Thermodynamics and Transport of Ultra-Confined Fluids using Nanotube and 2D Polyaramid Conduits

Nanotechnology has given us a large number of new materials with which to confine fluid phases, altering their thermodynamic and transport properties considerably from the corresponding bulk. Over the past decade, my laboratory at MIT has been centrally focused on quantitatively understanding these alterations, and ultimately using them to solve longstanding research challenges. We established the Center for Enhanced Nanofluidic Transport (CENT) at MIT with support from the U. S. Department of Energy (cent.mit.edu). In this presentation, I will highlight our use of two distinct platforms to this end: (1) the interior of carbon nanotubes as nanofluidic conduits, and (2) a newly discovered 2D polyaramid polymer recently synthesized by our team, a 2D version of a polymer analogous to Kevlar. We used carbon nanotubes as fluidic conduits to formulate and experimentally validate the first confined fluid Equation of State (EOS). Carbon nanotubes of precise diameters from 0.8 to 2.0 nm, filled with water and subjected to variable laser heating, were used to measure the confined fluid density using the vibrational frequency of the encapsulating graphene wall, mapping the phase behavior as a function of confinement diameter. The resulting traces of density versus temperature at constant pressure, or isobars, are well described by a confined fluid EOS that builds on the work of Sandler and co-workers. We find that for water, the entropy versus entropy of confined adsorption exhibits a linear compensation, similar to what is observed for activated carbon. Reformulating the EOS for a 2D slit shaped pore is able to predict the well-known maximum in capillary pressure at 1.3 nm spacing for a rectilinear graphene pore. The validation of this EOS for nanopore systems is a significant advance in engineering prediction for the narrowest and technologically important materials.

At the other extreme limit, confinement can be exerted as to preclude molecular transport entirely. All polymers exhibit fluid permeability at some level through the free volume of entangled polymer chains. However, two-dimensional (2D) materials including graphene stack densely and can exhibit molecular impermeability, allowing new types of fluidic manipulation. Solution-synthesized 2D polymers that exhibit the latter by poly- condensation have been a longstanding goal. In this talk, we demonstrate self-supporting, spin-coated 2D polyaramid nanofilms (Zeng, et al, Nature, 602, 91, 2022) that exhibit N_2 permeability below 3.1×10^{-9} Barrer, roughly 6500-fold lower than existing polymers, and similar for other gases. Optical interference during the pressurization of nanofilm-coated microwells allows measurement of mechanosensitive rim opening and sealing, creating gas-filled bulges stable exceeding 3 years. This discovery enables 2D polymer resonators with high resonance frequencies (~8 MHz) and Q factors up to 537, similar to graphene. A 60-nm coating of air-sensitive perovskites reduces the lattice degradation rate 14- fold with an O_2 permeability of 3.3×10^{-8} Barrer. Molecularly impermeable polymers promise the next generation of barrier materials that utilize exceedingly little polymer to maximize chemical rejection, ultimately contributing to sustainable materials development.