Simulations of ice using distributed computing

Andreas Pedersen, Jean-Claude Berthet and Hannes Jónsson
University of Iceland

Motivation
Methods
- Minimum-Mode Following
- Adaptive kinetic Monte Carlo

Three hexagonal (0001) ice surfaces

Water-Ice

Rich number of possible phases (more than 10). Hexagonal phase most stable at ambient conditions

Hexagonal Ice (I_h)

- Oxygen in hexagonal lattice
- Ice rule
  - 4 hydrogen bonds
  - No dipole moment
- Protons are disordered

Wide area of interest :

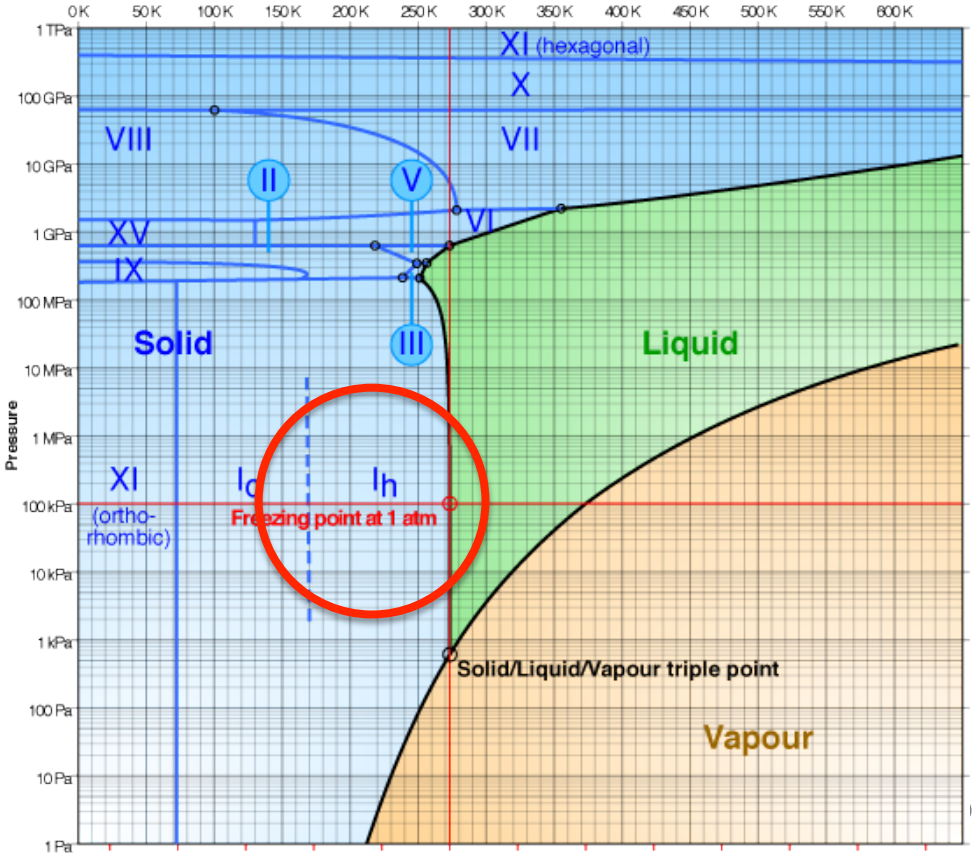
- Biology, Chemistry, Geology, Glaciology, …

Astronomy:

- Cold environment < 200 K
- HTST applies

Adaptive kinetic Monte Carlo:

