SCA SHORT COURSE, SYMPOSIUM 2018

WETTABILITY FROM NMR AND DIELECTRIC DISPERSION

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CONTENT

- Wettability for NMR
  - Based on wetted surfaces
  - Based on residence time
  - Examples
- Wettability from dielectric dispersion
  - Background and Principle
  - Examples

NMR BACKGROUND

$$\frac{1}{T_2} = \frac{1}{T_{2Bulk}} + \frac{1}{T_{2Surface}} + \frac{1}{T_{2Diffusion}}$$

$$\frac{\eta}{T} \qquad \frac{V}{S} \qquad (TE\ Grad)^2 D$$

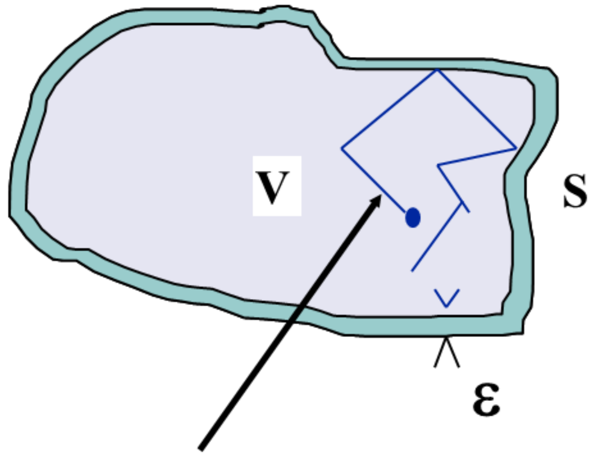
Viscosity

Pore size - Saturation
Permeability

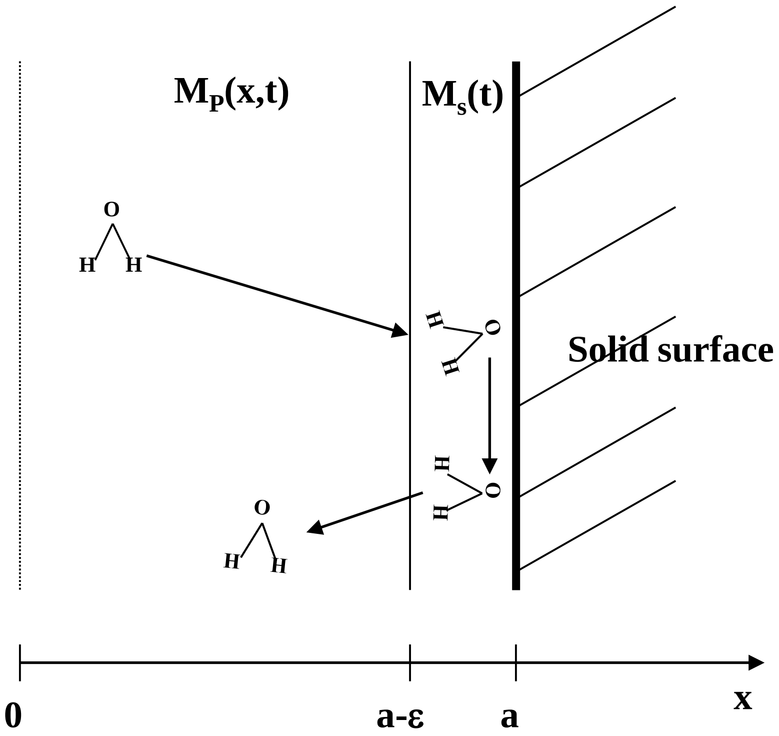
Increase contrast
D-T_2 logging

NMR BACKGROUND: SURFACE AND VOLUME DIFFUSION (SINGLE PHASE)

Saturated pore



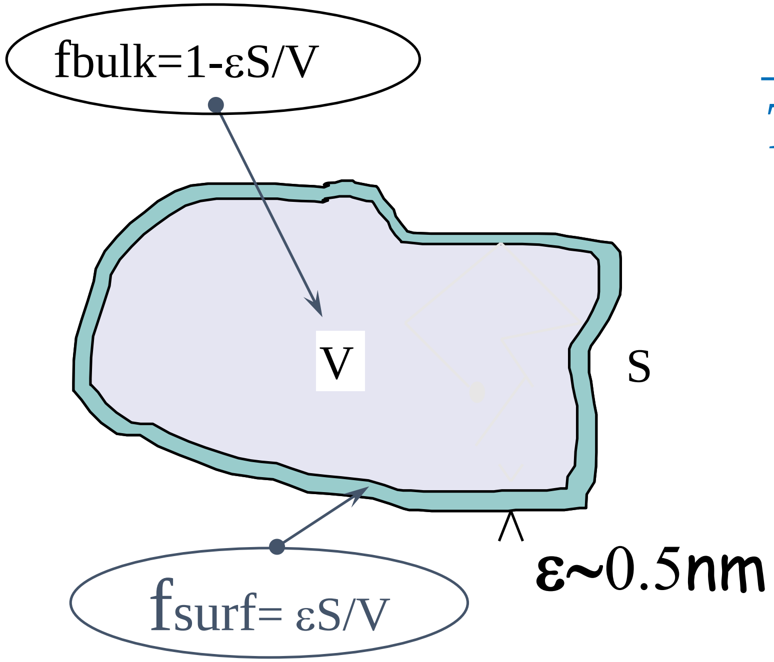
Spin carrying molecule diffusing and "colliding" the surface (*volume diffusion*)



Spin carrying molecule temporarily linked to the surface (*surface diffusion*)

NMR BACKGROUND: S/V MODEL (FAST DIFFUSION LIMIT)

not dependant on shape



$$\frac{1}{T_2} = \frac{f_{surf}}{T_{2surf}} + \frac{f_{bulk}}{T_{2bulk}} = \frac{1}{T_{2bulk}} + \frac{\varepsilon}{T_{2surf}} \frac{S}{V}$$

ρ_2: surface relaxivity

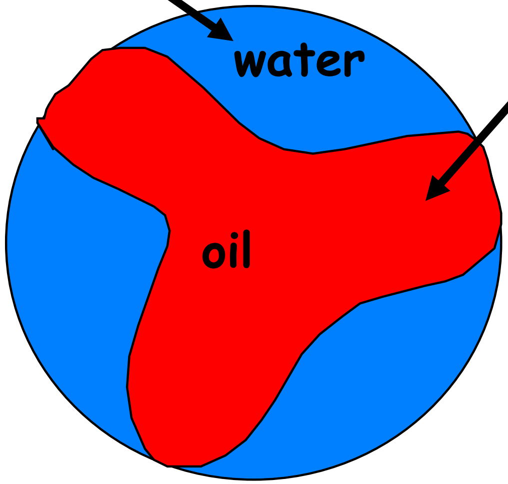
$$\frac{1}{T_2} - \frac{1}{T_{2B}} = \rho_2 \frac{S}{V}$$

WETTABILITY, STEP 1: BIPHASIC S/V MODEL

S w/o surface wetted by water/oil
V w/o volume of water/oil

$$\frac{1}{T_{2w}} = \frac{1}{T_{2Bw}} + \rho_{2w}\frac{S_w}{V_w}$$

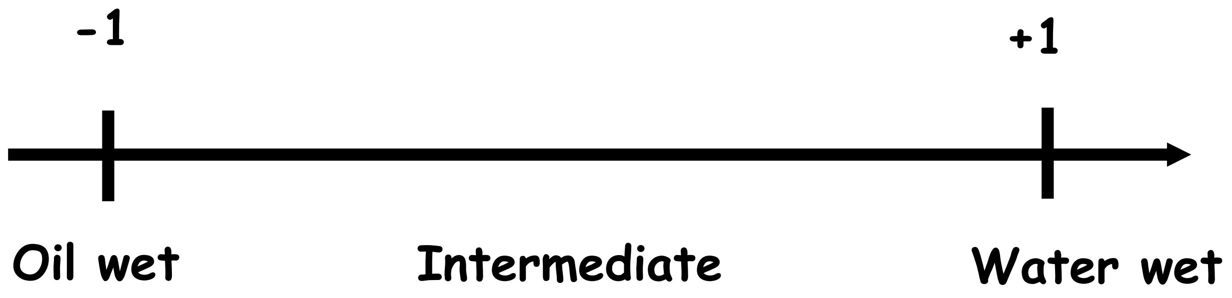
$$\frac{1}{T_{2o}} = \frac{1}{T_{2Bo}} + \rho_{2o}\frac{S_o}{V_o}$$



