Mixed Gas Diffusion Calculator

A tool to calculate the self diffusion constant of a mixture of two gas molecules through a metal organic framework

By Julian C. Umeh

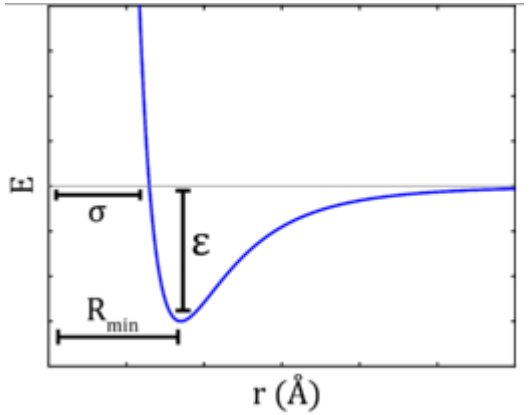
This tool employs the use of RASPA for its backend simulation. RASPA is a molecular simulation software for performing adsorption and diffusion calculations in nanoporous materials. It implements the state-of-art algorithms for Molecular Dynamics and Monte Carlo for various ensembles. In this simulation, we used molecular dynamics and the NVT ensemble.

- Every simulation is performed with production, equilibration and initialization cycles of 10000, 5000 and 5000 respectively.
  - Initialization cycles (monte carlo) set the configuration for the start of equilibration.
  - Equilibration cycles (molecular dynamics) warm-up the simulation.
  - Production cycles (molecular dynamics) are for the data collection.

- Transferrable Potential for Phase Equilibria (TraPPE) forcefield is used to define the molecular interactions for helium and methane.

Mol.	Definition	Ref
CH4	TraPPE	*J. Phys. Chem. B*, 1998, 102, 2569-2577
Ar	TraPPE	*J. Am. Chem. Soc.*,1992, 114, 10024-10035

Lennard-Jones Potential



https://upload.wikimedia.org/wikipedia/commons/thumb/f/fe/Schematic_of_the_Lennard-Jones_6-12_Potential.png/255px-Schematic_of_the_Lennard-Jones_6-12_Potential.png

- For the MOF, forcefield parameterized by the developers of RASPA was used.

Exceptional Negative Thermal Expansion in Isoreticular Metal–Organic Frameworks, Angew. Chem. Int. Ed. 2007, 46, 4496 –4499, DOI: 10.1002/anie.200700218.

MOF	Flexibility	Forcefield
IRMOF-1	Rigid	Dubbledam2007FlexibleIRMOF-1

- Lorentz-Berthelot's model was used as the general mixing rule for the Lennard-Jones potentials

$$\sigma_{ab} = \frac{\sigma_a + \sigma_b}{2} \qquad \varepsilon_{ab} = \sqrt{\varepsilon_a \varepsilon_b}$$

- There are two types of diffusion; self diffusion and collective diffusion.

Self diffusion is the movement of an individual molecule within the bulk of the substance and it is given by;

$$D_\alpha^S = \frac{1}{2dN_\alpha} \lim_{t\to\infty} \frac{d}{dt} \left\langle \sum_{i=1}^{N_\alpha} (r_i^\alpha(t) - r_i^\alpha(0))^2 \right\rangle,$$

Where N_α is the number of molecules of component $_\alpha$, d is the spatial dimension of the system, t is the time and r_i^α is the center-of-mass of molecule i of component $_\alpha$.

Collective diffusion also called transport diffusion describes the transport of mass in the system. It is given by;

$$D^T = \frac{\Gamma}{2dN} \lim_{t\to\infty} \frac{d}{dt} \left\langle \left(\sum_{i=1}^{N} (r_i(t) - r_i(0)) \right)^2 \right\rangle$$

Computing the diffusion constant

Einstein's equation of diffusion is used to calculate the self diffusivity

MSD = 6 D t + C

Where;

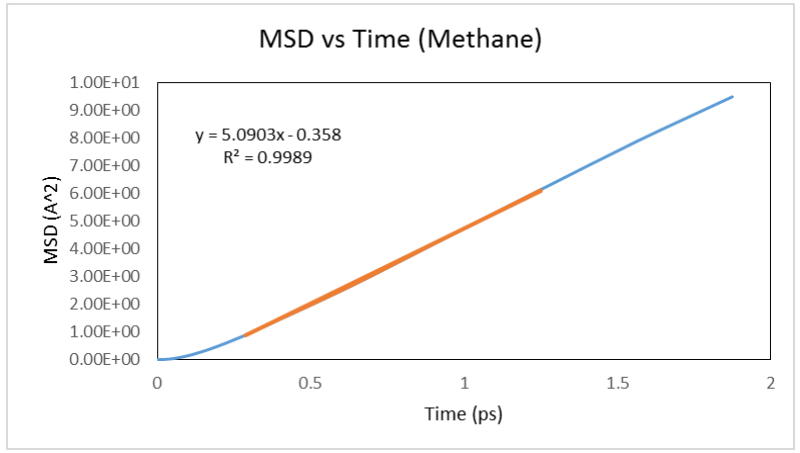
MSD = mean square displacement

msd = $\frac{1}{N}\sum_{j=1}^{n}([r_j(t) - rj(0)]^2)$

D = diffusion constant

t = time

C = constant



The diffusion constant is obtained from the $\frac{slope}{6}$ of the mean square displacement against time graph.

The initial and final few points were omitted and the center points fitted to a straight line.

Its unit is in squared angstrom per picosecond (A^2/ps).

In the graph above, the slope is 5.0903 and diffusivity is $\frac{5.0903}{6}$ = 0.848 A^2/ps

- Gases in nature almost never exist in a pure state, therefore it is important to run simulations of the diffusion of gas mixtures. The results from these simulations will differ from the results of the pure gas especially at higher temperatures where the larger gas molecule may give the smaller molecule the push needed to go through the MOF thereby increasing its rate of diffusion.

- Consider an example where we run a self-diffusion simulation of a gas mixture of helium and methane at 50% mole fraction each at 500 K in IRMOF-1. The diffusion constant for the methane gas is 5.54 A^2/ps and 25.34 A^2/ps for the helium molecule in the mixture containing 16 helium and 16 methane molecules per unit cell. In contrast, the self-diffusivity for methane only simulation is 5.44 A^2/ps and that of helium only is 13.62 A^2/ps for 16 molecules per unit cell.