SAMBa

Integrative Think Tank 6

EPSRC
Engineering and Physical Sciences Research Council

- **Surfactant design assisted by Molecular Simulation, the lost CMC!**
- **PSD by Tikhonov's regularization method. Can we do better?**

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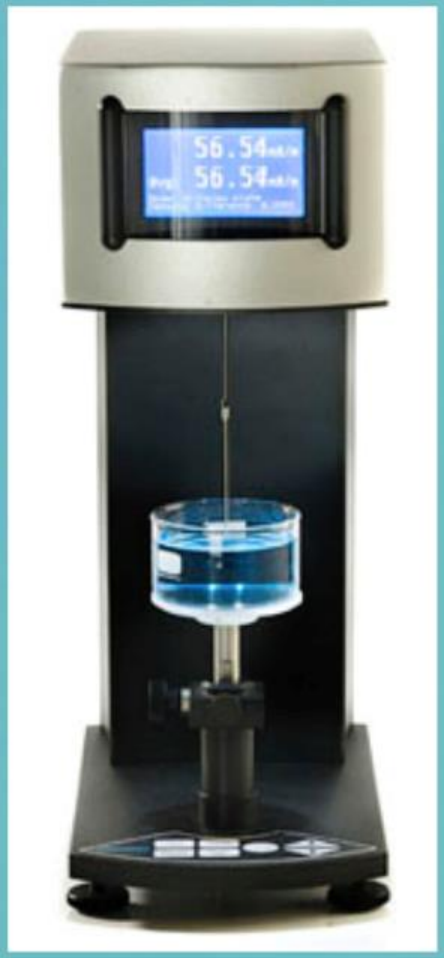
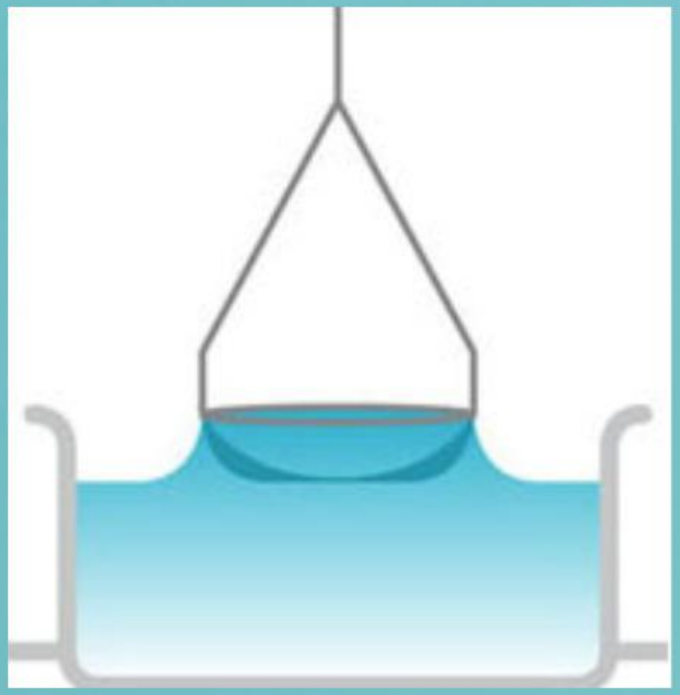
WH7.19

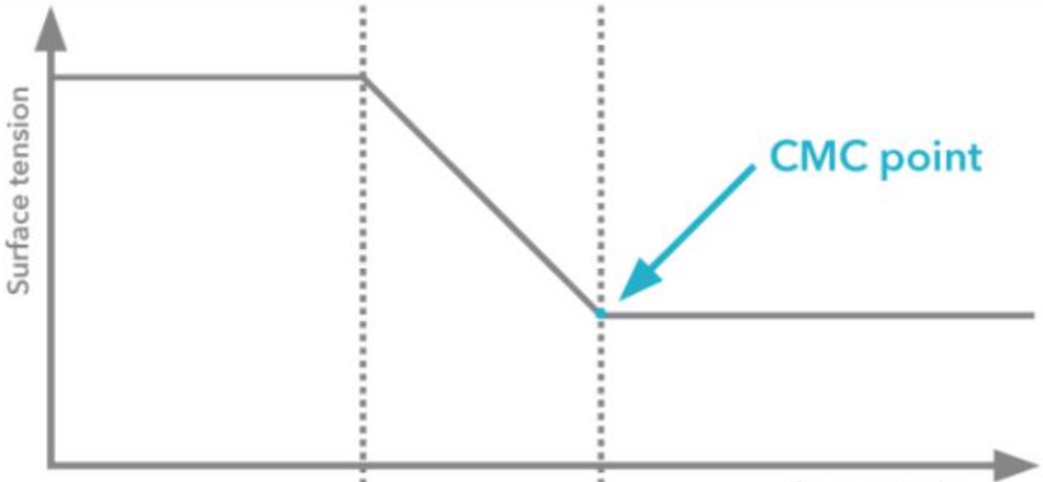
Surface tension measurement





www.attension.com

Surface tension measurement



[s] / [W]= 1 / 100 000
challenging for
molecular simulation!