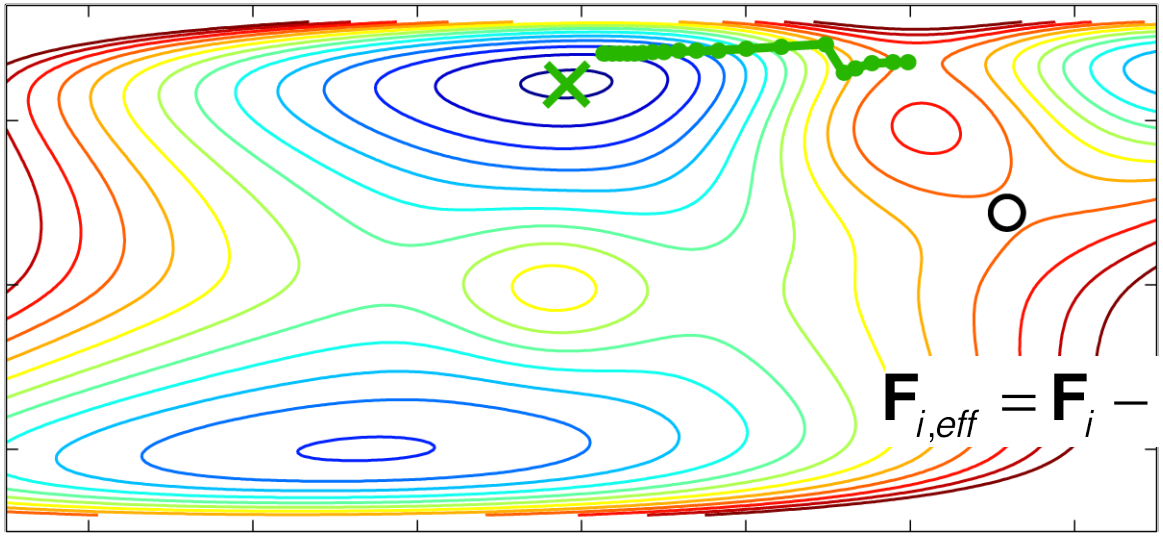
- Molecular system



Minimum-Mode Following Method

Minimum-Mode Following Method

- Displace system, using Gaussian random distribution
- A climb guided by the Hessian's Minimum-Mode
  - Minimum-Mode can be estimated using dimer or lanczos method
  - Hessian, matrix of second order derivative of the energy
- Locating Saddle Points in an unbiased way



$$\mathbf{F}_{i,eff} = \mathbf{F}_i - 2\left(\mathbf{F}_i \cdot \hat{\mathbf{v}}_{i,low}\right)\hat{\mathbf{v}}_{i,low}$$

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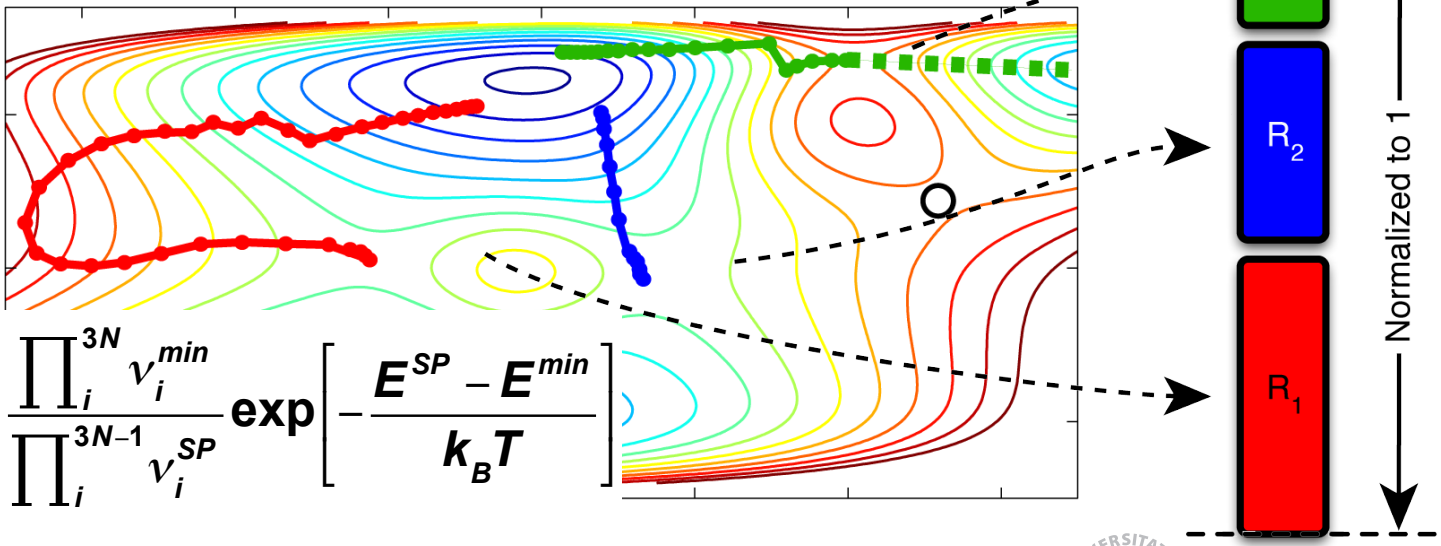
Ref: G. Henkelman and H. Jónsson, J. Chem. Phys. 111, 7010 (1999)

Adaptive Kinetic Monte Carlo

- Obtain Table of Events
  - Locate Saddle Point
  - Slide down Potential Energy Surface, to determine product
  - Rate for this mechanism estimated using HTST
- KMC pick among mechanisms



$$k^{HTST} = \frac{\prod_i^{3N} \nu_i^{min}}{\prod_i^{3N-1} \nu_i^{SP}} \exp\left[-\frac{E^{SP} - E^{min}}{k_B T}\right]$$

