Electronic Supplemental Information

Ferroelectric hexagonal and rhombic monolayer ices

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A. The molecular dynamics simulations for water confined between two single graphene sheets

Our previous study already demonstrates the formation of LD-48MI is insensitive to the atomic structure of the wall surface by using two structureless walls and two single graphene layers, respectively.[1] To confirm that the formation of the monolayer ice phase we observe within structureless walls is also insensitive to the atomic structure walls, we perform independent constant-volume and constant-temperature (NVT) MD simulations of 400 TIP5P[2] water molecules confined in two single graphene layers. The area densities of water are respectively 8.862, 11.037, 14.024, and 15.192 (nm^{-2}), corresponding to those for LD-48MI, MD-HMI, HD-fRMI, and HD-pRMI. The area density of 9.817 nm^{-2} is also carried out to study the formation of coexistence of LD-48MI and MD-HMI. For the system of area density of 15.192 nm^{-2}, the distance between the two graphens is fixed at 0.7 nm, and the distance is fixed at 0.6 nm for other four systems. The LJ parameters for carbon and oxygen interaction are $\sigma_{c\text{-}o}$ = 0.3257 nm and $\varepsilon_{c\text{-}o}$ = 0.4908 kJ/mol. The long-range electrostatic interactions are treated by PME method.[3] Spontaneous formation of LD-48MI, MD-HMI, HD-fRMI, HD-pRMI, and the coexisting LD-48MI/MD-HMI are observed depending on the area density of water (Movies S4-S8). It can be seen form Fig. S1 that these monolayer ice structures (other than some defects) are identical to the monolayer ice phases observed within structureless walls, indicating that structure of surface does not affect the phase stability and structure of confined water.

