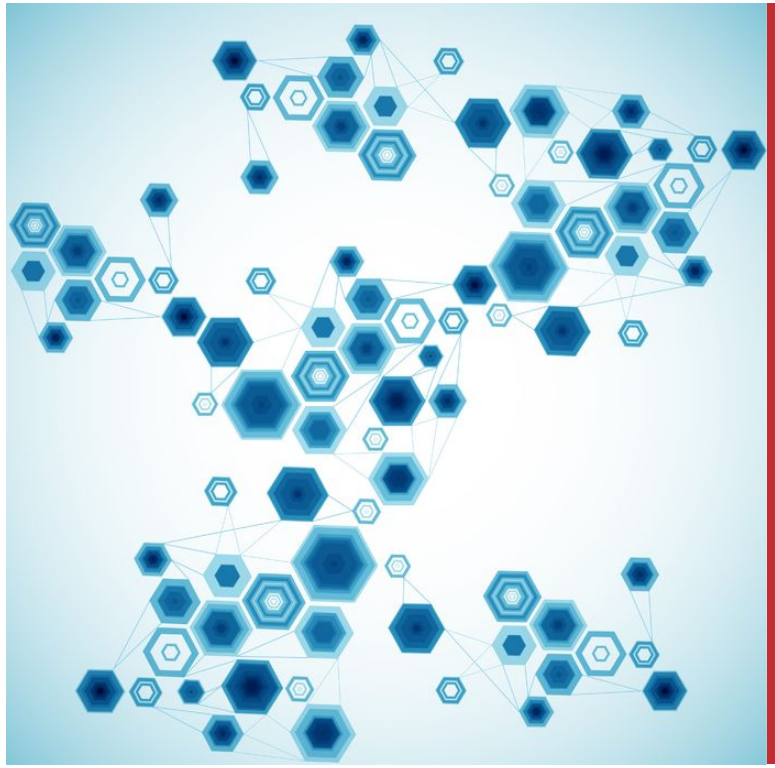

New ways to characterize 'hard' and 'soft' surface properties by IGC-ID

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Adscientis

Smart Inverse Chromatography

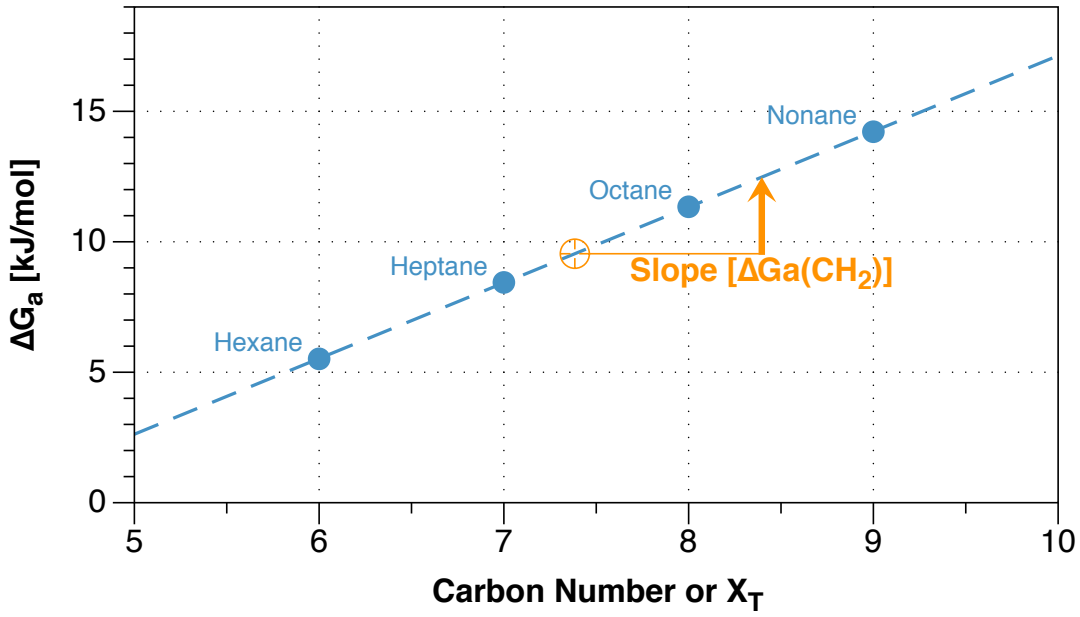
Content

- IGC at Infinite Dilution
  - Principle and Assumptions
- Real surfaces and accessibility
  - Morphology index (IM) and applications
- Real surfaces with ”Soft” material
  - Molecular mobility
  - Relative morphology index (RIM)
- Application of RIM to “Soft” and “Hard” surfaces
- Conclusions

IGC at Infinite Dilution

- Most used IGC technique
  - Mainly for the determination of the surface energy (γ_s^d)

- γ_s^d determination method:
  - Injection of an homologous set of alkanes probes (3 or more)
  - Plot ΔG_a versus Carbon Number



$$Measurement\ of\ t_N$$

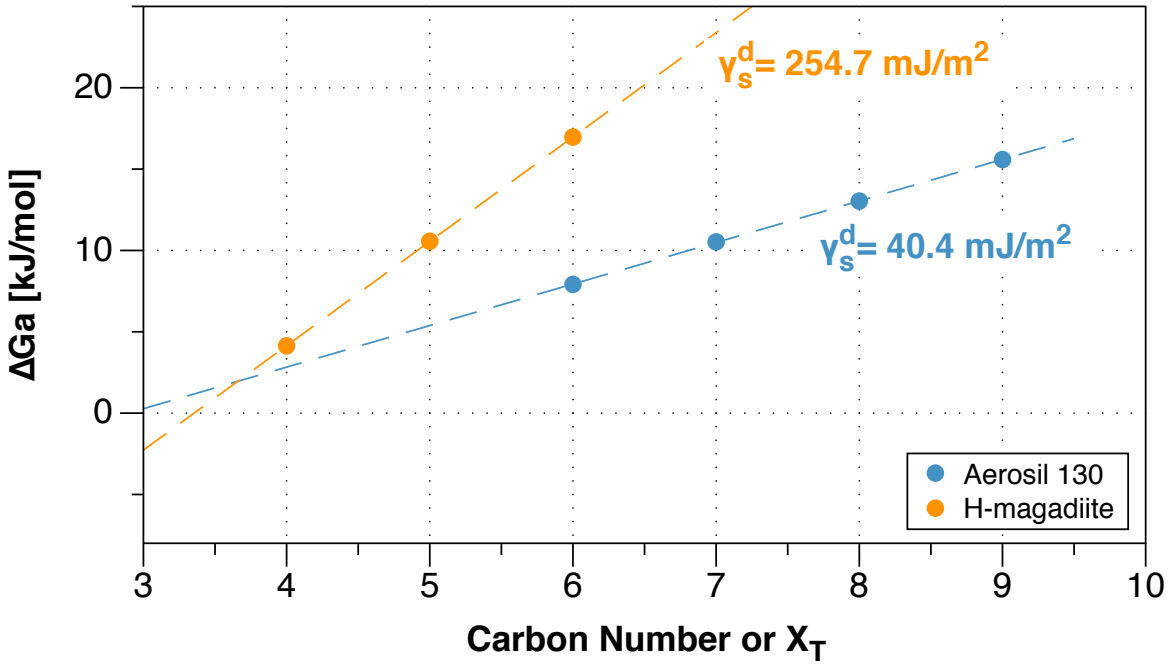
$$V_g = \frac{Flow_{corr}}{m_s}\frac{273.15}{T}.t_N$$

