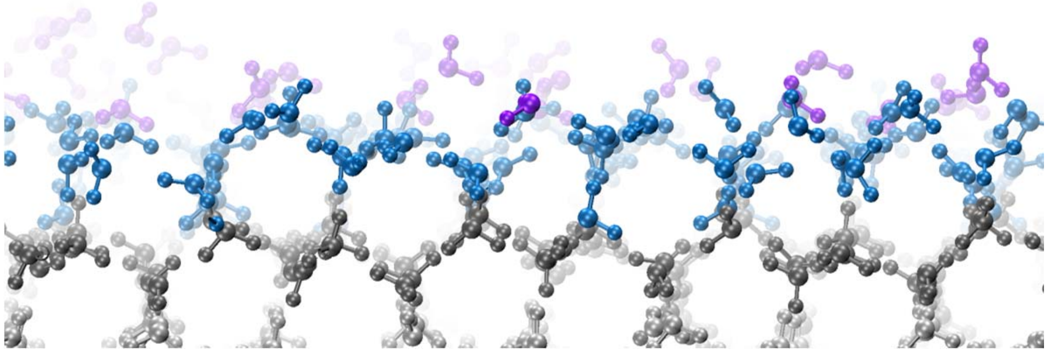
Molecular Dynamics Study of Basal, Prismatic, and Pyramidal Surfaces of Ice



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QLL

(surface premelting of pure ice)

- Surface premelting predicted by all water models in computer simulations (liquid-like layer develops spontaneously at the free surface of ice well below the melting point)
- QLL thickness <u>independent of water model</u> when compared at the same undercooling relative to the melting point of the model

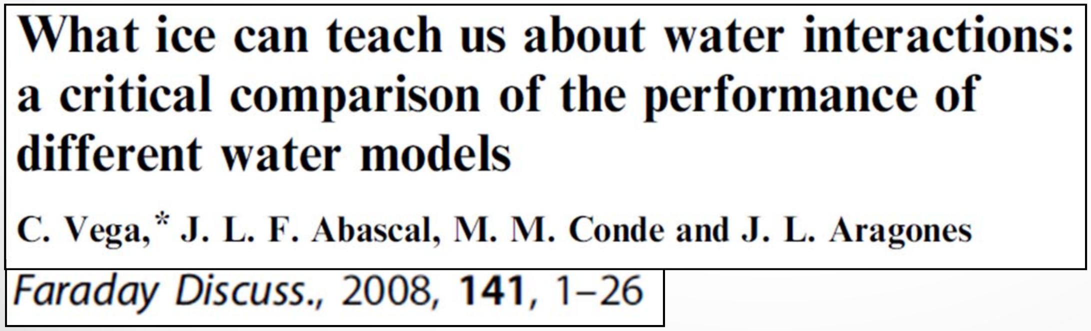
THE JOURNAL OF CHEMICAL PHYSICS **129**, 014702 (2008)

The thickness of a liquid layer on the free surface of ice as obtained from computer simulation

M. M. Conde,[1] C. Vega,[1,a)] and A. Patrykiejew[2]

[1]*Departamento de Quimica Fisica, Facultad de Ciencias Quimicas, Universidad Complutense, 28040 Madrid, Spain*

[2]*Faculty of Chemistry, MCS University, 20031 Lublin, Poland*

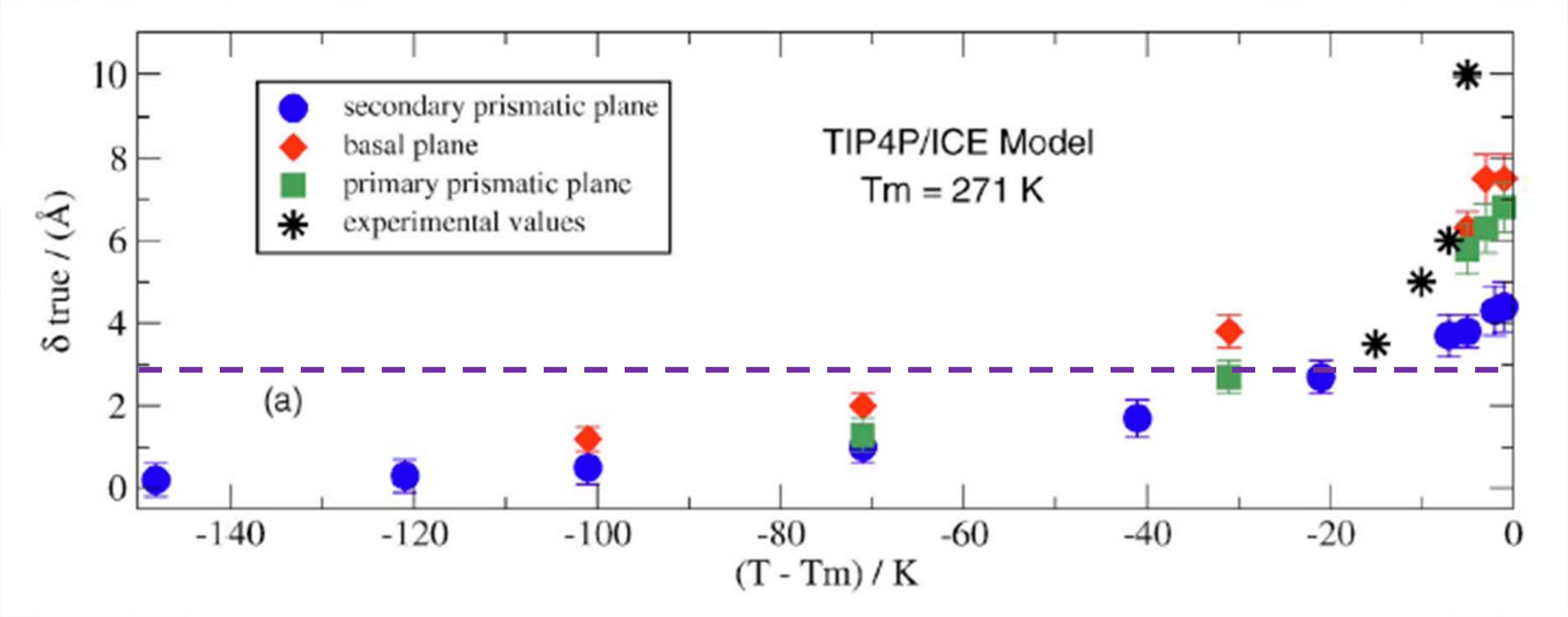


What ice can teach us about water interactions: a critical comparison of the performance of different water models

