Compelling evidence for fluid-solid transition of nanoconfined fluids

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It is well known that the behavior of fluids confined to the order of a few nanometers may differ greatly from that of the corresponding bulk fluid.(1) In the 1980s and early 1990s a large number of studies were reported on a variety of ultrathin liquid films confined between mica surfaces.(2) Although the fluids investigated ranged from linear alkanes(3) to cyclical(4) and globular(5) molecules, they exhibited one common feature: When their confinement reached the order of several molecular diameters, a rapid many-orders-of-magnitude increase in the viscosity of the confined fluid was observed, together with behavior typical of the stick-slip response of a crystalline solid structure.(6) However, no consensus as to the nature of this transition has been achieved and, for over a decade, there has been intense debate as to whether it is a first-order (crystallization) or second-order (vitrification) order phase transition. The increasing need to design and fabricate nanoscale devices adds urgency to the need to clarify this issue, and has motivated us to study confinement phenomena using computational molecular simulations, which inherently provide atomic resolution. Making use of high performance supercomputers, we utilize efficient parallel molecular dynamics simulations, coupled with fully-flexible atomistically-detailed molecular models, to show that when cyclohexane or dodecane are sufficiently confined between mica sheets, they undergo a robust phase transition to a layered and ordered solid-like structure. This provides compelling evidence in the debate over confinement-induced phase transitions and sets a new benchmark in the simulation of these systems.

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