Wetting and freezing transitions in Langmuir-Gibbs monolayers

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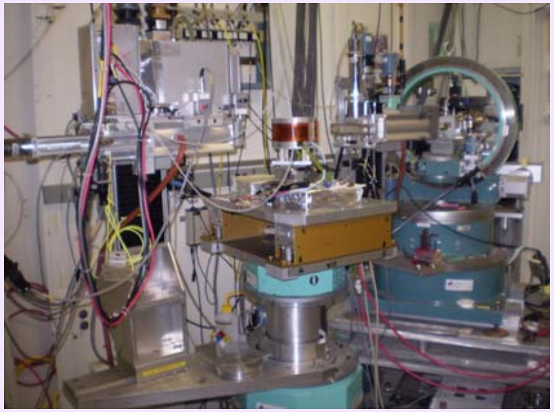
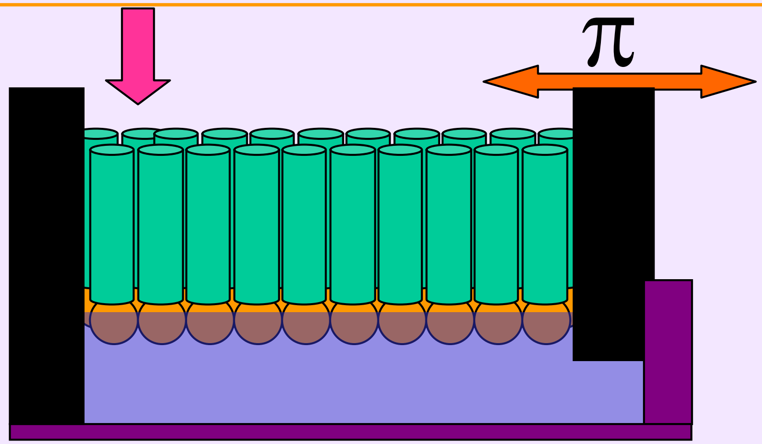
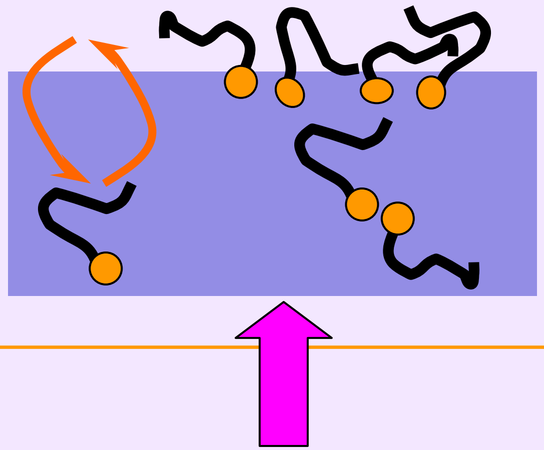


Langmuir Monolayers

- The molecules are amphiphilic & insoluble in the bulk subphase.
- Rich phase diagram (ordered phases).
- Large hysteresis.



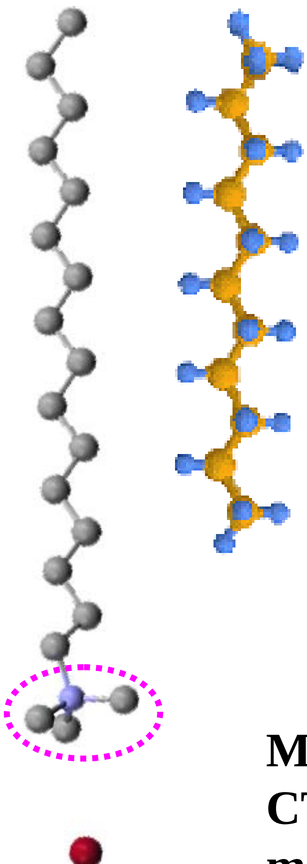


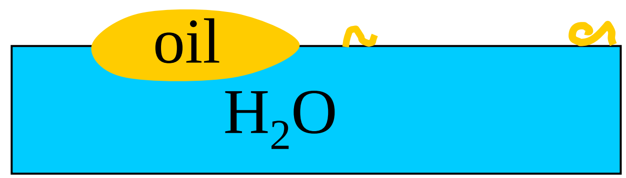
Gibbs Monolayers

- The molecules are soluble in the bulk phase.
- The surface adsorption is driven by Gibbs rule (Thermodynamics).
- No phase transitions. Disordered surface.