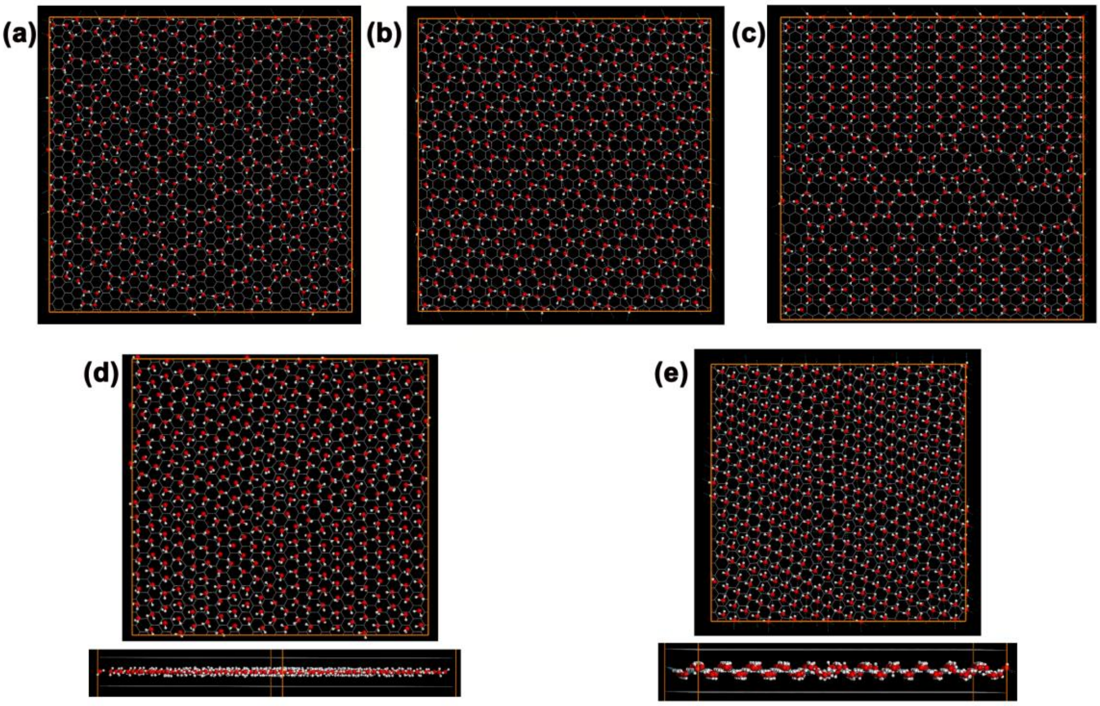
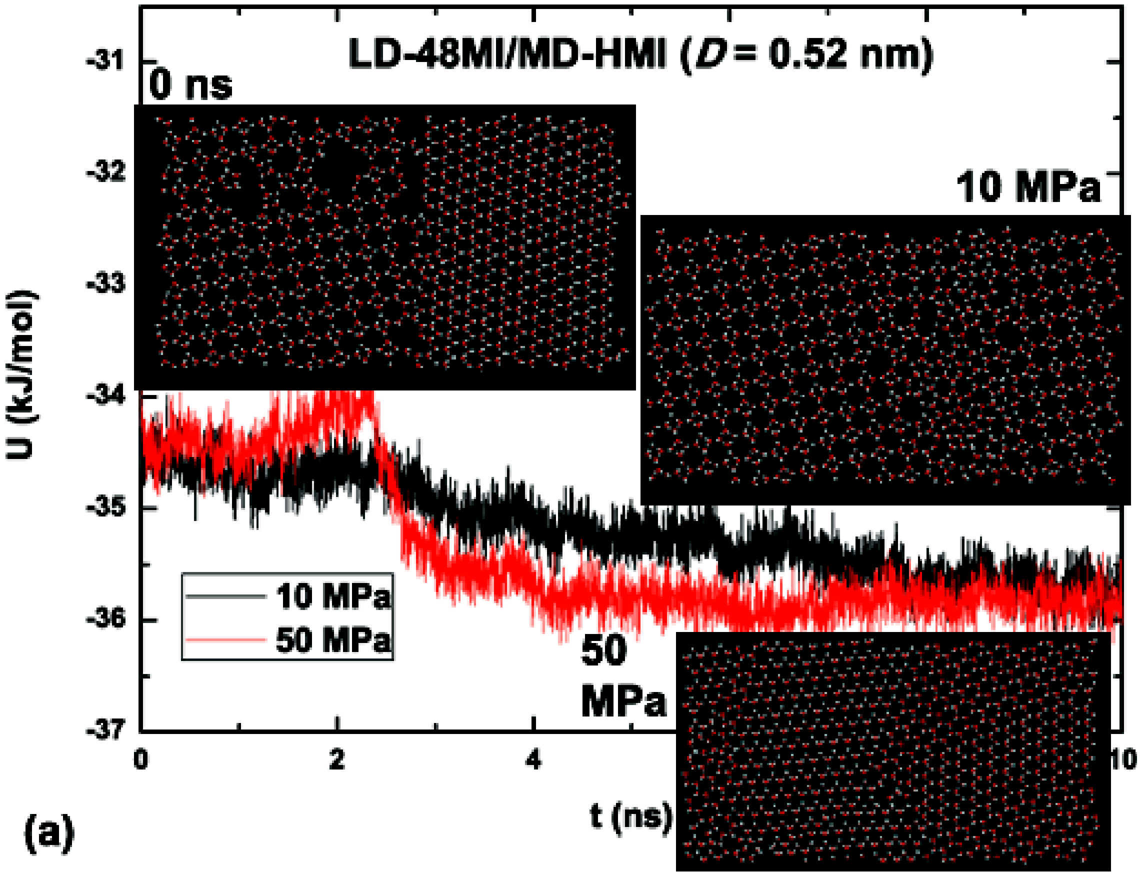
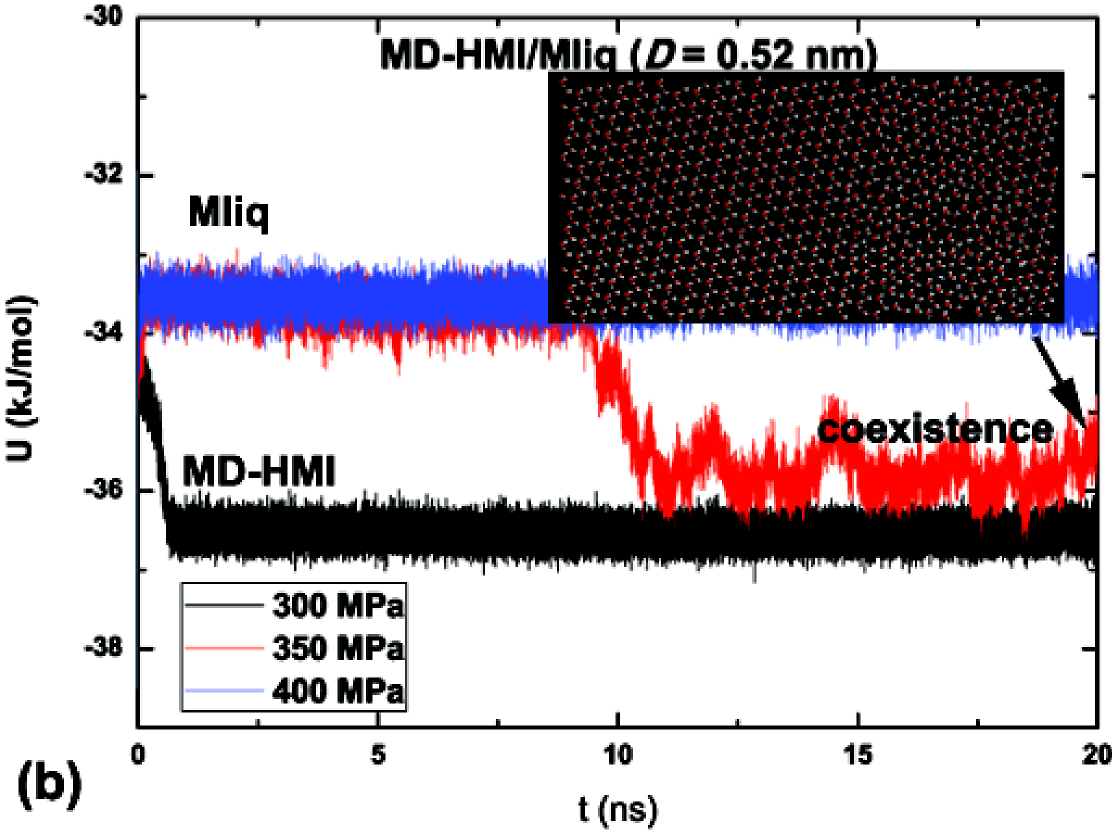