www.attension.com

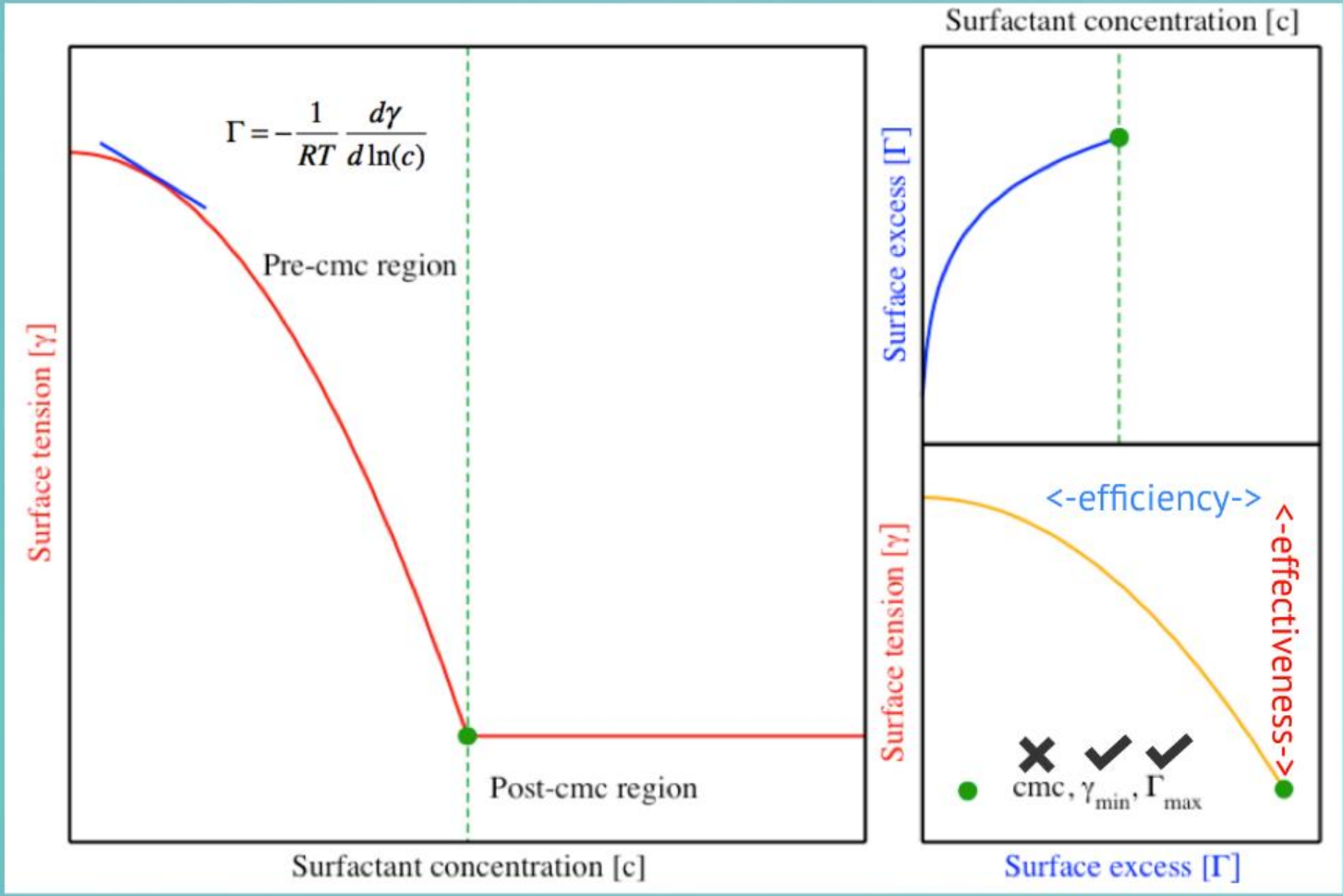
Surface tension

Incredible shot of US swimmer that perfectly shows the phenomenon of surface tension

