Statistical Mechanics of Multilayer Sorption: Surface Tension

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Organization

Why you should stay awake

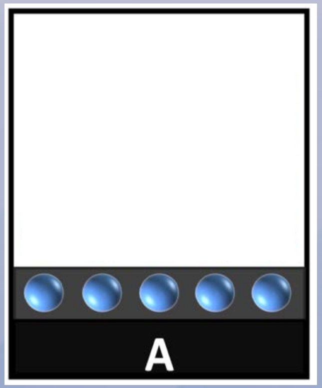
Solutions to Surfaces
- History
- The Concept
- The Derivation
- Some Examples
- Conclusions

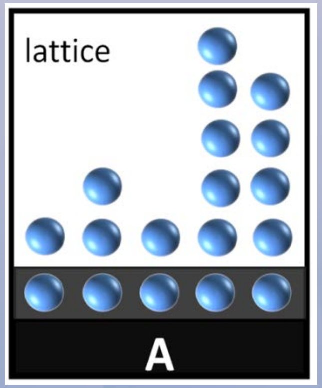
Motivation

Atmospheric Particles are Dynamic

Surface Properties are key to
- Nucleation
- Kelvin Effect – bistable sizes for small particles
- Cloud Activation
- Particle growth / Surface layers at RH below deliquescence
- Activation of Insoluble Dust Particles
- Reactions on Particle Surfaces

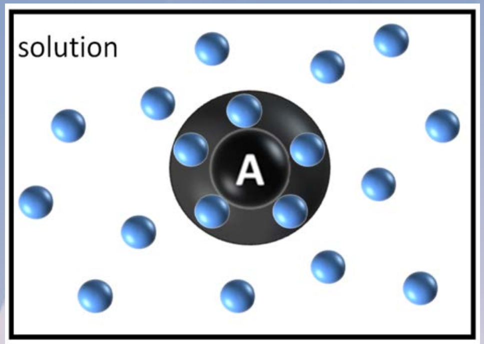
History

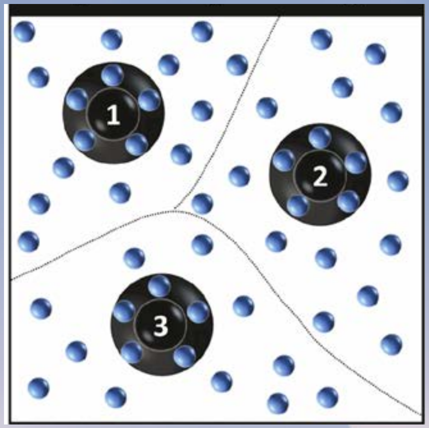




Brunauer, Emmett and Teller (BET): 1938
Guggenheim, Anderson, de Boer (GAB): Early 1940s

Langmuir: 1890's





Pauling, Stokes and Robinson: mid 1940s

Ally and Braunstein: 1998

The Concept

Model the arrangement of solute on the surface of a solution

Assume one sorption layer since we’re on the solvent surface

Let’s see what’s under the hood

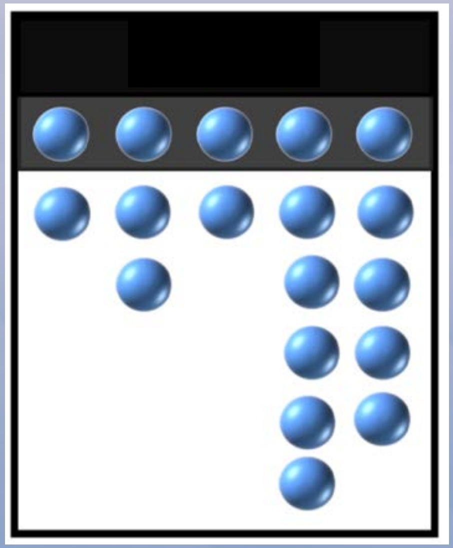
The Derivation

Surface layer partition function

$$\Omega_1 = \frac{N_{WS}!_{(r_A)}}{(N_{WS} - r_A N_{A1})!_{(r_A)}\,(r_A N_{A1})!_{(r_A)}}$$