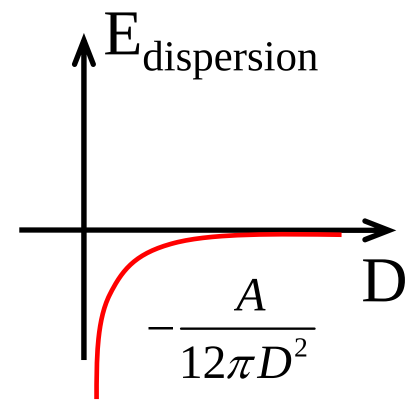
Langmuir-Gibbs films

Medium-sized alkanes $6 \leq n \leq 30$ do not spread on water

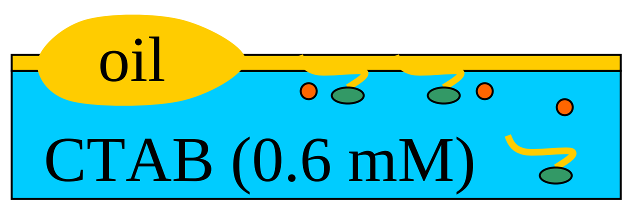




First order transition to the **pseudo-partial** wetting regime, upon increase in the concentration of CTAB. [1]

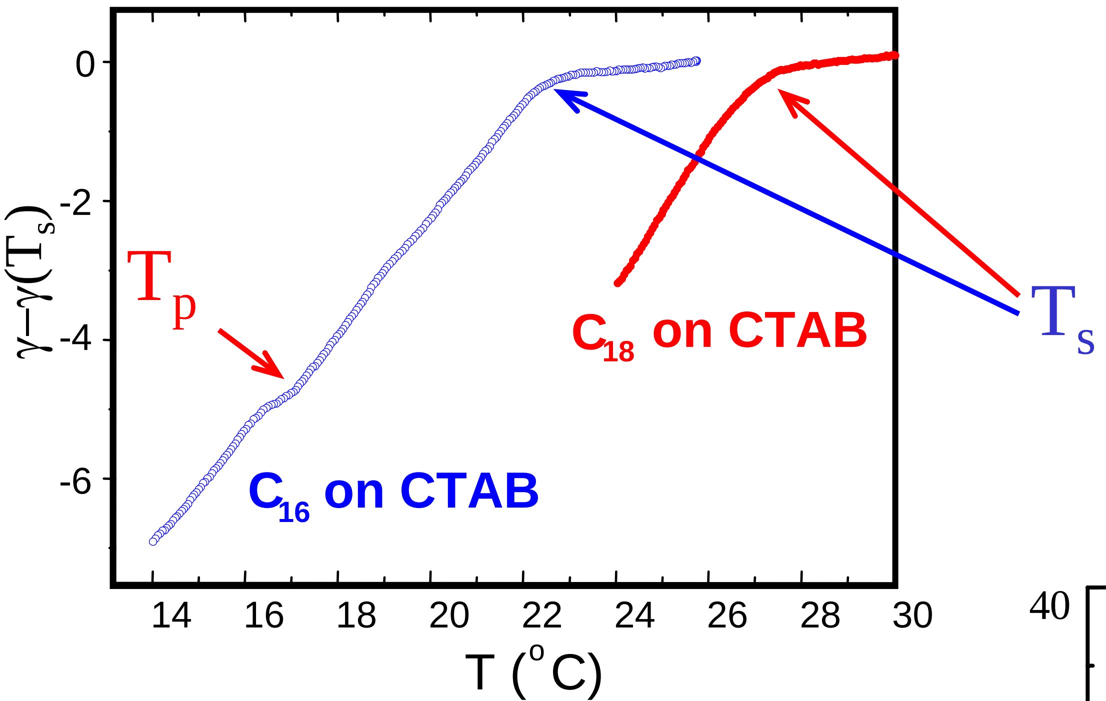


Mixed Langmuir-Gibbs CTAB + C_n disordered monolayer.

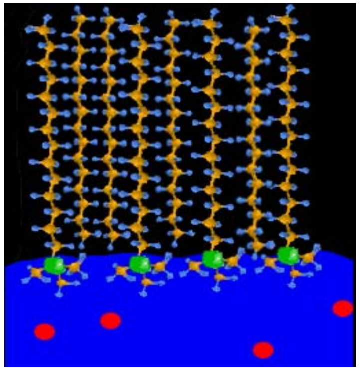


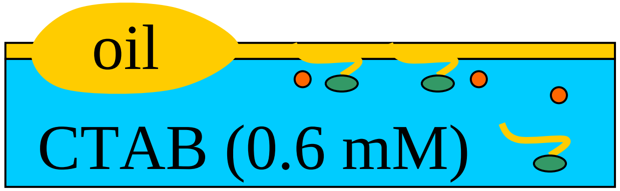
[1] K.M. Wilkinson, C.D. Bain, H. Matsubara, and M. Aratono, ChemPhysChem **6**, 547 (2005)

