DIFFUSION SEPERATION IN ZIFS: A BALANCE BETWEEN ENTHALPY AND ENTROPY

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To strive toward a greener future, a change in the energy consumption of industrial processes is necessary. One of these processes is the separation of small carbon species, found in crude oil, by cryogenic distillation. An improvement to this highly energetic process could be achieved by room temperature sieving[1,2]. One promising material for this is the zeolitic imidazolate framework-8 (ZIF-8).

In this research, the diffusion process of each species is modeled with force fields (FFs) generated with QuickFF[3,4], machine learning potentials (MLPs) derived with Psiflow[5] and ab-initio DFT with CP2K[6]. The simulation technique used to describe the diffusion behavior of the separate species is enhanced molecular dynamics (MD). This results in an efficient way of sampling the free energy profile (FEP) along the diffusion axis. The FEP can be further investigated by deconvoluting it into its enthalpic and entropic contributions as well as by deprojecting the1D-FEP into a 2D-FEP in terms of the diffusion progression as well as the gate size. The enthalpic contribution derives from the host-guest interactions and host deformations, while the entropic contribution entails the configurational freedom of the system and adsorbate and the amount of disorder in the system.

Using the methodology outlined above, the diffusion path of a guest molecule is investigated. Here, the maximum in free energy coincides with the maximum in enthalpy. If the deprojection is now applied, the host deformation portion of the enthalpy can be plotted as gate size increase, which is seen in figure 1. The entropy also has a maximum here, which is a result of the confinement of the guest molecule when diffusing through the gate. This gives insight into the physics of diffusion, which can be used to find and develop host molecules that are more efficient at the separation of small carbon species in crude oil.

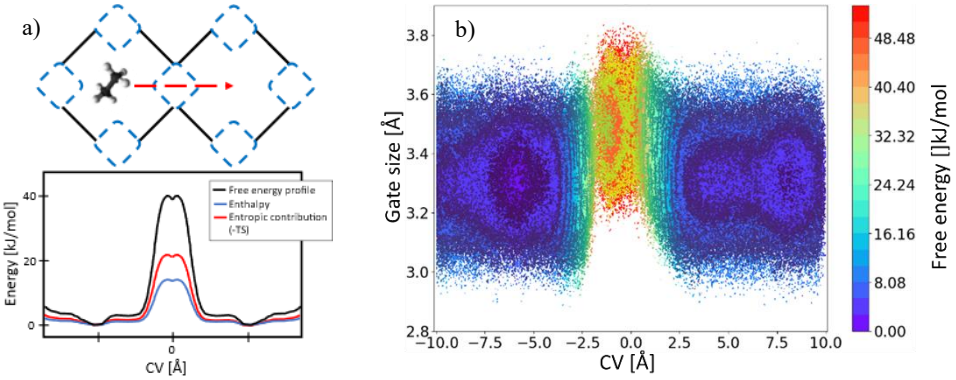

Figure 1: (a) Schematic view of an ethane molecule diffusing in a host molecule coupled with a schematic free energy profile and a sketch of the enthalpic and entropic contribution to the free energy profile. (b) 2D plot of the calculated gate sizes, colored in with the respective free energy of the system, against the CV, or position of the diffusing species in respect to the gate.

References

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