$$\Delta G_a = RT.Ln(V_g)$$

$$\gamma_s^d = \frac{1}{\gamma_{CH_2}}\left(\frac{\Delta G_a(CH_2)}{2N.a_{CH_2}}\right)^2$$

IGC-ID on silica

- Comparison of two silica
  - Pyrogenic Silica (Aerosil 130)
  - Crystalline and layered Silica (H-magadiite)
  - Same chemical composition, but different structures
- Measurements at 110°C
  - Huge difference in terms of γ_s^d values!



Why such differences?
What does it mean?

$$\gamma_s^d = \frac{1}{\gamma_{CH_2}} \left(\frac{\Delta G_a(CH_2)}{2N.a_{CH_2}} \right)^2$$

IGC-ID assumptions

- Dorris and Gray
  - Probes visit all the surface
  - Low probe amounts are injected to avoids the probe-probe interactions
  - Probes adsorb flat on the surface
  - Only adsorption occurs, i.e. 2D interactions (no absorption, i.e. 3D interactions)
  - The surface is homogeneous
    - **Topologically (flat)**
    - **Chemically**

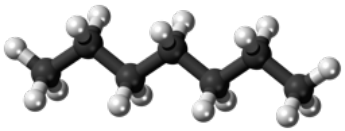
Also valid for contact angle measurements

- Real surfaces are seldom flat and homogeneous!

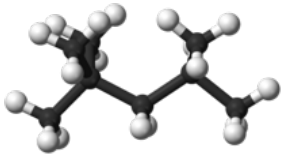
How assess if the surface is flat?

Real surfaces and accessibility

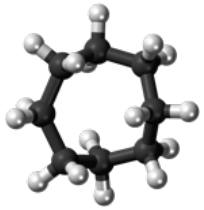
n-octane

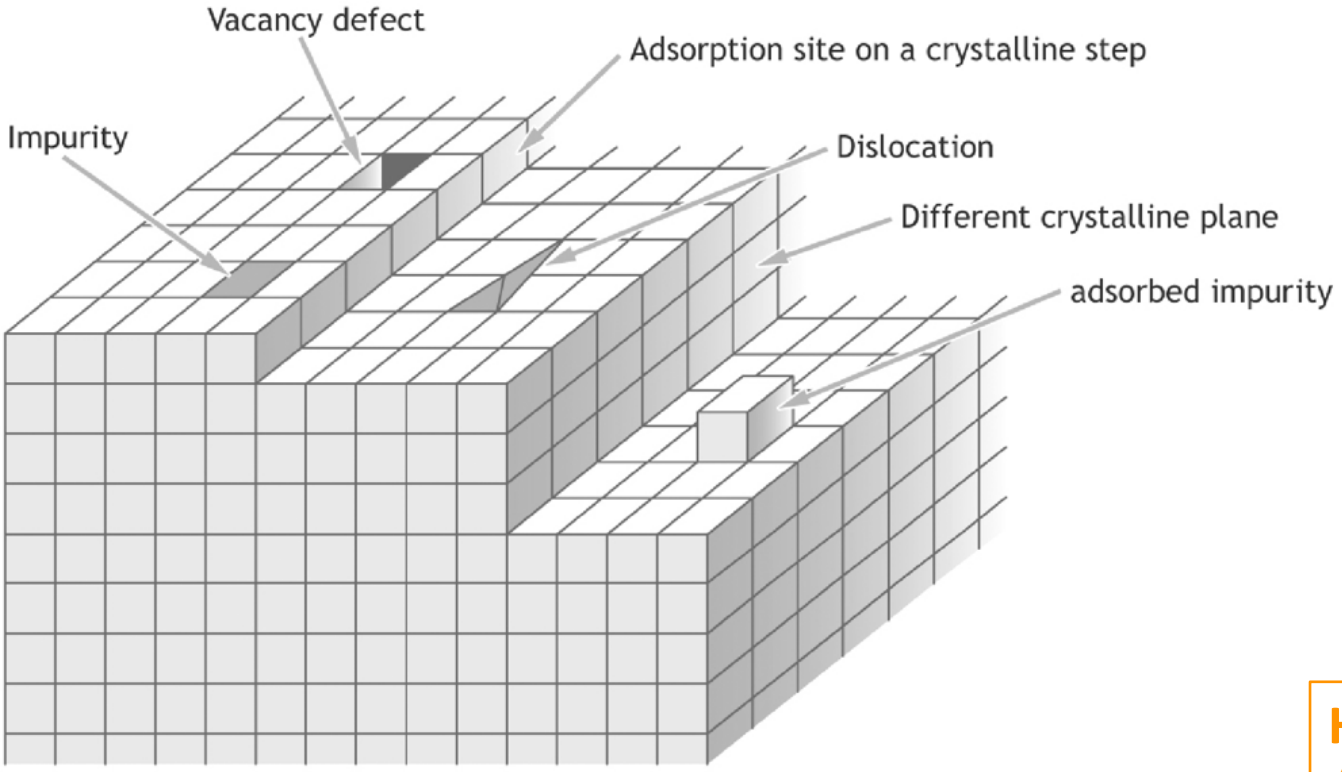


isooctane



cyclooctane





Depending on the molecular structure, the accessibility to the surface, i.e. the interaction energy, will no be identical

