

How to determine diffusion rates computationally?

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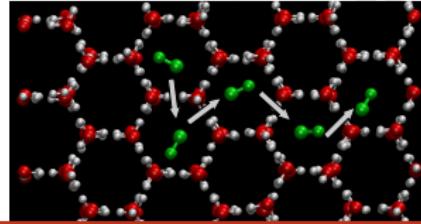
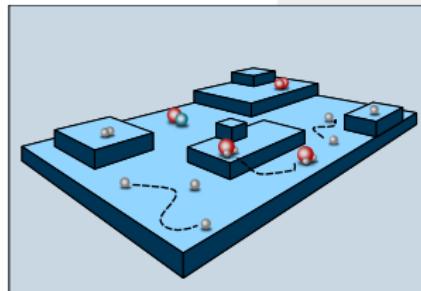
How to determine diffusion rates computationally?

- Diffusion is a fundamental process in solid state astrochemistry.
- Many rates and barriers are still missing in models and are (crudely) estimated.
- Experiments difficult to perform and often not available.



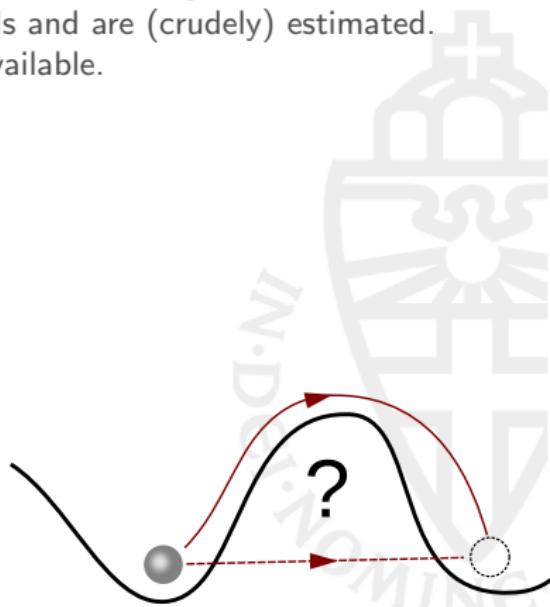
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 - Individual processes can be studied (experiments probe averages). Importance of quantum effects can be evaluated.
 - Differentiate between bulk and surface diffusion.



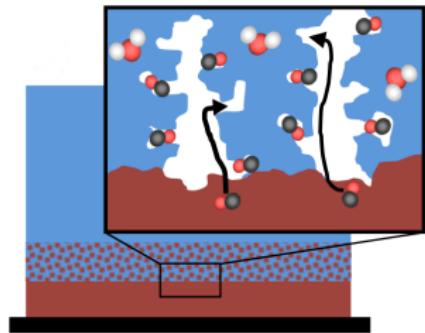
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Introduction

Analysis techniques

Simulation techniques

Conclusions

Challenges



Introduction

Analysis techniques

- Microscopic approach
- Mean squared displacement
- Velocity autocorrelation function
- Indirect methods

Simulation techniques

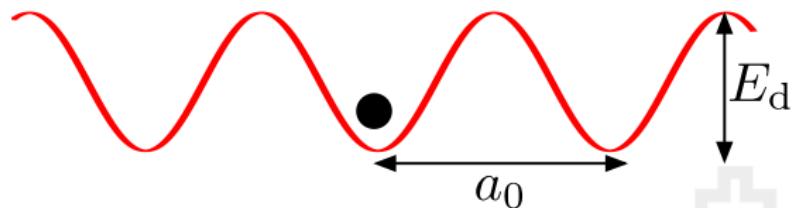
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Microscopic approach

Particle hopping in a periodic potential.



- Diffusion constant easily found:

$$D = a_0^2 k_{\text{hop}}$$

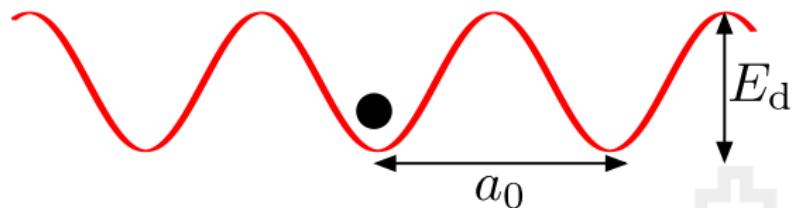
- k_{hop} and a_0 determined computationally.

$$k_{\text{hop}} = \nu \left(\frac{-E_d}{kT} \right) \quad \rightarrow \quad D = D_0 \exp \left(\frac{-E_d}{kT} \right)$$

Prefactor D_0 ($\sim 10^{-3} \text{ cm}^2\text{s}^{-1}$) combination of attempt frequency, jump distance a_0 and dimensionality.

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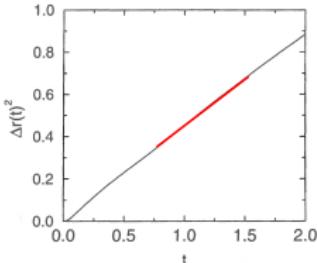
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Prefactor D_0 ($\sim 10^{-3}$ cm 2 s $^{-1}$) combination of attempt frequency, jump distance a_0 and dimensionality.

- ☺ Straightforward approach.
- ☺ k_{hop} and a_0 can be determined accurately, including quantum effects (possibly averaged).
- ☹ Only useful for very simple and crystalline systems.

Mean squared displacement



From a microscopic point of view, the Einstein relation relates the mean squared displacement of particles in time to the diffusion coefficient:

$$D = \lim_{t \rightarrow \infty} \frac{1}{2d} \frac{\partial}{\partial t} \langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle$$

d dimensionality of the system (2 for surface, 3 for bulk diffusion).

- 😊 Straightforward to implement.
- 😊 $\mathbf{r}(t)$ is usually available from simulations.
- 😢 **Long simulation times** needed for proper averaging (problematic for solids and at low temperatures).

Mean squared displacement is related to the velocity of the particles. In one dimension:

$$\begin{aligned}\langle x^2(t) \rangle &= \left\langle \left(\int_0^t v_x(t') dt' \right)^2 \right\rangle \\ &= \left\langle \int_0^t \int_0^t v_x(t') v_x(t'') dt'' dt' \right\rangle \\ &= 2 \int_0^t \int_0^{t'} \langle v_x(t') v_x(t'') \rangle dt'' dt'.\end{aligned}$$

But $\langle v_x(t') v_x(t'') \rangle$ only depends on $t' - t''$ so:

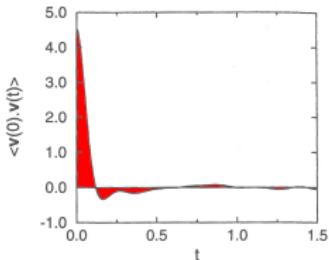
$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle.$$

From the Einstein relation:

$$D = \int_0^\infty \underbrace{\langle v_x(t) v_x(0) \rangle}_{\text{velocity autocorrelation function}} dt.$$



Velocity autocorrelation function



In general, Green-Kubo relation for the diffusion constant:

$$D = \frac{1}{d} \int_0^\infty \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle dt.$$

Vibrational power spectrum is also easily obtained:

$$P(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle e^{i\omega t} dt.$$

- 😊 Relation to the vibrational power spectrum of the system.
- 😢 $\mathbf{v}(t)$ not always available from simulations.
- 😢 Long simulation times needed to reduce noise.

