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Abstract:
We have observed fragile-to-strong dynamic crossover phenomena of alpha relaxation time and self diffusion constant in 1-d and 2-d confined supercooled water. The alpha relaxation time is measured by Quasi-Elastic Neutron Scattering (QENS) experiments and the self diffusion constant by Nuclear Magnetic Resonance (NMR) experiments. Water is confined in 1-d geometry in cylindrical pores of nanoscale silica materials, MCM-41 and in Single-wall and Double-wall Carbon Nanotubes. It is in 2-d geometry as the hydration water on surfaces of biopolymers, protein, DNA, and RNA. The crossover phenomena can also be observed by measuring the Mean Square Hydrogen Atom Displacement derived from Incoherent Elastic Neutron Scattering experiments and from appearance of a Boson peak in Incoherent Inelastic Neutron Scattering experiments.

We observe a pronounced violation of the Stokes-Einstein relation at and below the crossover temperature at ambient pressure. Upon applying pressure to the confined water, the crossover temperature is shown to track closely the Widom line emanating from the existence of a liquid-liquid critical point in an unattainable deeply supercooled state of bulk water. Relations of the dynamic crossover phenomena to the existence of a density minimum in supercooled confined water and to conformational flexibility of the hydrated biopolymers will be discussed [see 1, 2, 3, 4].

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References


Figure Caption:

Panel (A) shows the measured average translational relaxation time $\langle \tau_T \rangle$ of water confined in Double-Wall Carbon Nanotubes (DWNT) of inner diameter 16 Å plotted in a log scale against $1/T$. It shows a well-defined cusp-like dynamic crossover behavior occurring at $T_L = 190$ K. The solid line represents fitted curves using the VFT law, while the dashed line is the fitting according to the Arrhenius law. For comparison, panels (B1) and (B2) show the results of our previous experiments on super-cooled water confined in porous silica material MCM-41 with two different pore sizes, which show that the crossover temperature $T_L$ is insensitive to confinement pore sizes. From the results shown in the upper and lower panels, we estimate that water confined in a hydrophobic substrate (DWNT) has a lower dynamic crossover temperature by $\Delta T_L \approx 35$ K, as compare to that in a hydrophilic substrate (MCM-41) [5].
(A) \( T_L = 190 \text{ K} \)

\[ \langle \tau_r \rangle \quad (\text{ps}) \]

\[ T_0/T, \ T_0=146 \text{ K} \]

\[ E_A = 2.63 \text{ kcal/mol} \]

Hydrated DWNT

Exp. result
Arrhenius law
VFT law

(B1) \( \sim 18 \text{ Å pore size} \)

\[ \langle \tau_{1,3} \rangle \quad [\text{ps}] \]

\[ T_0/T, \ T_0=200 \text{ K} \]

Arrhenius
VFT \( D=1.47 \)

(B2) \( \sim 14 \text{ Å pore size} \)

\[ T_0/T, \ T_0=170 \text{ K} \]

Arrhenius
VFT \( D=4.62 \)