Estimating Diffusivity Coefficient by Molecular Dynamics Simulation

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Introduction: Statistical Mechanics

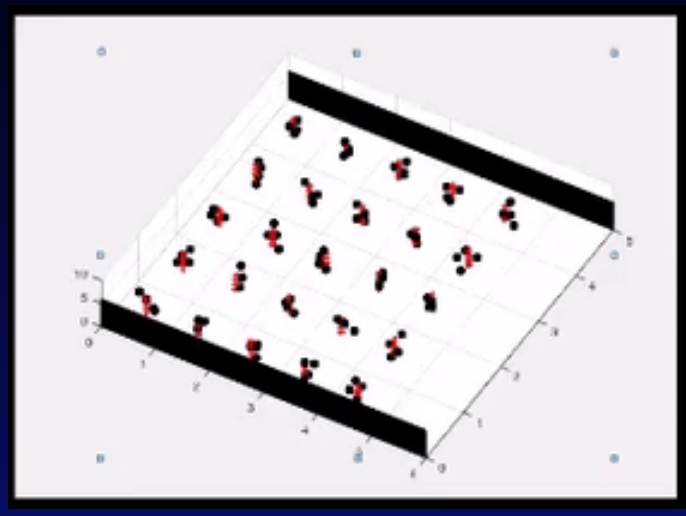
Monte Carlo Simulation

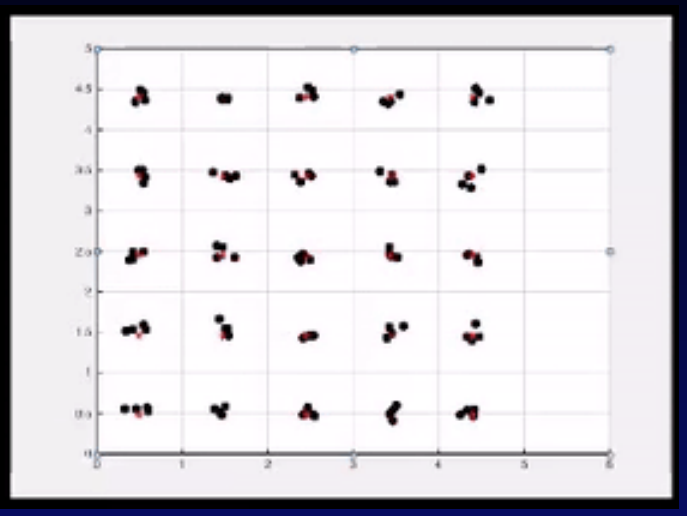
- Time independent
- Statistical ensemble and configurations are sampled by random walk, Metropolis, and Gibbs sampling approach
- Yields thermodynamic and structural properties

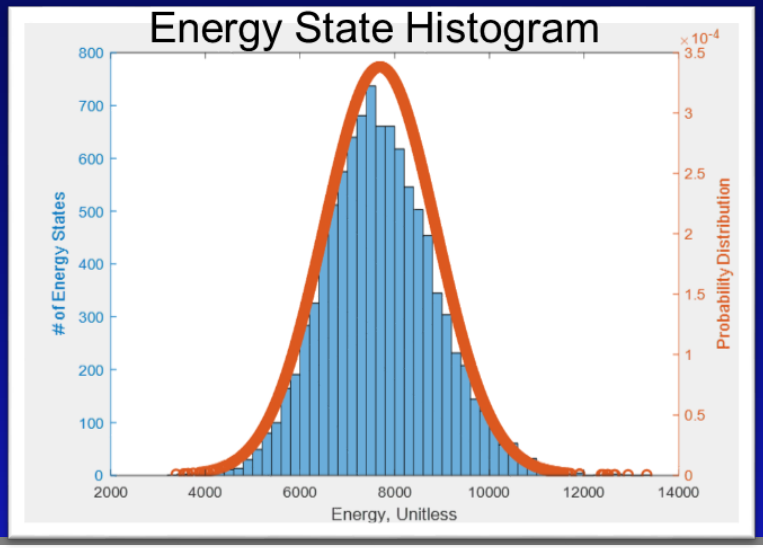
Molecular Dynamics

- Time dependent: the time step size varies from femtoseconds (10^{-15}) to nanoseconds (10^{-9})
- The algorithm solves Newton F=ma equation
- Yields thermodynamic, structural, and dynamic properties