Surface-Bulk partition function

$$\Omega_2 = \frac{N_A!}{N_{A\mathbf{1}}!\,(N_A - N_{A\mathbf{1}})!}$$



Energy

$$E = -N_{ws}\varepsilon_{ws} - N_{A1}\varepsilon_{A1} - N_A\varepsilon_A$$

Gibbs Free Energy is

$$\frac{G}{kT} = \frac{E}{kT} - \ln \Omega_1 \Omega_2$$

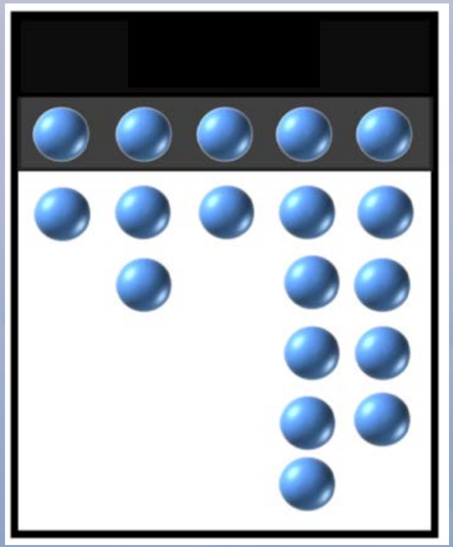
Glossary

N_{WS} – number of waters at the surface
N_{A1} – number of As sorbed in layer 1
N_{A2} – number of As sorbed in layer 2
N_A – total available A, so $N_A = N_{A1} + N_{A2}$
r_A – number of waters displaced from the surface by sorbent A
S_W – area occupied by a water molecule (about 0.1 nm^2)
A_T – total surface area
$A_T = S_W \cdot N_{WS}$
σ – surface tension of the solution
σ_W – surface tension of pure water
σ_A – surface tension of pure A

The Derivation

… lots of math …

$$\sigma(a_A) = \sigma_W + \frac{kT}{r_A S_W} \ln \frac{1 - K_A a_A}{1 - K_A a_A (1 - C_1)}$$



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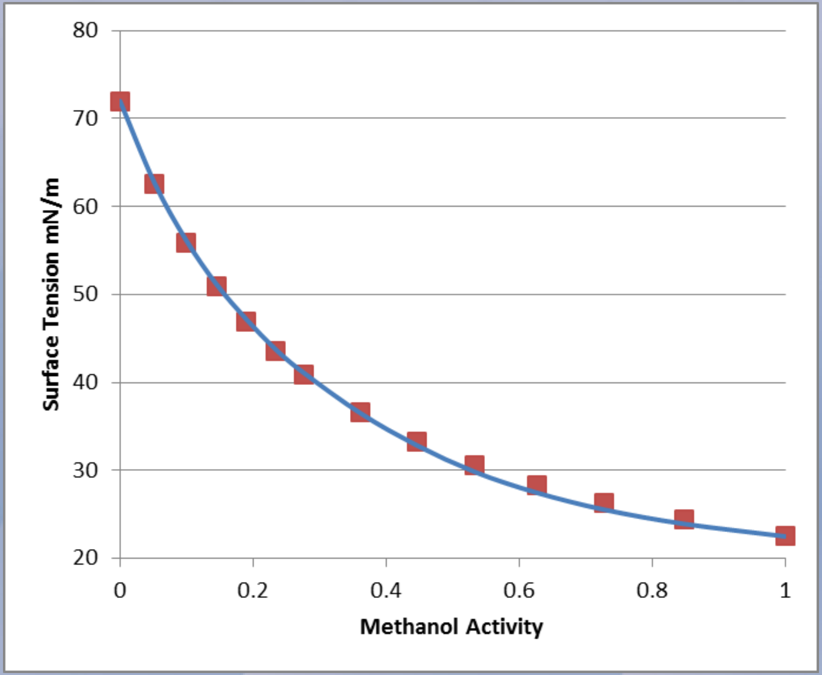
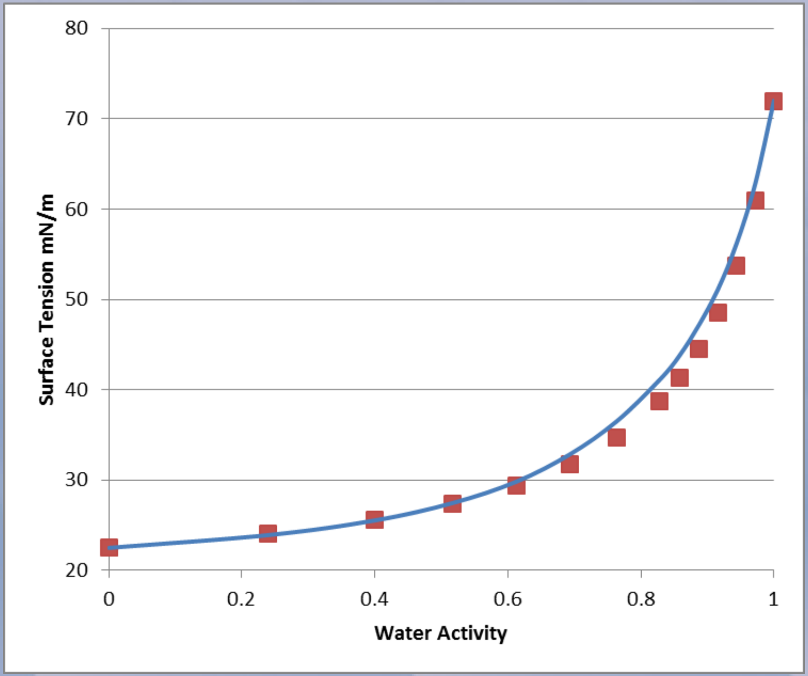
Examples