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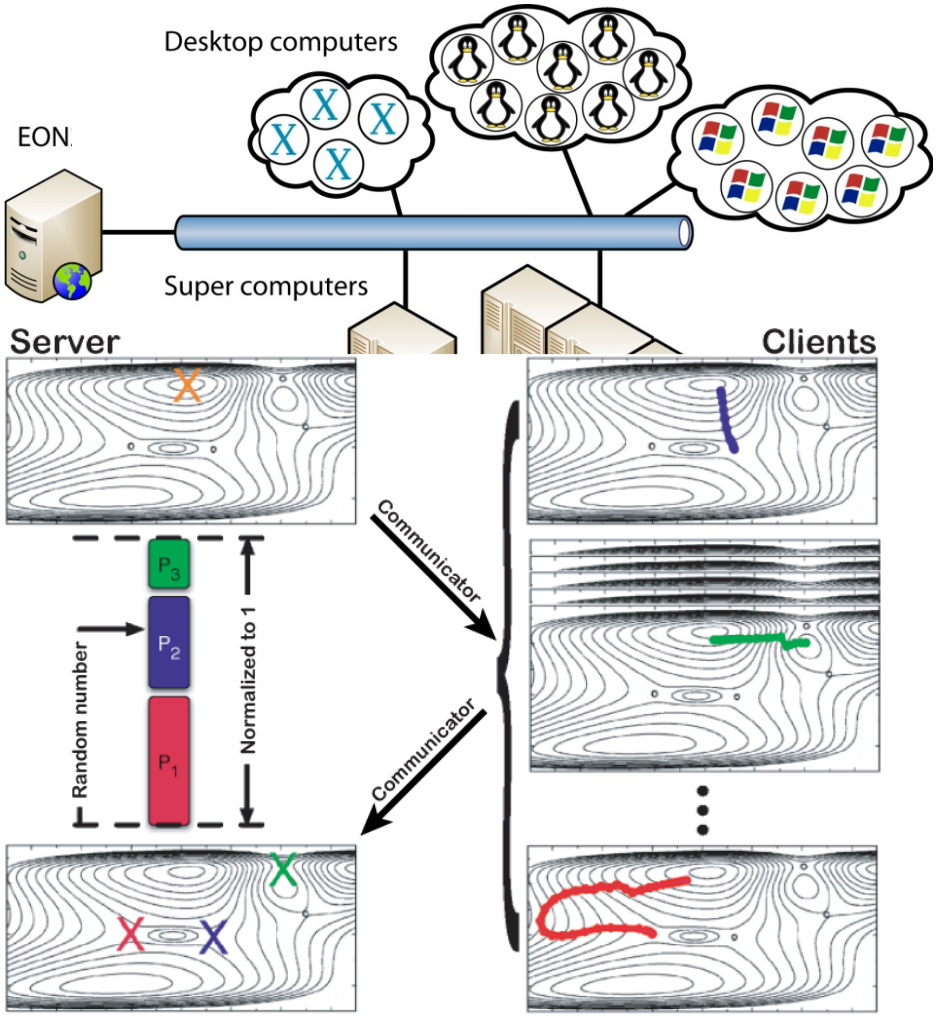
Ref: G. Henkelman and H. Jónsson, J. Chem. Phys. 115, 9657 (2001)

EON software

- Distributed implementation of the adaptive kinetic Monte Carlo method
  - SP search only relies on the initial displacement
  - A search should take more than 5 min.
- Communicators
  - BOINC
  - NORDUgrid
  - Amazon EC
- Implemented at U. Iceland in a collaboration with Henkelman research group (U. Texas, Austin)



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Ref: A. Pedersen and H. Jónsson, Math. Comput. Simulat. 80, 1487 (2010)