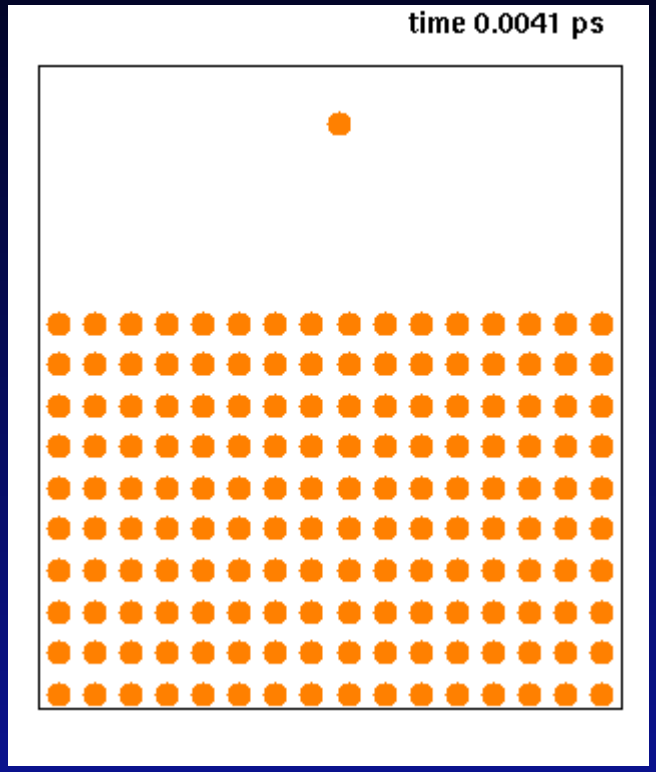
Introduction: Monte Carlo SImulation







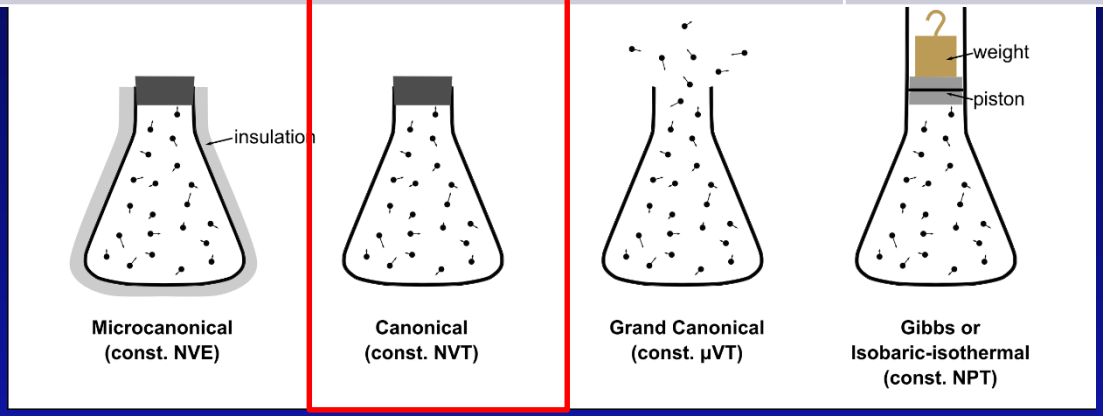
Introduction: Molecular Dynamics



Retrieved from, https://en.wikipedia.org

Introduction: Statistical Ensembles

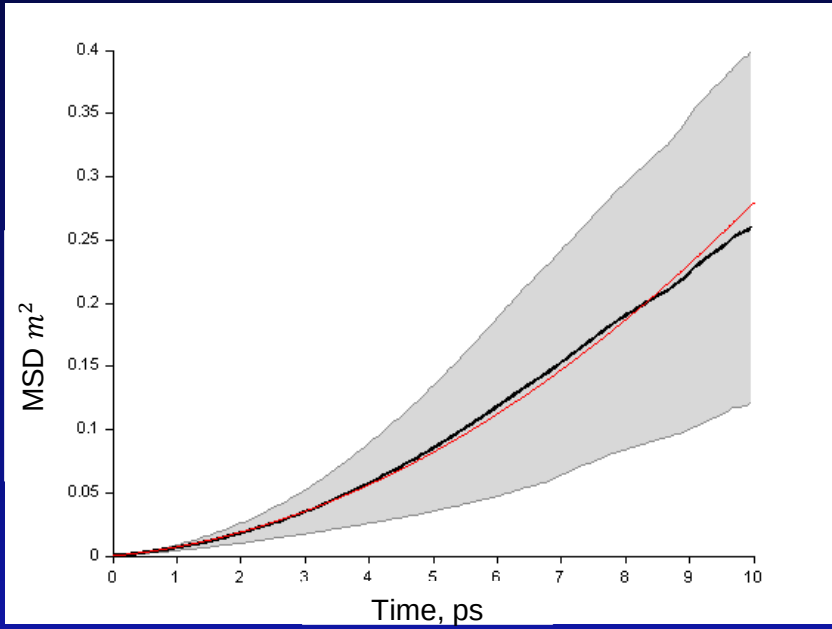
Microcanonical ensemble	Canonical ensemble	Grand canonical ensemble	Gibbs or isobaric-isothermal ensemble
Number of particles	Number of particles	Chemical potential	Number of particles
Volume	Volume	Volume	Pressure
Energy	Temperature	Temperature	Temperature



Modified from Wikipedia.com

Introduction: Mean Square Displacement (MSD)