C. Vega,* J. L. F. Abascal, M. M. Conde and J. L. Aragones

Faraday Discuss., 2008, **141**, 1–26

Thickness of QLL as a function of T

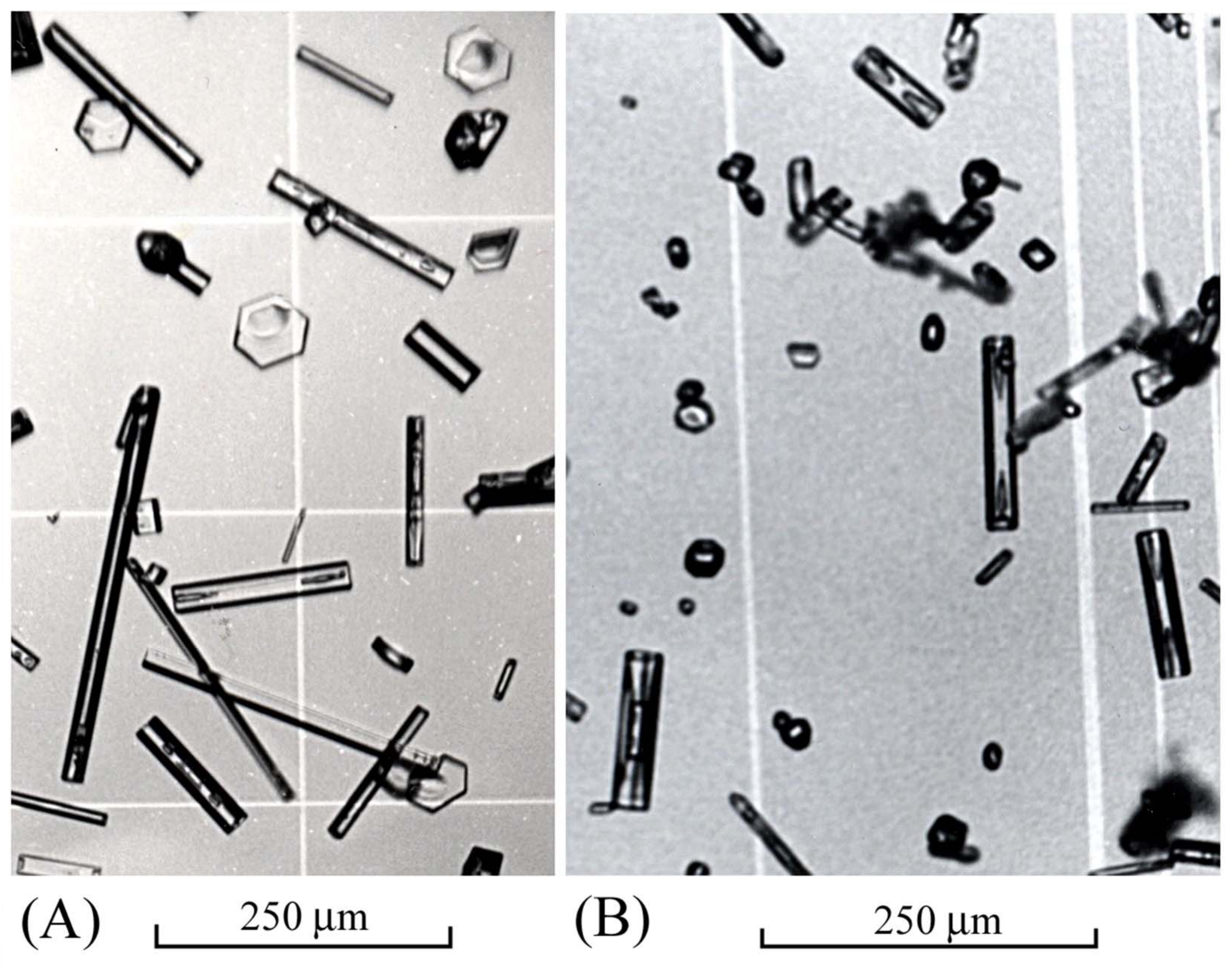


Conde, Vega, Patrykiejew (J. Chem. Phys. 2008)
* Experimental values by Bluhm et al. (J. Phys.: Condens. Matter 14, L227, 2002)

"liquid-like = molecules feel the underlying solid"

- QLL appearance starts at different temperatures depending on the ice facet exposed to vapor phase.
- At given T, the thickness of QLL differs for different ice facets.

