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Self-Diffusion Coefficients in Nanoporous Materials from Entropy Scaling

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Nanoporous materials such as metal-organic frameworks (MOFs) or covalent-organic frameworks (COFs) are gaining research attention due to its vast design space and versatility in various applications. Many screening studies have been performed on large databanks of these materials to identify best performing materials for specific adsorption applications. These screening studies were performed mostly on equilibrium properties such as selectivity or working capacities, as well as on process parameters without properly considering for kinetics in the process model itself. Predicting transport properties of fluids in nanoporous materials is desirable since it has been shown that many adsorption processes are affected by kinetics [1]. The state-of-the-art of predicting transport properties in confined spaces involves molecular dynamics simulations (MD) or Transition State Theory (TST), which are computationally resource intensive especially for high-throughput calculations. In this work, we propose a theoretical framework to predict diffusion coefficients based on entropies which is orders of magnitude faster than conventional MD or TST.

Entropy scaling [2] is a principle according to which transport properties such as self-diffusion coefficients, thermal conductivity, and viscosity are related to the residual entropy of the system. When these transport properties are normalized with a suitable reference, they can be described to good approximation as univariate functions of solely the residual entropy. Entropy scaling has been applied to self-diffusion coefficients for bulk systems [3], describing the self-diffusion coefficient as

$$\ln(D^*) = \ln\left(\frac{\rho D}{\rho D^{\text{ref}}}\right) = a - b(1 - \exp(s^*))(s^*)^2 + c(s^*)^3, \tag{1}$$

where a, b and c are adjustable parameters for each fluid in the Ansatz function, ρ *is the bulk density, and* D^{ref} as well as D are the Chapman-Enskog reference [4] and experimental self-diffusion coefficients, respectively. The residual entropy $s^* = s^{\text{res}}/(k_{\text{B}} m_i)$ was obtained from the PC-SAFT equation of state. Members of our group have recently extended this framework to predict local shear viscosity for inhomogeneous fluids near solid interfaces [5].

Classical density functional theory (DFT) is an efficient method to predict equilibrium properties of inhomogeneous fluids. In combination with entropy scaling, classical DFT can be used to predict transport properties of confined fluids. The grand potential functional can describe open systems in thermodynamic equilibrium, which is the case for adsorption,

$$\frac{\delta\Omega[\boldsymbol{\rho}(\mathbf{r})]}{\delta\rho_i(\mathbf{r})} = 0 = \frac{\delta F[\boldsymbol{\rho}(\mathbf{r})]}{\delta\boldsymbol{\rho}(\mathbf{r})} - \mu_i + V_i^{\text{ext}}(\mathbf{r}), \tag{2}$$

where Ω and F are the grand potential and Helmholtz energy functionals, $\rho_i(\mathbf{r})$ is the three-dimensional inhomogeneous molecular density, μ_i is the chemical potential of species i, and $V_i^{\text{ext}}(\mathbf{r})$ is the three-dimensional external potential which describes the interaction between the solid framework atoms and the fluid molecules. Classical DFT has been shown to be a predictive model for adsorption properties of small, non-polar adsorbates, while requiring only up to four orders of magnitude lower computational resources as conventional grand canonical Monte Carlo simulations [6].

Classical DFT does not only provide access to the inhomogeneous molecular density profiles, but also to the inhomogeneous entropic density profiles, which is used for entropy scaling. The inhomogeneous residual entropy is defined as

$$s^{\mathrm{res}}(\mathbf{r}) = -\left(\frac{\partial f^{\mathrm{res}}(\mathbf{r})}{\partial T}\right)_{\rho(\mathbf{r})}, \tag{3}$$

where $f^{\mathrm{res}}(\mathbf{r}) = f^{\mathrm{res}}[\boldsymbol{\rho}(\mathbf{r})]$ is the Helmholtz energy density, which is related to the Helmholtz energy according to $F[\boldsymbol{\rho}(\mathbf{r})] = \int f^{\mathrm{res}}(\mathbf{r}) d\mathbf{r}$. The reduced residual entropy is defined here as

$$s^{*,\mathrm{res}}(\rho(\mathbf{r}); \mu, T) = \frac{\int s^{\mathrm{res}}(\mathbf{r})/k_{\mathrm{B}}\, \mathrm{d}\mathbf{r}}{\int \bar{\rho}^{\mathrm{disp}}(\mathbf{r})\, \mathrm{d}\mathbf{r}}. \tag{4}$$

We first generated model graphene pores to calculate self-diffusion coefficients of a Lennard-Jones fluid at a reduced temperature of $T^* = 2.0$ using MD simulations. Self-diffusion coefficients were calculated using the mean-squared displacements and Einstein equation. We studied straight cylindrical pores of diameters and cylindrical pores with an aperture each of various diameters.

For entropy scaling, a suitable reference model for the self-diffusion coefficient is required. We tested a simplified version of the model proposed by Liu et al. [8], which uses a modified free volume (MFV) method as the reference self-diffusion coefficient. This model assumes that the bulk and wall contributions of self-diffusivity are additive, weighted respectively with free volume fractions and non-occupiable volume fractions. The bulk contribution can be approximated with the Chapman-Enskog model and the wall contribution with the Knudsen model [7]. We observed a relatively satisfying univariate relationship between the reduced self-diffusion coefficients in the model pores and the reduced residual entropies only for cases with moderate or large cylindrical pores or cylindrical pores with moderately large apertures. This shows that the combination of Chapman-Enskog and Knudsen reference models is not expected to perform reliably for pores with narrow apertures.

Future work includes considering models that consider “entropic barriers” instead of naïvely attributing all wall effects to the Knudsen model. A more comprehensive database is needed to derive a meaningful definition of residual entropy for inhomogeneous, porous systems. We apply the entropy scaling model to results from MD simulations of fluids in actual microporous materials, such as MOFs or COFs. The model will then be used to approximate Maxwell-Stefan diffusion coefficients, focusing on chemically and structurally similar species where this approach is expected to perform reliably.

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