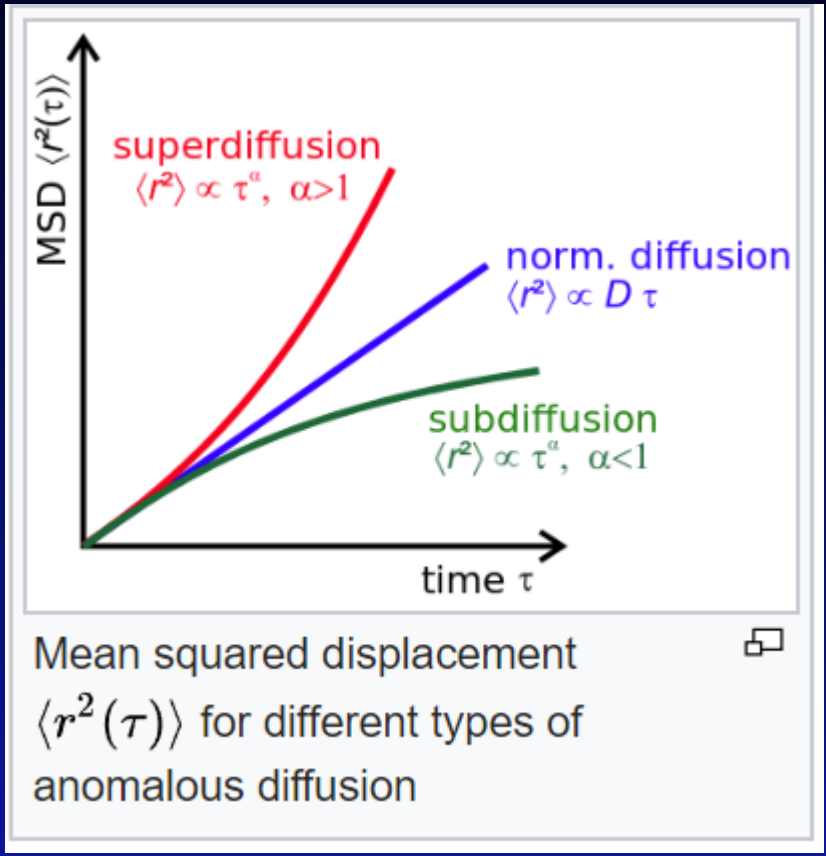
- The mode of displacement of particles with respect to a reference position over time. It determines if a particle is:
  - Freely diffusing
  - Transported
  - Bound and limited in its movement



Rerieved from mathworks.com

Introduction: Anomalous Diffusion

- The diffusion process is described by a power law
  - $MSD = \langle r^2 \rangle$
  - $\langle r^2 \rangle = Dt^{\alpha}$
  - $\alpha = 1$ normal diffusion
    - $\langle r^2 \rangle = Dt$
  - $\alpha < 1$ subdiffusion
    - $\langle r^2 \rangle = Dt^{\alpha}$
  - $\alpha > 1$ superdiffusion
    - $\langle r^2 \rangle = Dt^{\alpha}$



Mean squared displacement $\langle r^2(\tau) \rangle$ for different types of anomalous diffusion

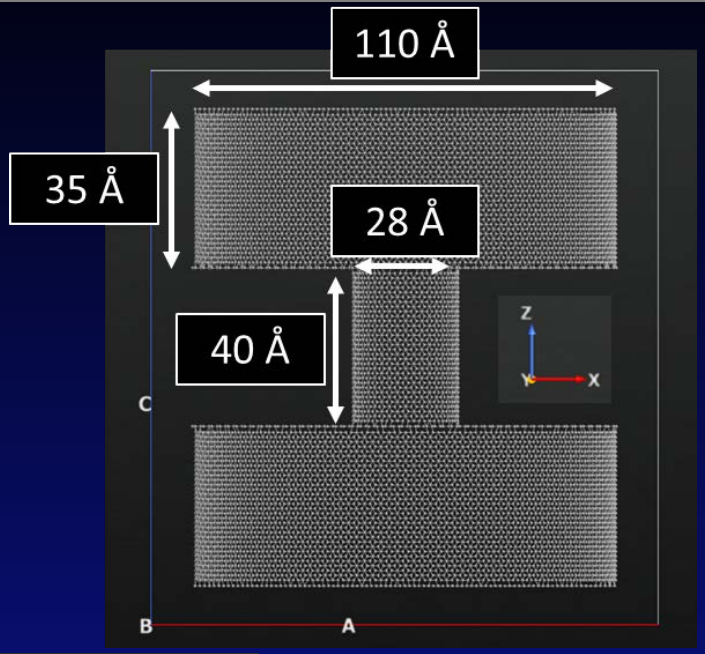
Retrieved from Wikipedia.com

Introduction: Diffusivity Coefficient Calculation

- $D = \frac{1}{2*n} \frac{\langle r(t) - r(t_0)^2 \rangle}{t - t_0}$
- $\langle r(t) - r(t_0)^2 \rangle = \mathrm{MSD}$, calculated by the molecular dynamics simulator
- $n = 3$, dimension of the system
- $t =$ time at which the diffusivity is calculated
- $t_0 =$ reference time

- The particles in the system must reach homogenous state, to use this equation.