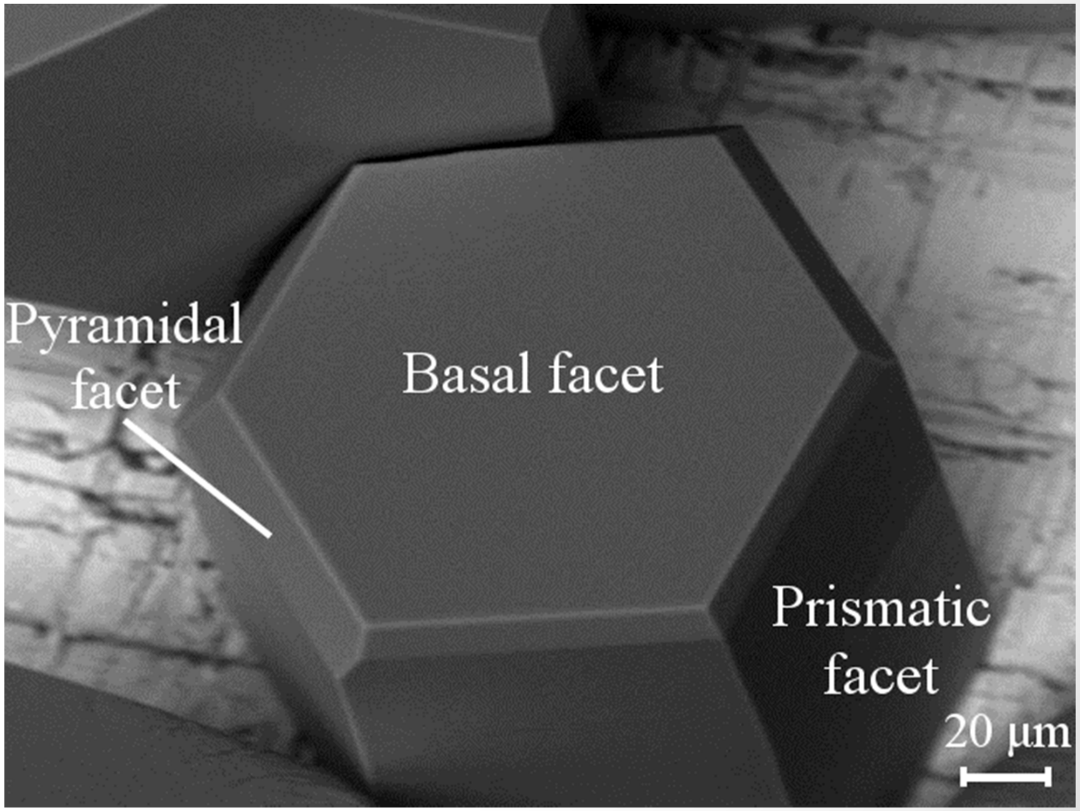
Cirrus ice crystals



(Walden *et al*. 2003)

Ice crystals grown by vapor deposition

- basal (0001)
- prismatic (10$\underline{1}$0)
- 28° pyramidal (10$\underline{1}$1)
- 14° pyramidal (20$\underline{2}$1)

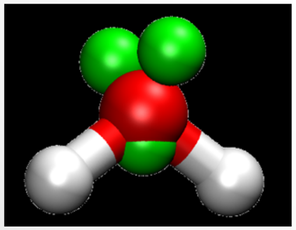


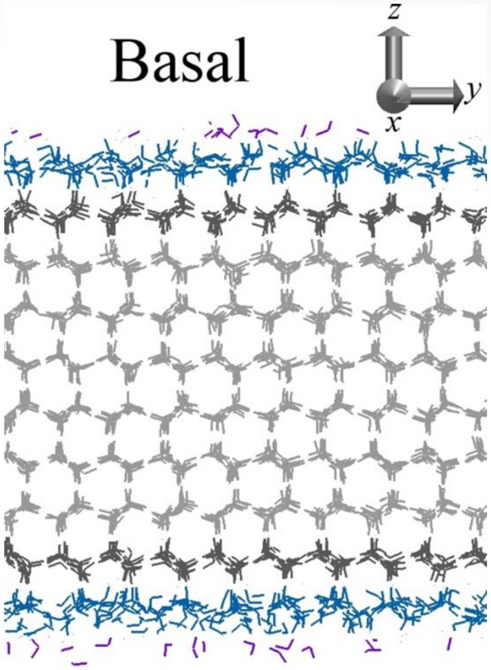
VP-SEM image

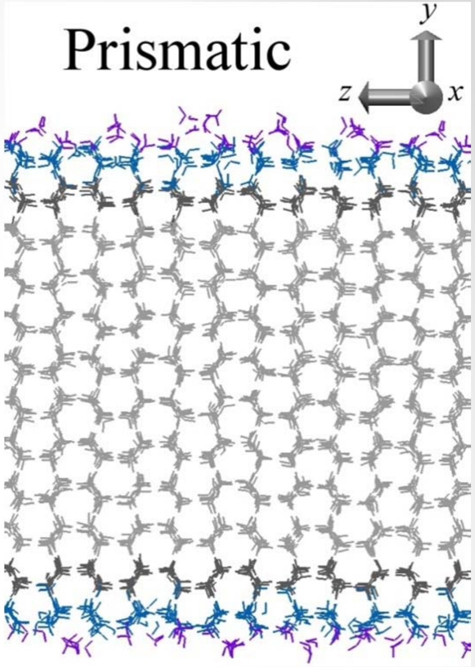
Pfalzgraff, Hulscher, & Neshyba, *Atmospheric Chemistry and Physics*, **2010**, *10*, 2927