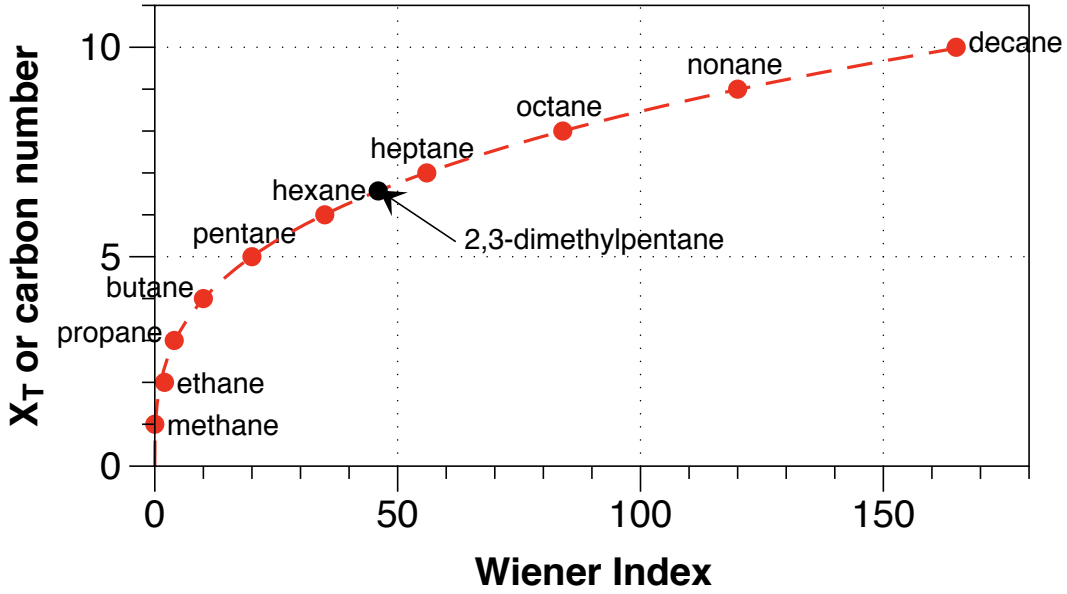
Comparing the behaviour of linear, branched and cyclic alkanes is able to deliver information about the surface nanoroughness

How to describe the molecules?
(i.e. taking into account their structure)

χ_T: Molecular descriptor

It is the oldest topological index related to molecular branching (1947)

- *W* is representative of the van der Waals volume of the molecule
  - Therefore representative of their dispersive interaction ability
  - *W* takes into account the structure of the molecules
- χ_T based on the Wiener Index (*W*) [X_T=f(*W*)]
- f(*W*) was developed so that χ_T = Nc (carbon number) for n-alkanes