Dimensions of the Carbon Nanotube System

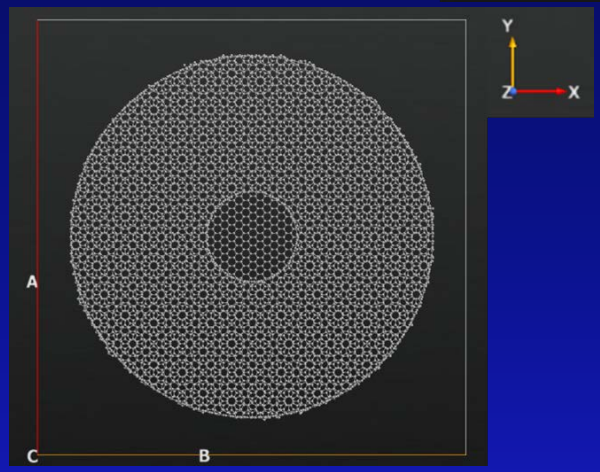


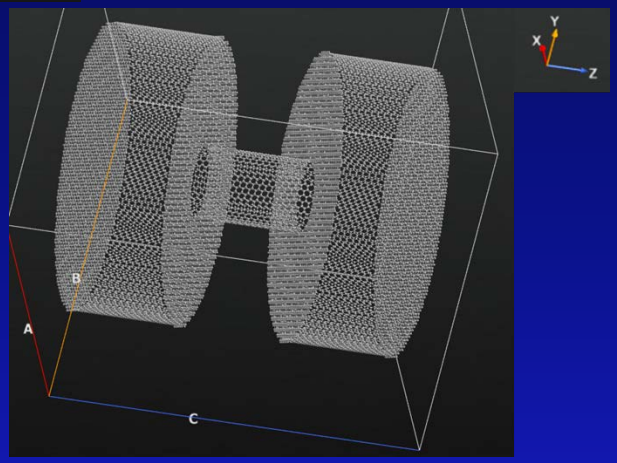
1st pore

2nd pore

3rd pore

Virtual NanoLab



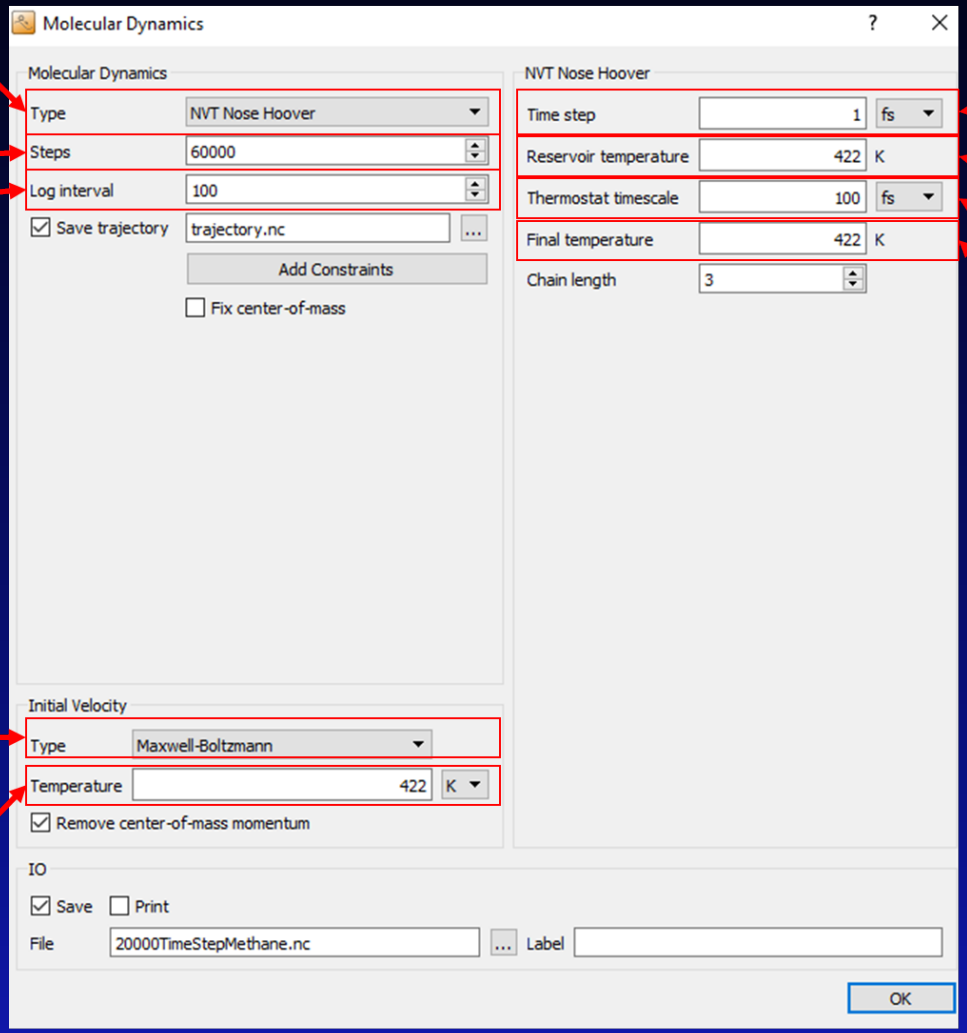


Sample Input

A deterministic algorithm for constant temperature case

Total steps

Resolution



Each time step is 1 femtosecond

Initial temperature of the system

Timescale to change the temperature

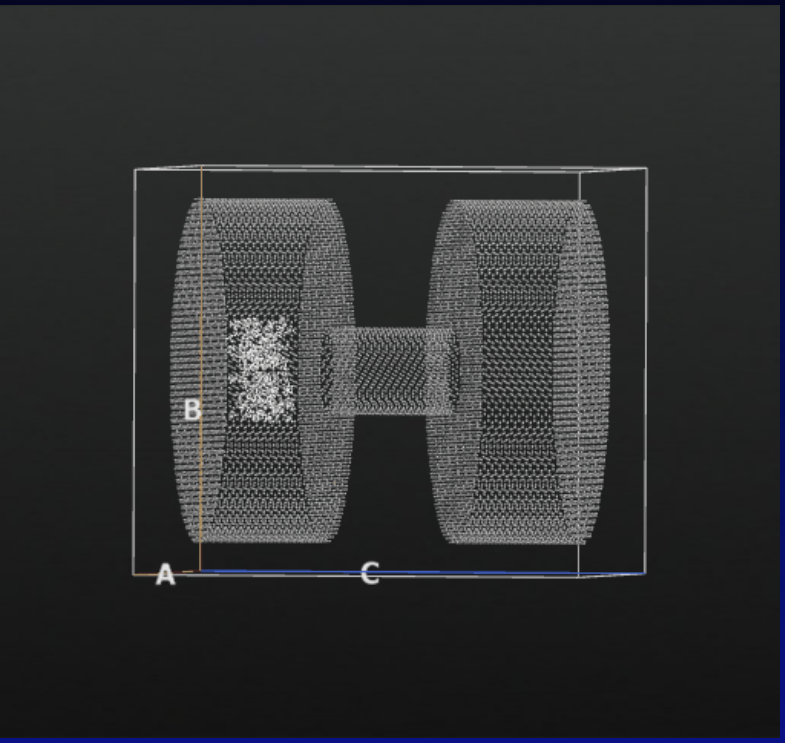
Final temperature of the system

Initial velocity calculation algorithm, The temperature of the system is fixed to 422 Kelvin