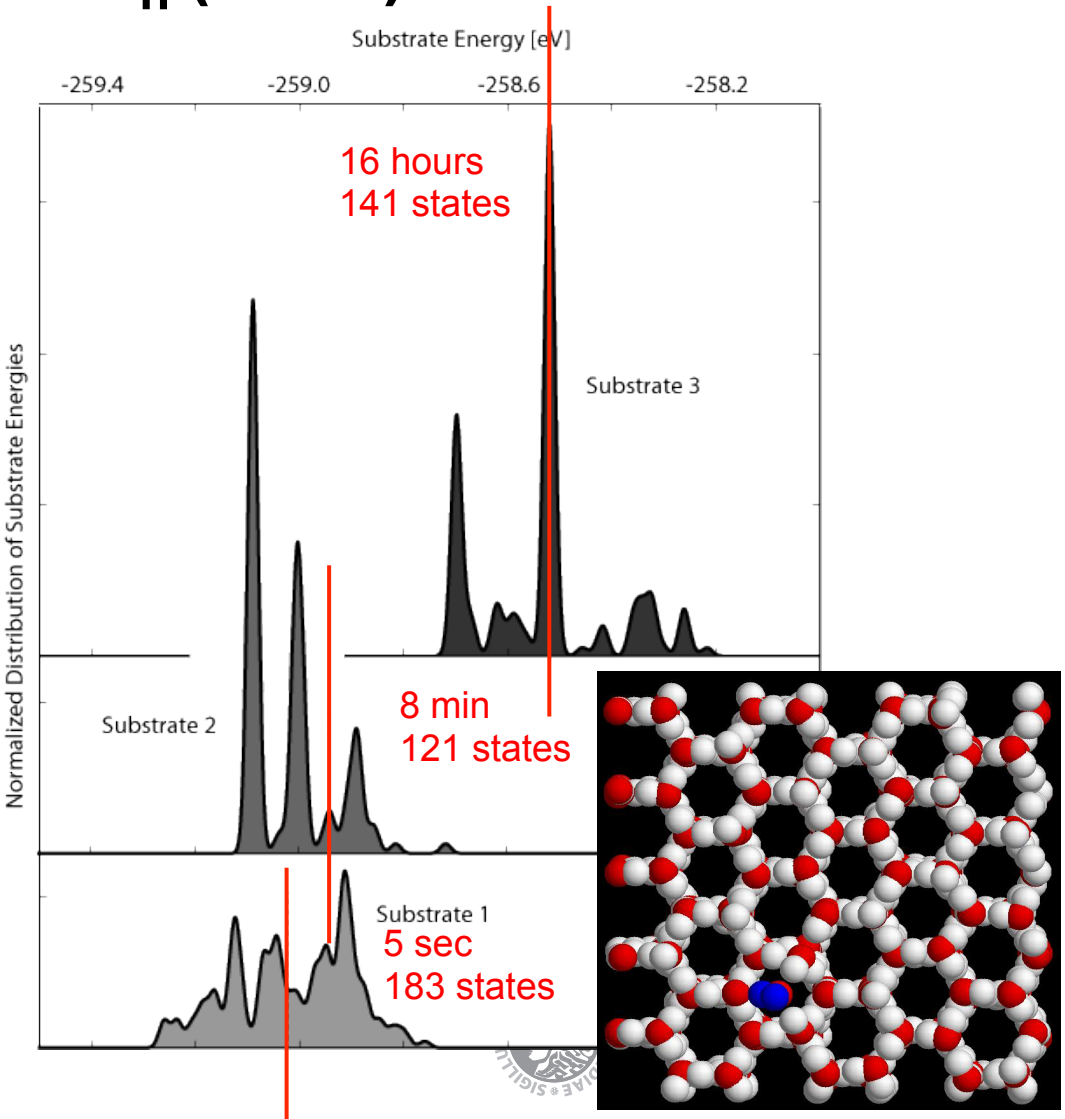
Add H_2O Molecule on I_h (0001) Surfaces

Min-mode estimation Lanczos

Atomic interactions
- TIP4P Inter-molecular
  - Cut-off 10 Å
  - Switching region 1 Å
  - Non-constrained
- CCL Intra-molecular

Three substrates
- 1 add-water molecule
- 360 substrate molecules
  - Surface area 23 Å X 22 Å
  - Bottom bi-layer frozen
  - 3 surface bi-layers free

