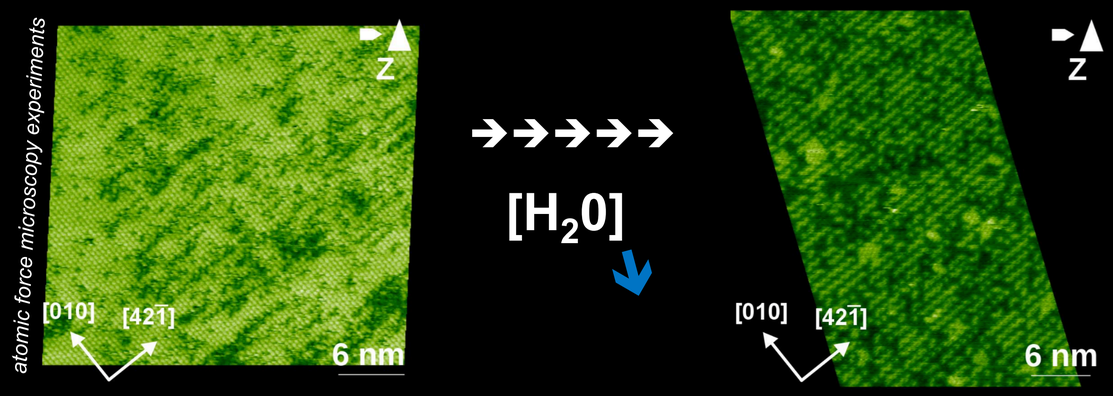
Ville Loukonen[1]
Peter Spijker[1]
Adam S. Foster[1]

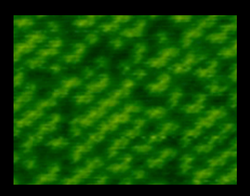
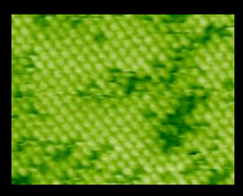
Felix Kling[2]
Ralf Bechstein[2]
Angelika Kühnle[2]

[1]*Department of Applied Physics, COMP Centre of Excellence, Aalto University, P.O. Box 11100, 00076 Aalto, Espoo, Finland*

[2]*Institut für Physikalische Chemie, Johannes Gutenberg Universität Mainz, Duesbergweg 10-14, 55099 Mainz, Germany*

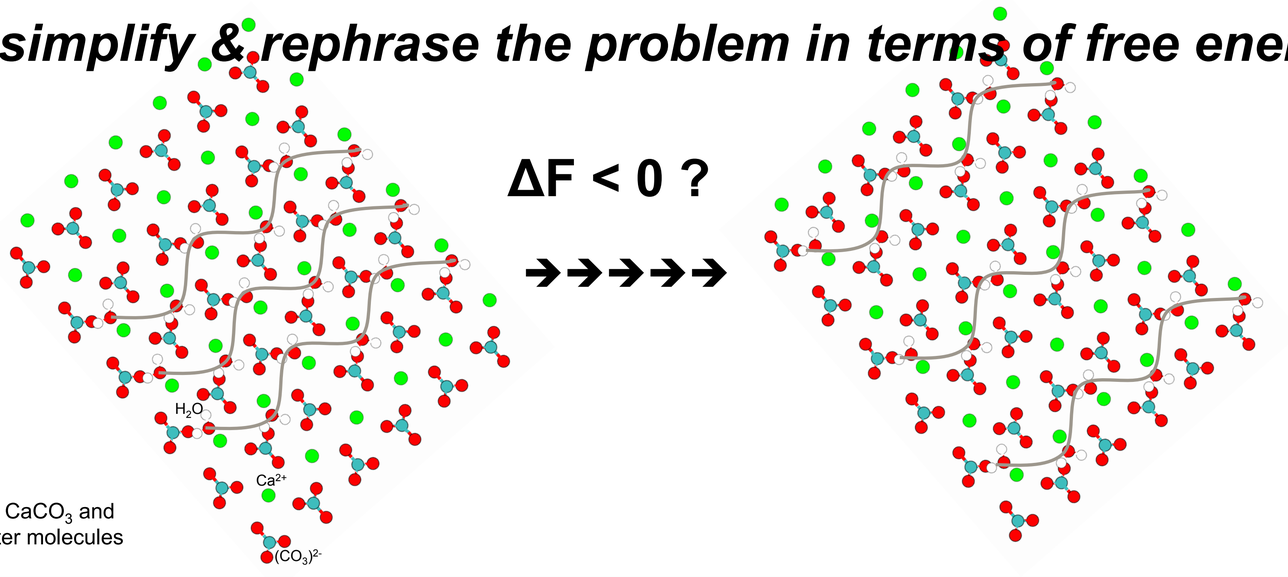
Entropy-driven self-assembly of water from first-principles?