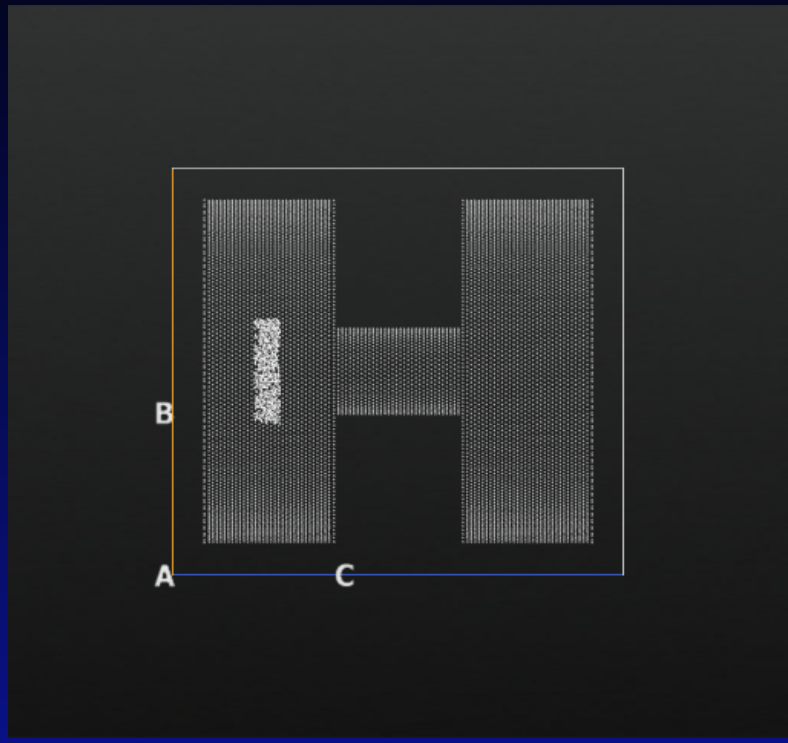
Velocity calculation temperature

Animation of the system

310 Kelvin

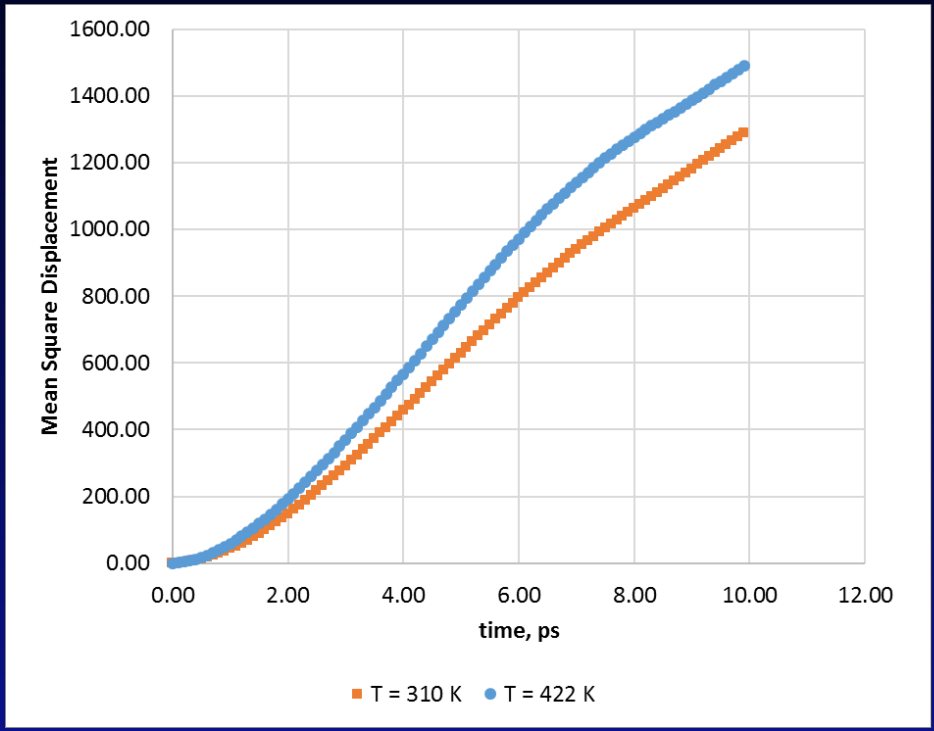


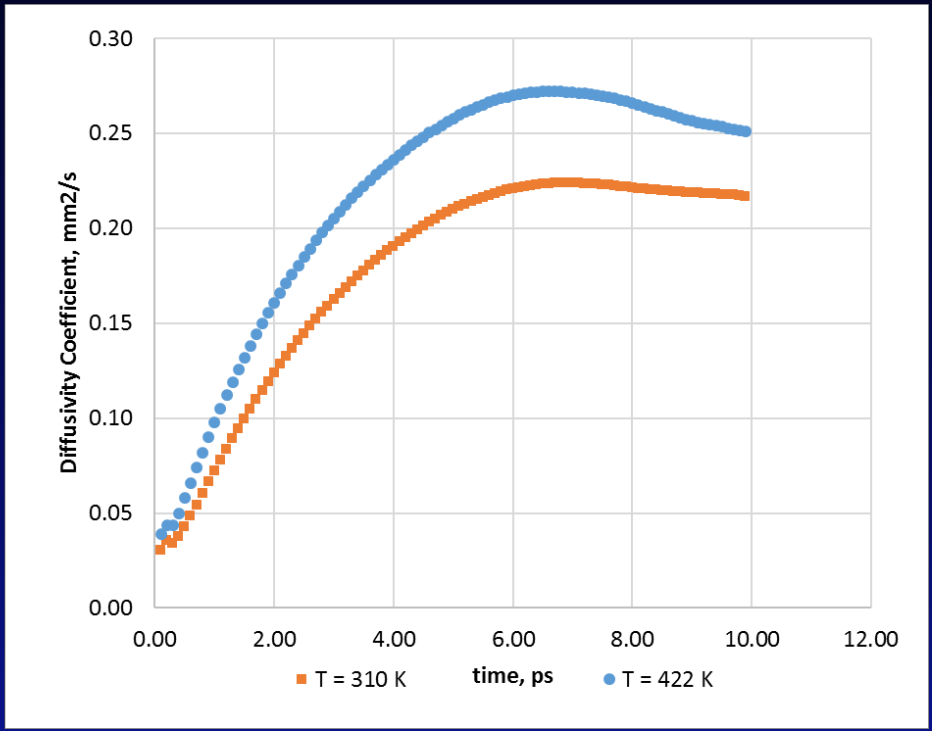
422 Kelvin



- 100 methane molecules simulated in each case
- Initial pressure of each system is 1690 psi (calculated by real gas law)