FIG. S1. The inherent structures of 2D monolayer ices formed between two graphene walls. (a) LD-48MI, (b) MD-HMI, (c) the coexisting LD-48MI/MD-HMI, (d) HD-fRMI, and (d) HD-pRMI.

B. Two-phase coexistence molecular dynamics simulations

We carry out two-phase coexistence MD simulations in NP_LT ensemble for the LD-48MI/MD-HMI, MD-HMI/Mliq, HD-fRMI/Mliq, and HD-pRMI/Mliq at T = 200 K, respectively. As shown in Fig. S2(a)–(d), for D = 0.52 nm, the phase boundary of LD-48MI/MD-HMI is between 10-50 MPa; that of MD-HMI/Mliq is between 300-400 MPa; and that of HD-fRMI/Mliq is between 450-500 MPa. For D = 0.62 nm, the phase boundary of HD-pRMI/Mliq is between 50-100 MPa. We also find that the LD-48MI and MD-HMI in the same nanoslit have nearly the same potential energy, so do the HD-fRMI and Mliq. This may be due to the framework of HD-HMI which meets the ice rule in a similar fashion as LD-48MI, while the framework of HD-fRMI is highly frustrated, like Mliq.


LD-48MI/MD-HMI (D = 0.52 nm)
0 ns
10 MPa
50 MPa
U (kJ/mol)
t (ns)
-31
-32
-33
-34
-35
-36
-37
0
2
4
10
10 MPa
50 MPa
(a)


MD-HMI/MIiq (D = 0.52 nm)
MIiq
MD-HMI
coexistence
U (kJ/mol)
t (ns)
-30
-32
-34
-36
-38
0
5
10
15
20
300 MPa
350 MPa
400 MPa
(b)