Indirect methods

The mean squared displacement (MSD) and velocity autocorrelation (VAC) methods are most used.

Other (indirect) possibilities:

- Model TPD experiments by Kinetic Monte Carlo with temperature dependent rate constants.
- Solve Fick's second law:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2},$$

with the appropriate boundary conditions to obtain $c(\mathbf{r}, t)$.

Solution can be fit to experiments.

- Rate equation models with diffusion parameter.

Introduction

Analysis techniques

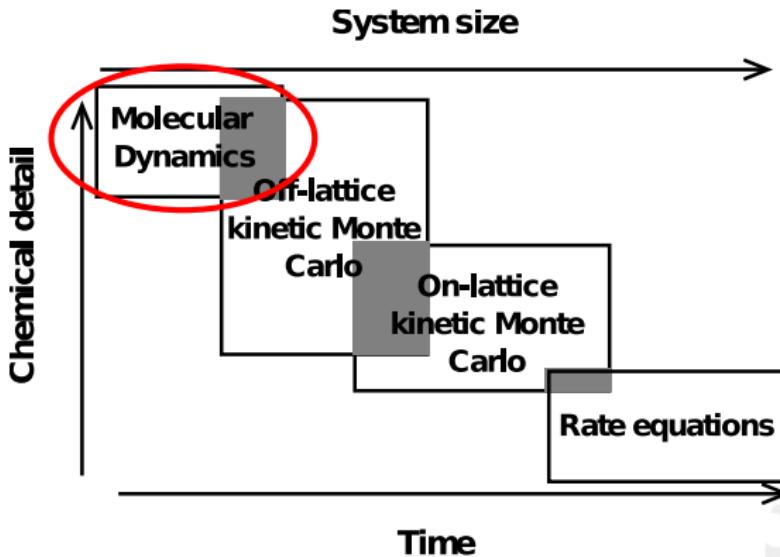
Simulation techniques

- Molecular Dynamics
- Kinetic Monte Carlo
- Indirect techniques

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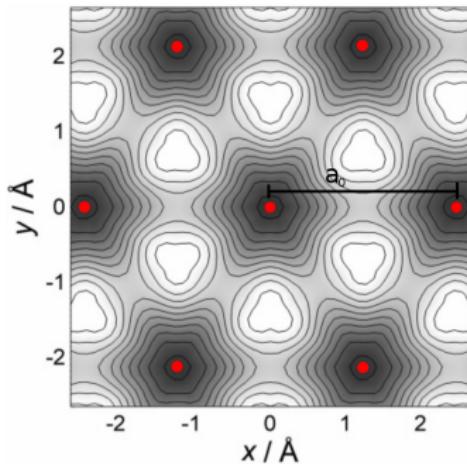


Molecular Dynamics:

- ☺ Atomistically detailed simulations possible.
- ☺ Interaction schemes of all accuracies (*ab-initio*, DFT, forcefields).
- ☺ Diffusion easily calculated from MSD of VAC.
- ☹ Long sampling is computationally expensive (problematic for dust grain simulations).

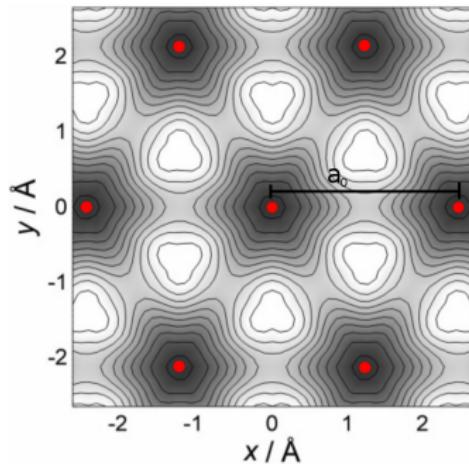
Quantum wavepacket dynamics for H atom surface diffusion on graphite
(Matteo Bonfanti and Rocco Martinazzo, *J. Phys. Chem. C.*, 111, 2007)

- Accurate *ab-initio* PES.
- Diffusion barrier determined (4 meV)
- Rate of single hopping/tunneling process, k_{hop} , calculated by wavepacket propagation.
- $D = a_0^2 k_{\text{hop}} = 1.7 \times 10^{-4} \text{ cm}^2 \text{s}^{-1}$.



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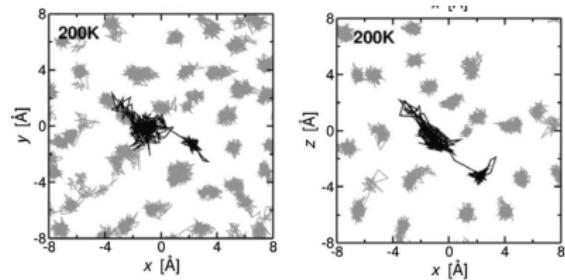
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- 😊 Very accurate description of interactions.
- 😊 Quantum approach.
- 😊 No 'real' dynamics simulation needed.
- 😢 Only possible from simple crystalline systems (defects not included).

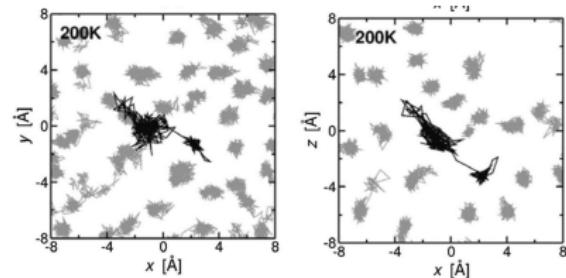
Classical Molecular Dynamics of atomic oxygen diffusion in amorphous solid water (Myung Won Lee and Markus Meuwly, *Faraday Discuss.*, , 2014).

- Individual jumps observed.
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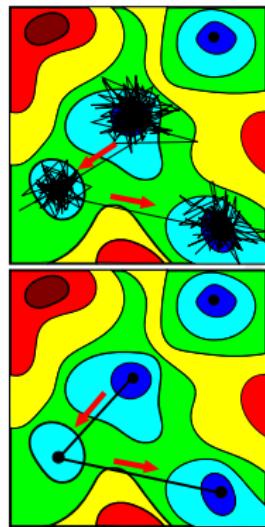
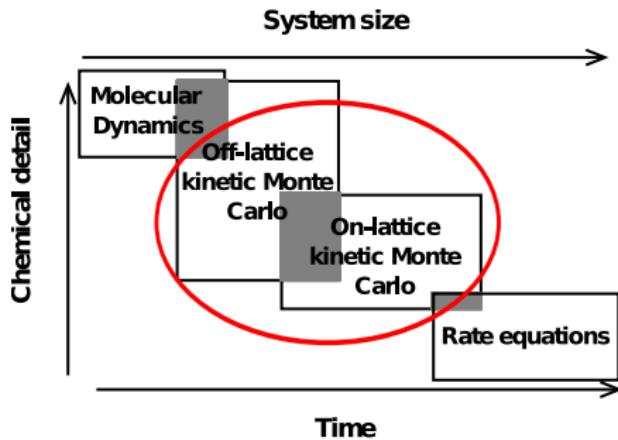


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- 😊 Accurate description of interactions.
- 😊 Diffusion mechanism can be understood.
- 😢 Temperature not low enough.
- 😢 Only limited number of jumps observed.
- 😢 System only partially sampled: possible bias.
- 😢 Simulation times not long enough to sample MSD.