Interfacial relaxivity is negligible

WETTABILITY, STEP 2: NMR INDEX

$$I_{NMR} = \frac{Surface\ \ wetted\ \ by\ \ water - surface\ \ wetted\ \ by\ \ oil}{Total\ \ surface} = \frac{S_w - S_o}{S_w + S_o}$$

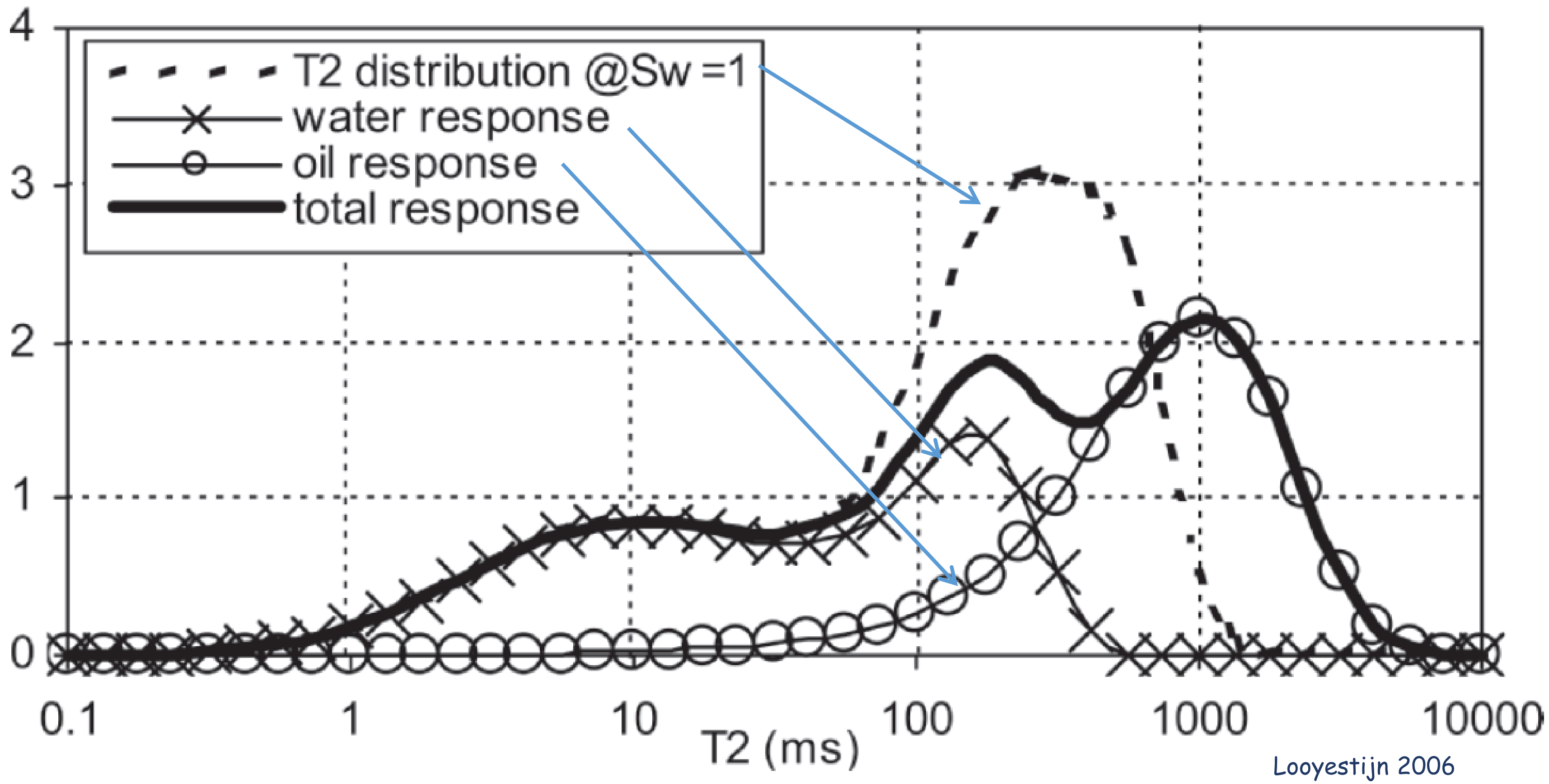


FROM THE PRINCIPLE TO THE APPLICATION

- Distribution of relaxation times due to
  - pore sizes
  - oil components for crude oils
- Need to distinguish water and oil contributions in T_2 distribution
- Need the ratio of surface relaxivity of water and oil
- At which saturation should the surfaces be measured ?

→ various ways of measurements, protocols or modeling

EXAMPLE OF THE NMR T_2 RESPONSE TO WETTABILITY (MODEL)



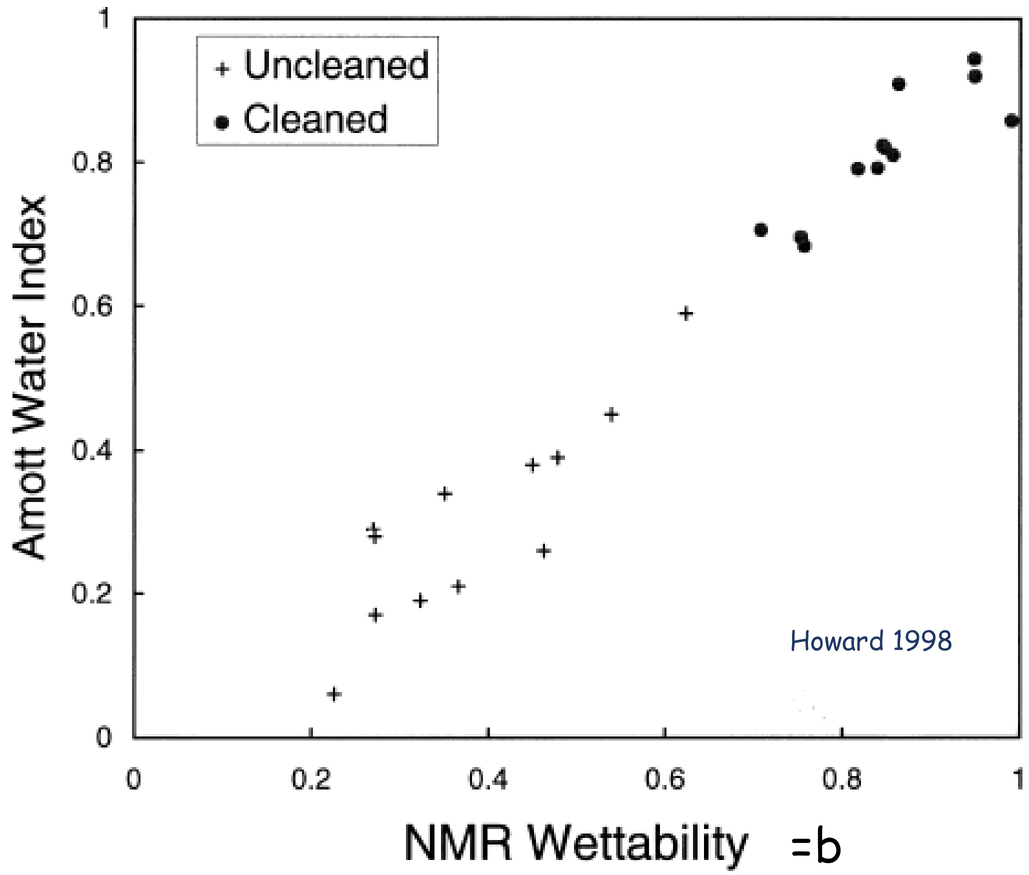
Looyestijn 2006

Fig. 3—S_w=0.5, I_w=0.0 (neutral, or intermediate-wet).