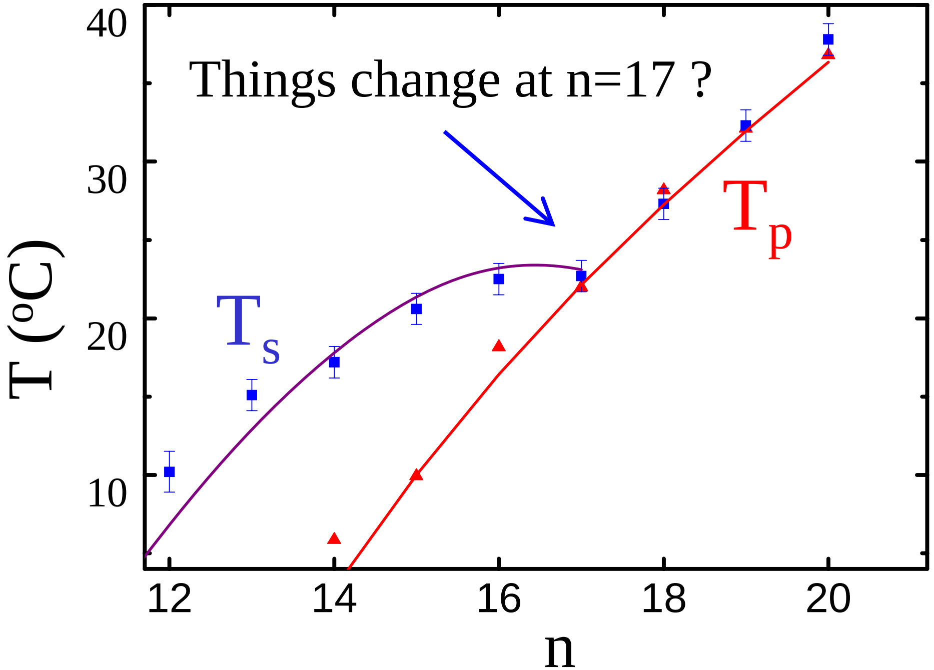
Thermodynamics of Liquid-Solid Transitions in Langmuir-Gibbs Films



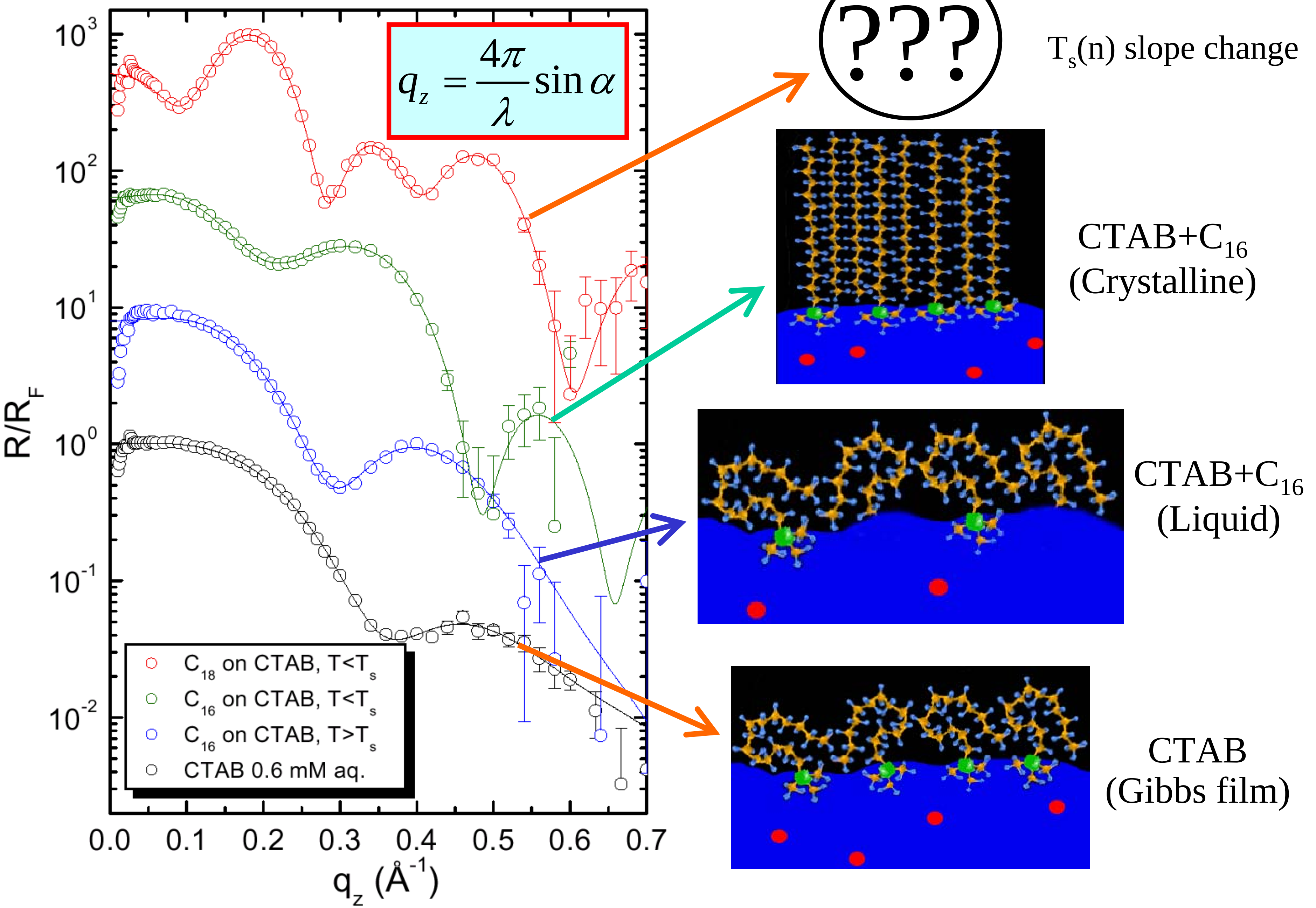
$$\Delta S = \left.\frac{d\gamma}{dT}\right|_{T<T_s} - \left.\frac{d\gamma}{dT}\right|_{T>T_s}$$



