

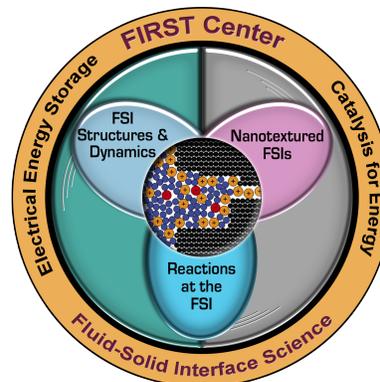
FIRST Center Research Perspective:

Effects of Nano-Confinement on the Fluid Interfacial Structure, Dynamics and Thermodynamic behavior

Ariel A. Chialvo
Oak Ridge National Laboratory

Peter T. Cummings
Vanderbilt University

Matthew C. F. Wander, Kevin L. Shuford
Drexel University



Research Summary: Our molecular dynamics (MD) simulations of graphene interactions with water and aqueous electrolytes probed how the compound effects of surface-type and confinement might be manipulated to engineer the fluid-solid interfacial behavior (e.g., surface wettability), the thermodynamic response functions, the dynamics of confined water, and the differential partition of ionic species from nano-confinement [1-4]. Current results indicate that fluid confinement between graphene sheets induces large enhancement of the isobaric and isothermal thermodynamic response functions of the aqueous phase, and significant slowdown of the water dynamics over that of the corresponding bulk counterparts, as well as preferential partition of polyvalent cations between confined and corresponding bulk environments. The detected enhancement of the graphene-water interfacial tension (*i.e.*, hydrophobicity) suggests that the surface lattice plays a decisive role in determining surface wetting and the onset of wet-dry transition.[5] Moreover, studies of aqueous electrolytes in contact with a family of porous carbon geometries provide an atomic scale depiction of ion transport dynamics in different environments to elucidate their influence on aqueous electrolyte supercapacitors.[6-8]

Technical Details: MD simulations of atom-explicit models of water and aqueous electrolytes were performed to determine the profiles of the potential of mean force (PMF) relevant to the process of graphene-plate association, involving unstrained flat, tensile-strained flat, and precisely defined corrugated surfaces. According to a proposed formalism [2] these profiles provided the avenue to define unambiguously the hydrophobic/hydrophilic nature of the fluid-surface interactions, without resorting to the usual definition of a contact angle, but instead, the change of sign of the solid-fluid interfacial tension or the logarithm of the corresponding residual association constant. Consequently, our simulations were able to capture the interfacial and wetting behavior of (flat) water at graphene multilayers grown epitaxially on silicon carbide single crystal surfaces, probed by contact wetting angle and synchrotron X-ray reflectivity measurements [5]. To manipulate the graphene-water interfacial, and consequent confinement, behavior either surface corrugation or biaxial tensile-strain (**Figure 1**) was introduced, which resulted in significant changes not only on the surface wettability, but also in the isothermal/isobaric thermodynamic

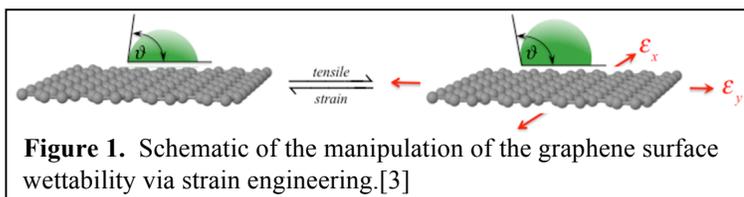
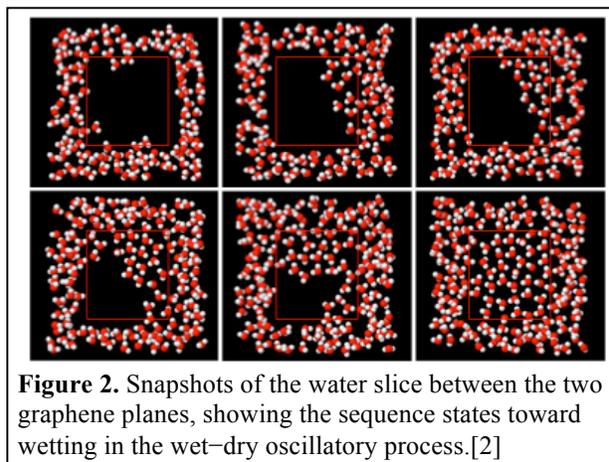


Figure 1. Schematic of the manipulation of the graphene surface wettability via strain engineering.[3]

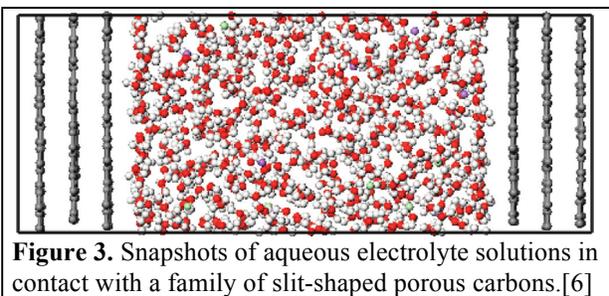
responses as well as in the dynamics of the confined water[2, 3].