A FEW WAYS OF CALCULATING I_{NMR}

- Brown and Fatt, 1956: effect of wettability on NMR relaxation
- Howard (1998): detect water shift only and calibrate it
- Fleury and Deflandre (2003): consider 4 saturation states obtained by centrifuge
- Al-Mahrooqi et al. (2006): consider 2 saturation states + modeling
- Looyestijn and Hofman (2006): perform inverse modeling from distribution data obtained at one saturation after aging (+ include 100% water and oil distributions)

- Other approaches more recently, but using the same principles

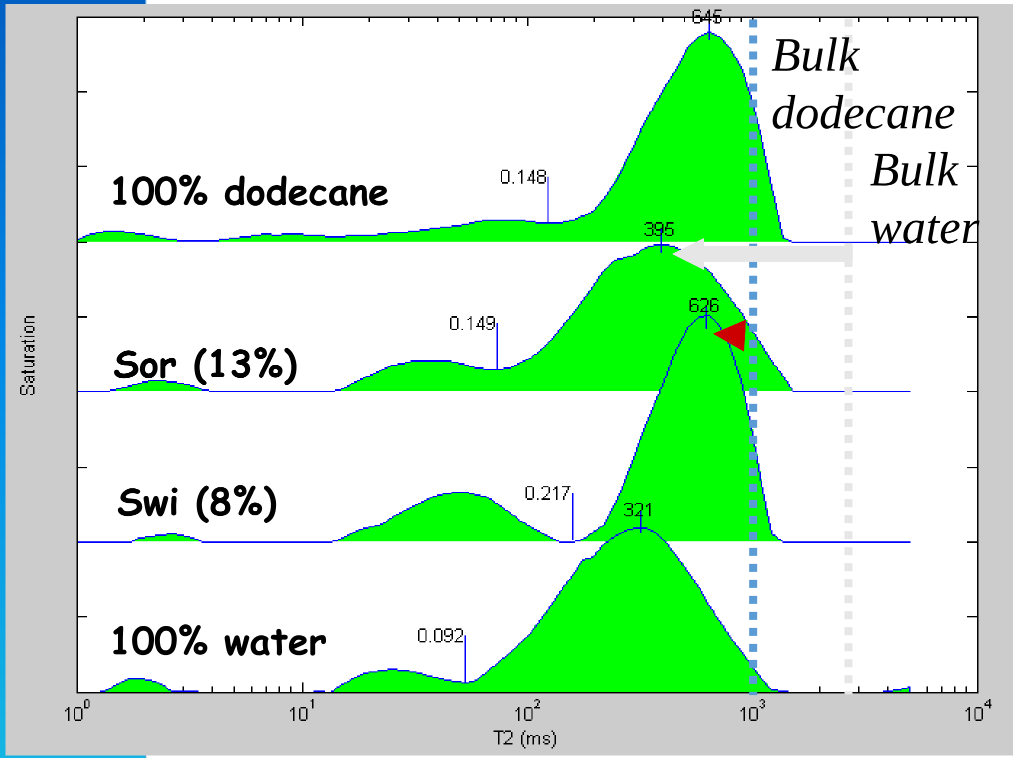


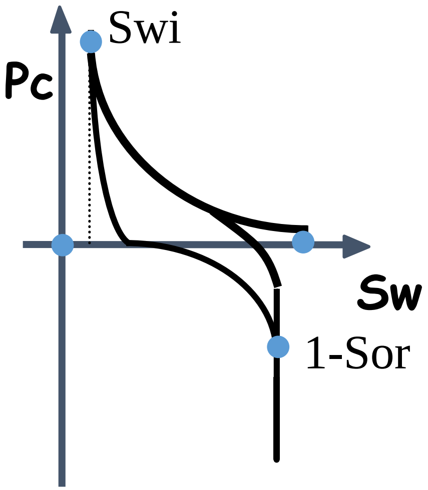
=b

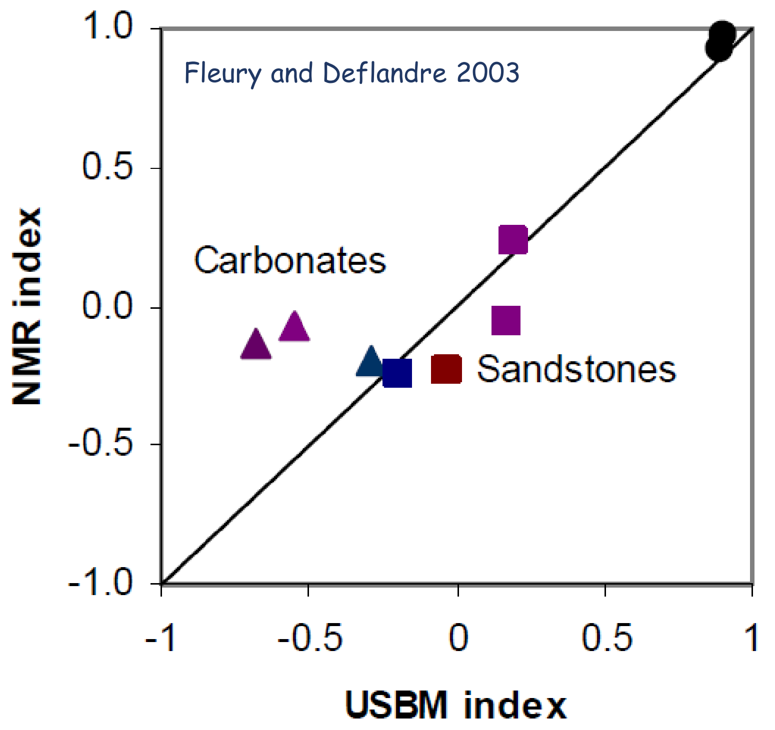
$$\frac{T_2(Sw)}{T_2(Sw=1)} = CSw^b$$

C and b must be tuned

Imbibition end points used for Amott and NMR







At Swi: mode of dist. is representative of the oil in the presence of a small amount of water