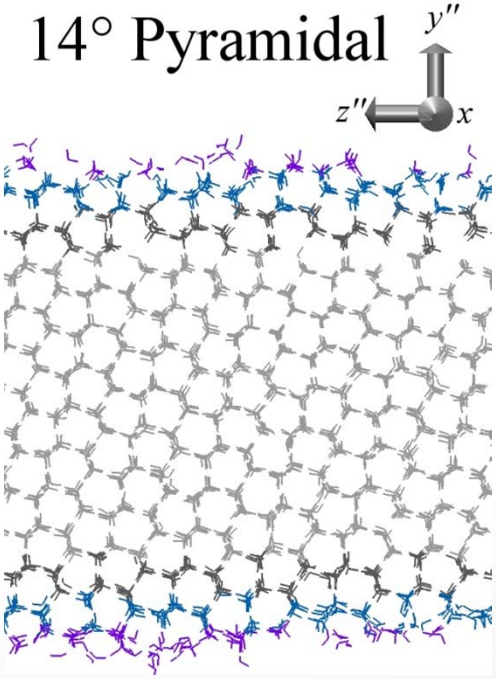
MD simulations

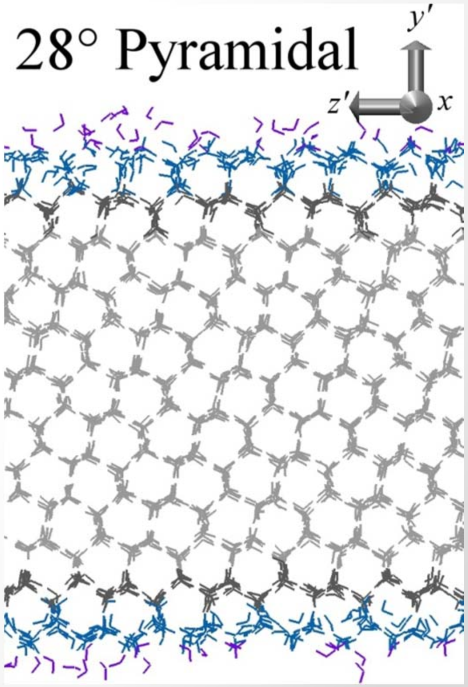
- Ice I_h slab
- 2880/3456 H_2O molecules
- Ice block dimensions:
  x, y, z ~ 4 – 6 nm
- 6-site water model
  Nada, van der Eerden,
  J. Chem. Phys. 2003, 118, 7410
- T_m = 289 K
  Abascal et al.,
  J. Chem. Phys. 2006, 125, 166101
- **T = 250 K** (~ -40 K)