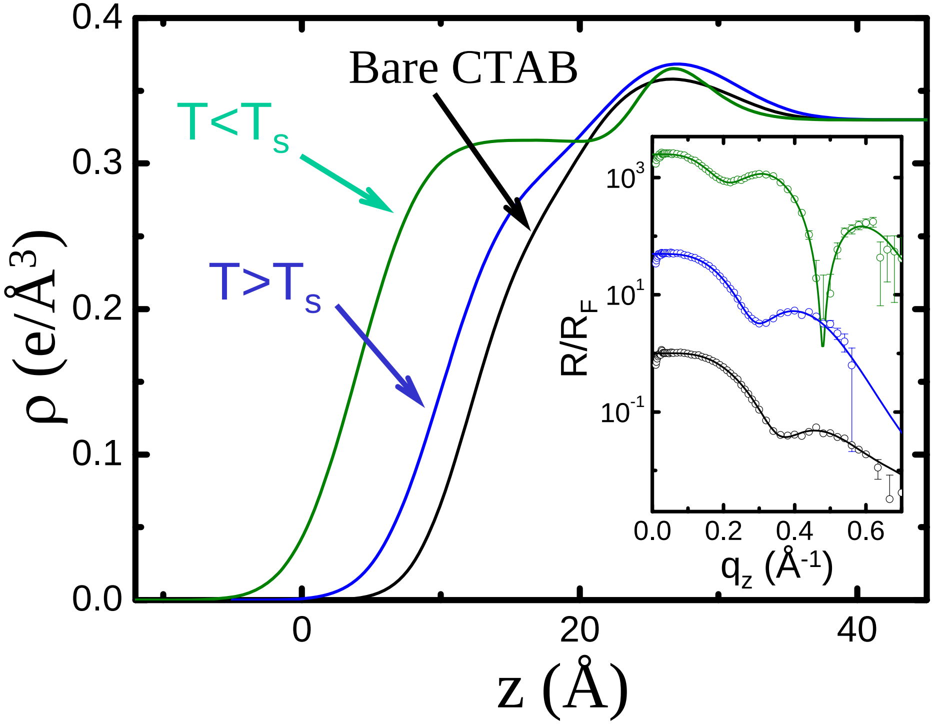




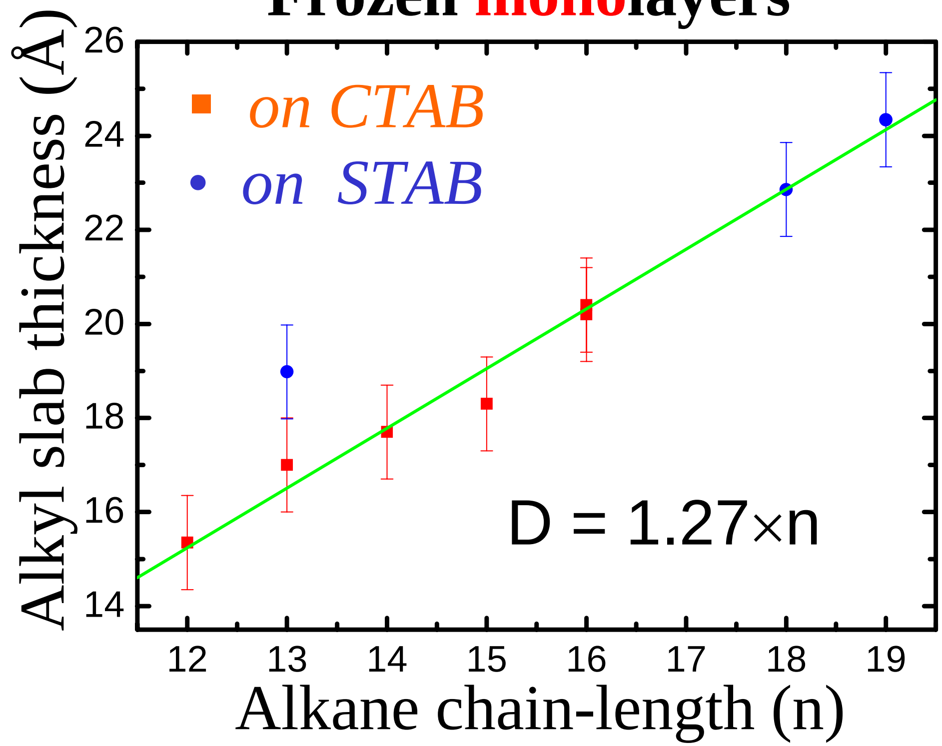
Fresnel-Normalized X-ray Reflectivity



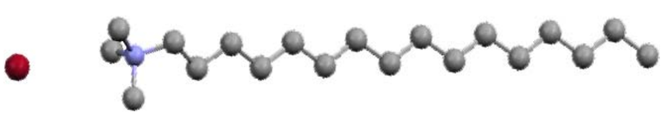
X-ray Reflectivity - Results



Frozen monolayers