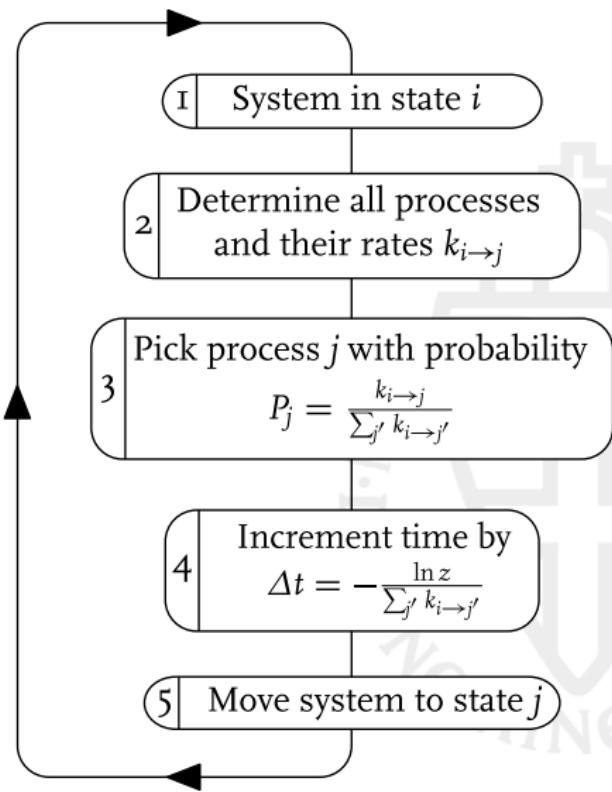


Kinetic Monte Carlo:

- ☺ Atomistic detail possible.
- ☺ Interaction schemes of all accuracies (*ab-initio*, DFT, forcefields, parametrized model).
- ☺ Diffusion easily calculated from MSD.
- ☹ Finding diffusion transition states is computationally expensive.
- ☹ Estimating rates not straightforward.



Kinetic Monte Carlo algorithm

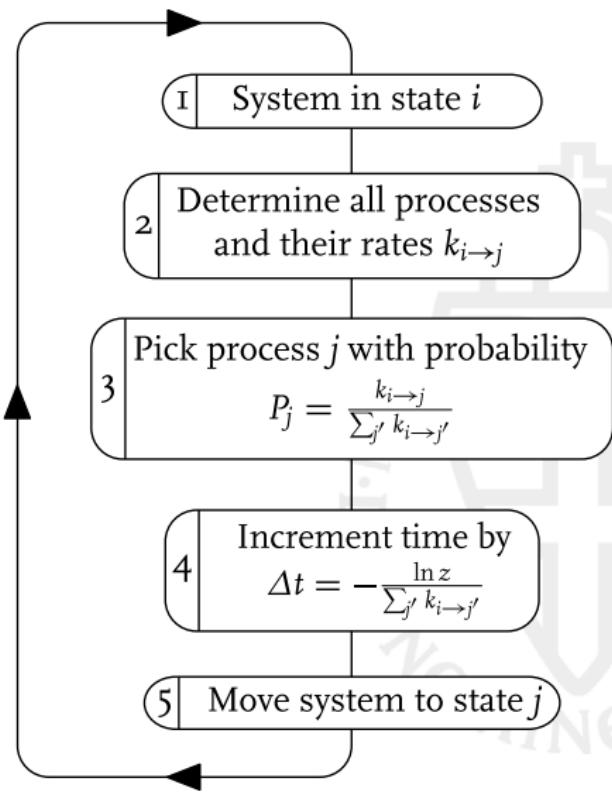


Kinetic Monte Carlo algorithm

Defining steps:

1 Define states

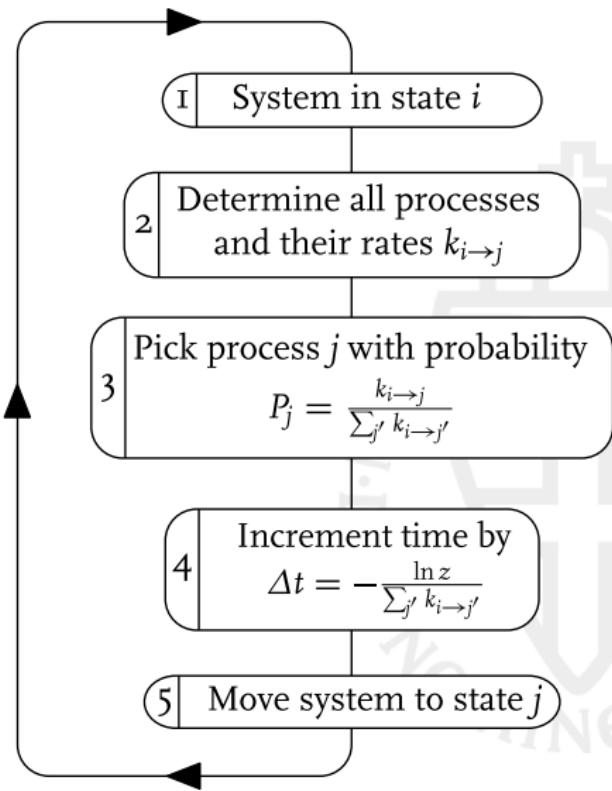
- Off-lattice (most structural detail)
- On-lattice (less structural detail)



Kinetic Monte Carlo algorithm

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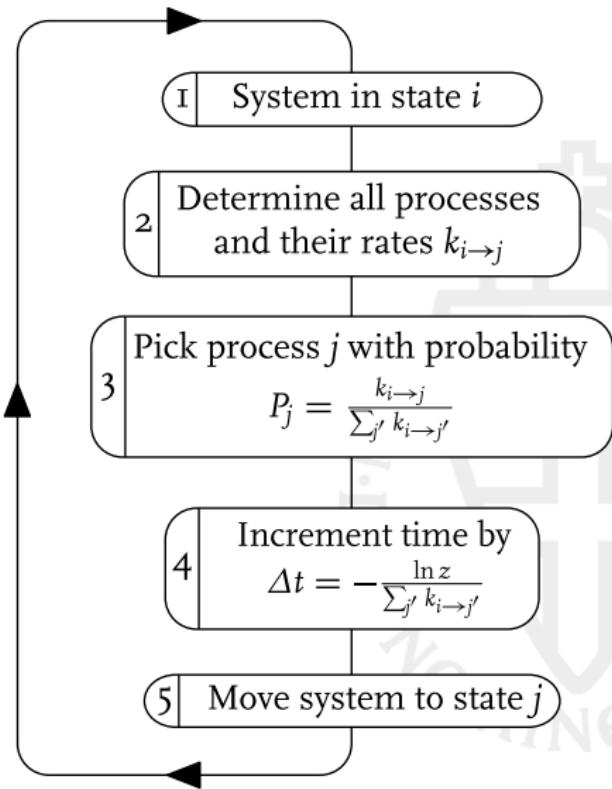
- 1 Define states
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 - On-lattice (less structural detail)
- 2 Determining processes:
 - Specify before simulation (lattice KMC, NEB)
 - On-the-fly (Adaptive KMC)
- 3 Determining rates:
 - Harmonic TST
 - Quantum Harmonic TST
 - Instanton theory
 - ...