Basal

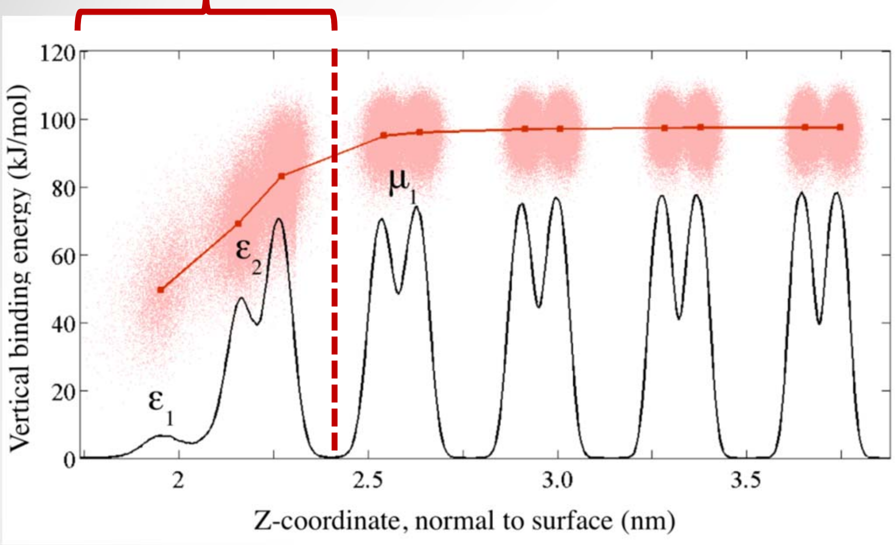

Prismatic


14° Pyramidal

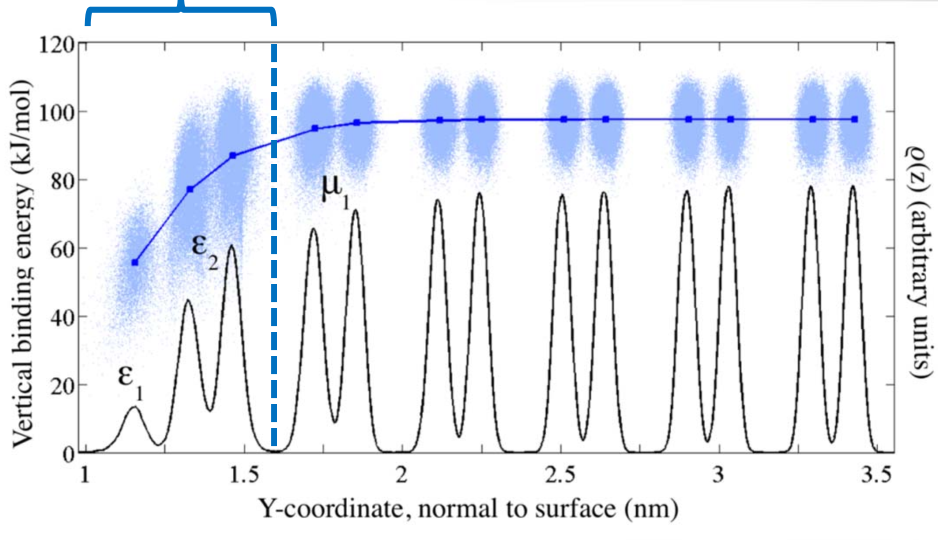

28° Pyramidal

Density profiles and vertical binding energies

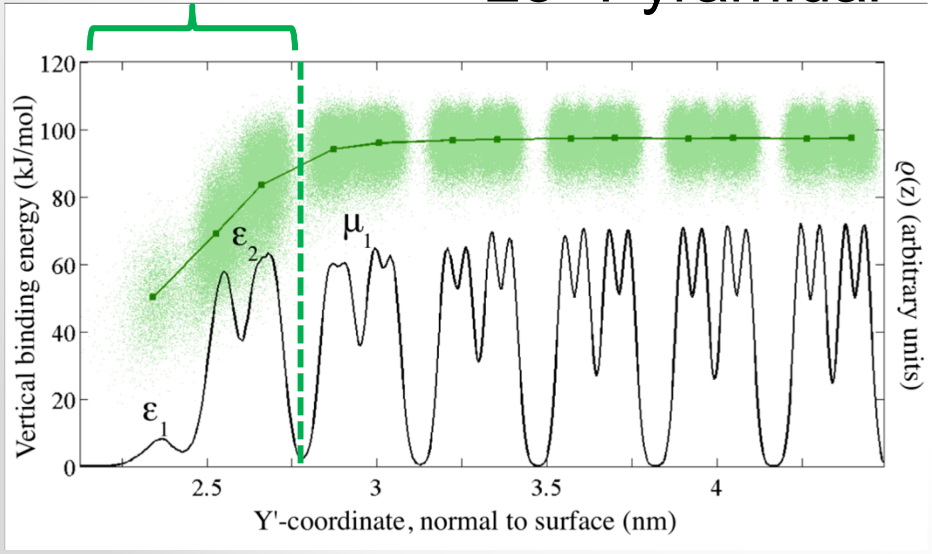
QLL (0.67 nm) Basal



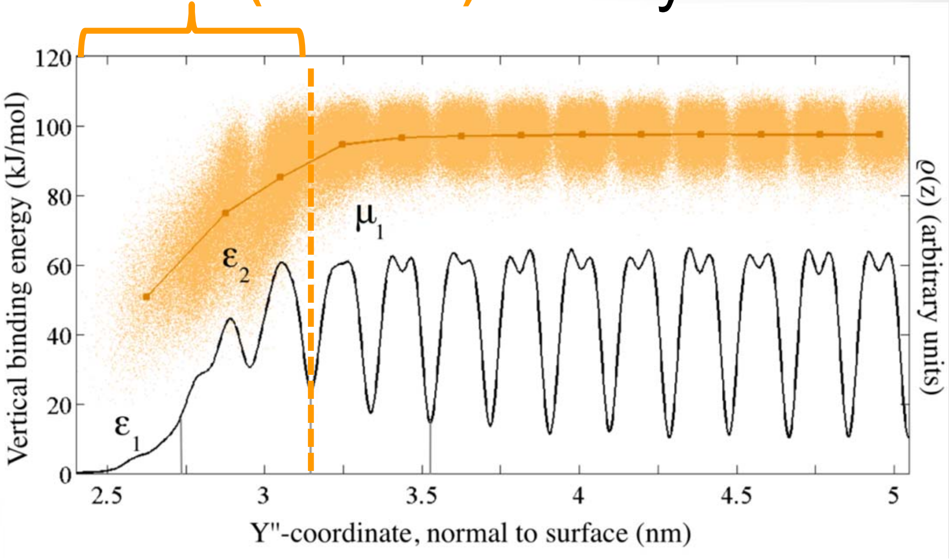
QLL (0.61 nm) Prismatic



QLL (0.63 nm) 28º Pyramidal

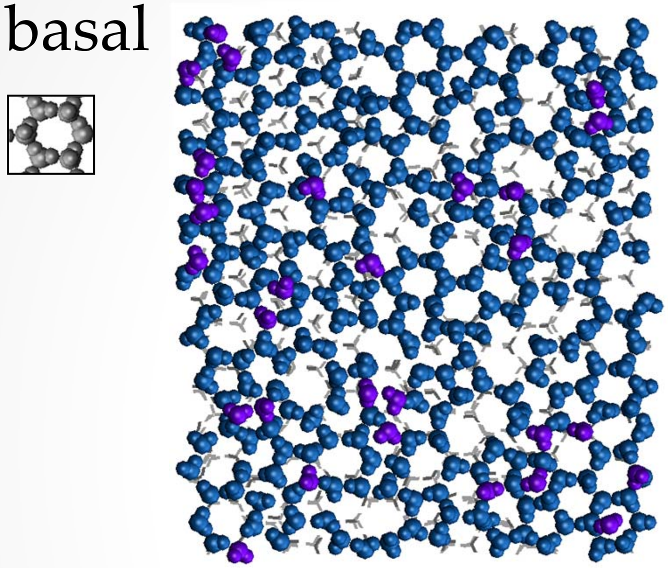


QLL (0.84 nm) 14º Pyramidal