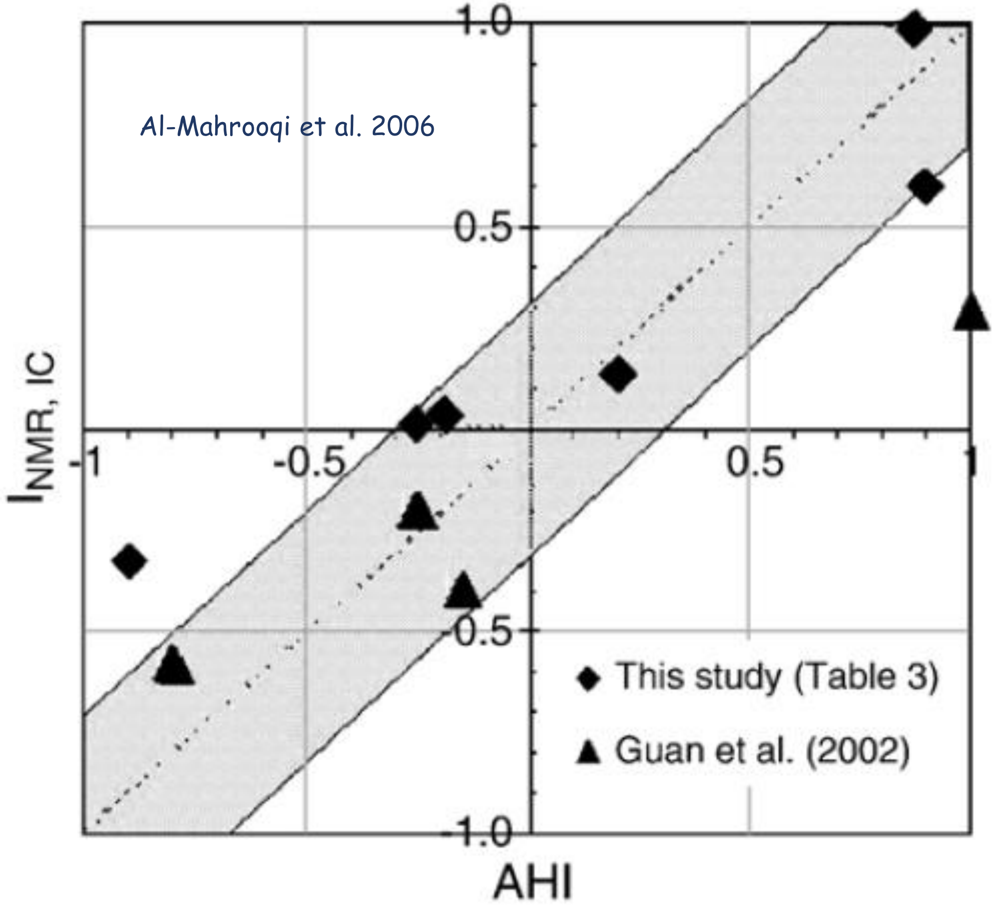
At Sor: mode of dist. is representative of the water in the presence of a small amount of oil

→ no need to distinguish water and oil contribution

→ a refined oil is recommended

$$I_{RMN} = \frac{Sw\left(\frac{1}{T_w} - \frac{1}{T_{bw}}\right) - C\rho So\left(\frac{1}{T_o} - \frac{1}{T_{bo}}\right)}{Sw\left(\frac{1}{T_w} - \frac{1}{T_{bw}}\right) + C\rho So\left(\frac{1}{T_o} - \frac{1}{T_{bo}}\right)}$$

$$C_\rho = \frac{\rho_w}{\rho_o} = \frac{1/T_{w100} - 1/T_{Bw}}{1/T_{o100} - 1/T_{Bo}}$$



$$I_{\mathrm{IC}}^{\mathrm{NMR}} = \left(\frac{T_{2m}^{S_{\mathrm{wi}}} - T_{2m}^{S_{\mathrm{or}}}}{T_{2m}^{S_{\mathrm{or}}}} \right)$$

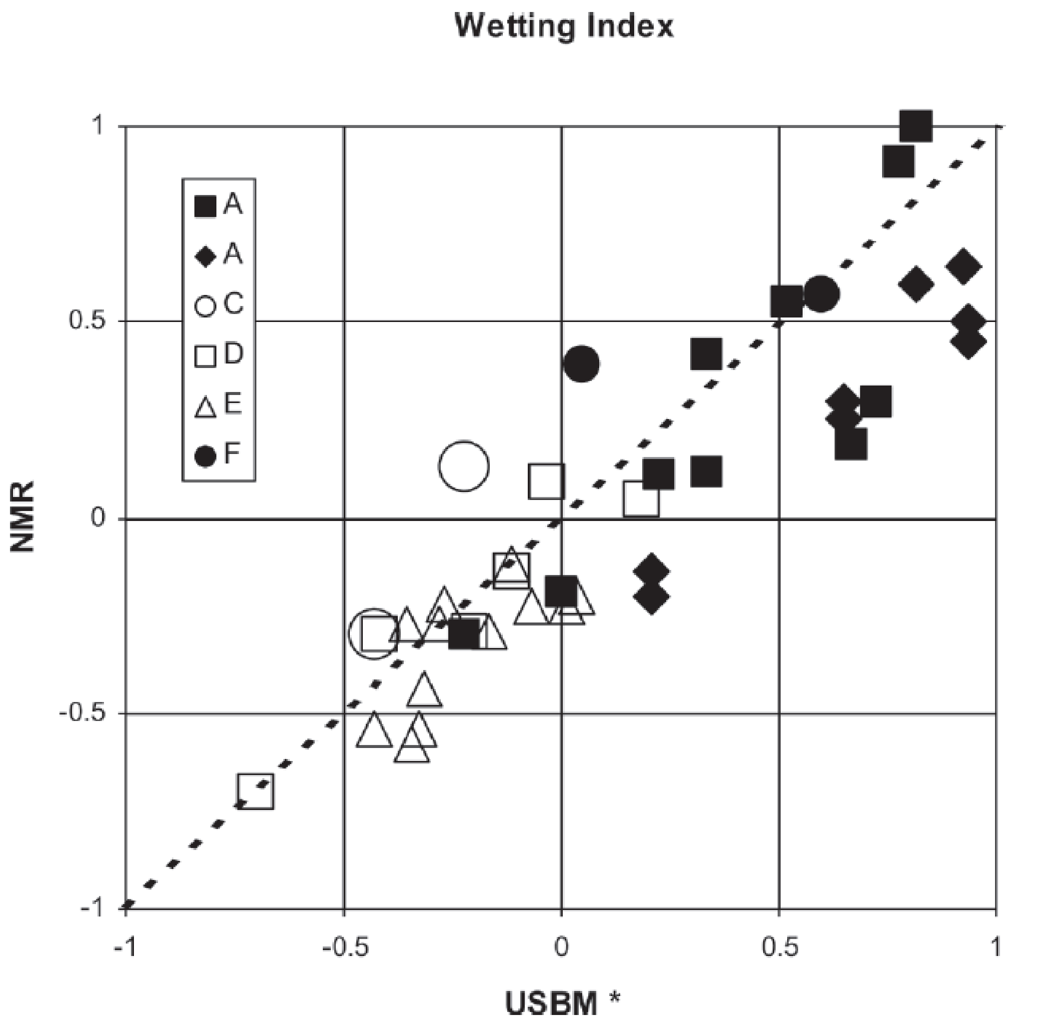


Fig. 15—Comparison of wetting index obtained by inversion of NMR and by standard core analysis, both defined on a [–1,1] scale for six different fields.

Need to define 3 distributions and associated parameters at a given saturation:

- for the distribution of water in water wetted pores
- for the distribution of oil in oil wetted pores
- for the bulk (crude) oil

Invert the parameters of the distribution to fit the distribution at a given saturation and obtain the wetted surfaces (and I_{NMR})

SUMMARY: WETTABILITY FROM T_2 DISTRIBUTION (WETTED SURFACE)

- Various ways of calculating wettability indexes based on the same principle
- Reasonably good relationship with standard methods (USBM – Amott)
- Attempts to minimize the number of experimental steps

"Ready to use"