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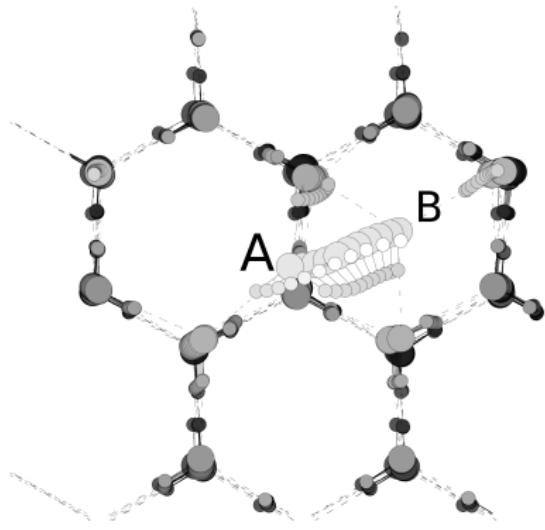
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- 4 All processes need to be known for proper time evolution.



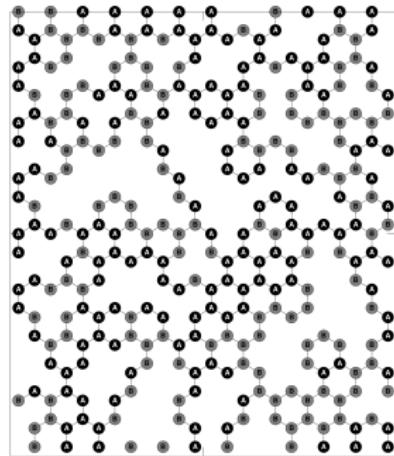
H₂O surface diffusion on ice 1h (E.R. Batista and H Jónsson, *Comput. Mater. Sci.*, 20, 2001)

- Binding sites explored in forcefield.
- Nudged elastic band calculation to obtain barriers.
- Harmonic rate constant:
 $k_{A \rightarrow B} = \nu \exp\left(\frac{-E_{A \rightarrow B}}{kT}\right).$



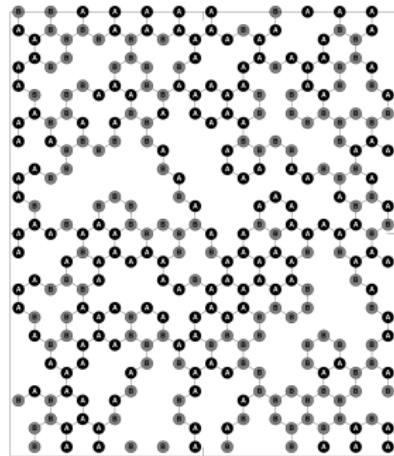
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($T = 140 \text{ K}$).
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H_2O surface diffusion on ice 1h (E.R. Batista and H Jónsson, *Comput. Mater. Sci.*, 20, 2001)

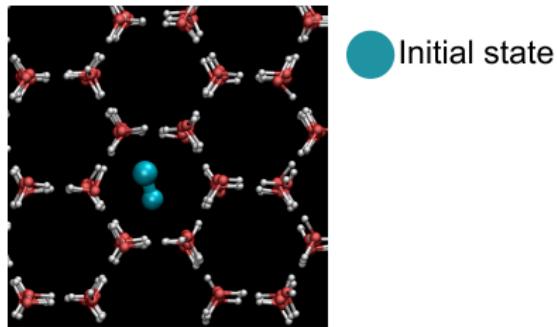
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- 😊 Accurate description of interactions (TIP4P forcefield).
- 😊 Long timescale simulations: sampling MSD possible.
- 😊 Crystal inhomogeneities included.
- 😢 Binding sites need to be known before the simulation (Some sites may be missed).

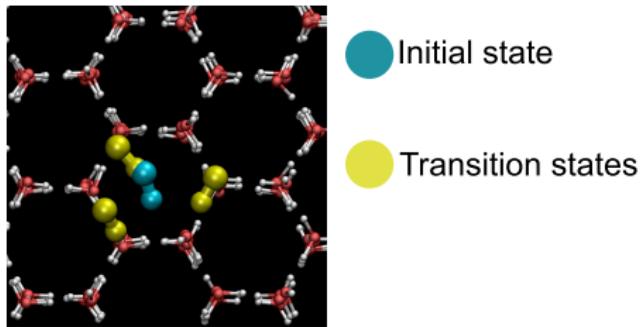
Adaptive Kinetic Monte Carlo

- No prior knowledge of diffusion steps
- Potential energy surface explored automatically, to find transition states.
- Example: CO diffusion on ice 1h (L.J. Karssemeijer et al., *Phys. Chem. Chem. Phys.*, 14, 2012).



