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Molecular Simulations on Gas Diffusion in Nanoporous Carbon

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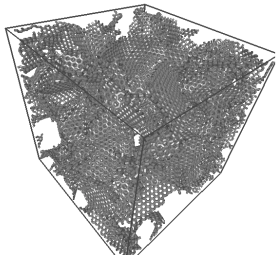
1. Introduction

In this work, we utilized molecular dynamics simulations to investigate gas diffusion in realistic nanoporous carbon models. We will focused on how the structure of the porous medium affects the gas diffusion. The porous structural features of interests include topological defects, dangling bonds, size and connectivity of the pores. Through a mimetic virtual synthesis routine, porous structures with distinct structural signatures will be generated. Gas molecules including argon and nitrogen are then introduced to those porous structures. Gas molecules are driven by a virtual membrane with asymmetric permeability, thus transport diffusivity are obtained and are correlated to the porous structure.

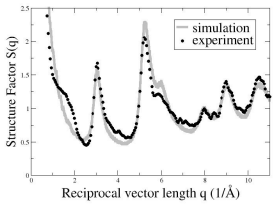
2. Mimetic sample preparation

One of the unique aspect of this work is that we utilize a mimetic sample preparation technique to obtain the nanoporous carbon model. Past attempts have focused on construction-type models [1], which aggregates certain building blocks [1], or reconstruction-type model [2], which recursively optimizes the atomic structure by targeting experimental measurements. Both approaches suffer from the lack of uniqueness and possible unphysical local atomic arrangements [3].

Recently, we constructed a physically motivated nanoporous carbon model that simulates the growth of nanoporous carbon network from random monatomic carbon gas [4]. This model reproduces the correct density and porosity without unphysical structures (i.e. 3- or 4-member rings). Most importantly, the obtained structural model has excellent agreement with activated saccharose cokes in terms of the experimental structure factor *s(q)* [5] as shown in Figure 1. This level of agreement to experiments has only been seen in the best reconstruction approach [2].



(a)



(b)

Figure 1. (a) Nanoporous carbon model from virtual synthesis [4]; (b) Structure factors as a function of reciprocal vectors from simulations (gray curve) and experimental activated saccharose cokes (black dots) [5].

3. Diffusivity and surface diffusivity measurement

A virtual membrane [6] is placed at the boundary of the simulation box to achieve steady-state diffusion of gas molecules in nanoporous carbon. This membrane has a direction-dependent permeability such that the flow from left to right is easier than the reverse direction. In this way, a chemical potential gradient is maintained across the simulation box, from which the transport diffusivity can be obtained.

During the mass-transport process, the guest molecules can either diffuse through the pore (Knudson diffusion or bulk diffusion), on the pore wall (surface diffusion) or a combination through desorption/adsorption processes [7]. We used a diffusion pathway analysis to extract surface diffusion contribution. The key is to determine whether the guest molecule is adsorbed on the porous surface along the trajectory. The isolation of surface diffusion contribution is critical since distinct diffusion modes behave very differently [8]. More importantly, it is likely that the surface diffusivity will correlate directly to the curvature/defects of the nanoporous surface, while pore size/connectivity will correlate to the rest of mass transport.

3. Conclusion

Transport diffusivity as well as the surface diffusion contribution of gas molecules in realistic nanoporous models are measured numerically using molecular simulation techniques. The transport properties are comprehended in terms of the nanoporous structures including atomic defects, ring defects and pore characteristics. Directions on how to control the transport properties of nanoporous carbon by tuning synthesis procedures will be discussed.

References

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