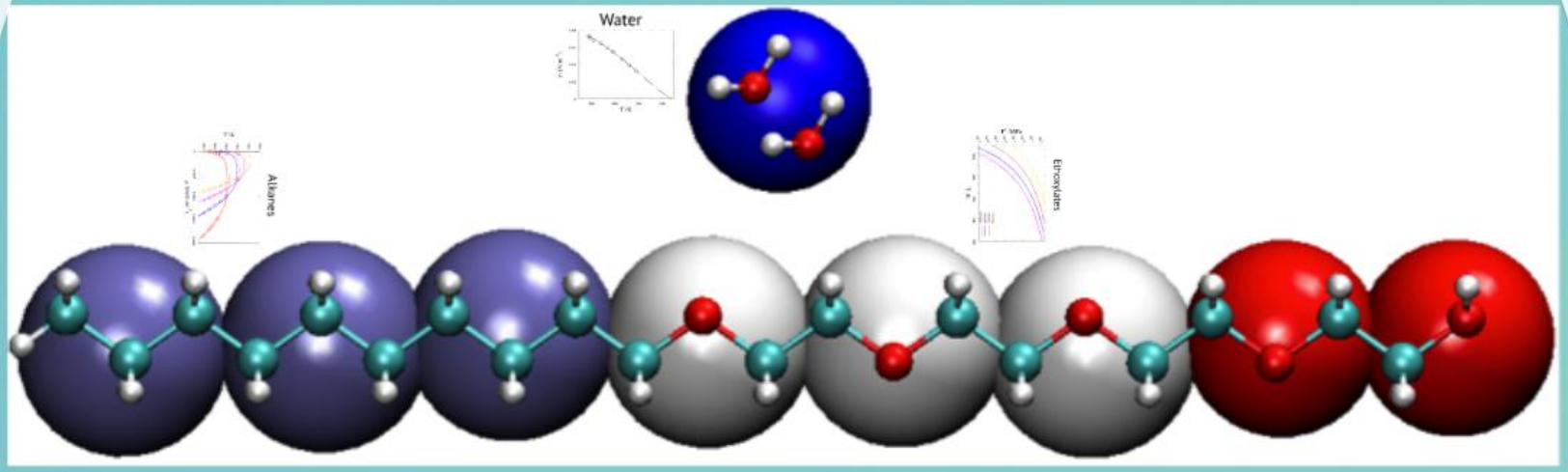
By JAMES NYE

PUBLISHED: 22:33, 17 August 2012 | **UPDATED:** 23:45, 17 August 2012

Our method


$\Gamma = -\frac{1}{RT}\frac{d\gamma}{d\ln(c)}$
Pre-cmc region
Post-cmc region
Surface tension [γ]
Surfactant concentration [c]
Surfactant concentration [c]
Surface excess [Γ]
<-efficiency->
<-effectiveness->
cmc, γ_{min}, Γ_{max}
Surface tension [γ]
Surface excess [Γ]

Our design drawing board



For the non-ionic surfactant tetraethylene glycol monodecyl ether ($C_{10}EO_4OH$,) at the air-water interface