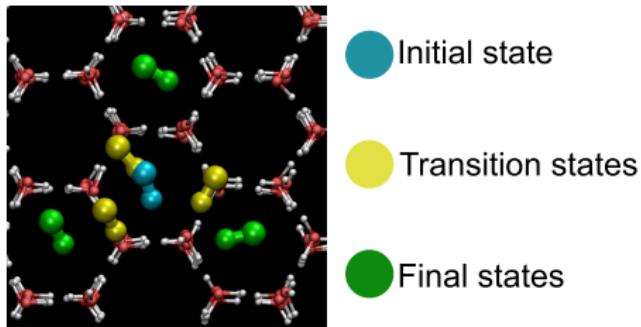
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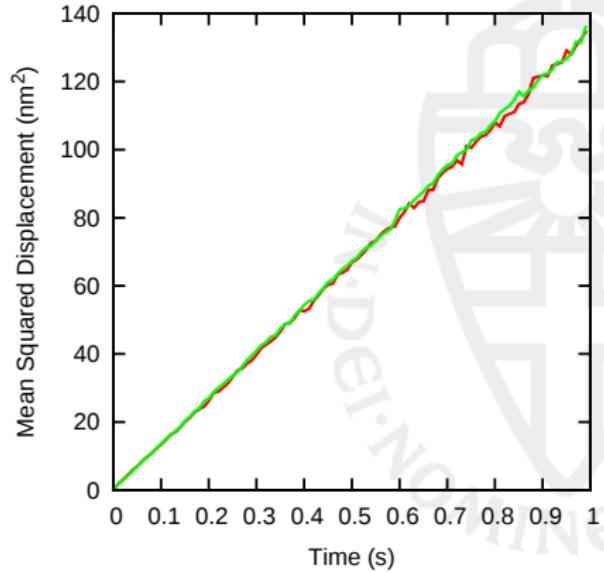
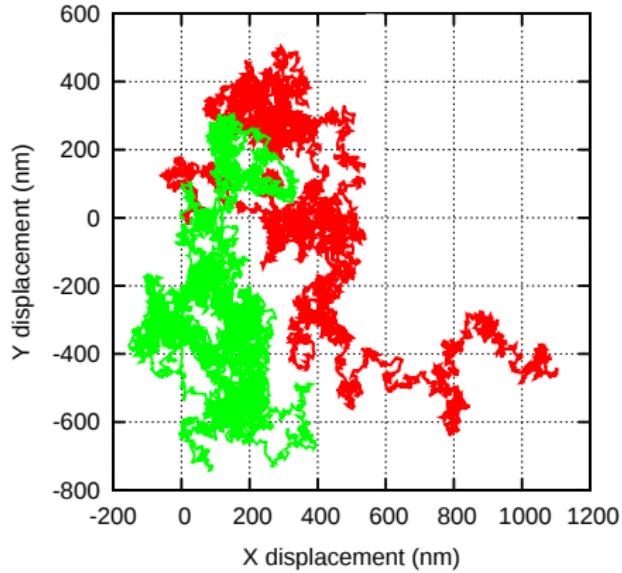
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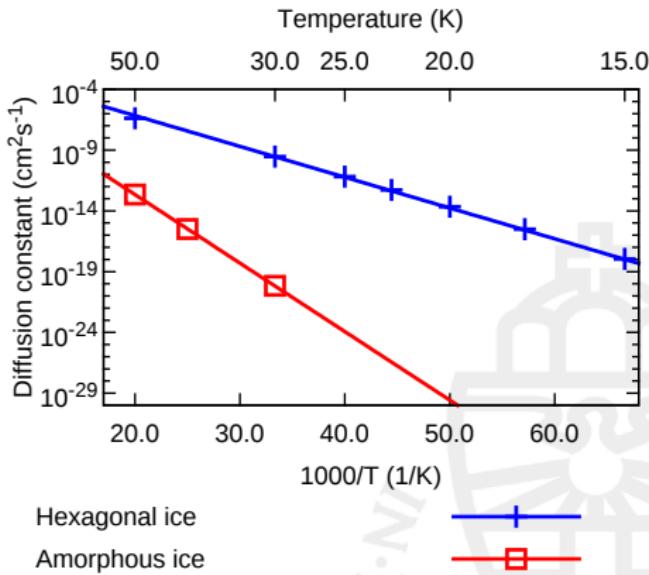


- KMC algorithm generates random walk trajectories of the CO molecule.
- Diffusion coefficient can be obtained from the mean squared displacement:

$$D = \lim_{t \rightarrow \infty} \frac{1}{4t} \langle |\mathbf{r}(0) - \mathbf{r}(t)|^2 \rangle.$$

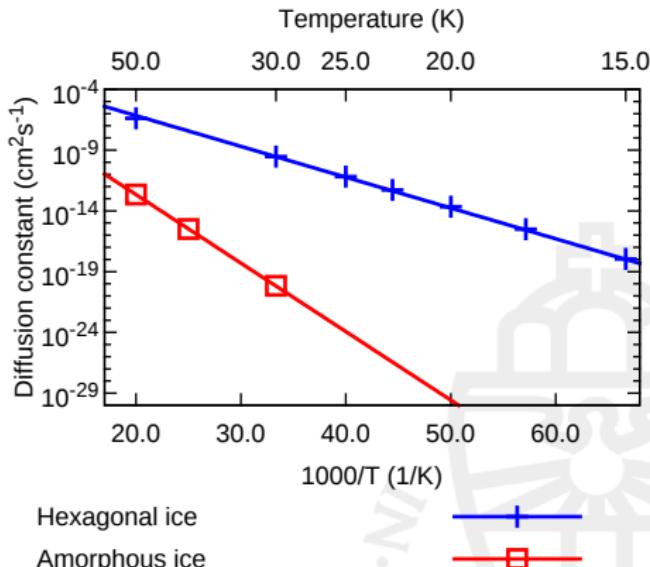
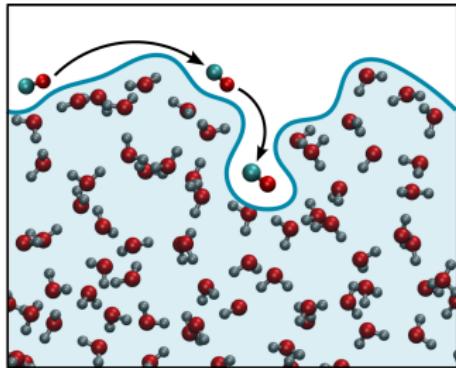


- Diffusion constant follows Arrhenius behavior.
- Effective energy barrier can be extracted.
- Diffusion on amorphous ice is impossible to simulate below 30 K.



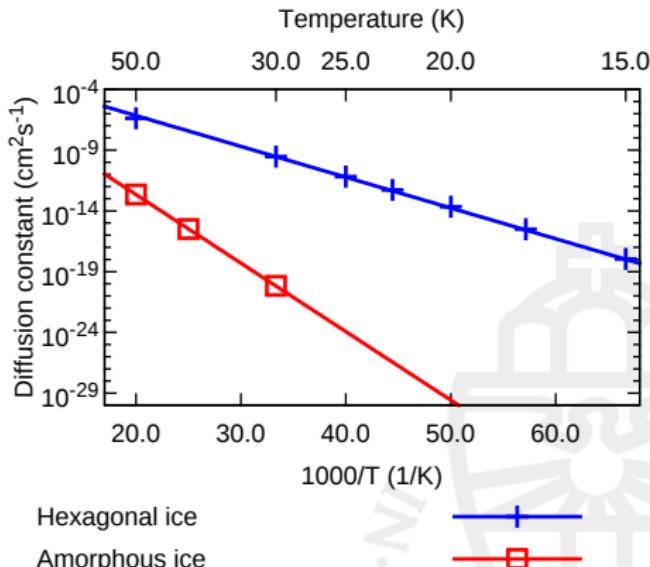
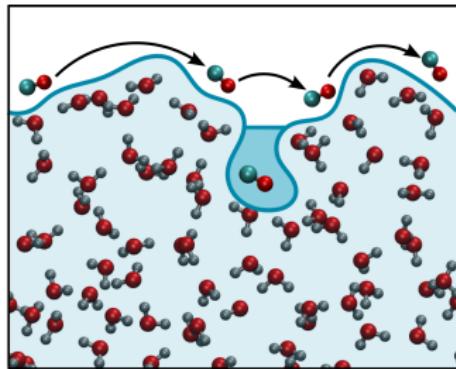
System	Effective diffusion barrier (meV)
Hexagonal ice	49 ± 2
Amorphous ice	103 ± 13

- On amorphous ice, diffusion is limited by strong binding pore sites.



System	Effective diffusion barrier (meV)
Hexagonal ice	49 ± 2
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- Increase CO coverage by occupying strong bonding sites to increase mobility.