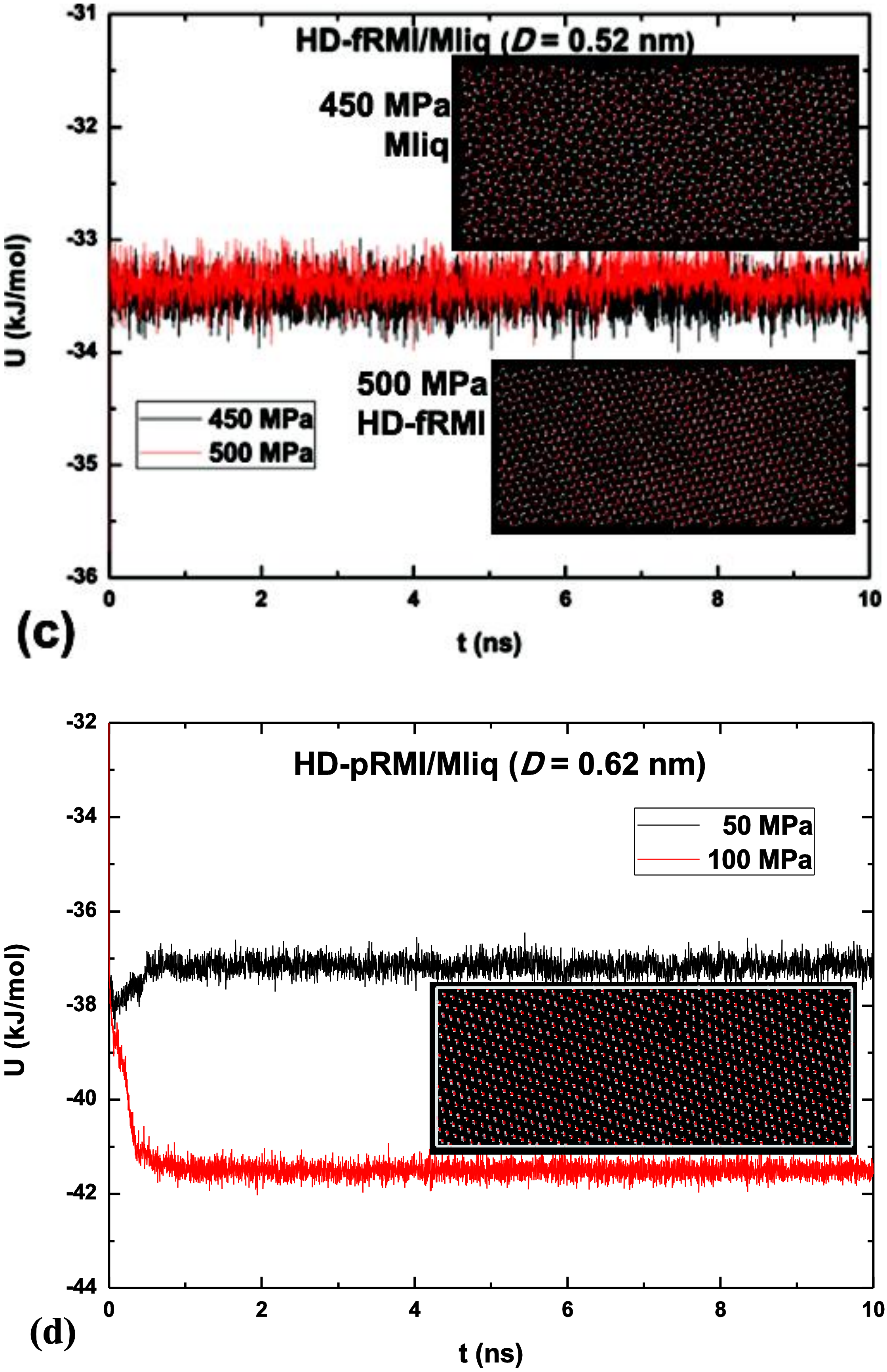


Fig. S2. Two-phase coexistence MD simulations in *NP_LT* ensemble for (a) LD-48MI/MD-HMI, (b) MD-HMI/Mliq, (c) HD-fRMI/Mliq, and (d) HD-pRMI/Mliq at $T = 200$ K.