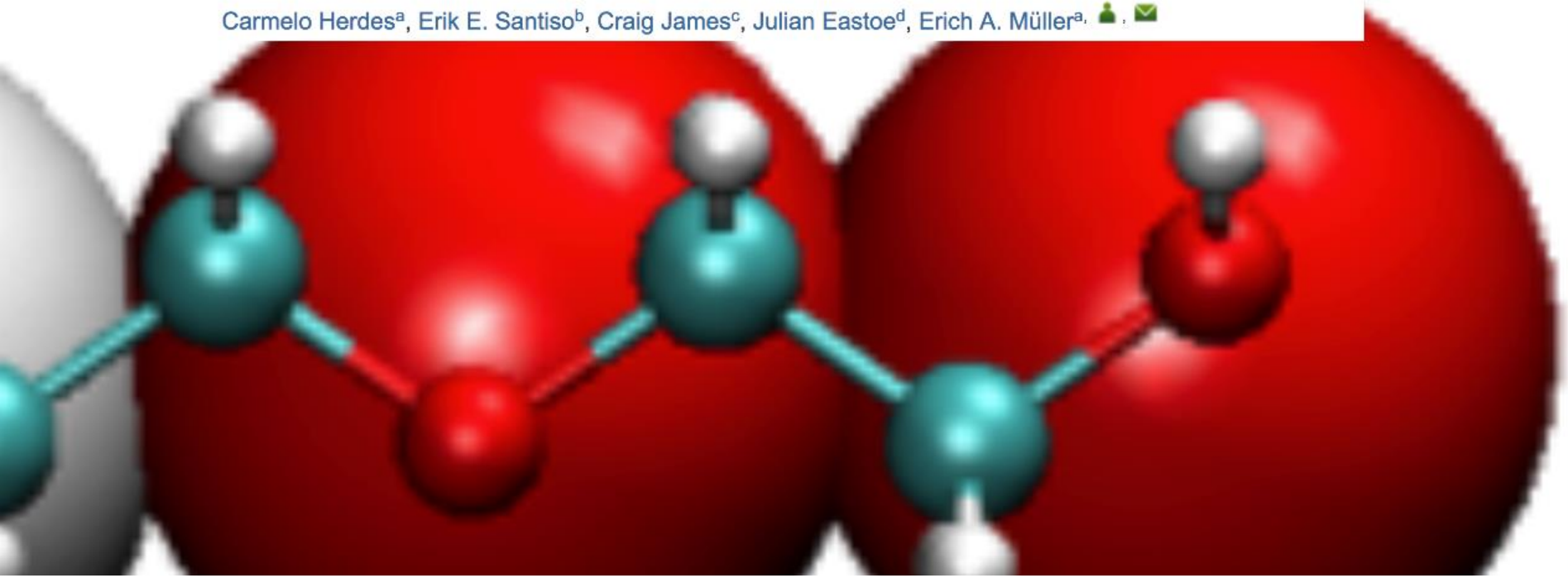
Parameterized by SAFT-γ Mie

Journal of Colloid and Interface Science

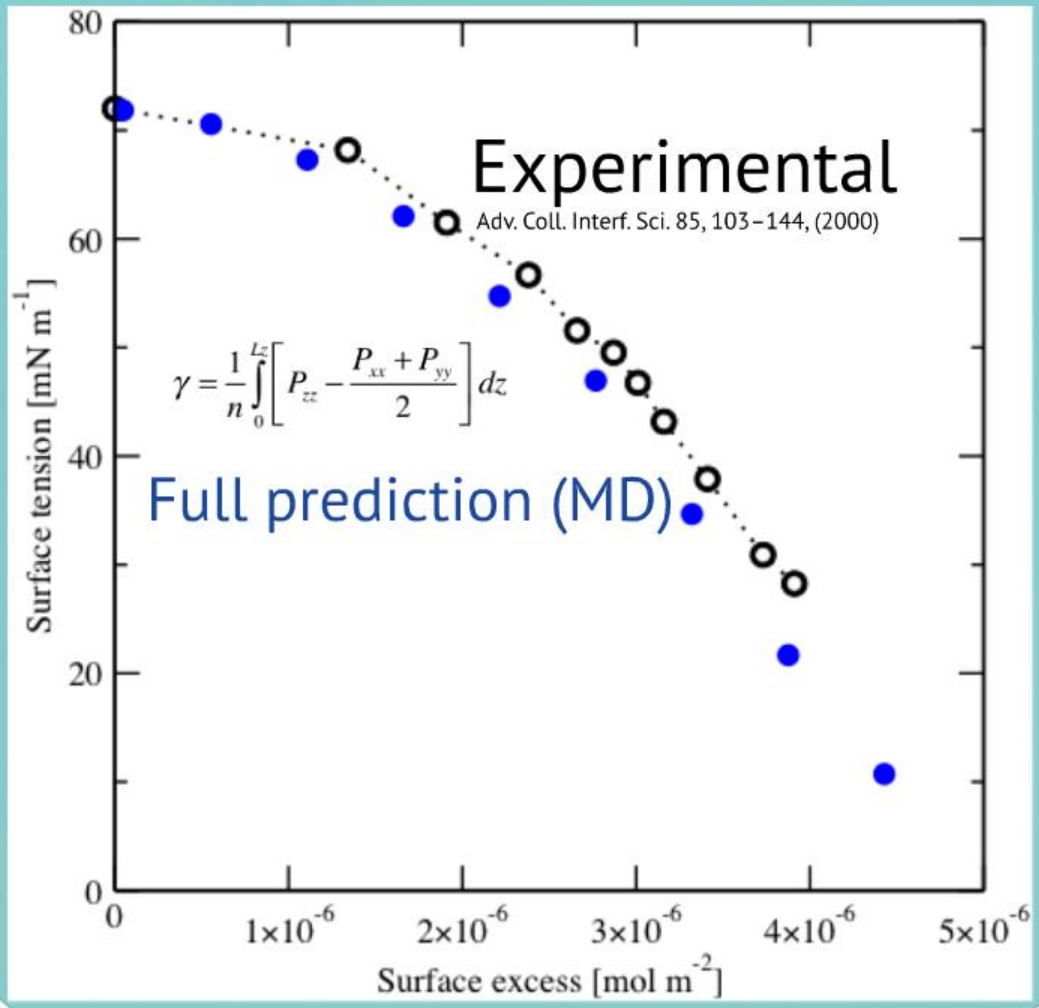
Volume 445, 1 May 2015, Pages 16–23

Modelling the interfacial behaviour of dilute light-switching surfactant solutions

Carmelo Herdes[a], Erik E. Santiso[b], Craig James[c], Julian Eastoe[d], Erich A. Müller[a],