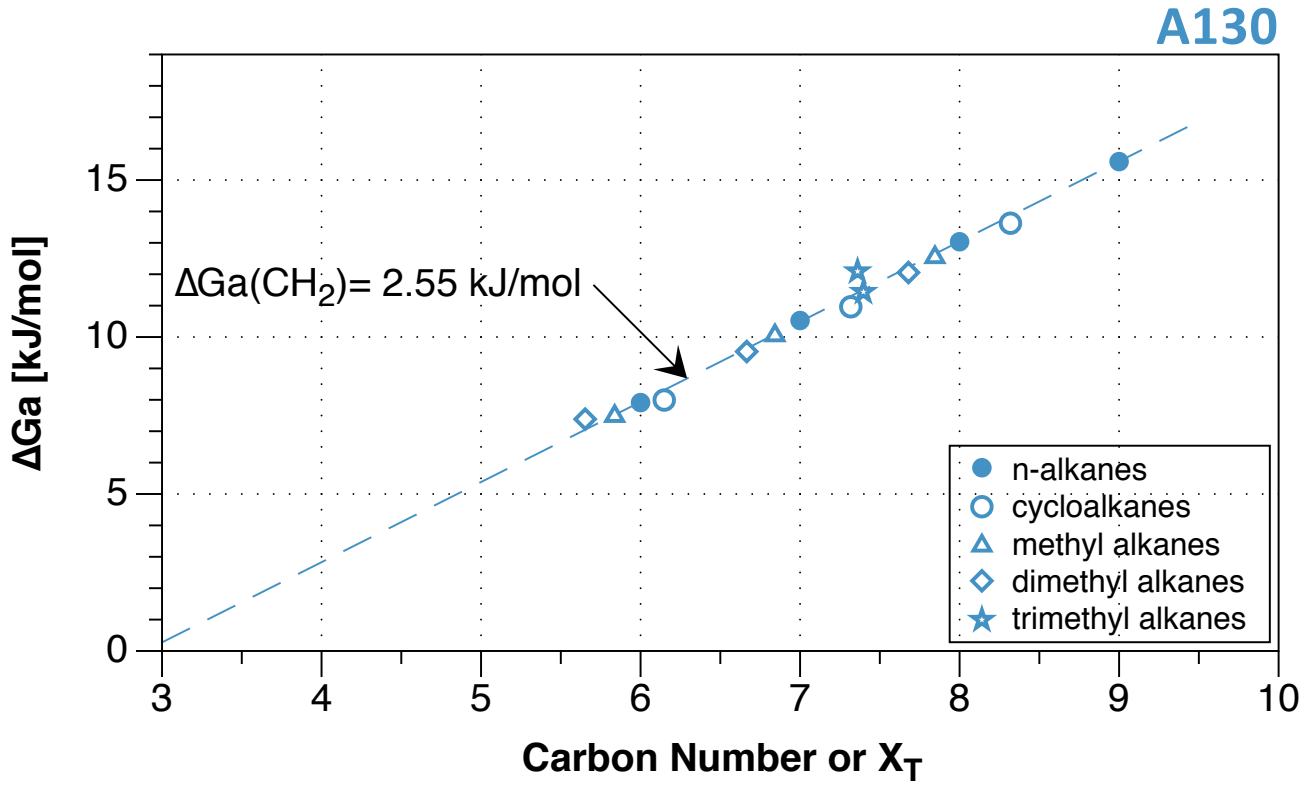
For 2,3-dimethylpentane *W*=46

$$\chi_T = 1{,}879 . W^{0{,}327} = 6{,}57$$

On Aerosil 130

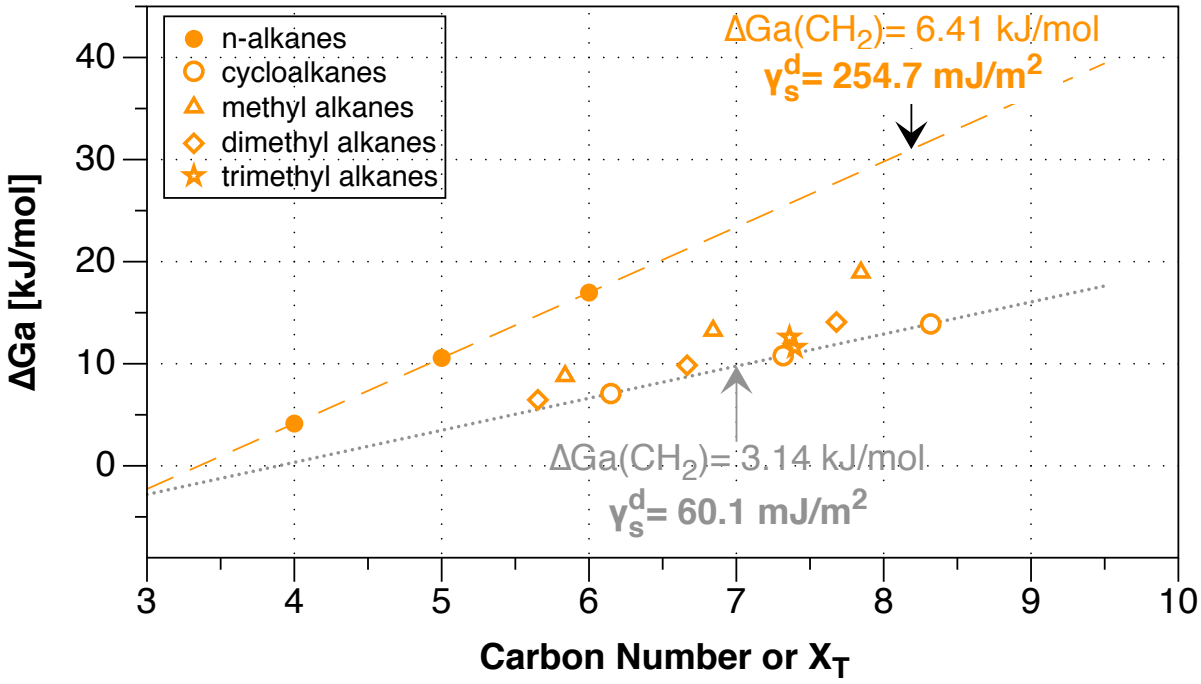
- Branched and cyclic probes are on the n-alkanes straight line
  - All the probes have the same accessibility to the surface

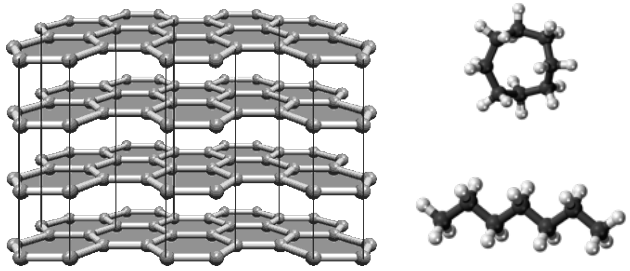
Aerosil 130 is flat at the molecular level



On H-magadiite

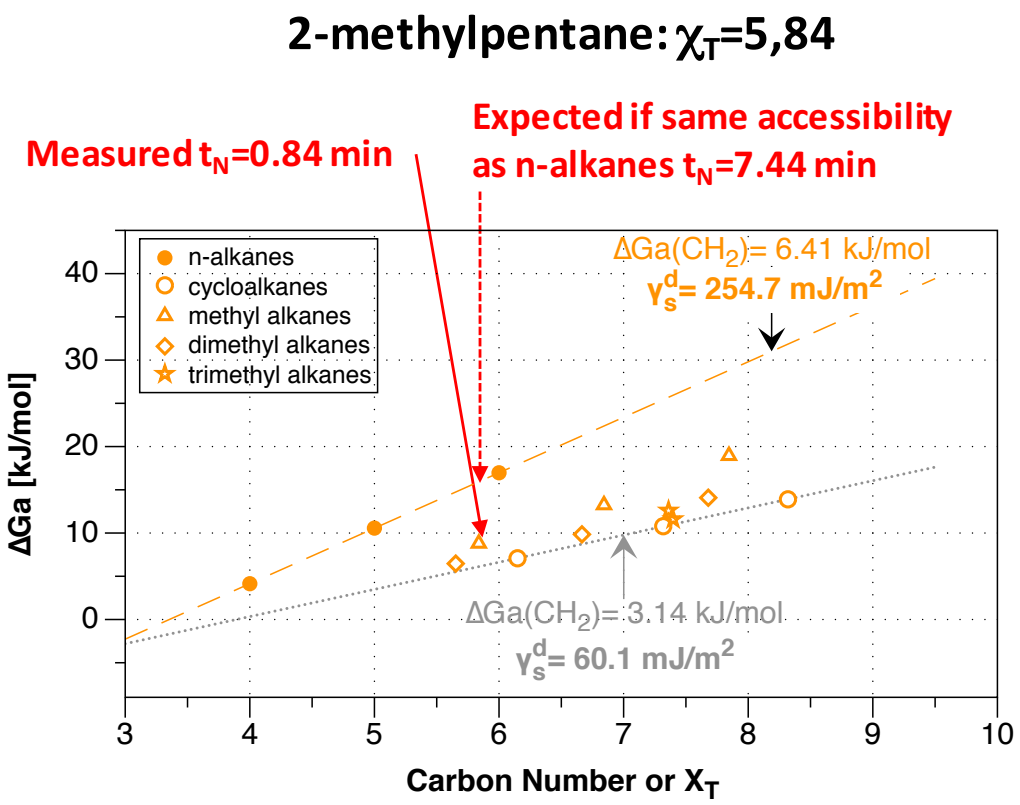
- Branched and cyclic probes are significantly below on the n-alkanes straight line
  - All the probes have not the same accessibility to the surface
  - Strong size exclusion effects exist
    - The most excluded are the cyclic probes
    - The less excluded are the 2-methylalkanes





How to characterize the size exclusion effects?