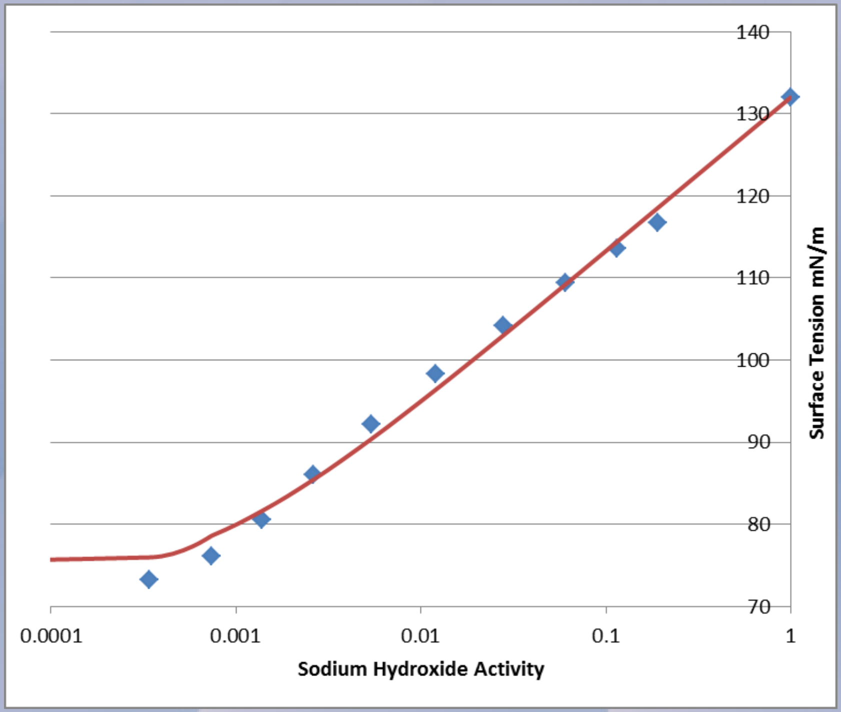


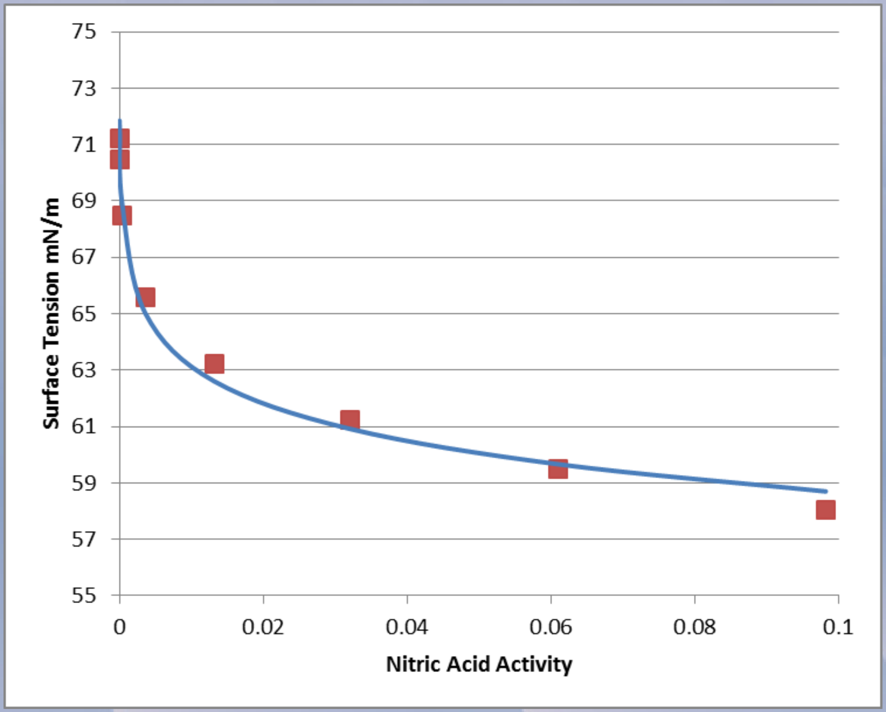
Methanol dissolved in water

Water dissolved in methanol

Ethanol and 1-propanol similar

Examples



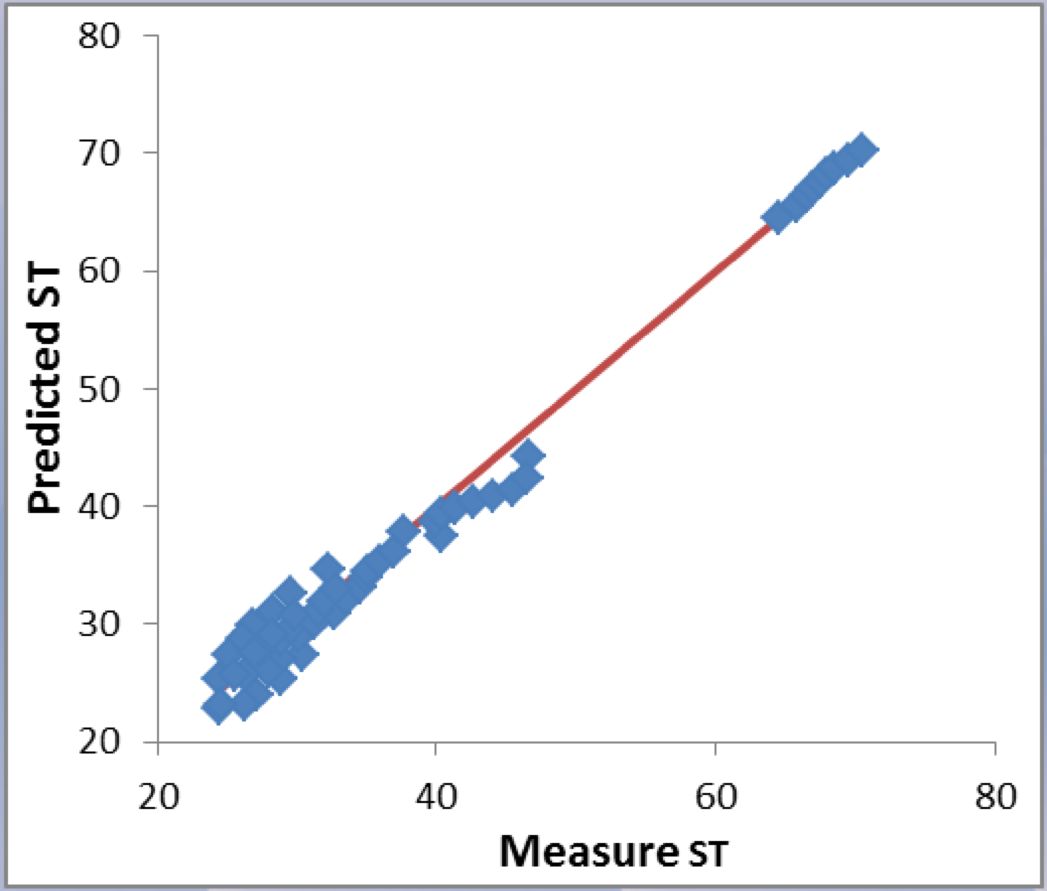


Sodium Hydroxide

Nitric Acid

Many other electrolytes too

Solutions to Surfaces: Examples



Water-Glycerol-Ethanol mixture
0-100% by weight each
Parameters from water-glycerol and water-ethanol mixtures