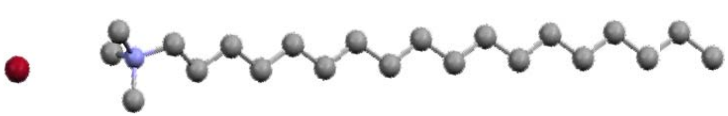


C_{16}TAB (CTAB)



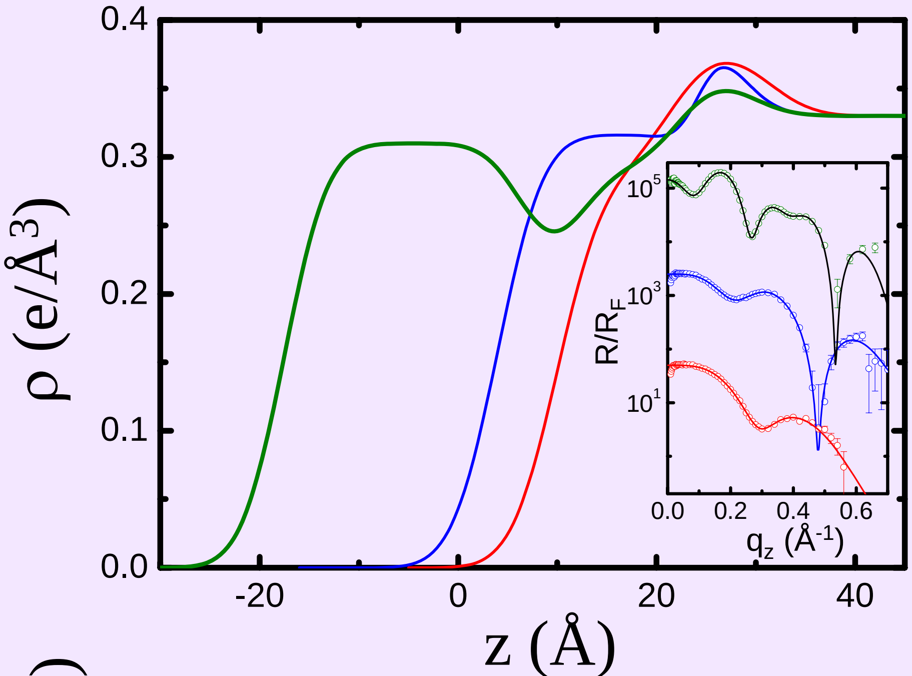
- Monolayers for alkanes with n≤17
- Mysterious “bilayers” for n > 17

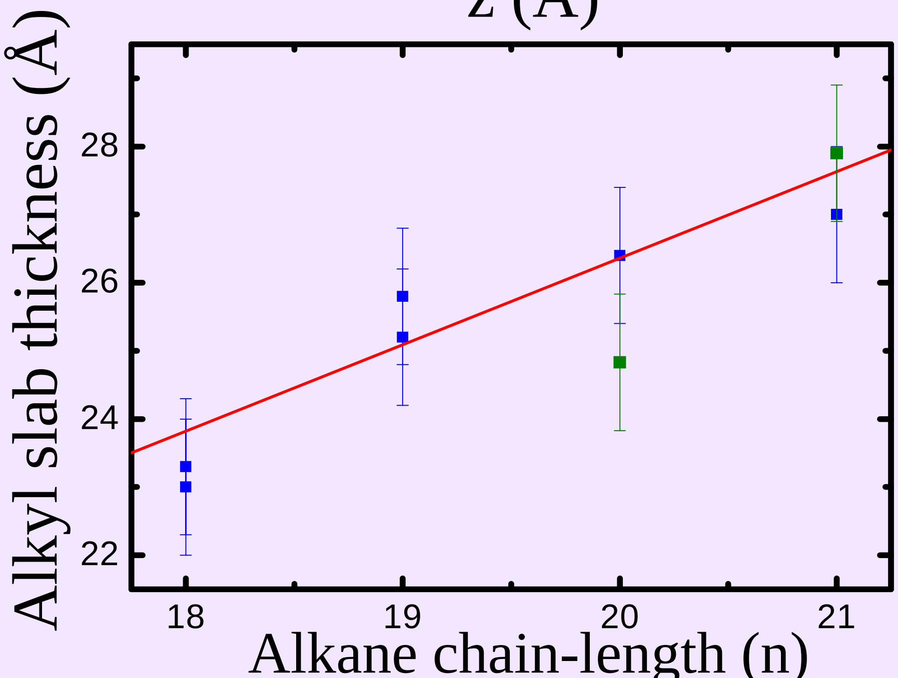
C_{18}TAB (STAB)