IM: Morphology Index



$$IM = \frac{t_N(measured)}{t_N(estimated)}$$

Assuming the same behaviour than n-alkanes

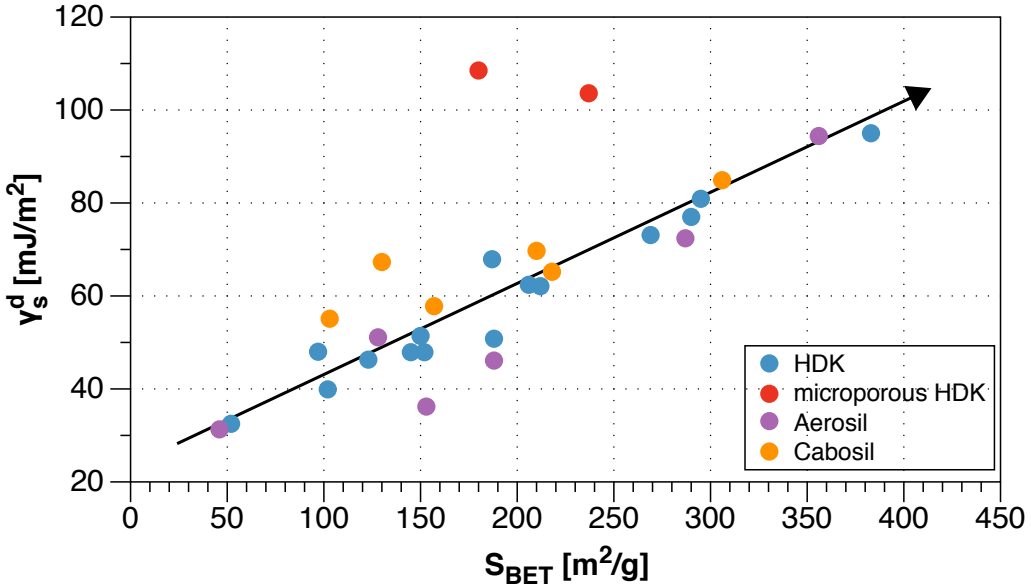
For 2-methylpentane: IM=0.11 (i.e. 11% of the expected t_N)

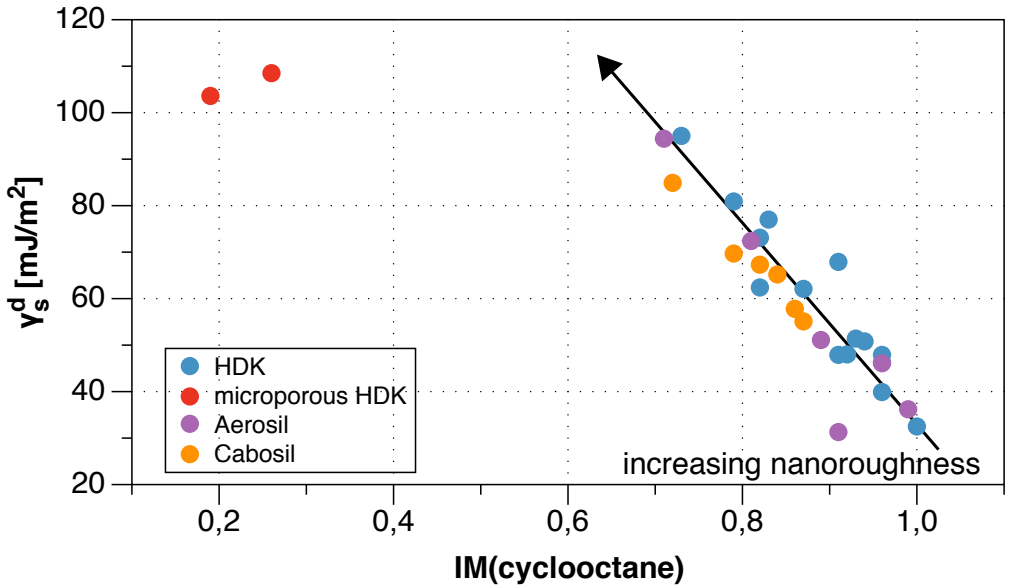
For flat surfaces IM≈1

- IM(2-MeC$_n$) > IM(2,2-diMeC$_n$) > IM(triMeC$_n$) > IM(cycloalkanes)

Pyrogenic Silica (amorphous)

- Comparison of samples issued from several manufacturers
- $50 < S_{BET} < 400\ m^2/g$
- Clear tendencies
  - γ_s^d values increase with S_{BET}
  - γ_s^d values related to the nanoroughness (IM(cyclooctane))
  - Microporosity strongly influences the measured γ_s^d value





Partial conclusions for hard and clean surfaces

- A lot of surface structures provide adsorption sites where the n-alkanes interact with several surfaces at the same time
  - Lead to stronger interactions

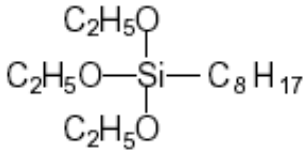
- The γ_s^d values are greatly influenced by the surface topology (nanoroughness)
  - Nanoroughness includes: porosity, microporosity, defects, specific structures …
- The use of branched and cyclic alkanes are efficient to describe the surface nanoroughness
- IM(cyclooctane) ≤ IM(isooctane) ≤ 1

What happens if the surface is organically modified?