C. Ferroelectric polarizations of monolayer ices computed from first-principles

To confirm ferroelectric properties of the monolayer ices observed in the classical MD simulations, we perform density-functional theory (DFT) structural optimizations of the four monolayer ice structures using the Cambridge Serial Total Energy Package (CASTEP) program.[4] To this end, the exchange-correlation functional is treated in the form of Perdew-Burke-Ernzerhof (PBE) generalized-gradient approximation (GGA).[5] The wave functions are expanded by using a plane-wave basis set with a kinetic energy cutoff of 380 eV. The ion-valence electron interactions are represented by an ultrasoft pseudopotential.[6] Because the monolayer ices are quasi-two-dimensional (Q2D), the supercell geometry is taken to be a tetragonal cell with the dimension $L_x \times L_y \times L_z$ where the z direction is chosen to be the normal direction of the monolayer surface. We use a 4-molecule supercell to simulate three monolayer ices: MD-HDI, HD-fRMI, and HD-pRMI, respectively. The fourth one, *i.e.*, LD-48MI, is built with 16 water molecules in the supercell. The Brillouin zone is sampled with $(3 \times 3 \times 1)$ k points of a Monkhorst–Pack grid.[7] In the structural optimization, L_z is chosen to be 20 Å and fixed, while L_x and L_y are independently relaxed to achieve the zero-pressure condition in the lateral directions. Convergence criterions are 5×10^{-6} eV/atom for total energy, 0.01eV/Å for the maximum force, and 0.02 GPa for the stress. The geometry optimizations confirm that three *free-standing* monolayer ices, HD-fRMI, HD-pRMI and LD-48MI, are locally stable in vacuum with similar structural features as those observed from the classical MD simulations (see Fig. 1). Minor changes in inner angles of rhombus of HD-fRMI and HD-pRMI are mainly due to the lack of the confining walls in the geometry optimizations.

Note however that the MD-HMI loses the two-centered hydrogen-bonding feature in the vacuum. To find out whether that the MD-HMI can maintain this feature between two confined walls, we place the MD-HMI between *two graphene* *monolayers* and perform the geometry optimization again using the DFT method. As the lattice of the graphene and that of MD-HMI mismatch with each other in the lateral directions, initial atomic positions of carbon and lattice parameters of the graphene are scaled to fit to the lattices of MD-HMI. Atomic fractional coordinates of the graphene with respect to the supercell lattices are fixed while lateral lattices of the supercell and atomic positions of MD-HMI ice are relaxed for the geometry optimization. Since L_z of the supercell is fixed, the separation between the two graphene layer is kept the same. When the separation between the two parallel graphene layers is set to 5 Å, MD-HMI confined to the graphene layers still loses the two-centered hydrogen-bonding feature. When the separation is reduced to 4.7-4.8 Å, the MD-HMI ice retains the structural features as seen from the classical MD simulation (Fig. 7b).

Mulliken charges of ions of monolayer ices are used to compute their ferroelectric properties. When computing the ferroelectric polarizations, the z dimension D' is set to be either the same as the nanoslit width in classical MD simulations, e.g., HD-fRMI, $D' = 0.52$ nm and HD-pRMI, $D' = 0.59$ nm, or the distance between the two graphene layer (MD-HMI, $D' = 0.47$ nm). The ferroelectric polarizations of MD-HMI, HD-fRMI, and HD-pRMI in these DFT calculations are 20 μC/cm^2, 22 μC/cm^2, and 23 μC/cm^2, respectively. We also optimize the all-atom planar structure using the DFT method, and find the structure is unstable.

D. A schematic plot to illustrate nonexistence of linear hydrogen bonds in any linear row of O atoms

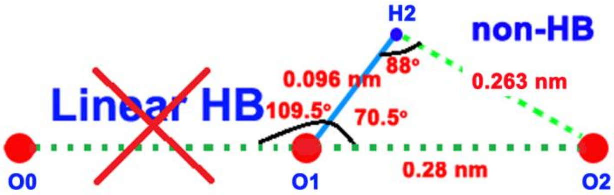


Fig. S3. A schematic plot where the H1 atom in the "linear hydrogen bond O0-H1-O1" is omitted because either O0 or O1 can be the proton-donor, making no difference to the discussion.