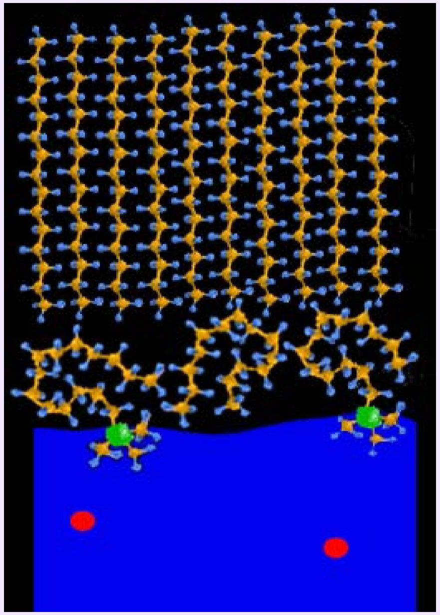
- Monolayers for alkanes with n ≤ 19
- Mysterious “bilayers” for n > 19

“Bilayers” mystery resolved

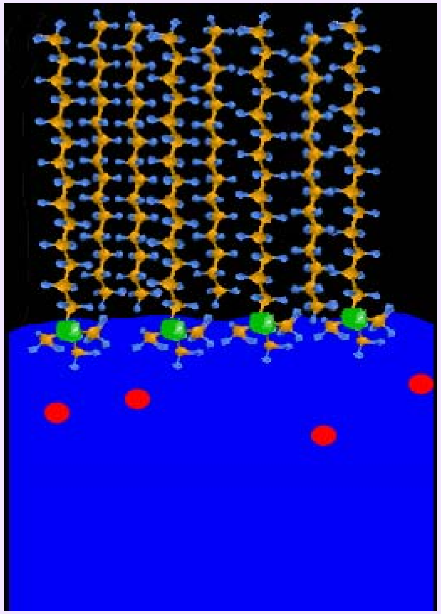




ΔS of a monolayer for all phases

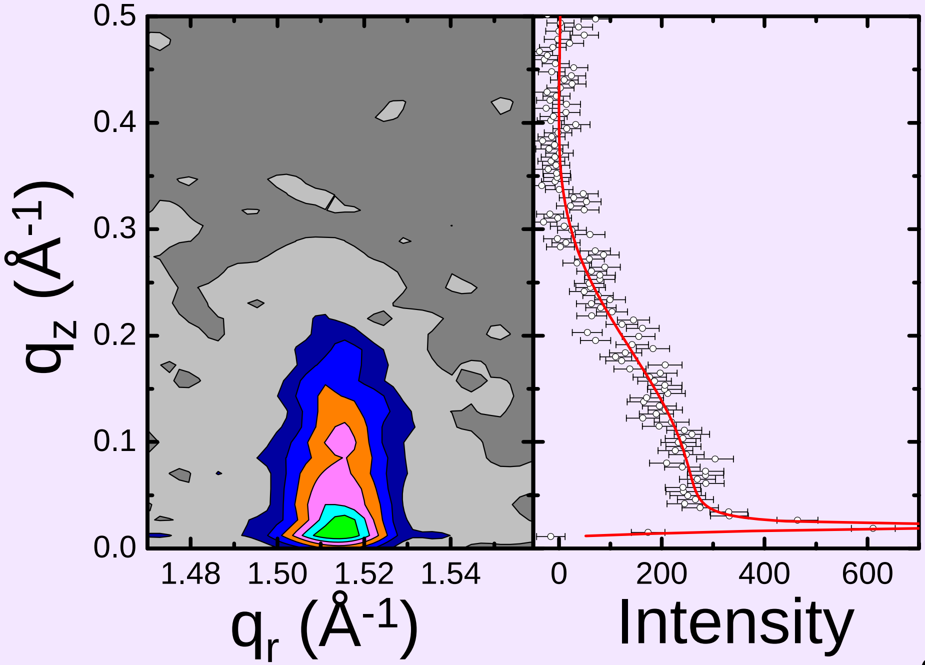


n > (m+1)