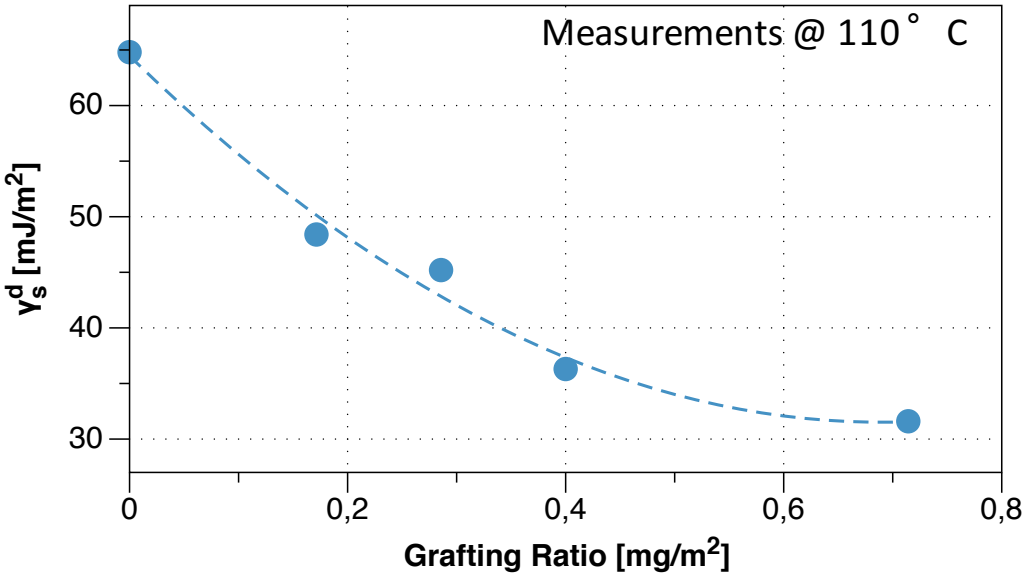
- **Grafted solid**
- **Coated surfaces**
- **Polluted surfaces**

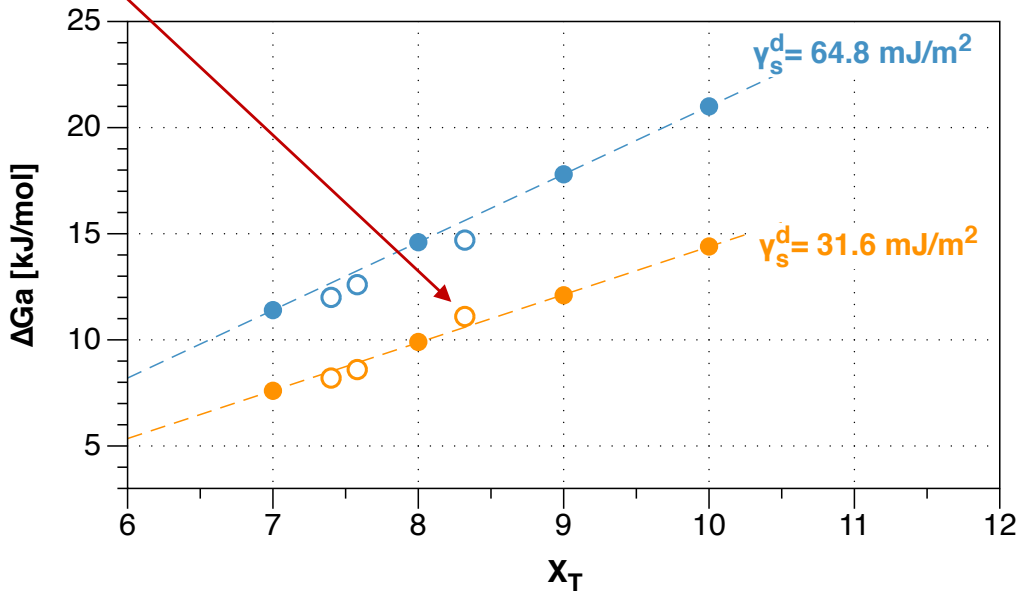
Silica grafting

- Octyltriethoxysilane grafting on SiO_2 (Ultrasil 7000 GR), $S_{BET} \approx 175\ m^2/g$

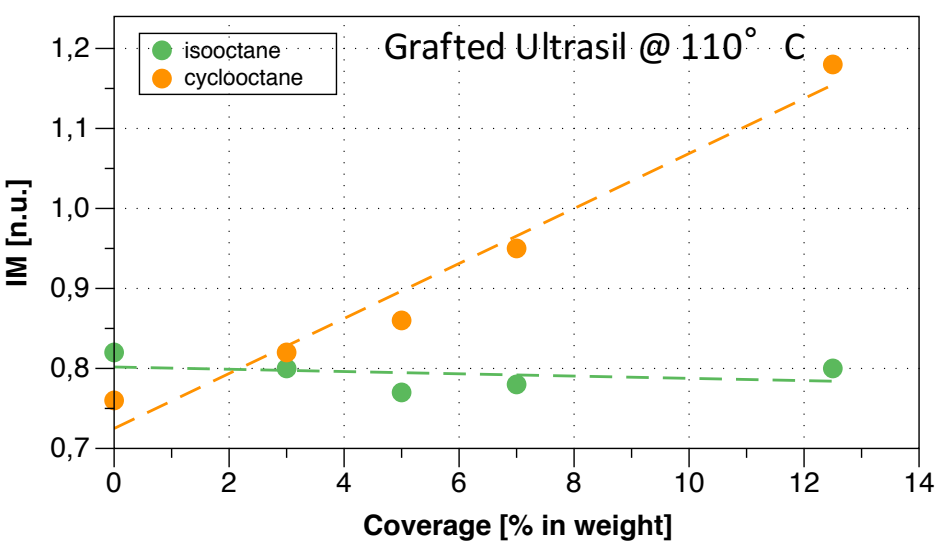


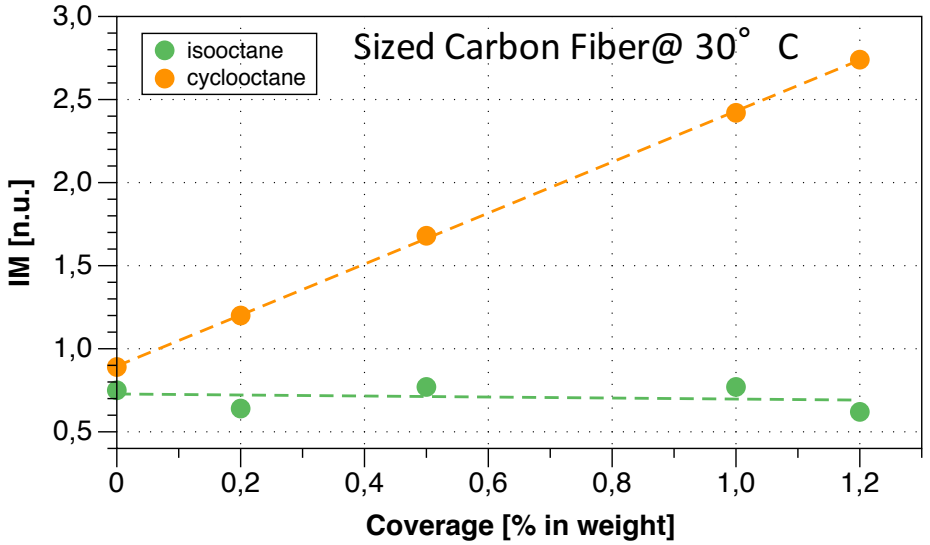
- Comparison of the γ_s^d value evolution according to the grafting ratio
  - Significant decrease of γ_s^d
  - On the starting sample, cyclooctane is below the reference straight line
  - On the most grafted sample, cyclooctane is **above** that line