E. The raw data determining the *D*-P_L phase diagrams of monolayer water with various values of lateral electric field

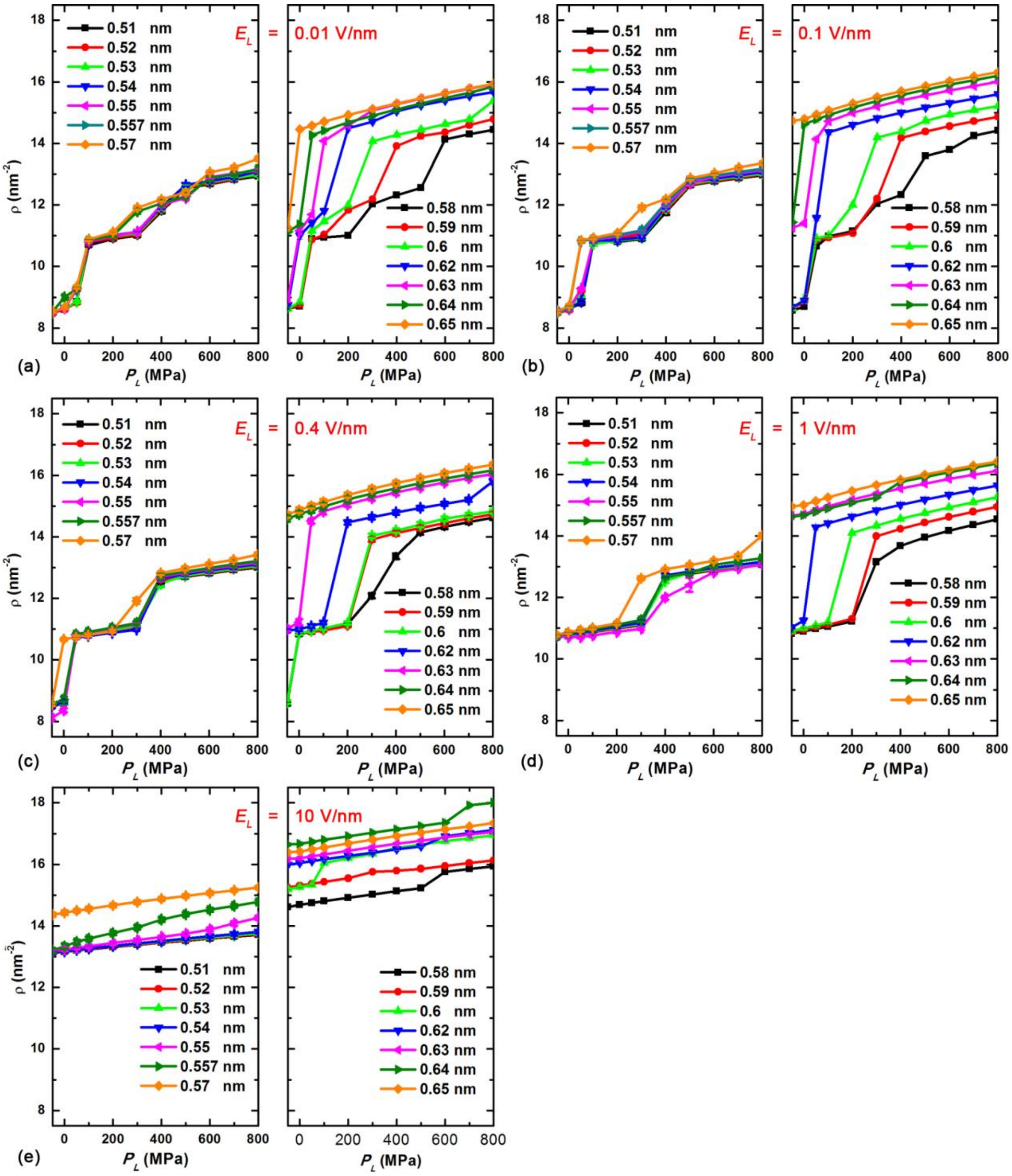


Fig. S4. The area density *ρ* of monolayer water *versus* the lateral pressure P_L for various *D* at 200 K and under different in-plane electric field: E_L = (a) 0.01 V/nm, (b) 0.1 V/nm, (c) 0.4 V/nm, (d) 1 V/nm, and (e) 10 V/nm.

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4) The CASTEP 6.1 software code is distributed and maintained by Accelyrs Inc.

5) J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865.

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