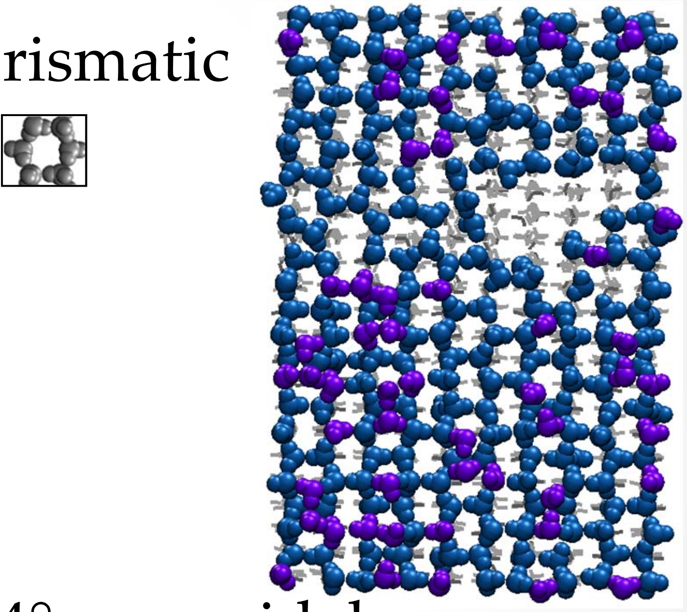


Top view

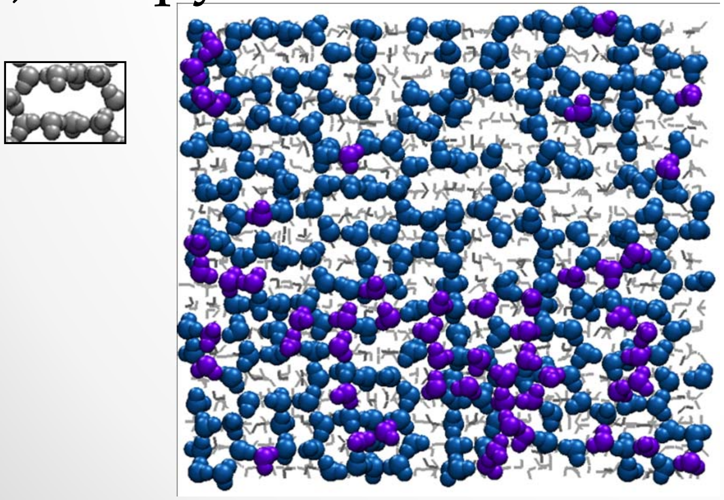
(a) basal



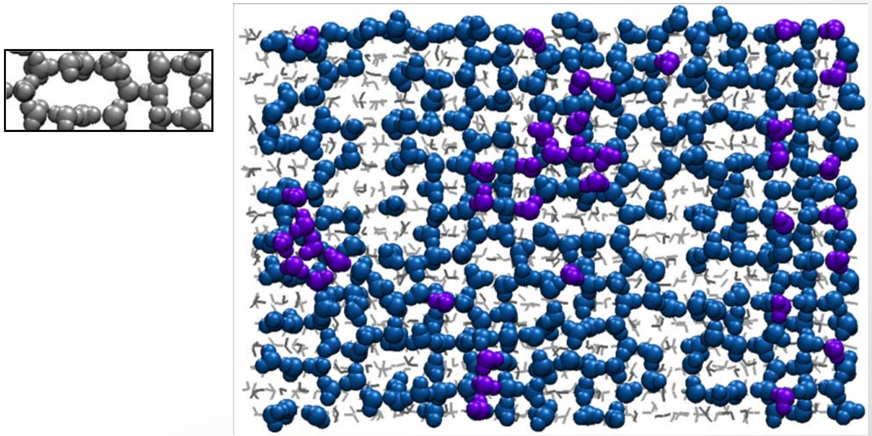
(b) prismatic



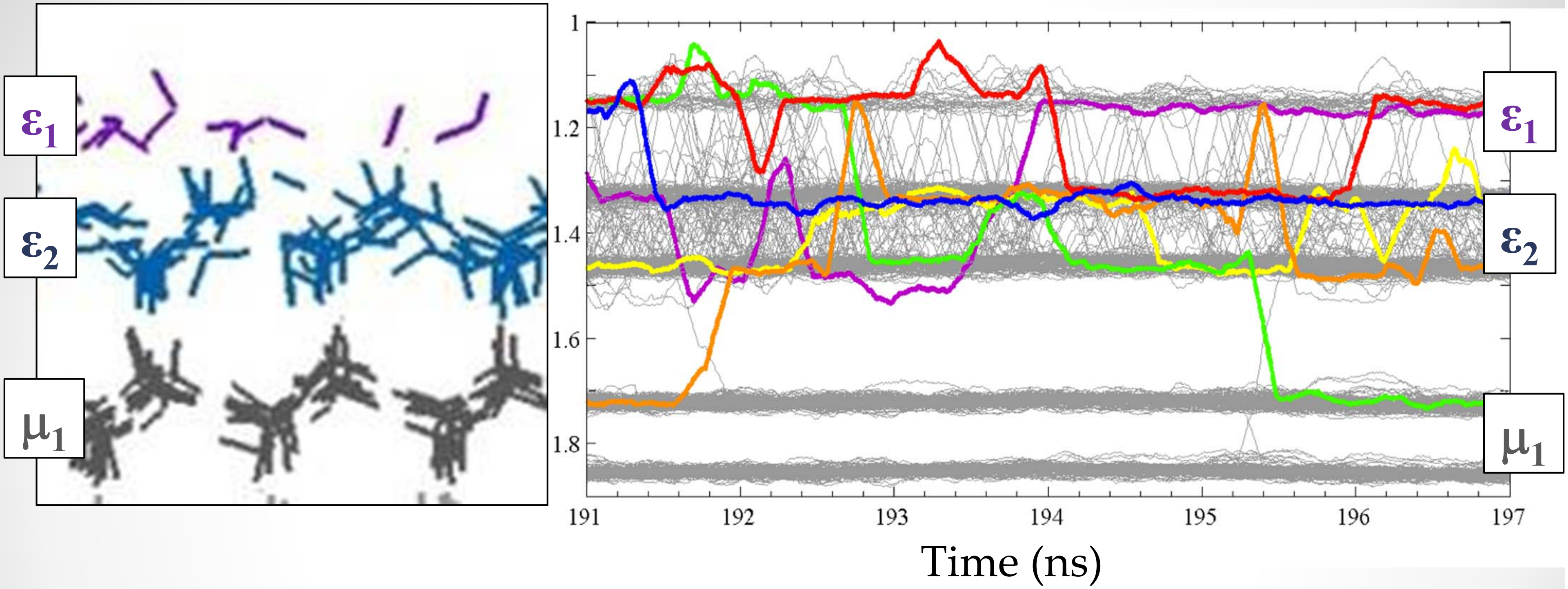
(c) 28° pyramidal



(d) 14° pyramidal



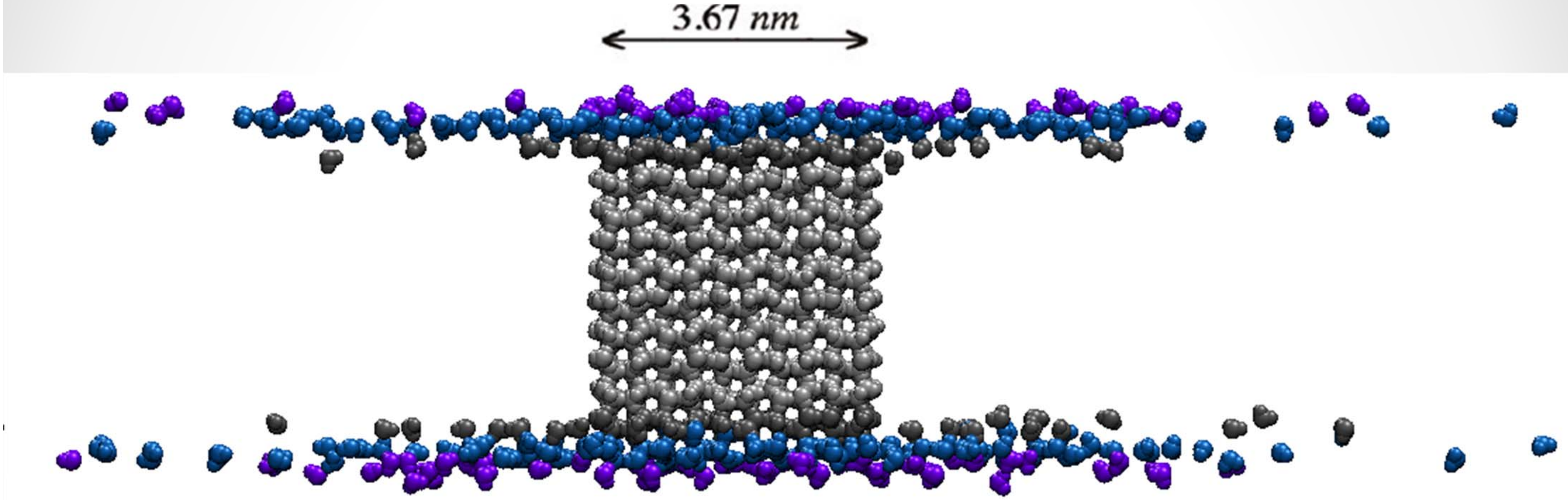
Inter-layer transitions



- $\varepsilon_1 \leftrightarrow \varepsilon_2$ mixing time (ε_2 "survival" time) ~ 10 ns
