Molecular basis of tetrahydrofuran-induced enclathration

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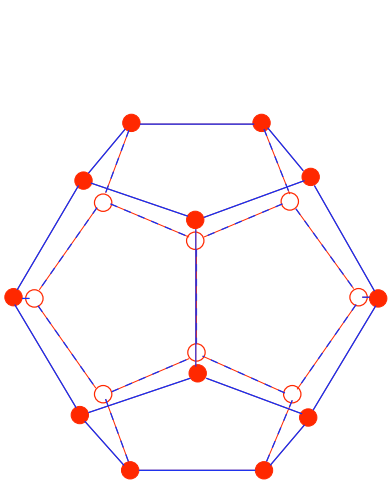
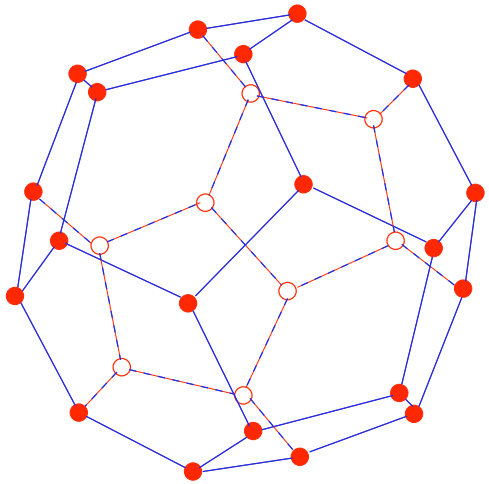
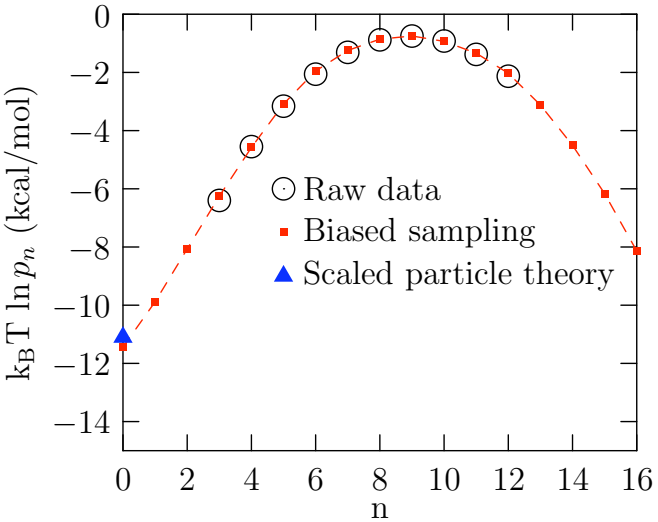
Clathrate hydrates are an important potential source of future energy supply. The clathrate framework is also promising as a molecular cage to sequester CO_2, a global warming gas. These cages, two of which are shown on the right, are made of water molecules (red circles) that interact amongst themselves via hydrogen bonds. The target solute, such as CH_4 or CO_2, occupies the space created in the center of the cage.



Dodecahedron



Hexacaidecahedron



To understand how the clathrate cages form in water, it is of first interest to understand how these cavities form in bulk water. We are studying this process by computer simulations. We have implemented a novel biased sampling technique to obtain the free energy of forming cavities in water, given by the p_0 term (figure on the right). Calculations show that it requires about 11.5 kcal/mol to create a cavity of radius 4 Å, of size similar to those of interest in clathrate hydrates.

☑ The theoretical developments provide novel insights into how the coordination structure of solutes impacts the free energy of the solute in bulk water.

☑ We are presently using these developments to understand the role of tetrahydrofuran on the solubility of CH_4.