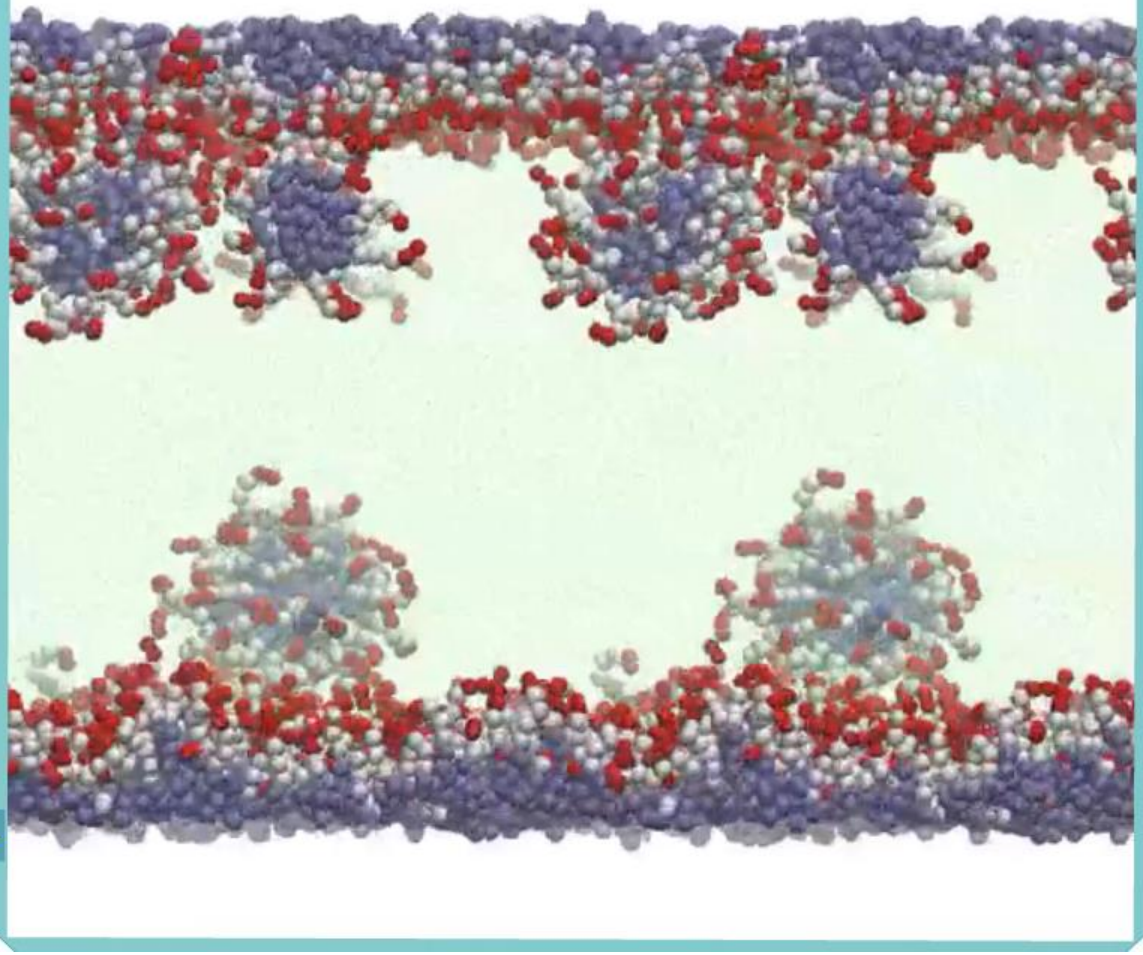


Proof on concept (I)



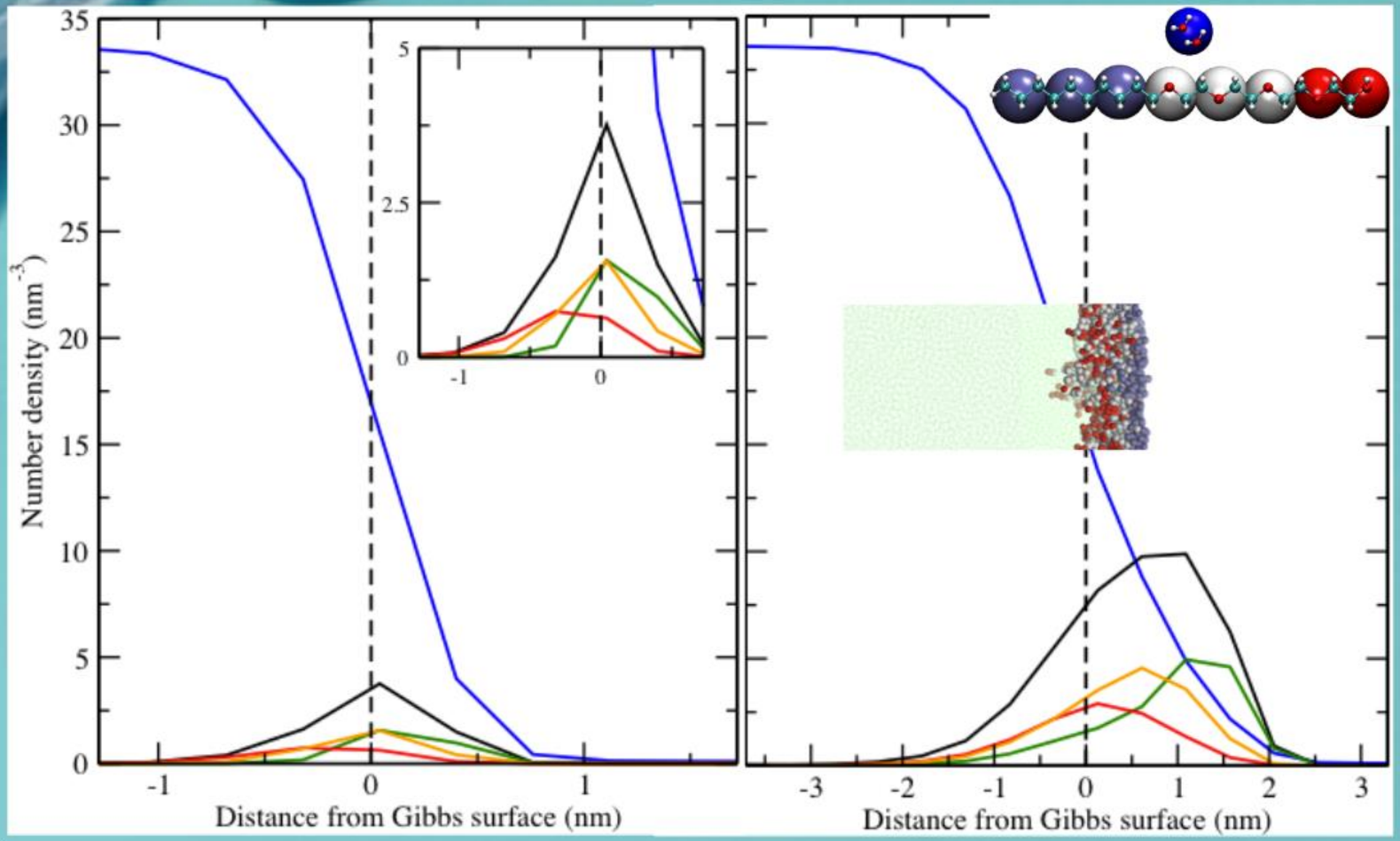
Proof on concept (II)

---> Then micelles are form and detached from the surface:



CLICK Here I am a movie!-->

Insights at the surface level



Can you help us predicting the CMC?