NMR BACKGROUND: T_1 , T_2 AND CORRELATION TIME τ_C IN LIQUIDS

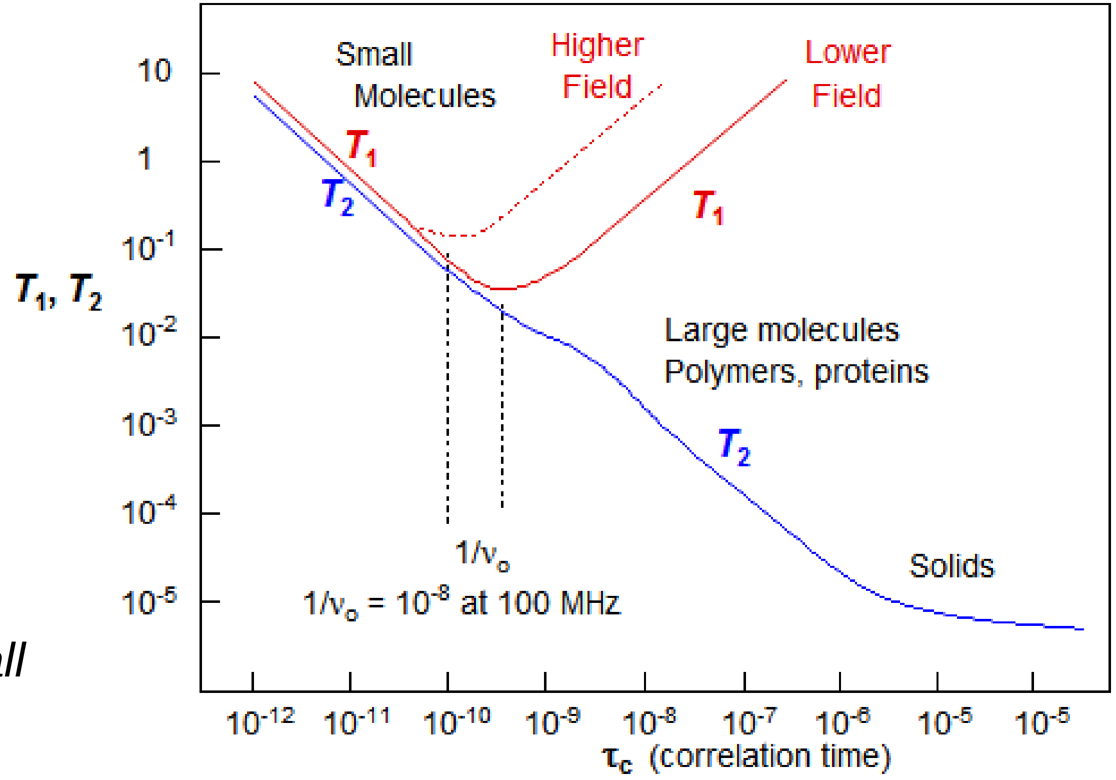
Correlation time of dipolar interactions: characteristic time for molecular re-orientation
Molecular motions strongly affect T1 and T2

$$\frac{1}{T_{1rot}} = C\left(\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{4\tau_c}{1+4\omega_0^2\tau_c^2}\right)$$

$$\frac{1}{T_{2rot}} = C\left(\frac{3}{2}\tau_c + \frac{5}{2}\frac{\tau_c}{1+\omega_0^2\tau_c^2} + \frac{\tau_c}{1+4\omega_0^2\tau_c^2}\right)$$

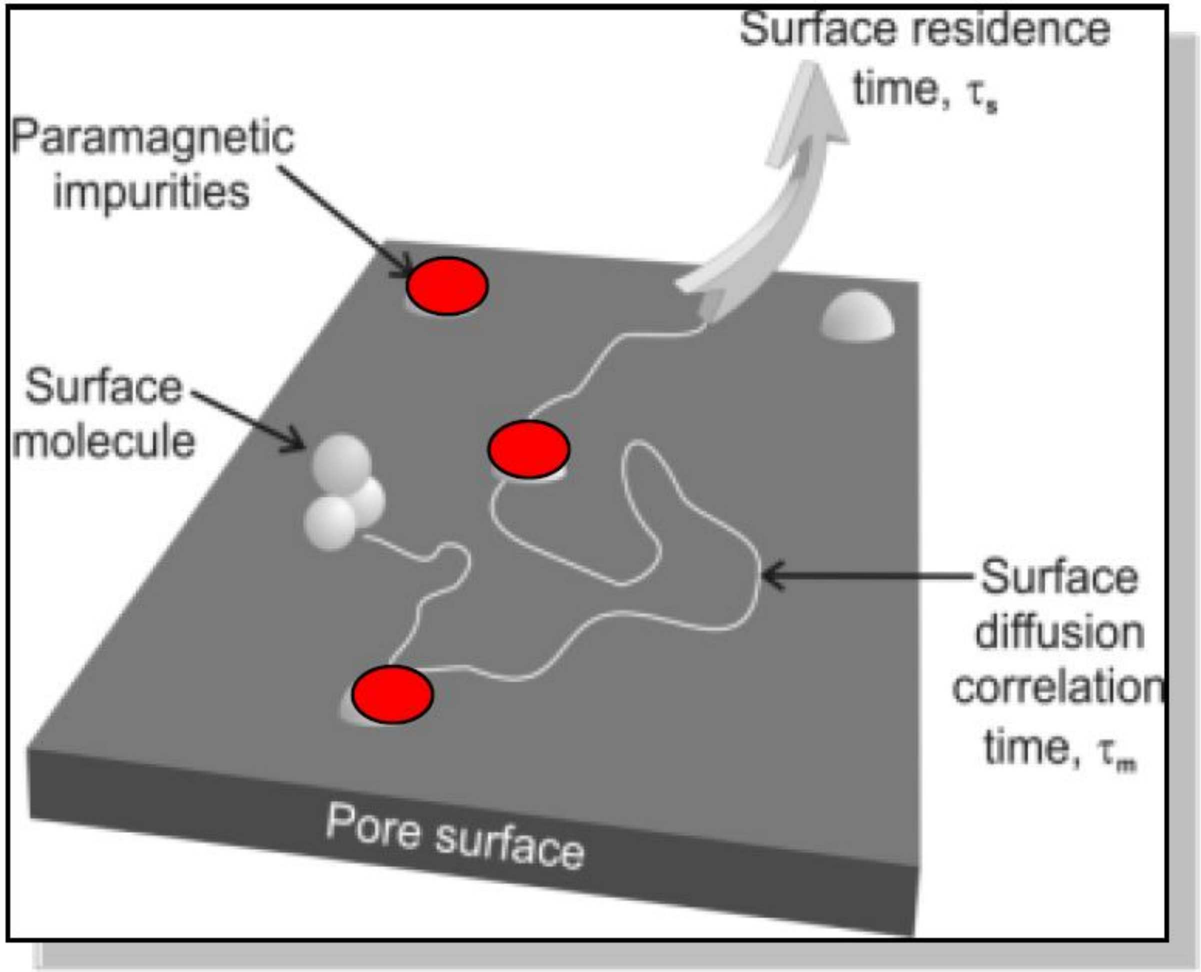
$$\text{with} \quad C = (N-1)\frac{3}{10}\left(\frac{\mu_0}{4\pi}\right)^2 \frac{\hbar\gamma^4}{r^6}$$

