

Correlations Between Static Thermodynamic Properties and Dynamic Transport Properties of Confined Fluids: Application to Adsorption and Diffusion in Porous Solids

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It is well appreciated that placing a fluid under confinement drastically alters both its static and dynamic properties relative to a bulk, unconfined fluid. However, predicting these changes (even semi-quantitatively) remains a scientific challenge, and thus, there exist fundamental knowledge gaps in a number of areas where confined fluids play a central role. Examples include lubrication, friction, and adsorption. In an effort to understand the impact of confinement on fluid properties, recent work has demonstrated that there exists a robust relationship between static fluid properties, such as excess entropy and insertion probabilities, and dynamic fluid properties, in particular, the self-diffusion coefficient, that is independent of the geometry of the system when the confinement is straightforward. However, such relationships have not been observed for confined fluids, which are prevalent in applications such as adsorption. Using Monte Carlo and Molecular Dynamics simulations in tandem, we perform this combined static-dynamic analysis to models of light gas adsorption in simple confinements such as graphitic carbon materials to systematically investigate the effect of the fluid-material interaction strength on the correlation of static and dynamic properties. We observe that fluids confined in strongly attractive pores display three distinct diffusive regimes when cooled below the critical point. These regimes are directly related to the structural arrangement in the pore, and hence, to the thermodynamic properties of the fluid. Even though weaker adsorbing pores exhibit a qualitatively different adsorption isotherm (e.g., the absence of multilayer adsorption), the relationship between the diffusive regimes and the underlying fluid structure is identical to that in strongly adsorbing pores. We perform additional analyses that allow for separation of the average dynamic properties into position-dependent dynamic properties through which we demonstrate how the three distinct diffusive regimes in adsorption processes are related to specific equilibrium structures at the relevant state points.