Temperature 100 K



Annealing, I_h (0001) Surface

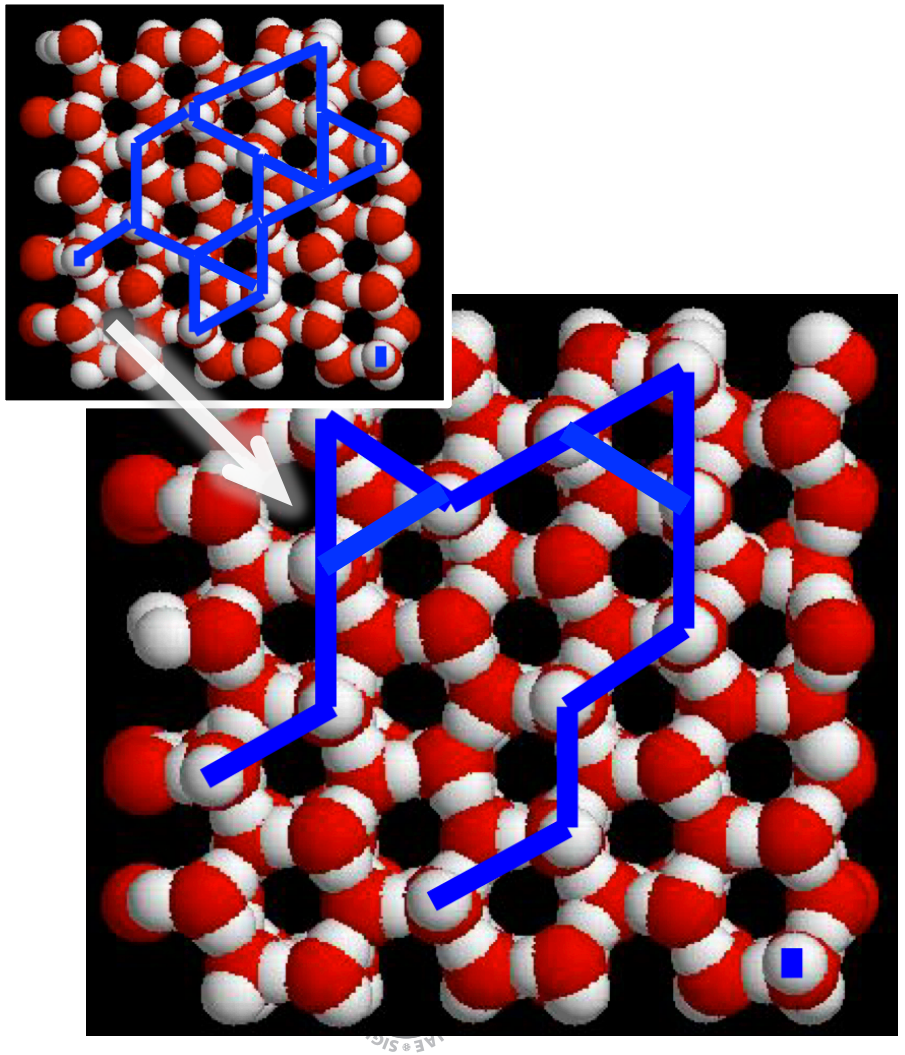
Transformation of surface

Dangling protons (charged) rearrange to decrease the number of nearest neighbors

Blue lines mark dangling protons

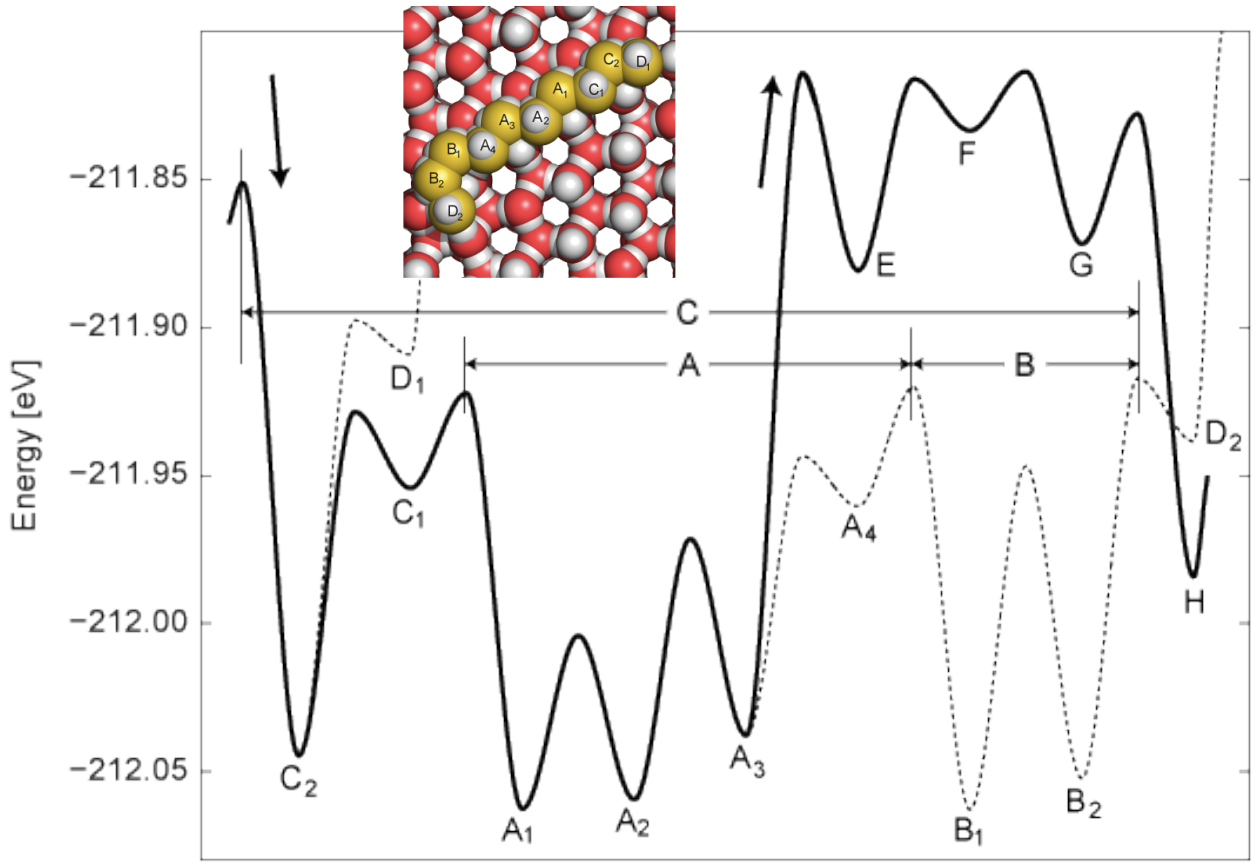
From area-like ‘disordered’