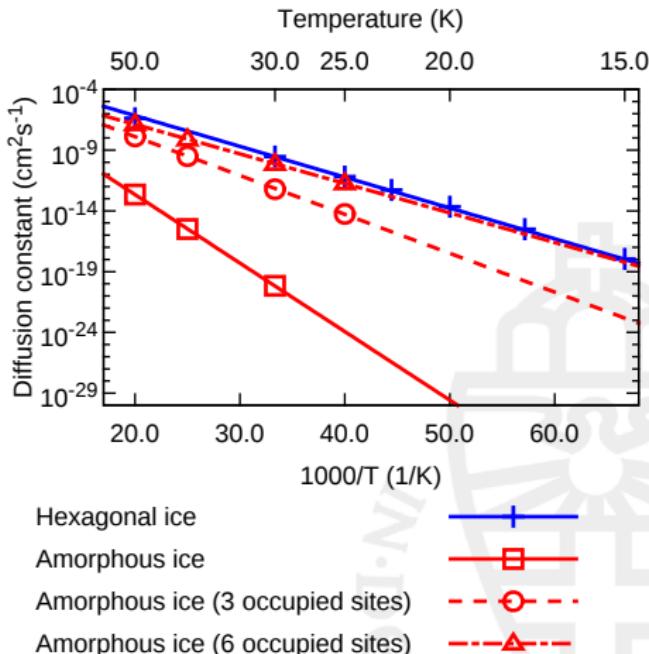
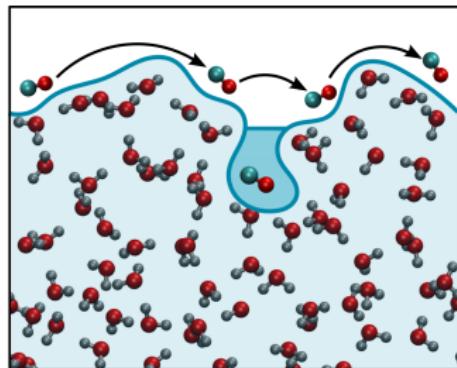


Hexagonal ice

Amorphous ice

System	Effective diffusion barrier (meV)
Hexagonal ice	49 ± 2
Amorphous ice	103 ± 13

- Three or six strongest binding sites are occupied with CO.
- One additional CO remains mobile.
- Occupying the pore sites increases mobility dramatically.



System	Effective diffusion barrier (meV)
Hexagonal ice	49 ± 2
Amorphous ice	103 ± 13
Amorphous ice (3 occupied sites)	67 ± 7
Amorphous ice (6 occupied sites)	64 ± 12

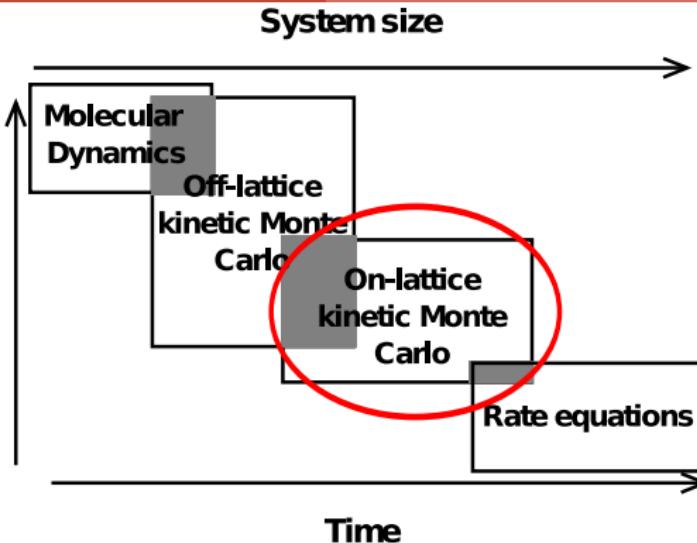
Off-lattice Kinetic Monte Carlo:

- 😊 Atomistic detail.
- 😊 Sufficiently long timescale to probe surface diffusion under astrochemical conditions.
- 😊 Can reveal mechanisms (trapping).
- 😢 Finding transition state computationally expensive.
- 😢 Bulk processes still beyond reach.



System size

Chemical detail



On-lattice Kinetic Monte Carlo:

- Larger systems than off-lattice KMC.
- Predefined event parameters.

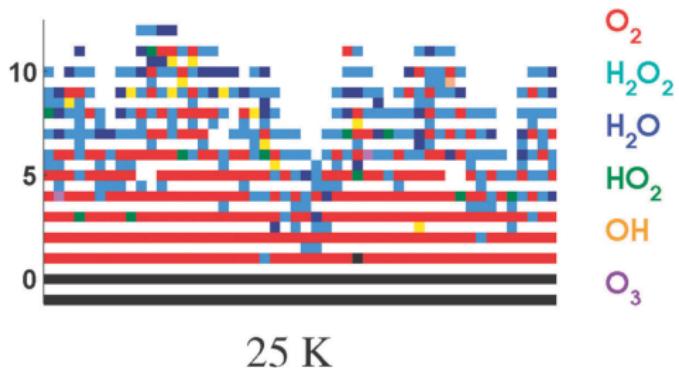


Figure: (Thanja Lamberts et al., *Phys. Chem. Chem. Phys.*, 15, 2013)

On-lattice Kinetic Monte Carlo:

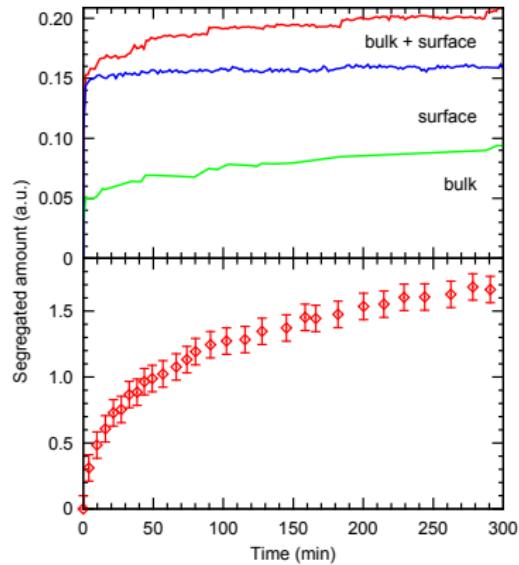
- Larger systems than off-lattice KMC.
- Predefined event parameters.
- Species confined to predefined lattice.
- No realistic interaction potentials.

Segregation in H₂O:CO₂ ice mixtures (K. I. Öberg et al., A&A, 505, 2009)

- Lattice KMC simulations.
- Diffusion included in bulk (swapping) and surface (swapping)
- Both bulk and surface processes needed to reproduce experiments.