As the interplate separation between two graphene surfaces is reduced, the fluid (water or aqueous electrolyte solution) is expelled from confinement, and ultimately, the subnanometer gap between graphene plates becomes empty. On the one hand, for pure water we detected that the expulsion of water from these finite-size slit pores proceeds as an oscillatory process of filling and emptying of the confined space with a nanosecond time scale. The oscillatory behavior is consistent with the evaporation mechanism of confined water between finite-size carbon plates whose small surface size does not allow cavity formation.



Consequently, water is expelled from confinement by density fluctuation (**Figure 2**). On the other hand, as the interplate distance becomes similar to the size of hydrated ionic species, the differential hydration of these species would prevent local electroneutrality in these open systems through the selective expulsion of ions bearing larger hydration shells from the confined spaces, and resulting in a significant ion partitioning between the confined and bulk environment.[1] The magnitude of the ion partition exhibits a very strong dependence with the surface type and the interplate distance, as a manifestation of the degree of overlapping of approaching interfacial structures upon confinement.[4] Evidence from or simulation and experimental sources from elsewhere suggest that the enhancement of the thermodynamic response functions of confined water depend primarily on the degree of fluid confinement, whereas the nature of the fluid-substrate interactions – hydrophobic versus hydrophilic – plays a secondary role. We should be cautious about these observations, however, in that the relative contributions to the compound (confinement plus substrate type) effect might depend strongly on the interplate distance h , *i.e.*, on the degree of interfacial overlapping or the ability of the system to accommodate fully- or partially-overlapped water layers.

A variety of alkali halide, aqueous electrolyte solutions in contact with neutral and charged planar-graphite slit-pores were modeled by MD simulation (**Figure 3**). Firstly, many ions show distinct behavior relative to the baseline of the NaCl brines: Li^+ displays particularly good ion pairing behavior; K^+ shows some particularly interesting properties relative to Na^+ electrolyte brine, and for certain applications, the benefits may outweigh the costs; F^- is a particularly bad choice for capacitive energy storage, as it is likely to precipitate fully in the slits under low voltage; Br^- is at least as good a performer as Cl^- , but I^- displays lower conductivity despite the low ion pairing results.[6] Secondly, size trends in structure and transport properties are examined by varying the choice of ions among the alkali metal and halide series.[7, 8] As with the uncharged pores, system dynamics are driven by changes in hydration behavior and specifically by variations in the number of hydrogen bonds per water molecule, and the larger ions diffuse more rapidly under high surface charge



conditions than the smaller ions. Finally, a quantitative fit to the interfacial charge structure confirms the presence of two distinct types of layers (i.e., the structured adsorption layer and diffuse layer) in an aqueous interface.[8]

Significant Impacts on Science and Technology: The approach pursued in this research effort has provided a versatile tool to gain fundamental understanding of aqueous/graphene fluid-solid interfacial and confined fluid behavior through the interrogation of the system response to perturbation of defining parameters such as graphene surface lattice, degree of fluid confinement, state condition and fluid composition. The outcome of this effort has been **(a)** the proof of principle for the modification and eventual control of the wettability of graphene surfaces based on the manipulation of the graphene lattice, and **(b)** the detection of unexpected microscopic behavior with profound thermodynamic relevance for the macroscopic modeling of confined fluids. In brief, we observed *(i)* strong effects of corrugation and tensile strain on the solid-fluid interfacial tension, the surface association, and the thermodynamic response functions; *(ii)* a strong effect of confinement on the dynamics of water, but weak to negligible dependence on surface type; *(iii)* a strong effect of surface type on ion partitioning into graphene slit pores; *(iv)* oscillatory wet-dry transition in subnanometer graphene slit pores as a manifestation of density fluctuations within finite confinement. This model indicates that the chemistry of the interface is able to create a small interfacial potential, and it shows how water molecules can rotate to increase charge separation in response to a surface potential. Furthermore, the investigations of comparing different alkali halide solutions help to determine their interfacial and confinement properties with regards to the capacitive electrical energy storage and discharge capabilities at fixed porous carbon electrode surfaces.

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