- Binary exchanges QLL ($\varepsilon_1 + \varepsilon_2$) ↔ μ_1 …char. time ~ 10^2 ns
- Important for surface diffusivity

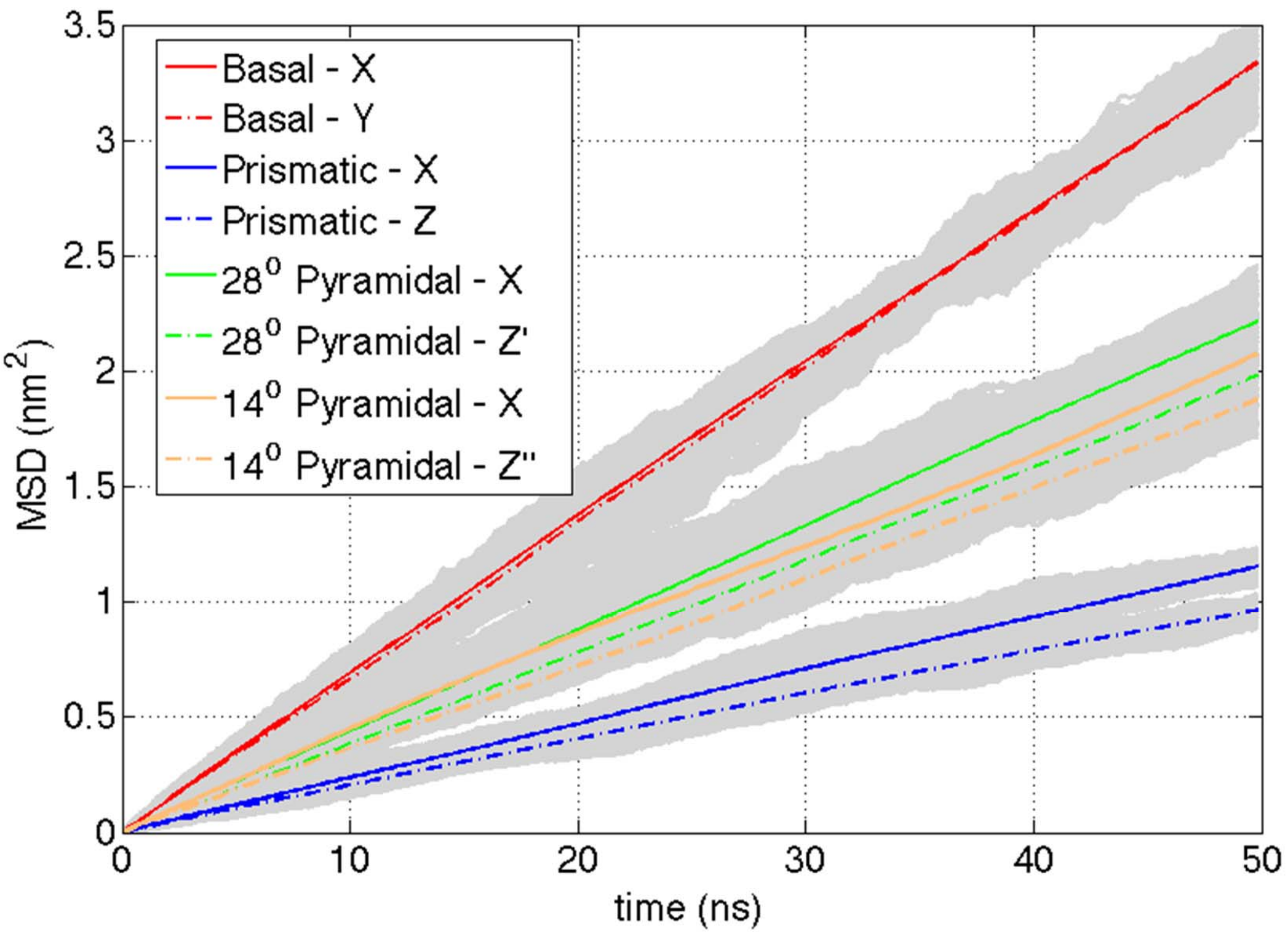
  Bolton and Pettersson, J. Phys. Chem. B 2000, 104, 1590
- Time scales facet-specific

Surface diffusion



Prismatic surface after 100 ns, viewed along the secondary prismatic axis. Molecules crossing periodic boundaries are depicted in neighboring domains.