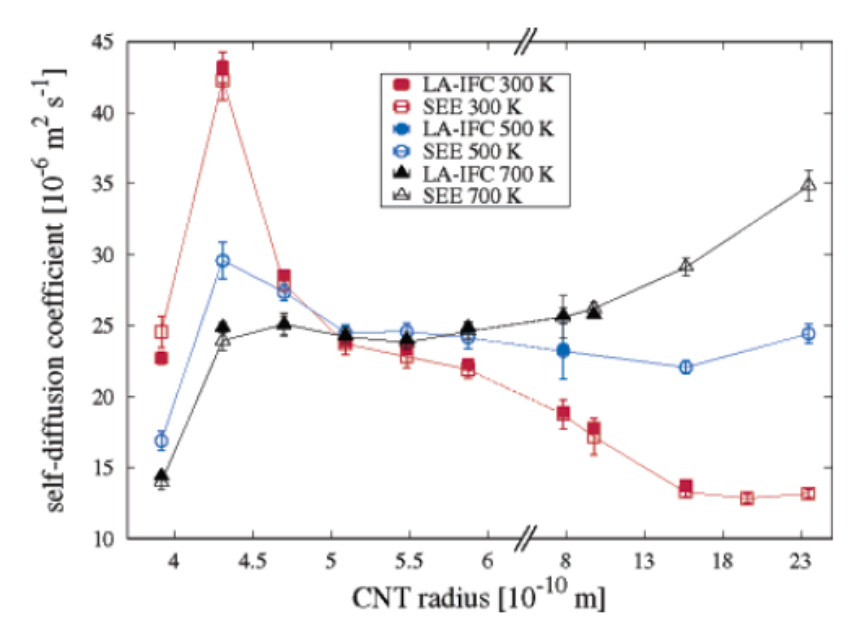
Results: Two pores connected with a nanotube

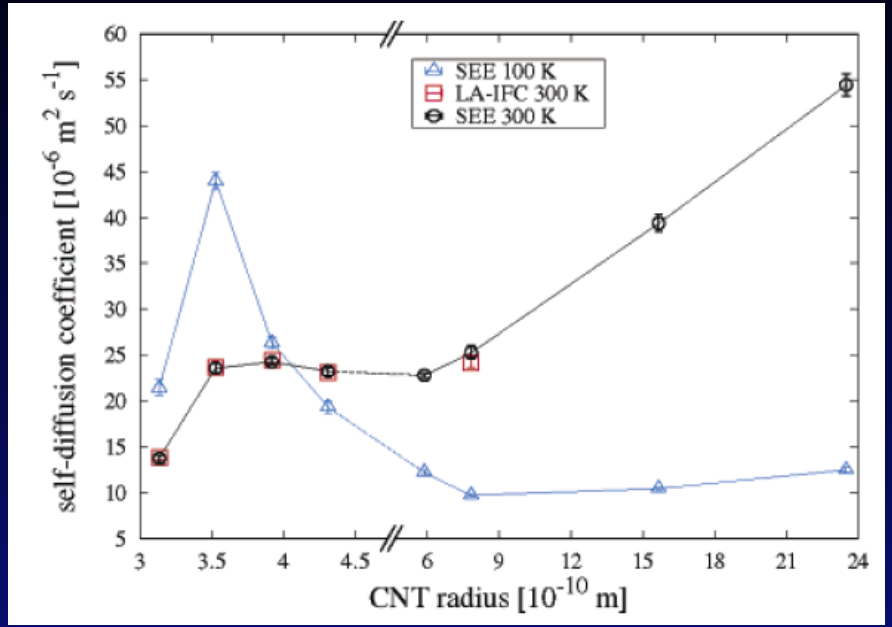




- Sub-diffusion observed in both cases
- The 1st pore is huge compared to the 2nd pore. The output of the simulation is dominated by the 1st pore, where the initial configuration was set.