Objective: to develop a fully predictive molecular-experimental framework for the design of surfactants

Challenge: the modeling will be incomplete until the CMC could be predicted

Key question: are we missing something obvious?

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Research Article

Previous A

Pore Size Distribution Analysis of Selected Hexagonal Mesoporous Silicas by Grand Canonical Monte Carlo Simulations

Carmelo Herdes ,[†] Miguel A. Santos ,[‡] Francisco Medina ,[§] and Lourdes F. Vega *[†]
Institut de Ciència de Materials de Barcelona, (ICMAB-CSIC), Consejo Superior de Investigaciones Científicas, Campus de la U.A.B., Bellaterra, 08193 Barcelona, Spain, Center for Computational Biology, The Hospital for Sick Children, Toronto, Ontario, Canada M5G 1X8, and Departament d'Enginyeria Química, ETSEQ, Universitat Rovira i Virgili, Avda dels Països Catalans, 26, 43007 Tarragona, Spain

Langmuir, **2005**, *21* (19), pp 8733–8742
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Publication Date (Web): August 13, 2005
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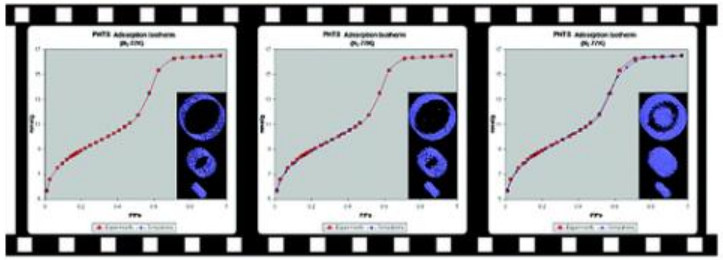
links

Abstract



PSD our approach

How to obtain the Pore Size Distribution?

•Experimental Isotherm

$$N_T(P) = \int_{H_{min}}^{H_{max}} f(H)\rho_T(P,H)dH$$

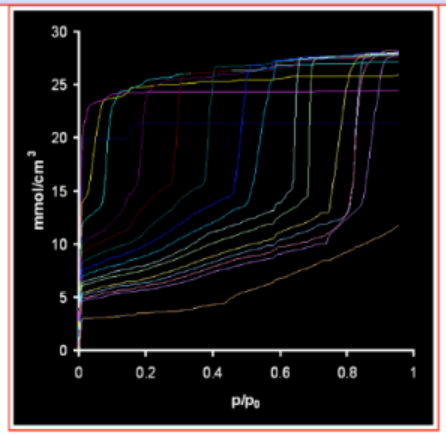
•PSD

•Kernel of Single Isotherms (DFT , **GCMC**)

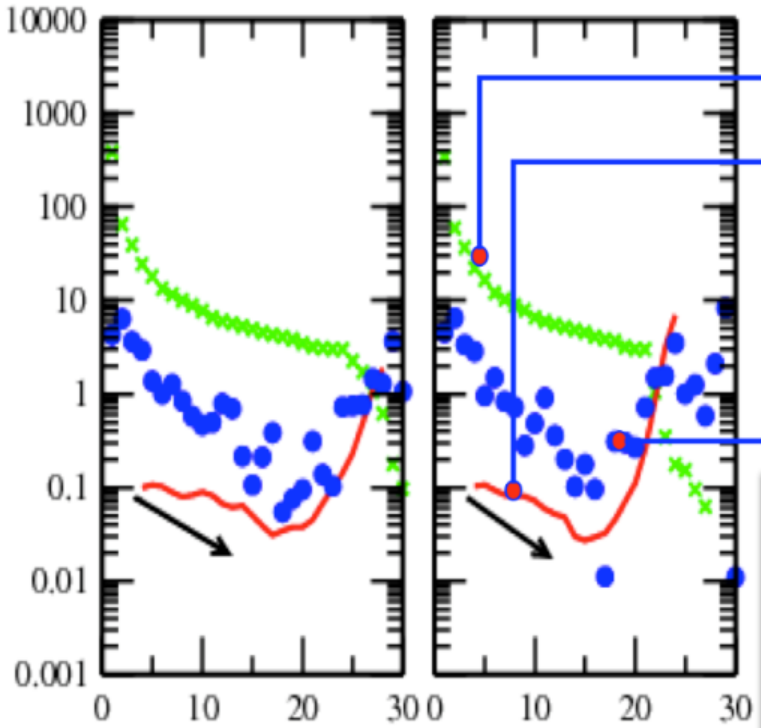
- Ill-posed problem!
- Possible solution:
- A regularization procedure

Suppositions

- Unique Pore Geometry
- Homogeneous Surfaces



The Discrete Picard Condition (DPC)