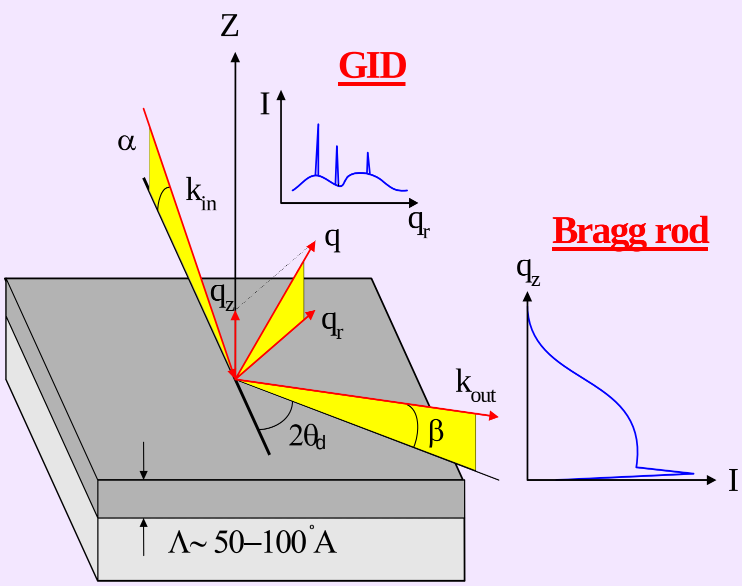


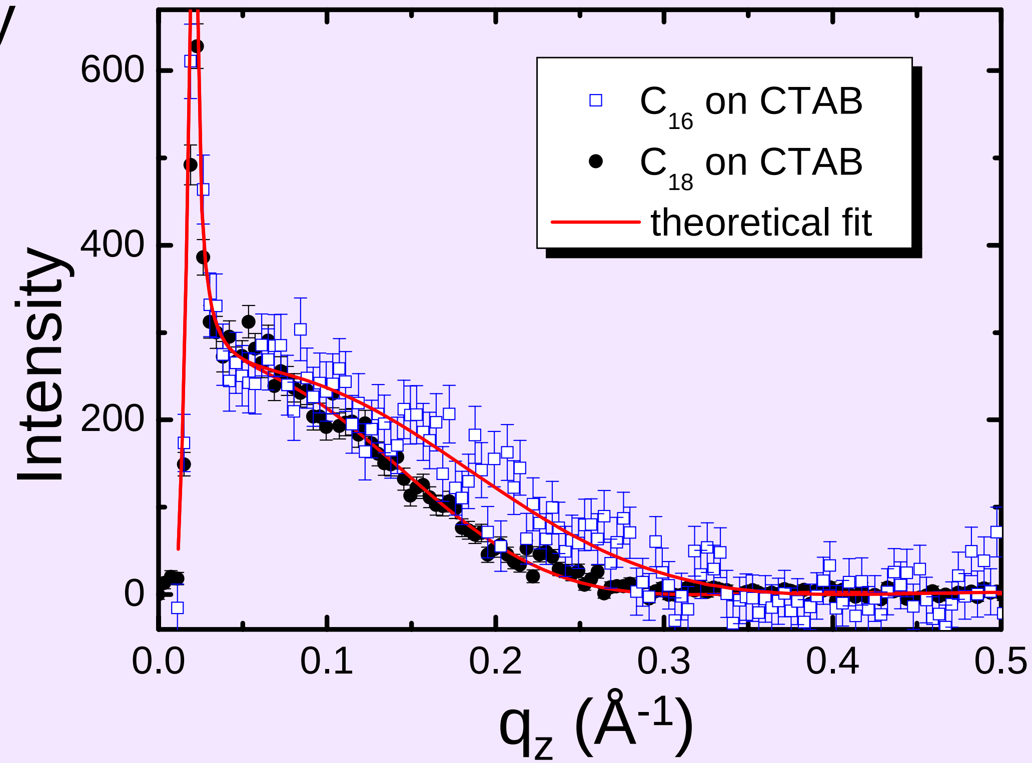
n≤(m+1)

Sloutskin et al., *PRL* **99**, 136102 (2007)