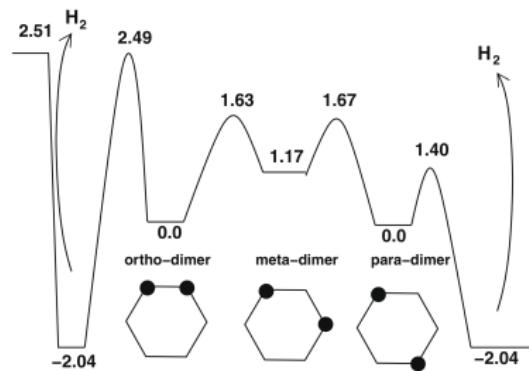
Predefined event parameters:

Barrier type	Energy / K
$E_{\text{binding}}^{\text{H}_2\text{O}-\text{H}_2\text{O}}$	1000
$E_{\text{binding}}^{\text{CO}_2-\text{CO}_2}$	500
$E_{\text{hop}}^{\text{H}_2\text{O}}$	2400
$E_{\text{hop}}^{\text{CO}_2}$	1200
$E_{\text{swap}}^{\text{H}_2\text{O}-\text{CO}_2}$	3600
$E_{\text{swap}}^{\text{CO}_2-\text{H}_2\text{O}}$	3600



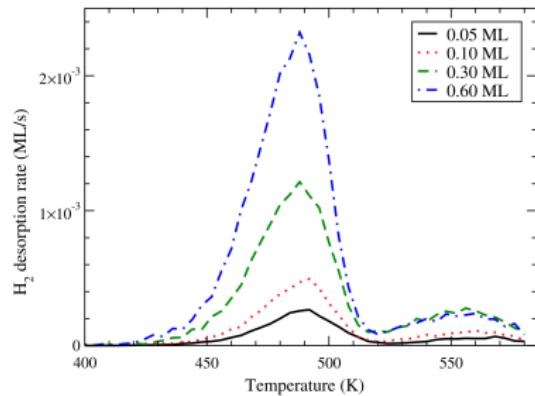
Lattice KMC simulation of TPD experiments (E. Gavardi et al., *Chem. Phys. Lett.*, 477, 2009)

- KMC simulation with varying temperature (A.P.J. Jansen, *Comput. Phys. Commun.*, 86, 1995).
- Binding energies and diffusion barrier from DFT simulations.
- KMC simulates H₂ formation and TPD profiles are obtained.
- Ortho- to para-dimer diffusion gives second peak in TPD.
- Insight in process obtained from KMC simulation.



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On-lattice Kinetic Monte Carlo

- 😊 Long timescales, can probe bulk processes.
- 😊 Computationally efficient.
- 😊 Rates as input: close relation to rate equation models.
- 😢 Assumptions have to be made on mechanisms.



Indirect computational methods to find diffusion parameters

- Solutions to Fick's second law to understand experiments:
 - Simple analytical solution, can be fit to experiments.
 - Gives quantitative understanding.

Possible future methods?

- Extracting diffusion constants from MSD in lattice KMC simulations.
- Analyzing power spectrum from MD simulations.



Fick's second law:

$$\frac{\partial c(x, t)}{\partial t} = D(T) \frac{\partial^2 c(x, t)}{\partial x^2}.$$

General solution:

$$c(x, t) = \sum_{i=-\infty}^{\infty} [A_i \sin(\lambda_i x) + B_i \cos(\lambda_i x)] \exp(-\lambda_i^2 D t).$$

Initial value problem: boundary conditions and initial concentration profile determine full solution.

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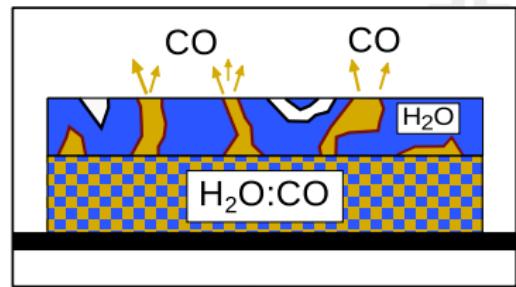
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Initial value problem: boundary conditions and initial concentration profile determine full solution.

- Isothermal desorption experiments through ASW ($\text{CO}, \text{NH}_3, \text{H}_2\text{CO}, \text{HNCO}$) (F Mispelaer et al., *A&A* A13, (2013); L.J. Karssemeijer et al., *ApJ* 781, (2014)).
- Mixing experiments: CO into ASW (Lauck, Öberg et al, 2014, in prep).

CO diffusion and desorption through ASW
(L.J. Karssemeijer et al., *ApJ*, 781, 2014).



- Boundary conditions:

- Initial concentration in bottom slab:

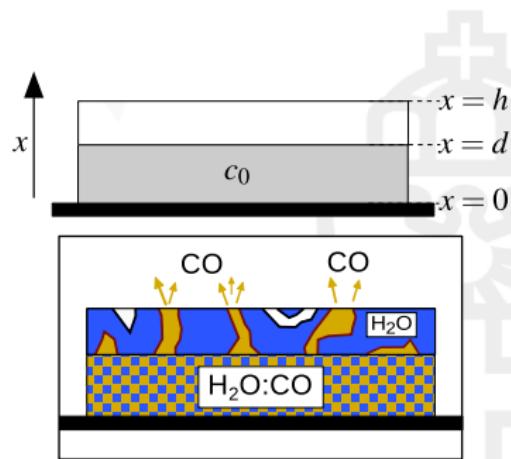
$$c(x, 0) = \begin{cases} c_0, & \text{if } 0 < x \leq d, \\ 0, & \text{if } d < x < h. \end{cases}$$

- Desorption at $x = h$:

$$c(h, t) = 0.$$

- No flux at $x = 0$:

$$\frac{\partial c(0, t)}{\partial x} = 0.$$



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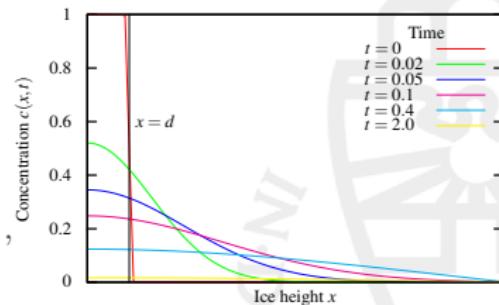
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- Solution ($\mu_i = (2i + 1)\pi/2h$):

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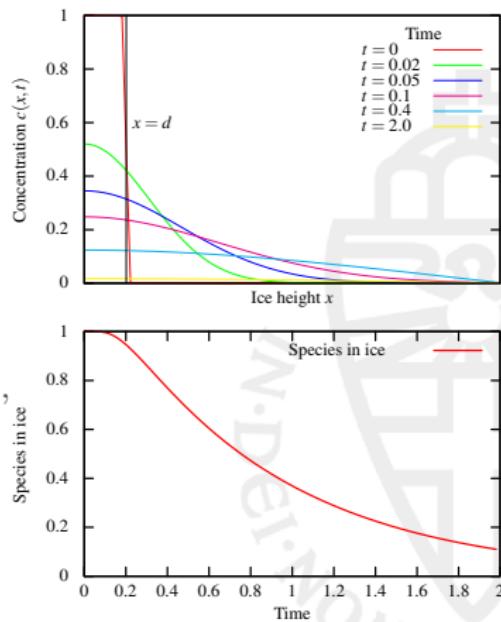
$$\frac{\partial c(0, t)}{\partial x} = 0.$$