Conclusions

Surface and Solution Models are One

- Solutions in previous publications and poster here
- Approaching Gibbs energy description of surface and bulk

Electrolyte and Organic Surface Tension Models are One

One Sorption Layer is Enough at the Surface

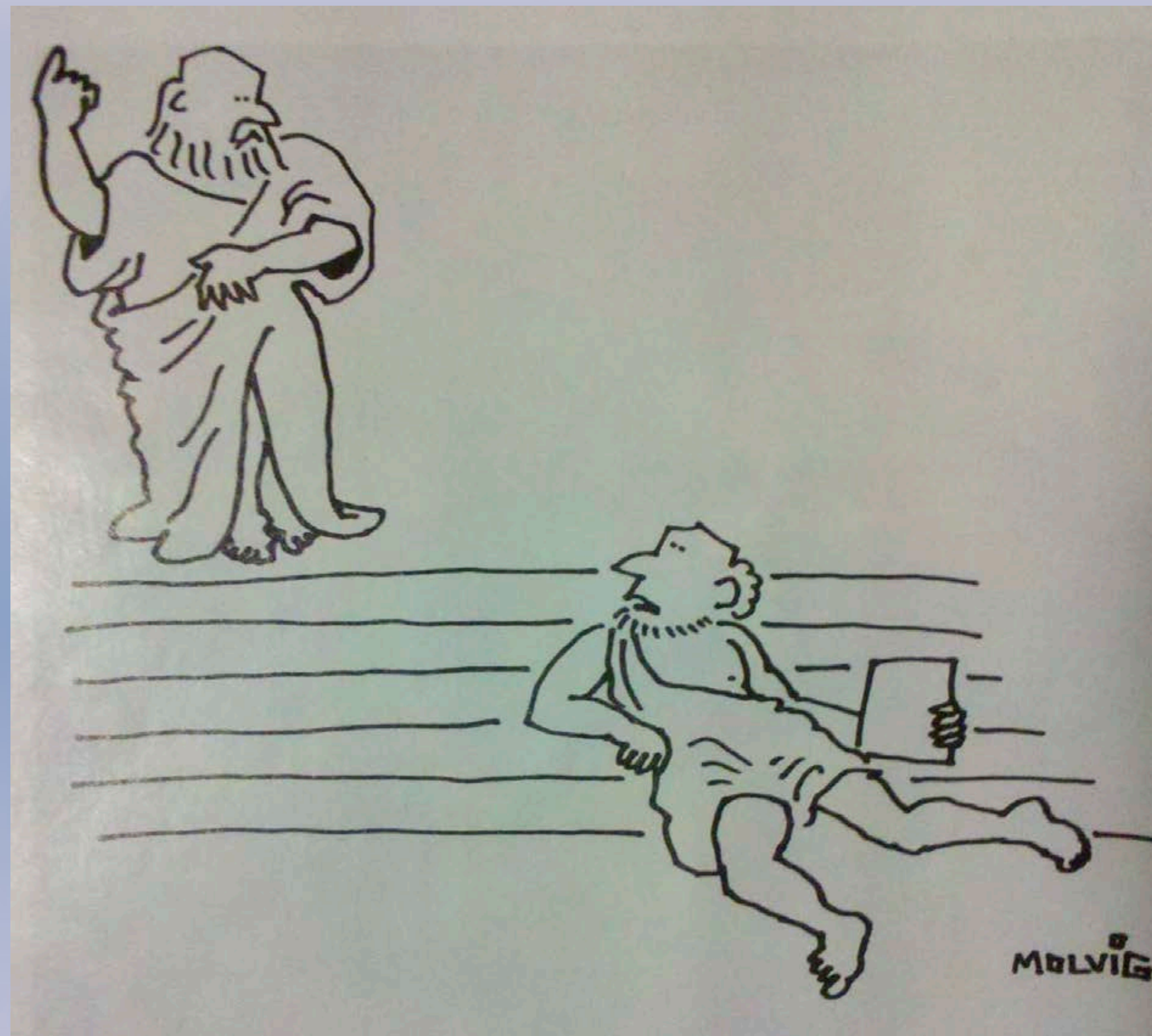
Statistical Mechanics is my Shepherd, I shall not want

Still Need to

- Improve the multisolute model
- Relate Parameter Values to Physical Chemical Properties
- Develop Temperature Dependence

Questions?

Thanks for listening



"Is this going to be on the midterm?"