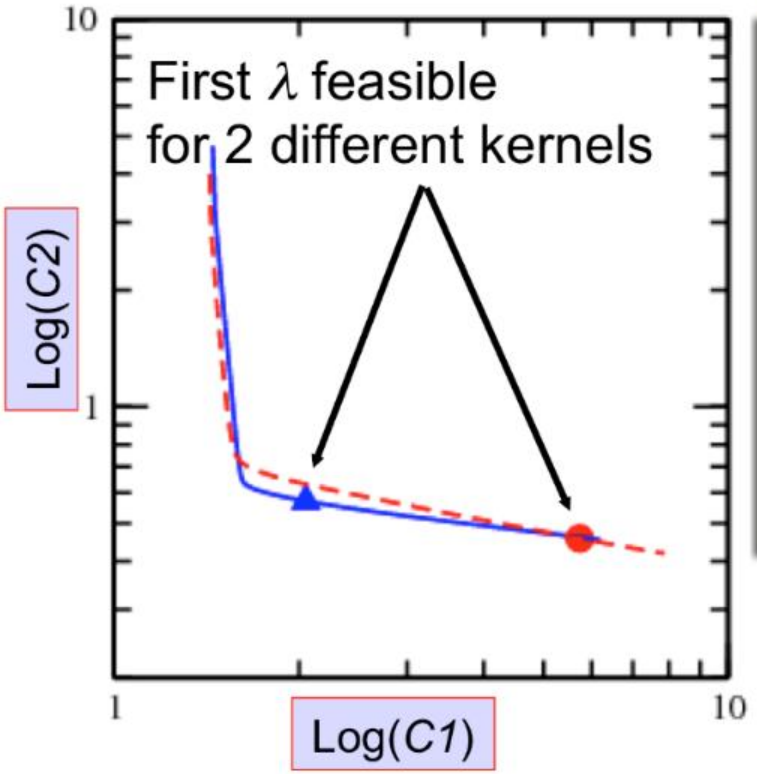


$$r_i \equiv s_i^{-1} \left(\prod_{j=i-q}^{j=i+q} |\mathbf{u}_i^T \mathbf{a_e}| \right)^{1/(2q+1)}$$

The discrete Picard condition (DPC)

r_i : tells how "good" the couple kernel – experimental data is. The red line should have in "average" a negative slope

The L-curve criterion



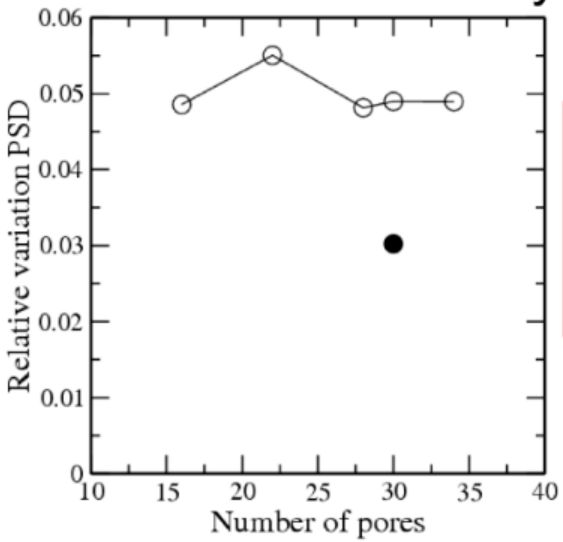
The L-curve
Depicts many calculated possible solutions in a given range of λ values.
The results of C1, C2 are plotted using log-log axis.

C1 C2

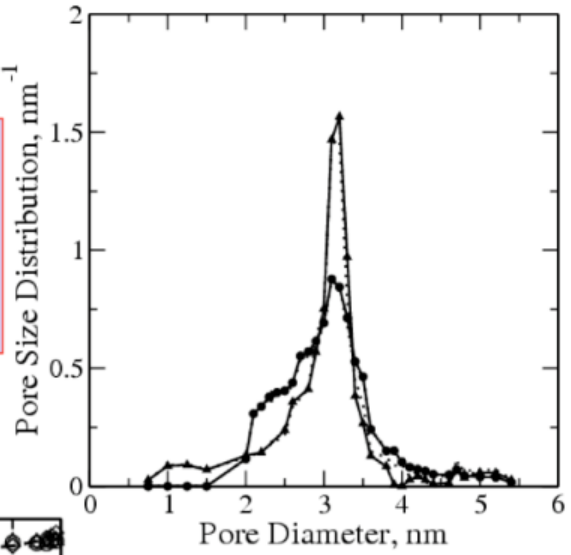
$$\min_{\mathbf{x}} \left\{ \left\| \mathbf{a_e} - \mathbf{A_s}\,\mathbf{x} \right\|_2^2 + \lambda^2 \left\| \mathbf{R}\,\mathbf{x} \right\|_2^2 \right\}$$

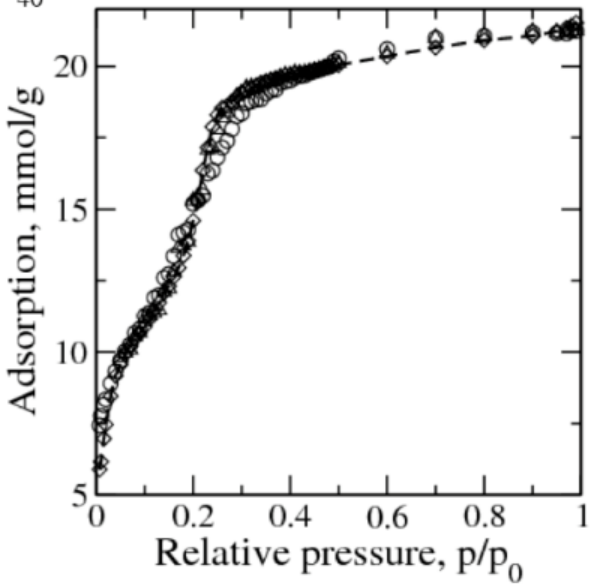
PSD analysis for Silica Based Materials (II)