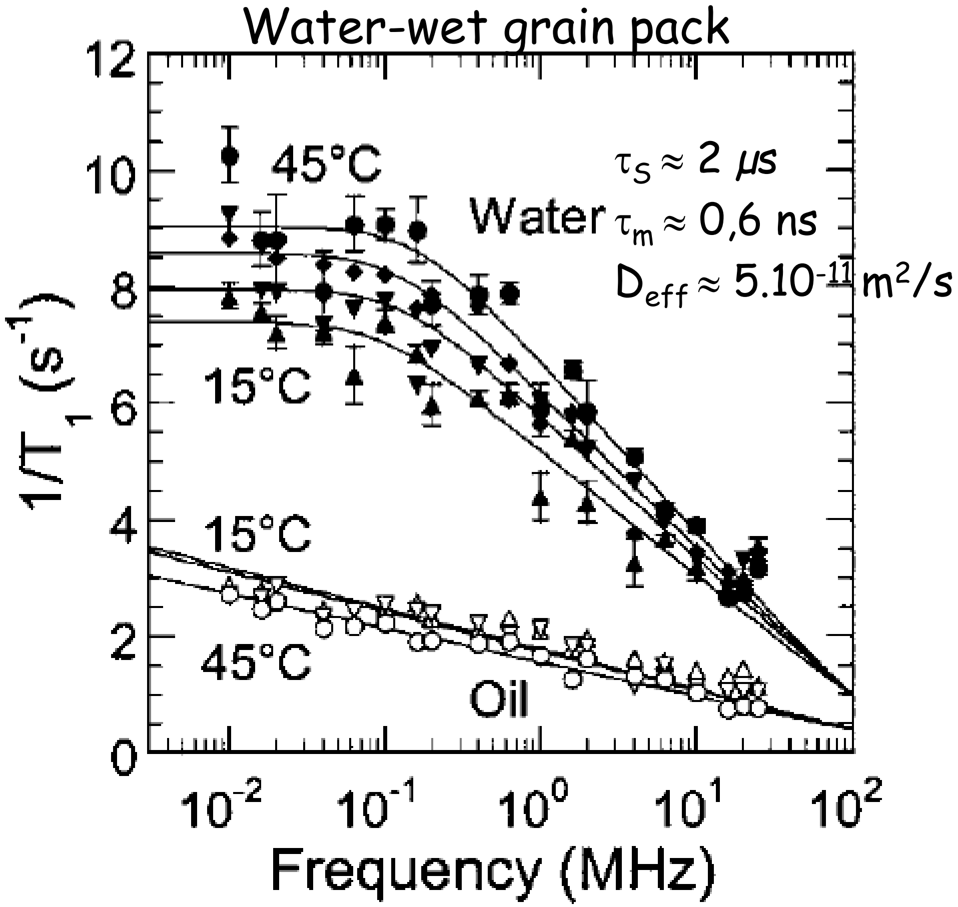
Theory originally designed for small idealized molecules applicable to larger ones due to short range interactions



E.M. Purcell, R. V. P. Relaxation Effects in Nuclear Magnetic Resonance Absorption. *Phys. Rev.* 679–746 (1948).

NMR BACKGROUND: T_1 DISPERSION IN POROUS MEDIA





Godefroy et al. . *PRE 2001*

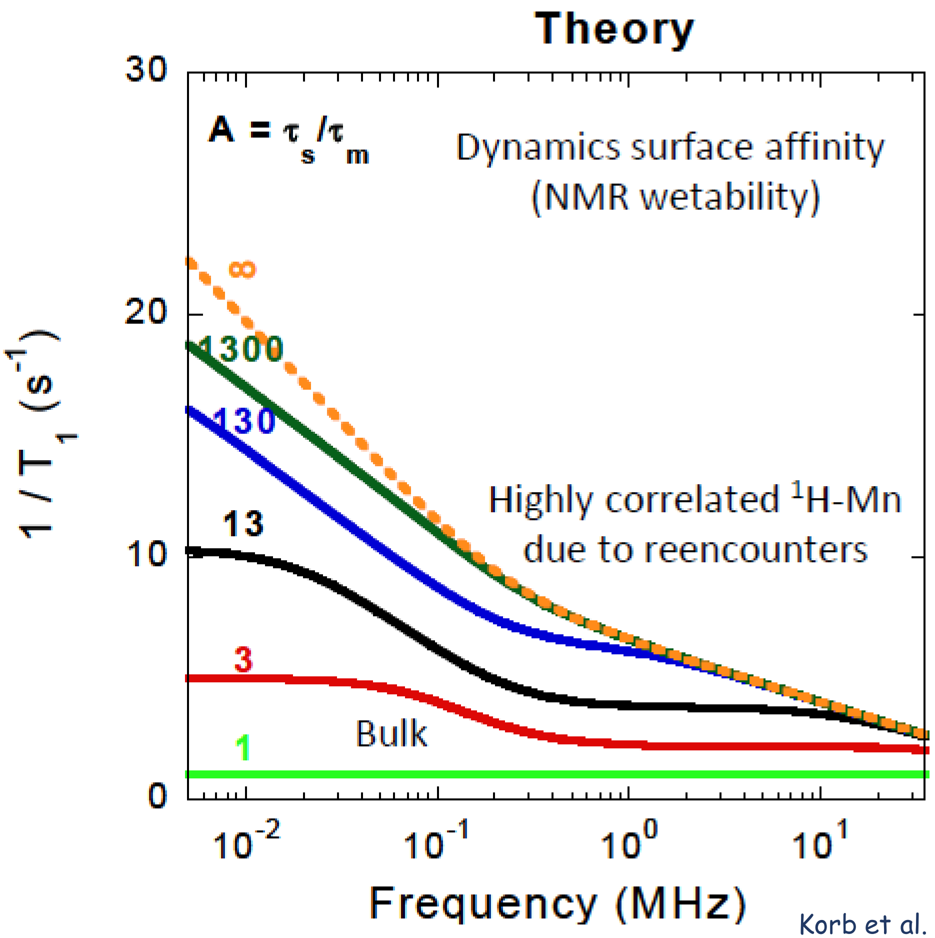
NMR WETTABILITY BASED ON RESIDENCE TIME

$$A = \frac{\tau_S}{\tau_m}$$

Correspond to the number of diffusing steps on the solid surface

Depends on temperature

Also valid in the absence of paramagnetic impurities (e.g. catalyst support, D'agostino et al. 2014)



Korb et al. 2009

FROM THE PRINCIPLE TO THE APPLICATION

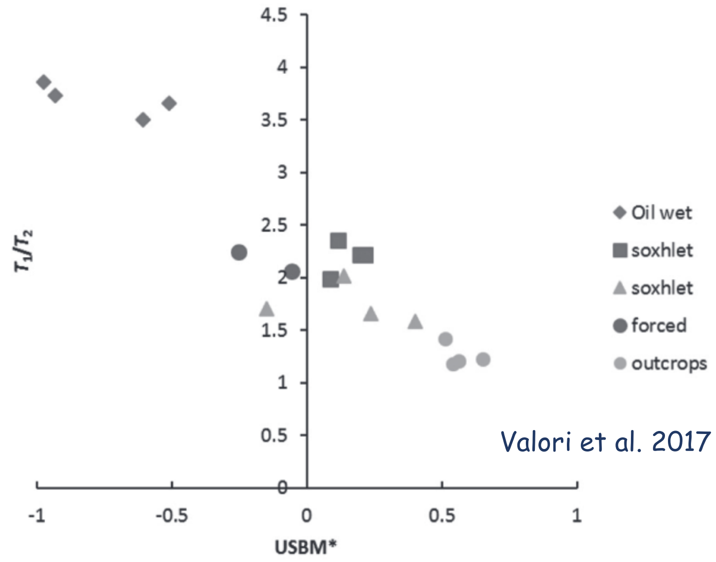
- Measure dispersion curves $T_1(\omega_0)$
  - Need a field cycling instrument
  - Need to separate water and oil contributions
  - Scaling theoretically between 1 and ∞

- Measure T_1/T_2 ratio

$$\frac{T_1}{T_2} \propto -\frac{\ln(\tau_m/\tau_S)}{\ln(\omega_0\tau_m)}$$

$$providing\ (\tau_m/\tau_S)^2 \ll (\omega_0\tau_m)^2 \ll 1$$

Using oil average T_1/T_2



Valori et al. 2017

SUMMARY: WETTABILITY FROM RESIDENCE TIME

- Affinity parameter linked to the time of residence of a molecule at the solid surface
- Need to separate oil and water contributions
- T_1/T_2 as a proxy seems the most promising solution, especially for logging application

WETTABILITY FROM DIELECTRICS - GENERAL

Current density Electric field

$$J = (\sigma + i\omega\varepsilon_0\varepsilon)E$$

Conductivity Permittivity

Wettability influences the electrical properties of rocks at both low and high frequencies.

kHz MHz GHz

Low frequencies (< 100 kHz) wettability mainly controls the dc electrical conductivity of rock.

Governing factor : tortuosity - continuity of the water phase.