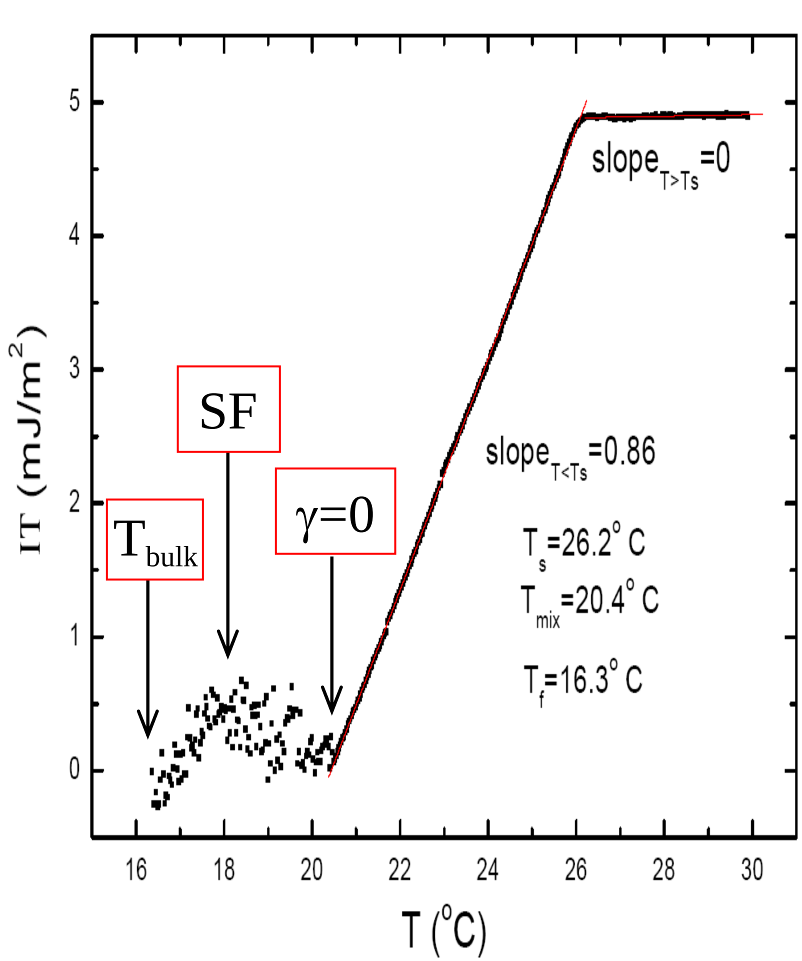


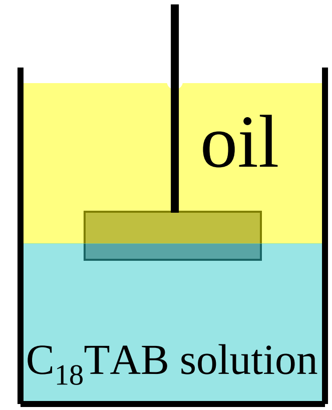
- **Surface normal molecules**
- **Hexagonal packing**
- **Single frozen layer in all phases**





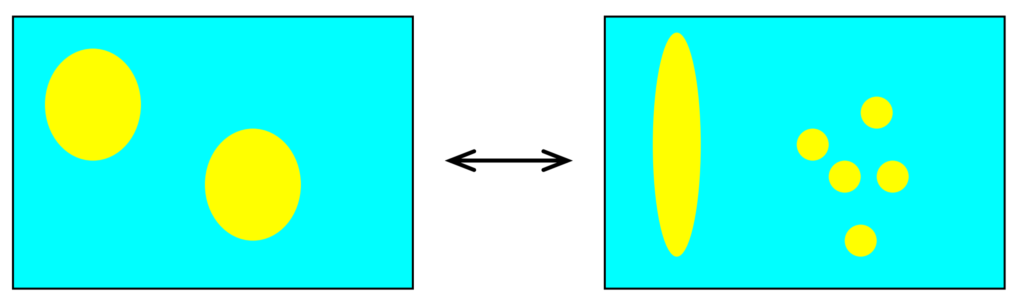
Interfacial freezing at a liquid-liquid boundary





- **Spontaneous emulsification, tunable by T.**
- **Emulsion stable.**
- **Small droplets preferred.**
- **Non-spherical droplets.**

Implication for bulk emulsions:



E. Sloutskin et al., *Faraday Discuss.* **129,** 339 (2005).

Interfacial freezing : The γ_i=0 region (visual)

$C_{16}/H_2O/C_{18}TAB$: **0.4 mM (nominal!) , 25°C (re-heated)**

10 μm

Conclusions

- Sub-mM concentrations of CTAB induce spreading of an alkane monolayer on water.
- Above T_s the monolayer is liquid.
- Below T_s , the molecules are ordered, vertically aligned, hexagonally packed, with large crystalline coherence lengths.
- The length mismatch between alkyl tail of CTAB determines the structure of a frozen LG film:
  - n-alkanes with $n \leq 17$ form monolayers
  - n-alkanes with $n > 17$ form bilayers
- LGF crystallization at the liquid-liquid interface induces spontaneous emulsification.

Thanks …

- **J. D. Baumert award committee.**
- **Audience at CFN/NSLS.**
- **Prof. M. Deutsch (Bar-Ilan University, Israel).**
- **Dr. B. M. Ocko (BNL, USA).**
- **Prof. C. D. Bain (Durham U., England).**
- **Z. Sapir (Intel, Israel)**
- **L. Tamam (Bar-Ilan University, Israel).**
- **S. Yefet (Bar-Ilan University, Israel).**