Protocol PSD analysis over AM-5



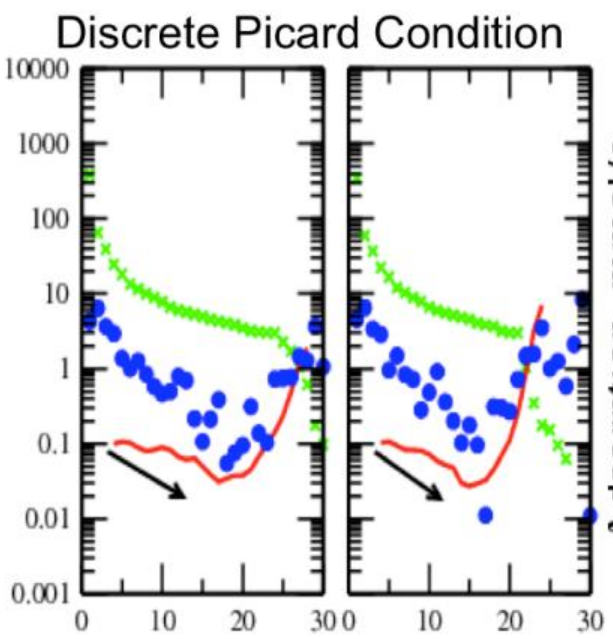
Robustness of the proposed PSD versus errors in the experimental data

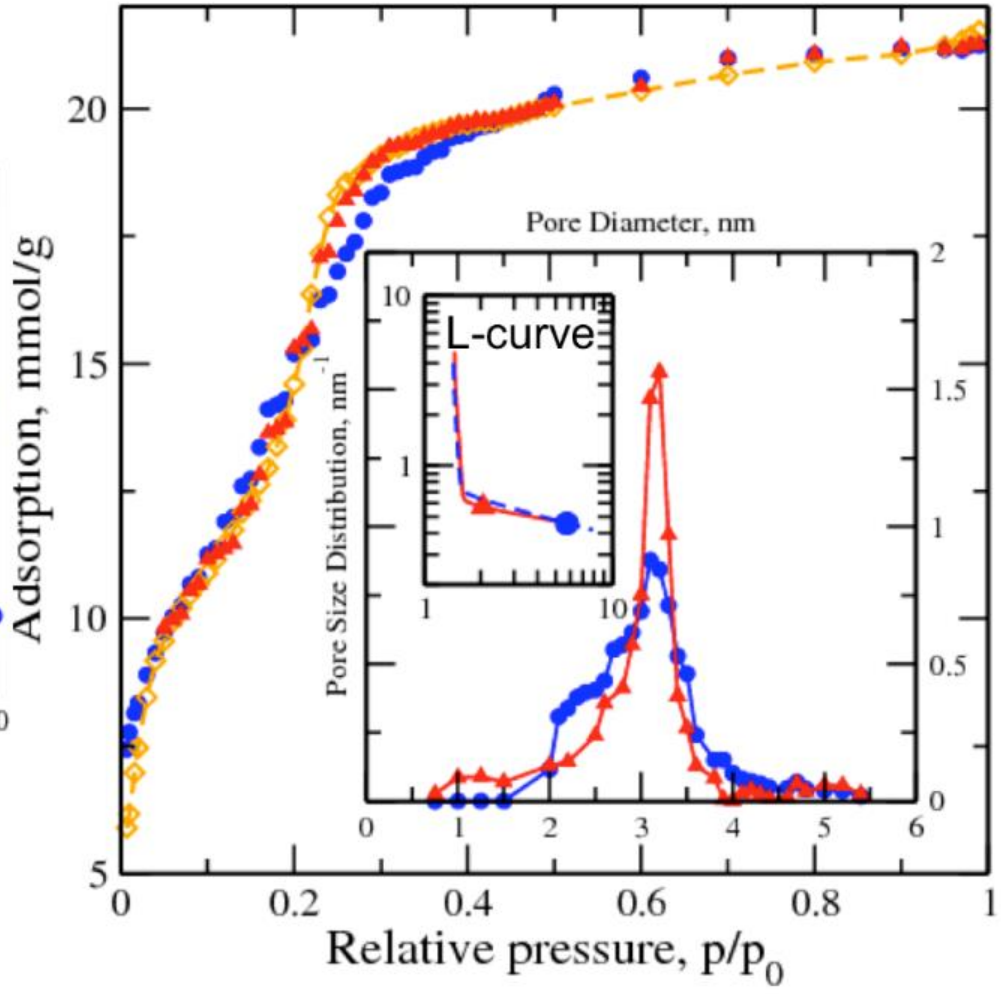




PSD analysis for Silica Based Materials (I)

Protocol PSD analysis over AM-5





Thank you for your attention!

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