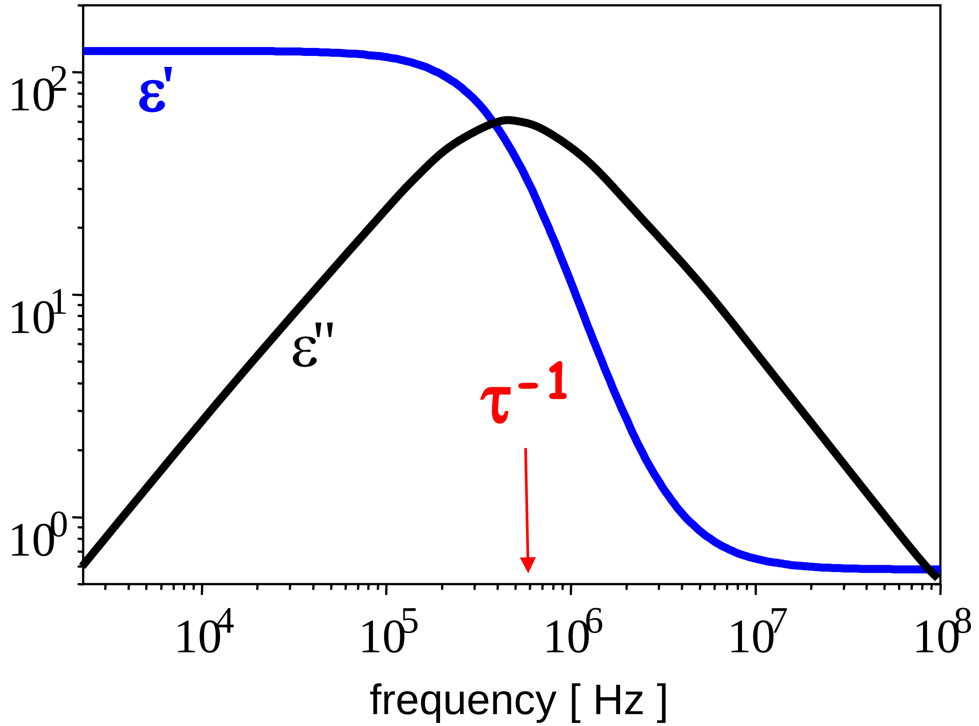
High frequencies (> 1 MHz) wettability mainly controls the dielectric permittivity ε

Governing factor: shape of the water phase rather than continuity

DIELECTRIC PERMITTIVITY

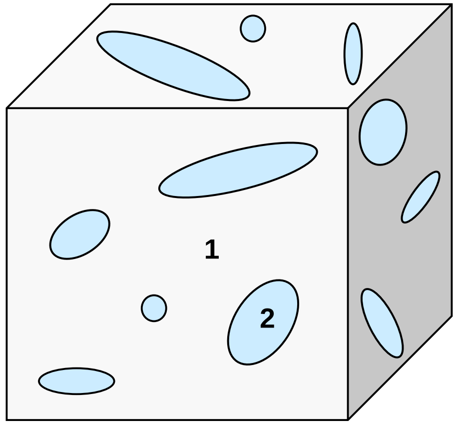
- ε is a complex function of frequency and consists of a real part ε' and an imaginary part ε".
- The real part decreases monotonically with increasing frequency. The imaginary part exhibits peaks at characteristic frequencies.
- The reciprocal of the frequency at which a peak in ε" is observed is called dielectric relaxation time τ.

- ε" peaks when the oscillations of the applied electric field become too fast for the charges to be able to follow them. Charges tend to accumulate at interfaces



PRINCIPLE OF DIELECTRIC WETTABILITY TEST

- Rocks at Swi conditions are modeled as a distribution of water inclusions imbedded in an insulating medium. Each inclusion has a shape factor μ.
- μ is an increasing function of the surface-to-volume ratio of the inclusion. A linear relation between μ and the relaxation time of the inclusion exists (Lysne, 1983).
- A distribution of water shapes results in a distribution of relaxation times. Water-wet rocks have higher μ's and longer τ's than oil wet rocks.



1 INSULATING PHASE (MATRIX + OIL)
2 WATER

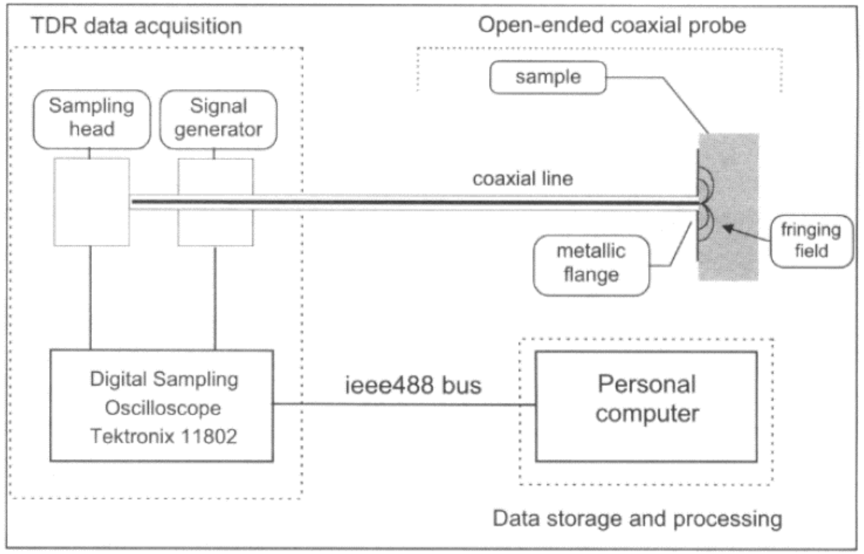
$$\tau(\mu) = \varepsilon_0 \frac{\varepsilon_m(\mu - 1) + \varepsilon_w}{\sigma_w}$$

WETTABILITY FROM DIELECTRICS - METHOD

- $\varepsilon(\omega)$ is measured under cleaned conditions and re-measured after aging the sample. Water saturation must be close to Swi in both measurements. Time domain reflectometry is commonly used to measure $\varepsilon(\omega)$ in the MHz-GHz range.

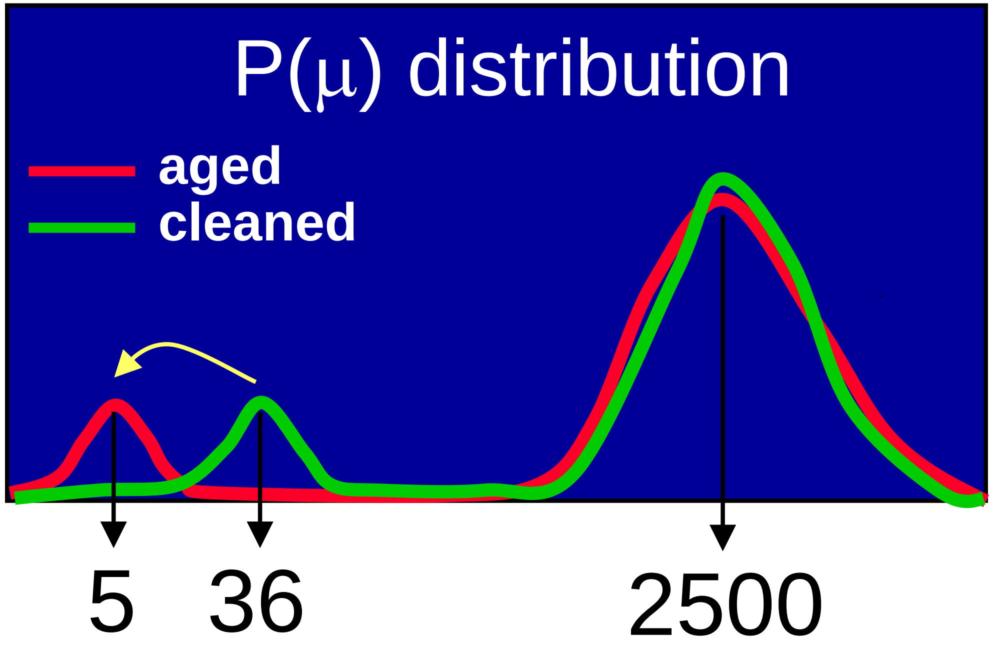
- The dielectric permittivity $\varepsilon(\omega)$ is expressed in terms of the μ-distribution P(μ).