Different perception





- Comparison of the evolution of the IM according the grafting ratio
  - IM(isooctane) remain constant
  - IM(cyclooctane) increases according the grafting ratio (even >1 for the highest ratio)
  - IM(cyclooctane)>IM(isooctane) with increasing grafting ratio
- Also observed for coated surfaces and polymers near their T_g
  - Sometimes IM(cyclooctane)>2.5 (i.e. t_N is 2.5 times higher as expected according n-alkanes)

Why ?

The solubility parameters of the n-alkanes, branched alkanes and cyclic alkanes explain their different behaviours

$$\delta_{cyclic} > \delta_{n\text{-}alkanes} > \delta_{branched}$$

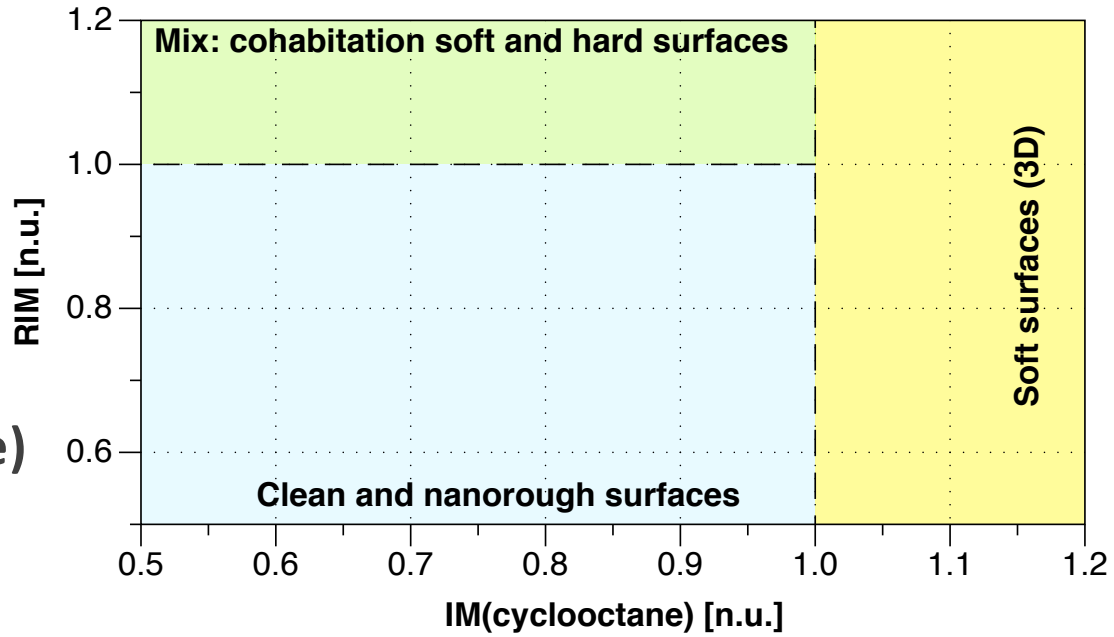
The RIM index

Cases	Surfaces	Molecular Mobility	IM behaviour
Liquids, molten polymers Highly coated surfaces	"Soft"	High (3D)	**IM(isooctane) < 1 < IM(cyclooctane)**
Clean solids (crystalline or not) Mineral amorphous solids	"Hard"	None (2D)	**IM(cyclooctane) < IM(isooctane) ≤ 1**
Polluted solid surface Partly coated surfaces Organic amorphous solids	"Hard + Soft" or amorphous + crystalline	Mixed	**IM(isooctane) < IM(cyclooctane) ≤ 1**

Definition of the RIM index:

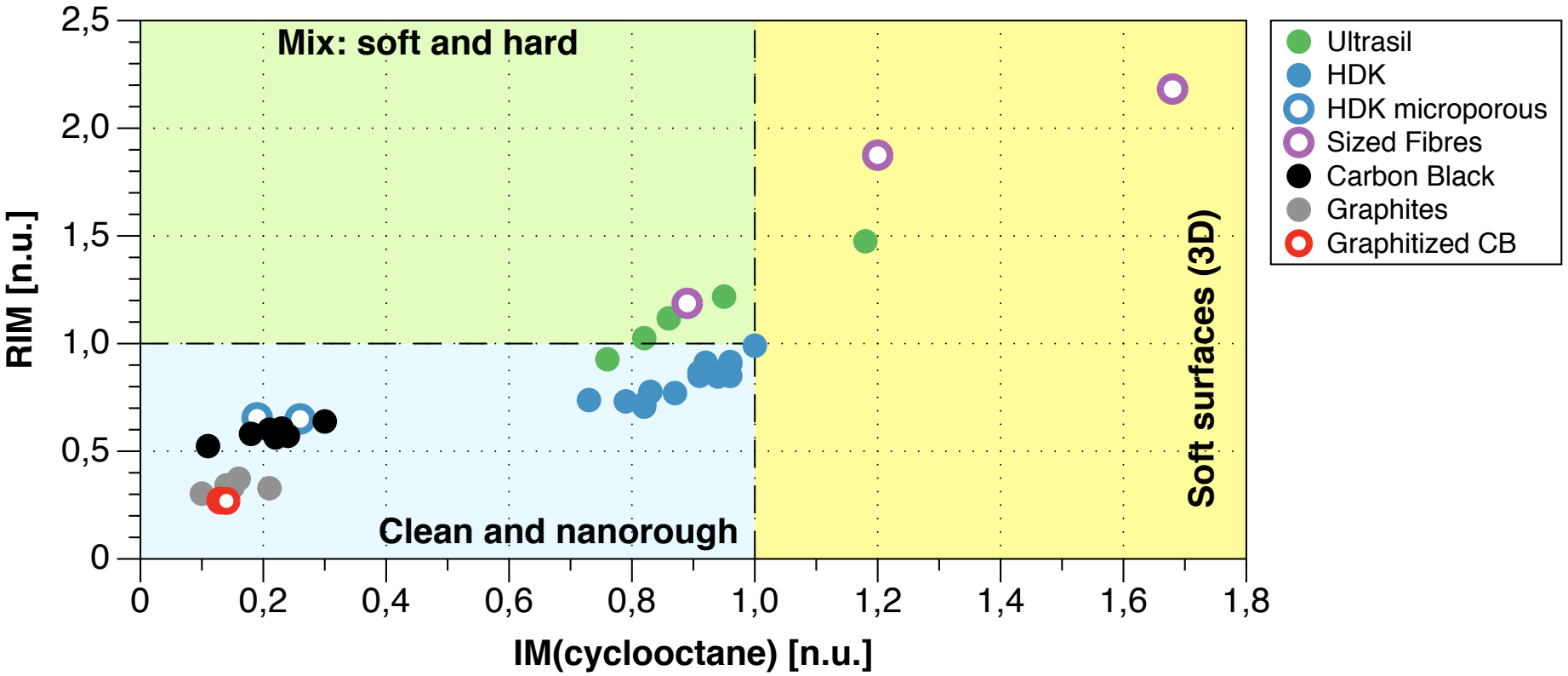
$$RIM = \frac{IM(cyclooctane)}{IM(isooctane)}$$