Why this "sparse"  *rather than this* "dense"  *even at low* [H_2O]?

…an entropic effect?

simplify & rephrase the problem in terms of free energy



calcite $CaCO_3$ and 18 water molecules

ΔF < 0 ?

for a spontaneous transition, the free energy change **ΔF** is negative:

ΔF = ΔE – TΔS < 0

➔ **ΔS > ΔE/T**

ΔX = X(sparse) – X(dense)

	ΔE	ΔS	ΔF = ΔE – TΔS
free energy truth table	negative	positive	always negative! best scenario!
	negative	negative	not entropically favored
	positive	positive	not energetically favored
	positive	negative	always positive! no transition!

in these cases ΔS > ΔE/T determines what happens ➔➔➔ *ΔE is easy to evaluate, ΔS very non-trivial!*

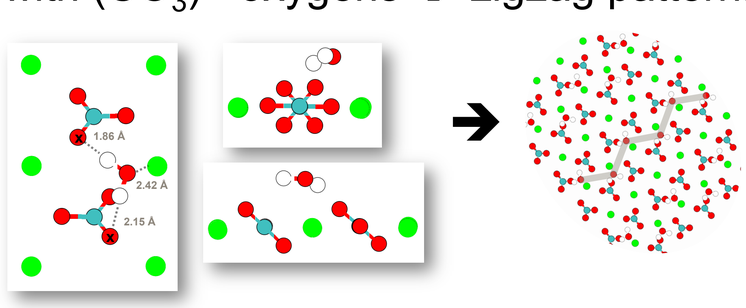
T=0 K – *energetics without entropy*

ΔE = +0.11 eV
➔ "dense" state is slightly favoured, but only slightly

adsorption energy E_{ads} ~ 1 eV
➔ agrees well with experimental extrapolation to T=0 K limit

bonding patterns

Ca^{2+} ions accommodate water oxygens and water hydrogens try to bond with $(CO_3)^{2-}$ oxygens ➔ zigzag pattern!



computational details

PBE-D3/DZVP/500 Ry,
four layers of calcite
+ 18 waters = 720 atoms,
0.5 fs timestep in MD runs,
2 ps of equilibrium simulations
at T = 300 K

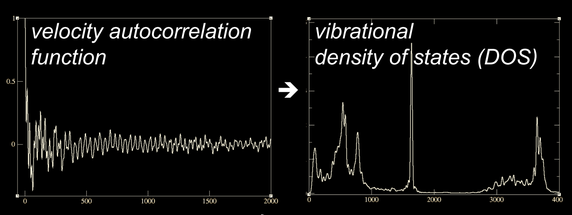
www.CP2K.org

T=300 K – *include thermal motion*

ΔE = -0.22 eV
➔ now the "sparse" state is slightly favoured, but again, only slightly

approximating entropy†

vibrational modes are independent quantum harmonic oscillators



➔ $\ln[Z] = \int \mathrm{DOS}(\omega)\ \ln[z_{qho}]\ d\omega$

➔ $S = k_B \ln[Z] + k_B T \partial_T \ln[Z]$

†Lin et al., *J. Chem. Phys.*, **119**, 11792-11805, 2003

➔ **ΔS** = +0.17 meV/K
➔ *best case scenario! however*
…very small differences,
this yields **ΔF** ~ -0.3 eV
…need longer trajectories

ville.loukonen@aalto.fi

This work was supported by the Academy of Finland through its Centres of Excellence Programme (2012-2017) under Project No. 251748.

CSC – IT Center for Science is acknowledged for computing time and services