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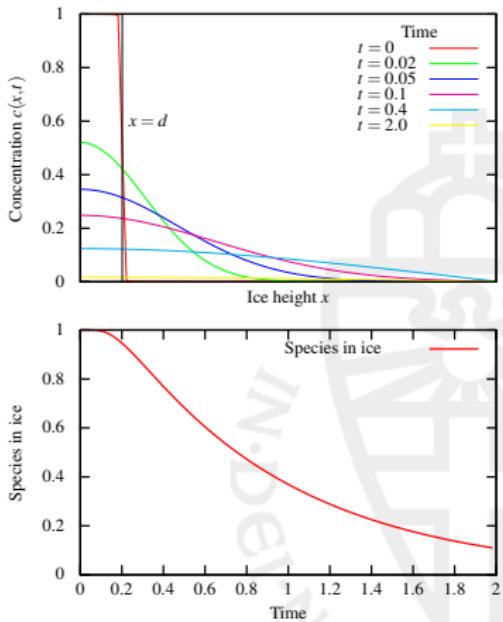
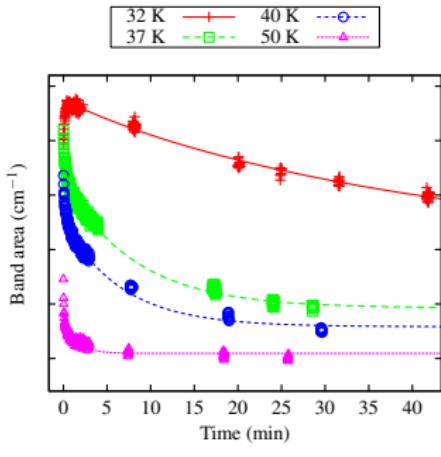
$$c(x, t) = \sum_{i=0}^{\infty} \frac{2c_0}{\mu_i h} \sin(\mu_i d) \cos(\mu_i x) \exp(-\mu_i^2 D t),$$

- Species in ice (~IR band area):

$$\begin{aligned} A(t) &= \int_0^h c(x, t) dx \\ &= \sum_{i=0}^{\infty} \frac{2c_0(-1)^n}{\mu_i^2 h d} \sin(\mu_i d) \exp(-\mu_i^2 D t) \end{aligned}$$



- Solution fit to experimental results.



Solutions to Fick's second law to understand experiments

- 😊 Useful to quantitatively understand experiments.
- 😊 Simple model, little parameters.
- 🙁 Fit to IR band area gives a lot of uncertainty.
- 🙁 How applicable is the model?
 - 🙁 Diffusion not the only process.
 - 🙁 Only one diffusing species.
 - 🙁 No concentration dependence in the model.
- 🙁 Complicating model does not necessarily improve understanding.



Conclusions

- Several analysis techniques and simulation methods available.
- Computer simulations can help unveil properties of molecular diffusion on the atomic scale.
- Tradeoff between **detail/accuracy** and **system size/timescales** (limits on included local structure, inhomogeneities, trapping, restructuring, crystallization)
- Long timescales under astrophysical conditions problematic.
- Lot of recent work and work in progress.
- Diffusion is still too poorly understood.

Challenges for computing diffusion processes



Challenges for computing diffusion processes

- How to simulate bulk processes?

- Is there real bulk diffusion or effective surface diffusion along pores?
- Lattice Kinetic Monte Carlo, but...
 - Unclear what processes to include?
 - What parameters to give them?
- Molecular Dynamics...
 - Time scales long enough?
 - Accelerated methods?



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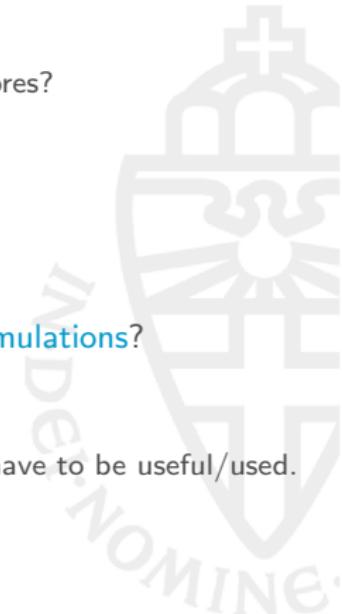
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- What structure of the ice to include in atomistically detailed simulations?

- What are the essential physical processes?

How to input detailed simulation results into simplistic models

- More detailed simulations can give a lot of insight, but results have to be useful/used.



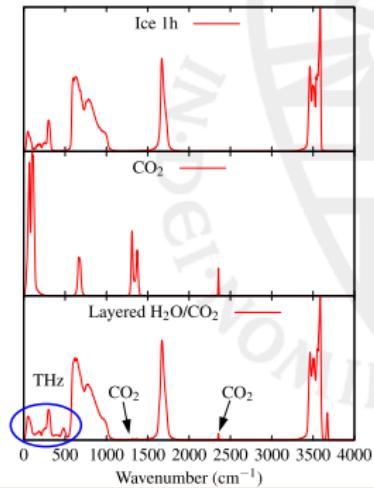
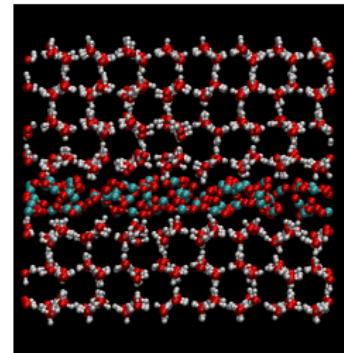
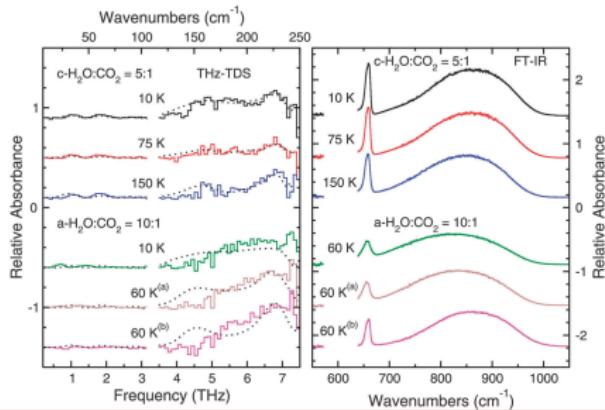
Thank you for your attention

Questions?



VAC and Power spectrum

- VAC also gives power spectrum $P(\omega)$.
- Maybe used for interpretation of new THz ice results (M.A. Allodi et al., *Phys. Chem. Chem. Phys.*, 16, 2014).
- Possible new way to characterize bulk diffusion?
- Requires accurate potentials...

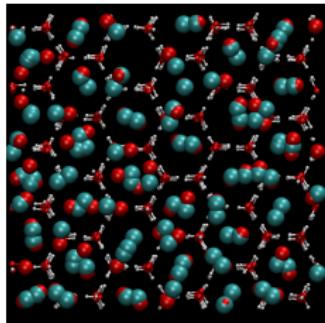


Adaptive Kinetic Monte Carlo

CO diffusion on water ice.

- Amorphous and crystalline samples.
- Binding energies evaluated.
- Nanoporous sites important.

Hexagonal ice



Amorphous ice