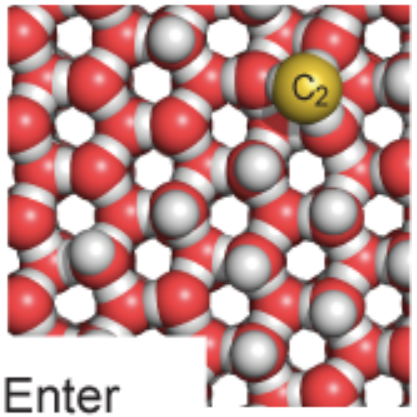
To line-like ‘ordered’

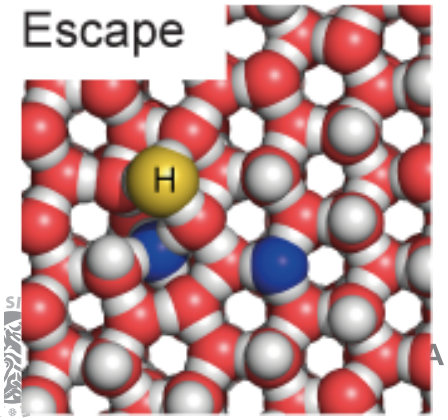


Annealing, Observed Proton Swapping

Blue molecules with dangling proton are swapped, metastable configuration where a molecule is within a hexagonal hole, effective barrier 0.25eV

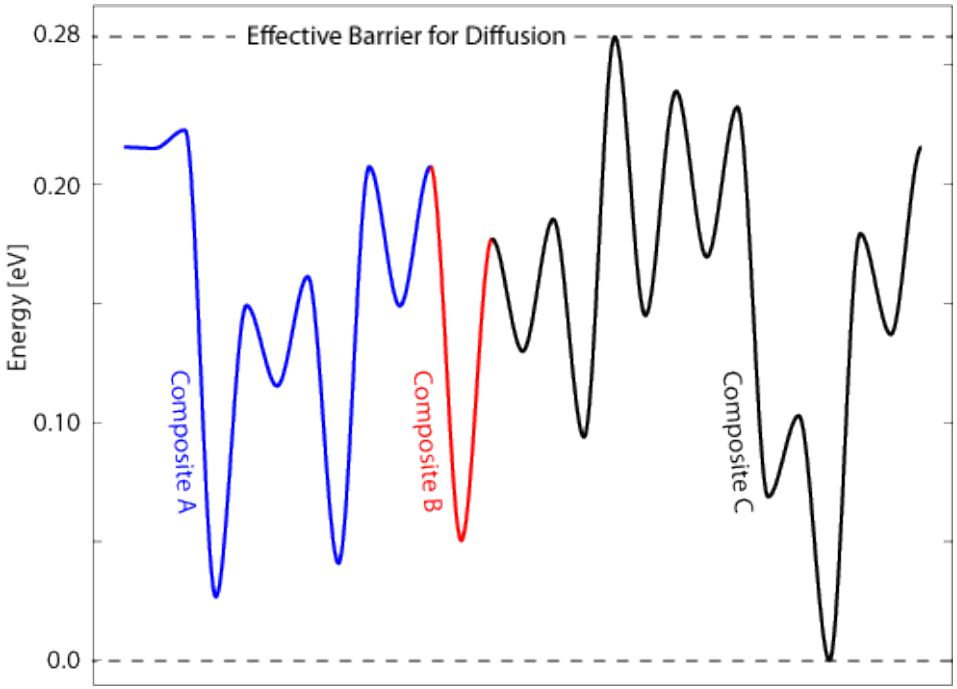






Diffusion, Effective Barrier

At 100K substrate 2 was sufficiently stable for limited resampling (~4 hours). Size of composite states limited to max 8 microstates. The resulting trajectories were highly anisotropic (1D). Backbone energy landscape for migration has been extracted, effective barrier 0.28 eV

