Path Sampling Calculation of Methane Diffusivity in Natural Gas Hydrates

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Natural gas is one of our most abundant fossil fuels, but the majority of gas reserves are in clathrate-hydrate form. Transport properties in these materials are important for many potential technologies, but measurements are complicated by the need for high pressures, low temperatures, and single crystal samples to separate diffusion along grain boundaries from diffusion within the crystal. This research uses a path sampling method for computing free energies [R. Radhakrishnan and T. Schlick, J. Chem. Phys. 121 2436 (2004)] with reactive flux and kinetic Monte Carlo simulations to estimate the methane diffusivity within a structure I gas hydrate crystal. The calculations support a water-vacancy assisted diffusion mechanism where methane hops from an occupied “donor” cage to an adjacent “acceptor” cage. For pathways between cages that are separated by five-membered water rings, the free energy landscape has a high barrier with a shallow well at the top. For pathways between cages that are separated by six-membered water rings, the free energy calculations show a lower barrier with no stable intermediate. Reactive flux simulations confirm that many reactive trajectories become trapped in the shallow intermediate at the top of the barrier leading to a small transmission coefficient for these paths. Stable intermediate configurations are identified as doubly occupied off-pathway cages and methane occupying the position of a water vacancy. Rate constants are computed and used to simulate self-diffusion with a kinetic Monte Carlo algorithm. Self-diffusion rates are slower than the Einstein estimate because of lattice connectivity and methane’s preference for large cages over small cages. Specifically, the fastest pathways for methane hopping are arranged in parallel (non-intersecting) channels, so methane must hop via a slow pathway to escape the channel. In a hydrate I crystal at 250K with nearly all cages occupied by methane, we estimate D ≈ 7•10-15 X m2/s where X is the fraction of unoccupied cages.