New representation: RIM vs IM(cyclooctane)



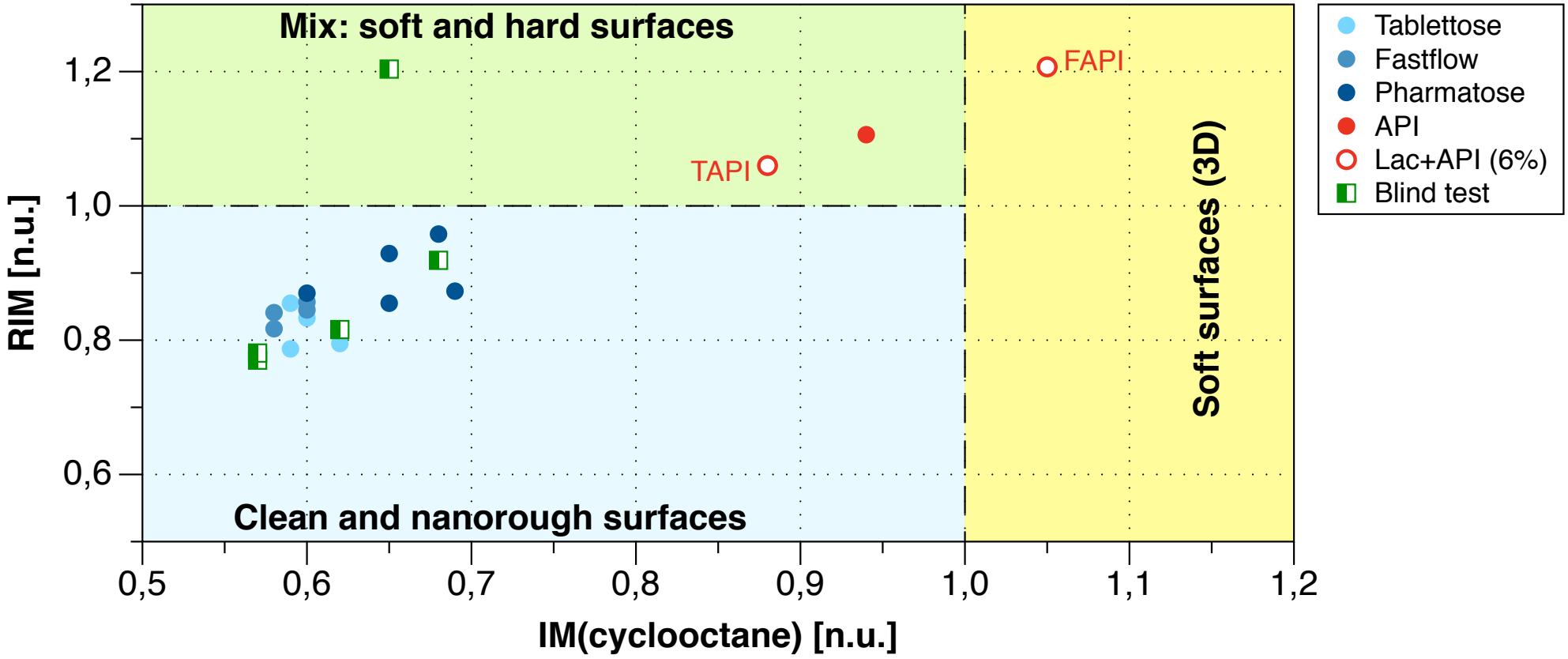
RIM: Application to the previous examples

- A clear picture of the different behaviours is obtained
  - The effect of microporosity (Carbon Black, Graphites, microporous HDK)
  - The effect of slight nanoroughness (pyrogenic silica)
  - The presence of soft material (grafted or coated)



RIM: Application to Lactose

- Easy distinction between the lactose samples
  - From one provider to the other
  - Sample showing a divergent behaviour
  - The presence of soft material (API)



Conclusions

On hard and clean surfaces

- The morphological index is able to describe the surface nanoroughness
  - IM(cyclooctane)≤IM(isooctane)≤1
- The γ_s^d values are significantly impacted by the surface nanoroughness

On soft or organically modified surfaces

- The RIM index is able to detect and describe the influence of molecular mobility
  - The cyclic probes interact more strongly with the soft materials (dissolution)

Opens the way to promising applications:

- Characterisation of the surface cleanliness
- Estimation of the amorphous contains (ex: lactose)

Perspectives

- Neuronic: a solution for automated IGC measurements
  - Simultaneous and independent measurements on two samples (2 analytical channels)
  - Up to 30 test solvents available (up to 45)
  - Working temperature (20-350°C)
  - Reduced dead-volume for high efficiency
  - Real IGC-ID measurements
    - γ_s^d, nanoroughness (IM & RIM), acid-base, diffusion, HSP…
  - IGC-FC measurements
    - Desorption isotherm, specific surface area, surface heterogeneity (AEDF) and thermal desorption

- Example of performance
  - HSP determination on two samples (liquids) using 20 test solvents within a working day (repeatability tests included)