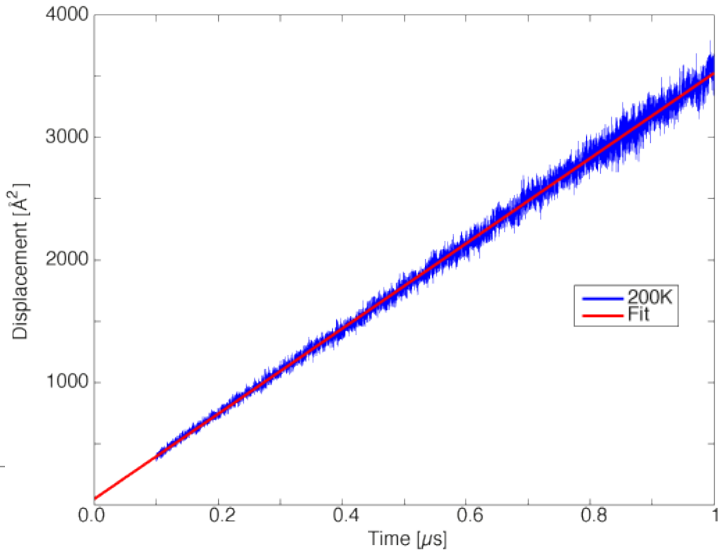


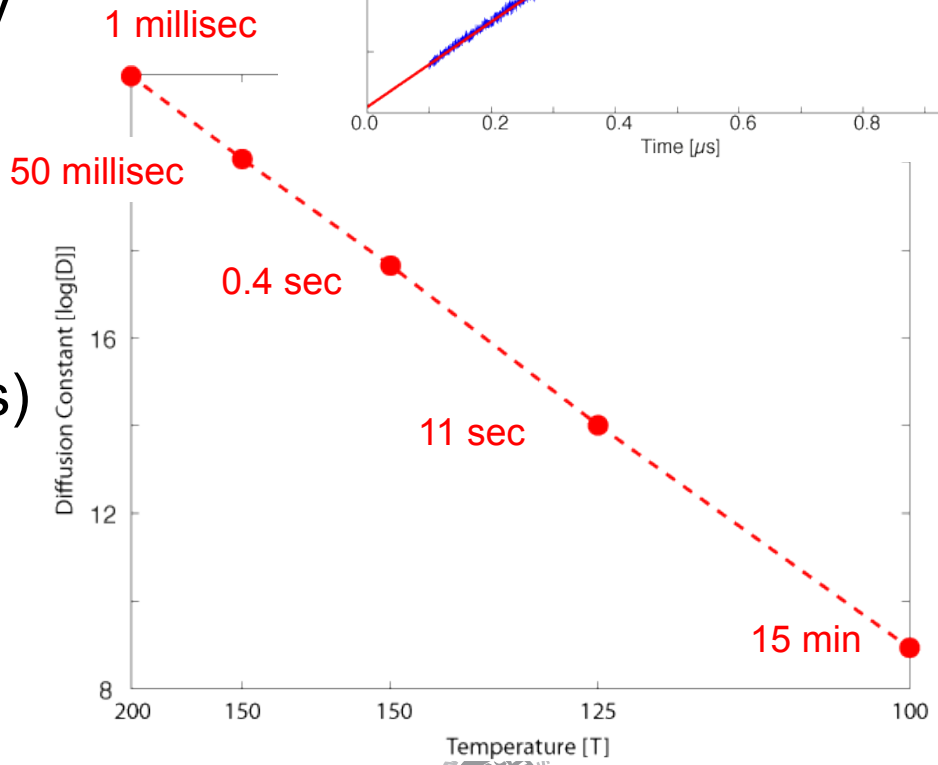
Rate at 100K and 200K:

- 100 meV ~ 10^{8}, 10^{10}
- 280 meV ~ 10^{-1}, 10^{6}

The Fletcher Phase

Dangling protons are aligned in rows, DFT calculations by Pan *et al.* shows it is an energetically favorable configuration





Simulations

- Sufficiently stable for extensive resampling (5 mio. KMC steps, 77 states) in interval from 100K to 200K
- Trajectories are isotropic
- Diffusion barrier 0.23eV