- $\varepsilon(\omega)$ is inverted to find the P(μ) distribution. Then the two distributions are compared. If they are similar, the rock is considered to be water-wet. If they are different, there is an indication of a non water-wet condition.



$$\varepsilon(\omega) = \int_1^{\infty} \frac{P(\mu)d\mu}{1 + i\omega\tau(\mu)}$$

EXAMPLE 1 – MIXED-WET SAMPLE

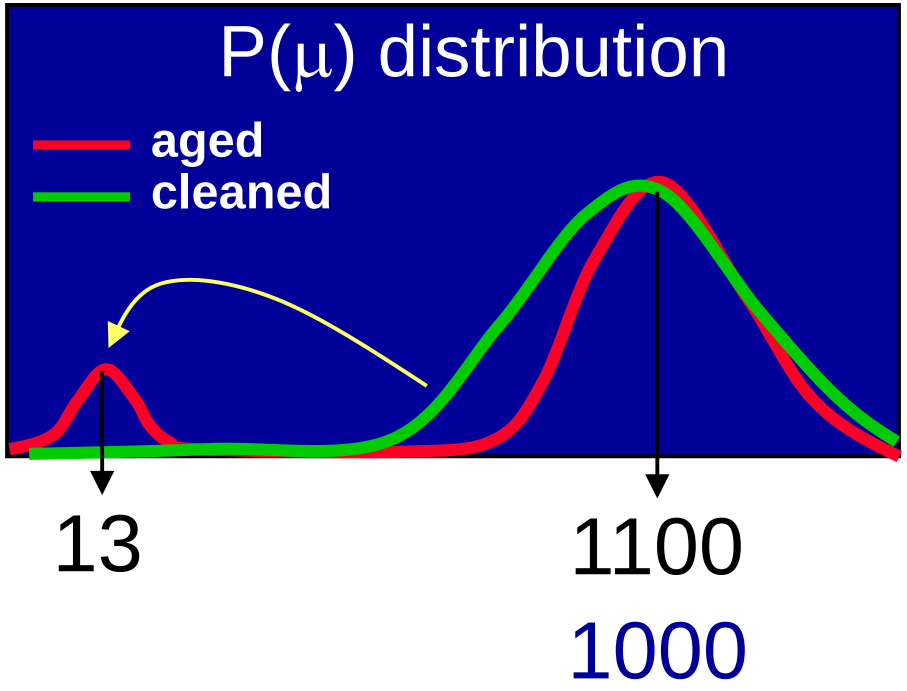


Low S/V
(large pores)

High S/V inclusions
(micropososity)

- The ageing of the sample reduced the S/V ratios of the water contained in the larger pores. The S/V ratios of water in microporosity did not change
- Conclusion: the larger pores became oil-wet, the micro-pores stayed water-wet

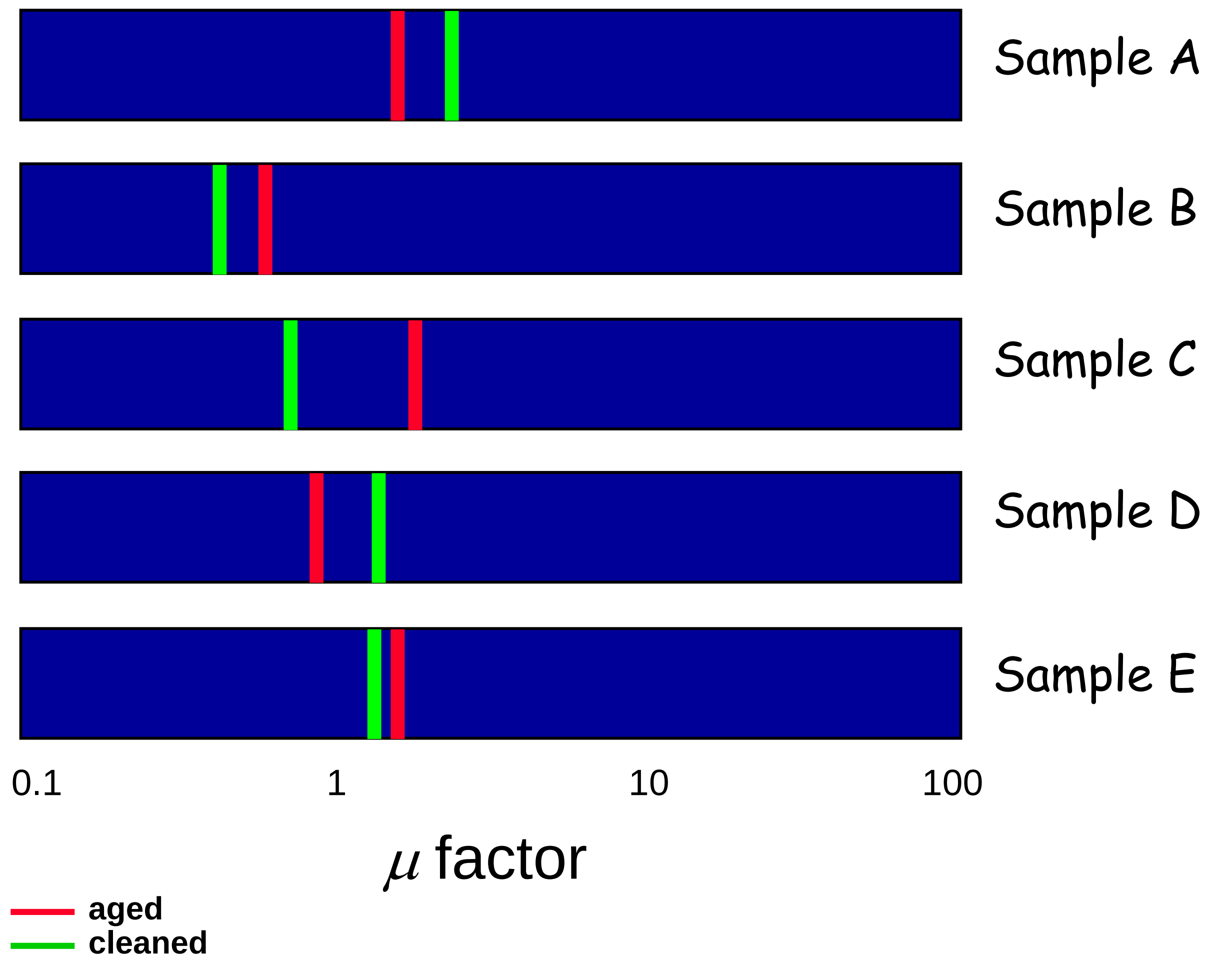
EXAMPLE 2 – MIXED-WET SAMPLE



- Under cleaned conditions (green curve), this sample exhibits a monomodal water shape distribution.
- The ageing of the sample generated a low S/V peak (red). This indicates that part of the pores became oil-wet.

EXAMPLE 3 – WATER-WET SAMPLES

- All these samples exhibited monomodal water shape distributions. Instead of showing the μ-distributions, we only present their peak values (green and red bars)
- The ageing did not significantly modify the μ factors and so the samples were all classified as water-wet.



SUMMARY: WETTABILITY FROM DIELECTRIC

- Compare spectra measured at one saturation (Swi) before and after ageing
- Detect the change of water inclusions
- No index available
- Recent development in relation to the new dielectric logging tools