Results from literature



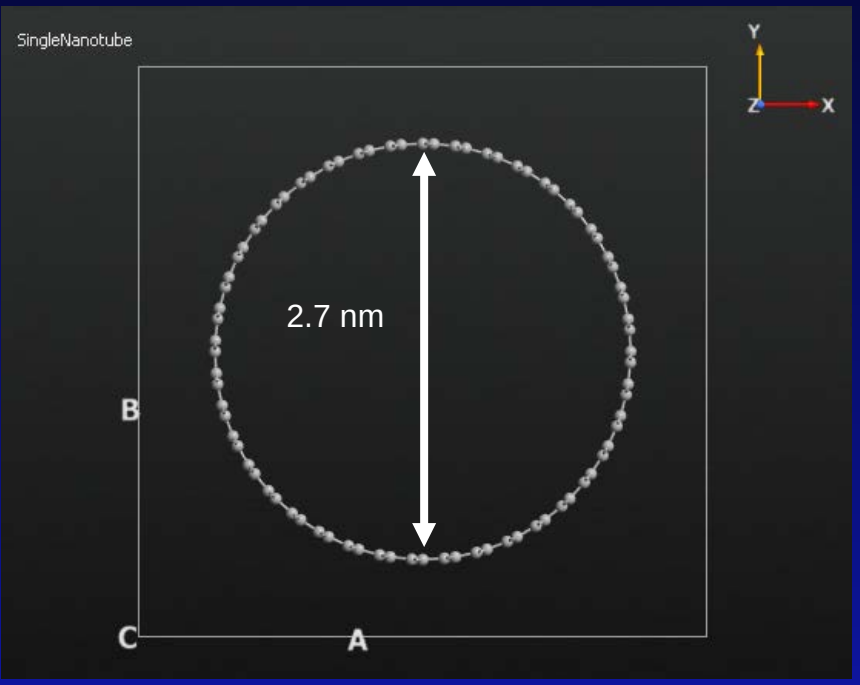


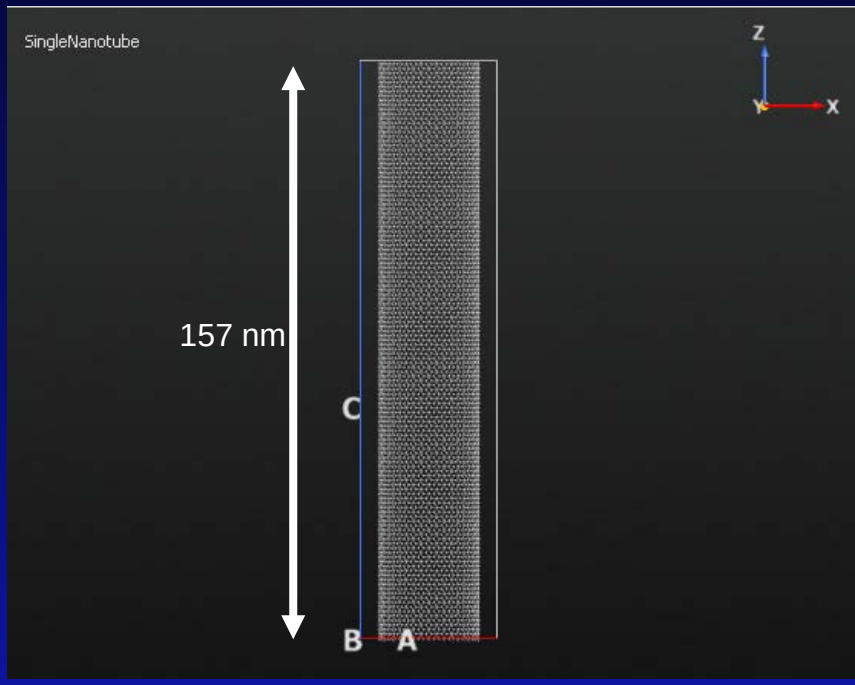
Retrieved from Jakobtorweihen et al.