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Ref: Ding Pan *et al.*, Phys Rev Lett 101, 155703 (2008)

Conclusions

Hexagonal ice surface, annealing

- Transforms toward line-like proton order

Hexagonal ice surface, barriers

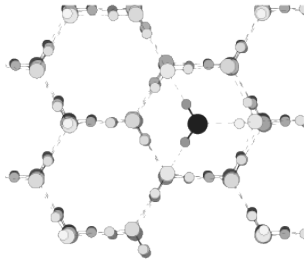
- Substrate annealing ~0.25 eV
- Add molecule diffusion ~0.25 eV

Coarse graining required

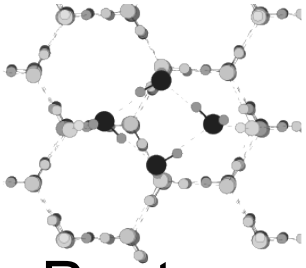
Supported by The Icelandic Research Fund

Clusters on an I_h Surface

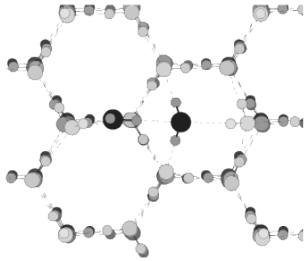
Monomer



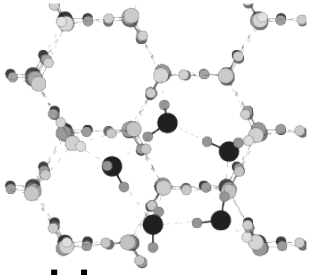
Tetramer



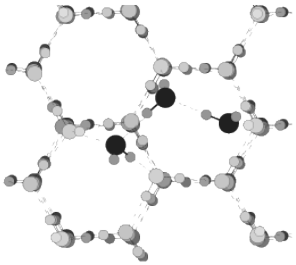
Dimer



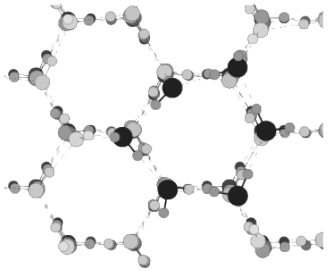
Pentamer



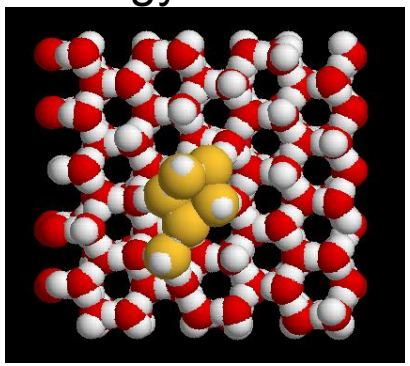
Trimer



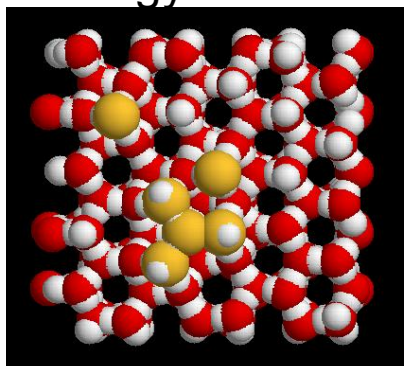
Hexamer



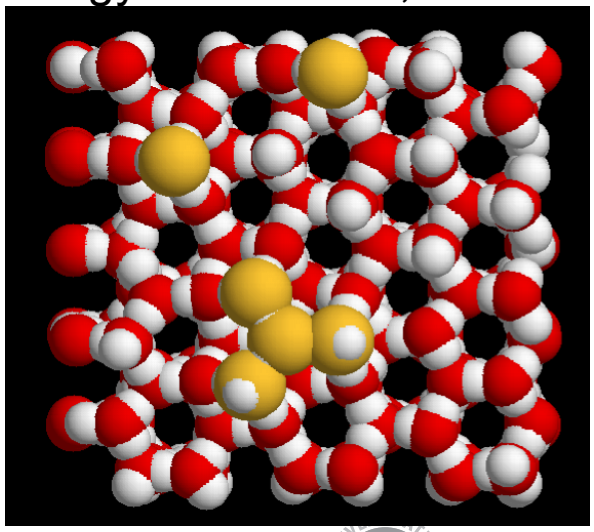
Energy: -215.02 eV



Energy: -215.24 eV



Energy: -215.39 eV; Time 2.5 ns



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Leftmost figure: E. Batista and H. Jónsson, Comp. Mater. Science 20, 325 (2001)