Mean squared displacement



1-D diffusivity on ice surfaces

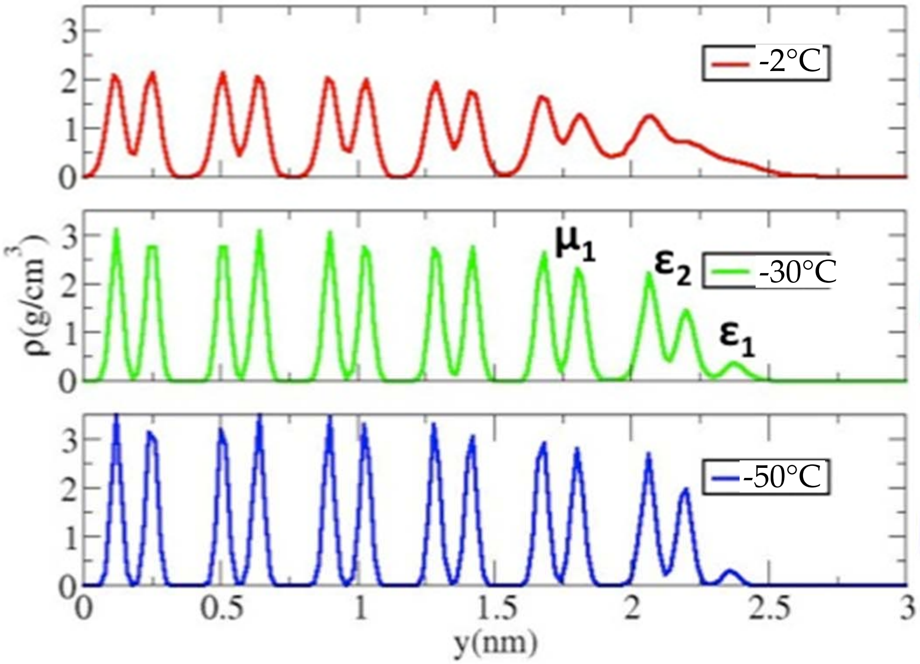
Facet exposed	Direction of diffusion	Q	1-D diffusivity, D^* ($cm^2/s \times 10^{-6}$)	Diffusion length, x_s (nm)
Basal	x	1/5	1.67	14.3
	y	1/5	1.68	14.3
Prismatic	x	1/6	0.70	9.9
	z	1/6	0.58	9.0
28º Pyramidal	x	1/6	1.34	15.1
	z'	1/6	1.20	14.3
14º Pyramidal	x	1/6	1.21	12.5
	z''	1/6	1.13	12.0

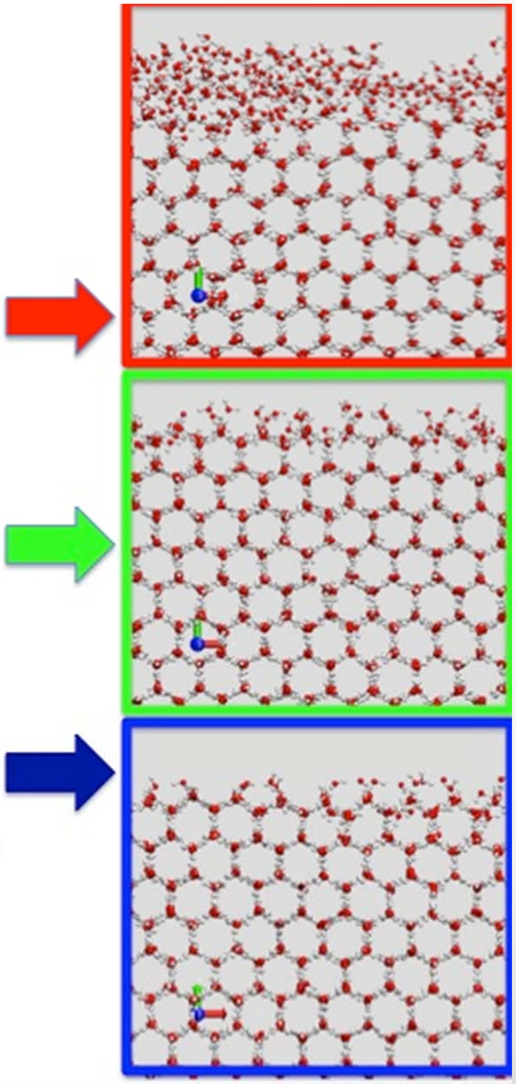
experiment - liquid water: $D = 1.6 \times 10^{-6}\ cm^2/s$ (-35°C)
$D = 12.0 \times 10^{-6}\ cm^2/s$ (0°C)
$D = 18.9 \times 10^{-6}\ cm^2/s$ (20°C)

Price et al., J. Phys. Chem. A **1999,** *103,* 448-450

Work in progress: Temperature dependence of diffusivity

Arrhenius analysis to determine the activation energy





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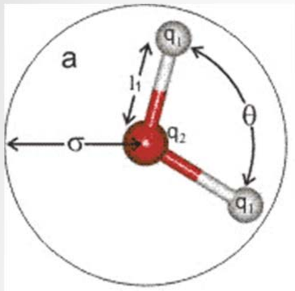
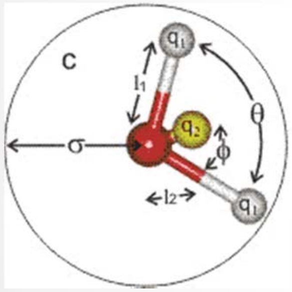
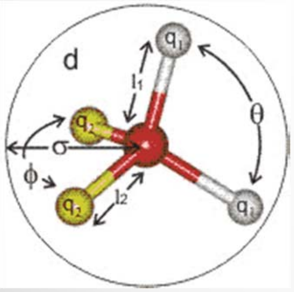
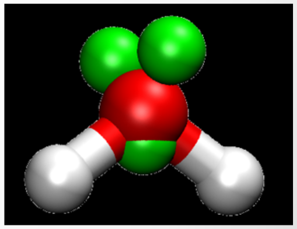






Water model	Melting temperature (K)
TIP3P	145
SPC	190.5
SPC/E	215
TIP4P	230
TIP4P/Ew	243
TIP4P/Ice	271
TIP5P	272
NE6	275 (289)
Expt.	273.15



Vega et al., Mol. Phys. 2006, 104, 3583
García Fernández et al., J. Chem. Phys. 2006, 124, 144506