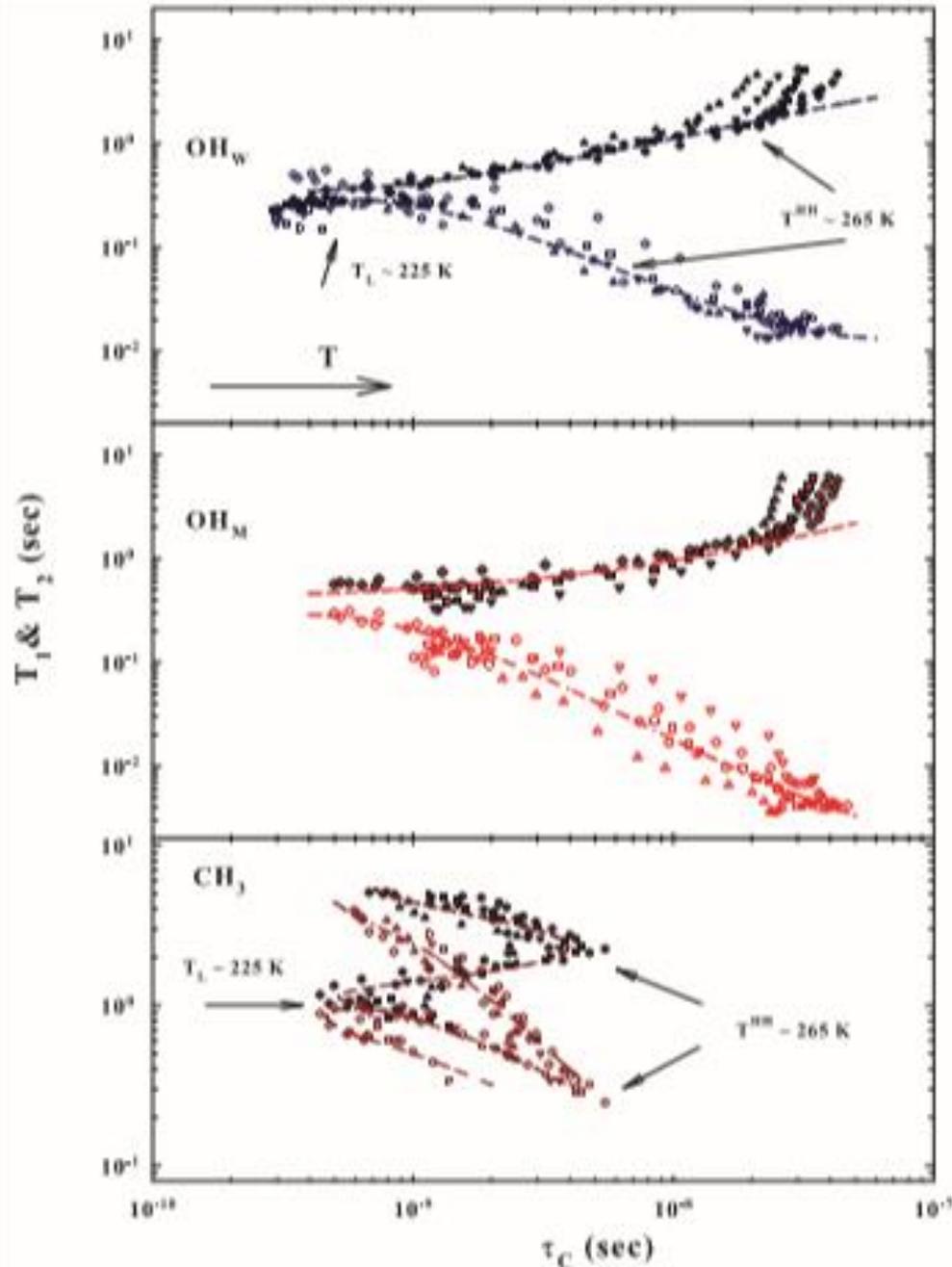
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T_1 and T_2 Vs τ_C : solutions

$$T_L \sim 225K$$

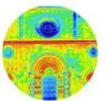
$$T^{HH} \sim 265K$$



Finally the same analysis for the different concentrations shows how the relaxation times of the methanol methyl group (lower panel) show a cuspid behavior both at T^{HH} and at T_L . This indicates their importance, especially in systems with simultaneous hydrophilic and hydrophobic interactions.

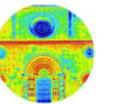
Concerning the two hydroxyl groups, these show an analogous trend in which it is evident a variation of behavior in T_1 at the corresponding T^{HH} which corresponds to an inflection point in the values of T_2 .

At low temperatures, on the other hand, the data relating to the water hydroxyl (OH_W) better reproduce the hyperbolic behavior predicted by the BPP theory compared to the hydroxyl of methanol (OH_M).



Conclusions

- ***Our results indicate that when HB interactions that facilitate clustering in water solutions compete with interactions with opposite behaviors, e.g., hydrophobicity, the effects of these latter interactions become relevant for temperatures where the water tetrahedral network is no longer stable.***
- ***We show how the temperature-concentration evolutions of T_1 and T_2 as far as the measured τ can be used to explain how the HB interactions, that create the characteristic water tetrahedral transient network, affect the methanol methyl, and how methanol influences the water structure.***
- ***The analysis in terms of τ_c , which encompasses all local structural configurations, allowed the analysis of the dynamical behavior of the properties at the considered conditions, pointing out the temperatures able to describe the competition between hydrophobicity and hydrophilicity.***
- ***This competition between is one of the most challenging research subjects of modern statistical physics.***
- ***In the overall our data show that the temperature increase progressively reduces the lifetime of the hydrogen bond interactions with the consequent decoupling in the dynamic modes of the system. Specifically, at temperatures above about 265 K, hydrophobicity becomes progressively stronger and governs the physical properties of the solutions.***





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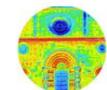
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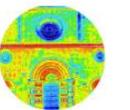
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- **All the authors are grateful to Profs. Ben Widom (Cornell) and Sidney Yip (MIT) for proposing the important theme of hydrophobicity and for all the suggestions.**
- **We thank the staff of SIF (Società Italiana di Fisica) and the organizers of the 105th Congress of Physics and all of you.**

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