- The temperature influence is not uniform throughout different pore sizes
- Diffusivity decreases as temperature increases in smaller pores (<5 nm)
  - Due to competing influences of collision frequency and temperature
- At larger pores temperature increases the diffusivity (>5 nm)
  - Due to increase in the velocity (competition between the molecules is negligible)

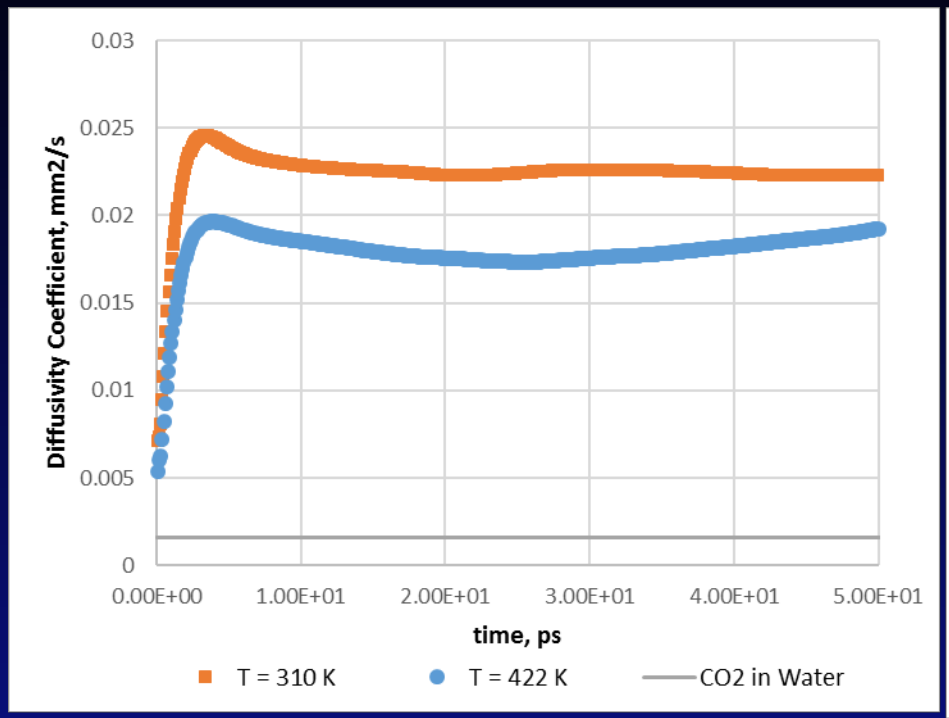
Dimensions of a single nanotube system

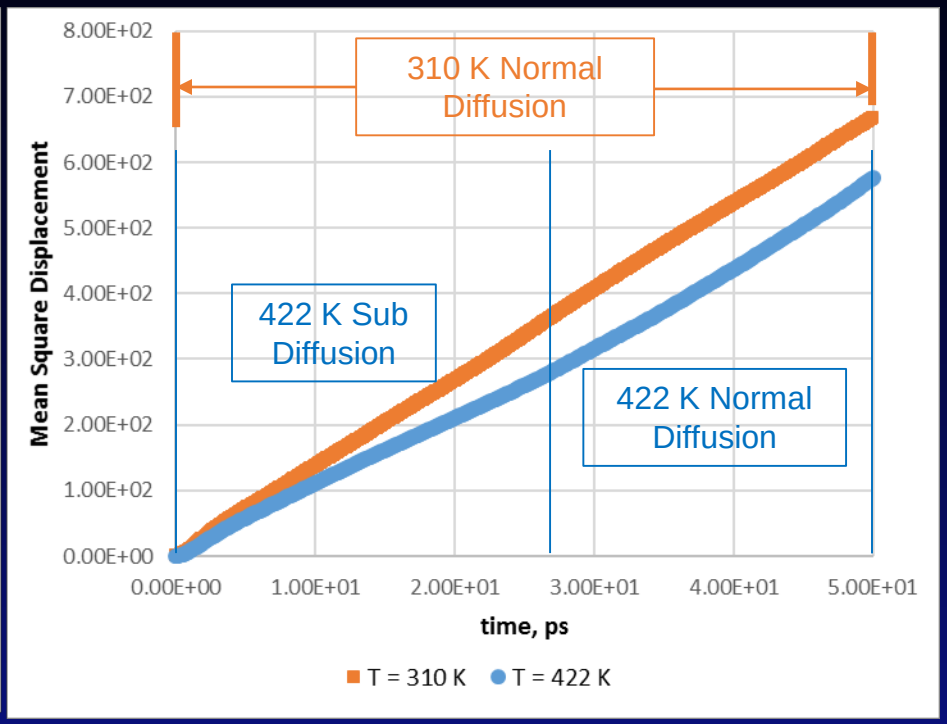
- 2.7 nm diameter
- 157 nm thickness
- Periodic boundary condition





Results: 2.7 nm Nanotube





- Normal diffusion at 310 Kelvin
- Sub diffusion at early times of 422 Kelvin, then normal diffusion after 29 ps.

Conclusion

- Diffusivity of methane in nanotube was studied in terms of:
  - Effect of the pore geometry
  - Effect of the temperature

- At smaller pores (2.7 nm in this study) it is favorable to decrease the temperature, which prevents the molecules from competing and allows them to diffuse faster.

  - At lower temperature (310 Kelvin) → normal diffusion
  - At higher temperature (422 Kelvin) → anomalous diffusion

- At larger pores (11 nm in this study) increasing temperature enhances diffusivity by increasing their energies.
  - Due to the pore geometry, diffusion at both 310 K and 422 K was anomalous diffusion
    - No periodic boundary conditions
    - The system was closed by a carbon wall, which confines the particles

Future Studies

- Create 10 different nanotube systems, of which pore diameters vary between 1-10 nm
  - For each of them, run simulations at 300K, 400K and 500K
  - Create a graph similar to published literature

- Increase the complexity of the system by connecting two or more pores with different diameters
  - Check the effect of the temperature

- Include clay minerals in the pores
- Include large hydrocarbons (representing kerogen)
- Simulate a methane-heptane mixture and check if there is any difference between the diffusivity rates

THANK YOU