Supplementary Information for

Phase transitions of water overlayer on charged graphene: From electromelting to electrofreezing

Xueyan Zhu, Quanzi Yuan, Ya-Pu Zhao*

State Key Laboratory of Nonlinear Mechanics, Institute of Mechanics, Chinese Academy of Sciences, Beijing 100190, China
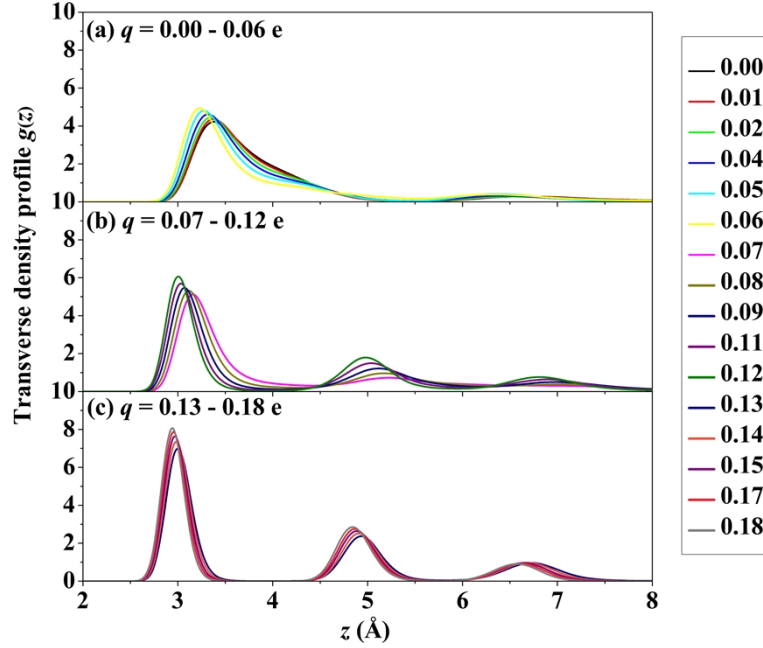
SI 1: Transverse density profile

Fig. S1 Transverse distribution of the density of oxygen atoms for different charge values, q.

To explore the transverse changing of the water film in the course of charging graphene, we plot the evolution of the transverse density profile (TDP) $g(z)$ with respect to q as shown in Fig. S1. For $q = 0.00 - 0.06$ e, the TDP exhibits unimodal distribution, indicating monolayer water film. This is attributed to the fact that the structure of the initial water monolayer is hardly damaged in this range. As q approaches the ice-to-liquid transition point (around $q = 0.07$ e), the distribution starts to develop two peaks. In this case, some water molecules escape from the first layer and form a second layer due to the destruction of the hydrogen bonds (H bonds). With further increase of q, the TDP gradually develops three peaks, the positions of which decrease simultaneously. Moreover, these peaks become higher and narrow during this process, indicating the enhanced layering effect. The origin of these phenomena is the change of the water-water interaction from being attractive to repulsive, which induces the increase of the distance between water molecules, and the strengthened water-graphene interaction as q increases.

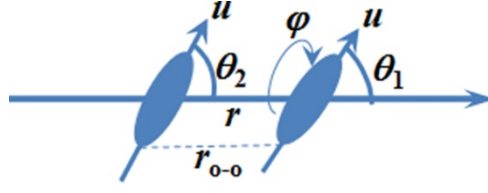**SI 2: Derivations of the interaction energy between two water molecules**

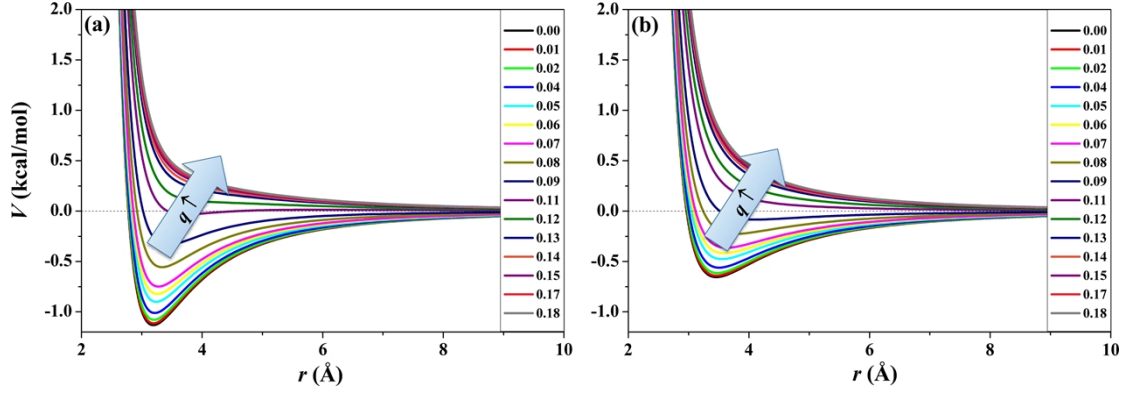**Fig. S2** Schematic diagram of the interaction between two water dipoles.

Fig. S3 Water-water interaction energy V calculated from equation *
MERGEFORMAT (S1), (a) with and (b) without considering r^{-6} term, respectively.

It has been known that a water molecule, due to its shape, is a polar molecule with oxygen atom negatively charged and hydrogen atoms positively charged. Thus, the interaction energy between two water molecules comes from three parts: the induction force, the orientation force and the dispersion force[1]. For SPC/E water model, the equation for calculating the interaction energy can be expressed by

$$V = -\frac{Cu^2}{r^3}\left(2\cos\theta_1\cos\theta_2 - \sin\theta_1\sin\theta_2\cos\varphi\right) + 4\varepsilon_{O\text{-}O}\left[\left(\frac{\sigma_{O\text{-}O}}{r_{O\text{-}O}}\right)^{12} - \left(\frac{\sigma_{O\text{-}O}}{r_{O\text{-}O}}\right)^{6}\right], *$$

MERGEFORMAT (S1)

where C is the Coulomb's constant, u the dipole moment of a water molecule, $\varepsilon_{O\text{-}O}$ and $\sigma_{O\text{-}O}$ are the Lennard-Jones parameters for oxygen atoms (Fig. S2). In our simulations, water molecules are usually parallel to each other, in which case, $r_{O\text{-}O} \approx r$. In equation * MERGEFORMAT (S1), the r^{-12} term represents repulsive interaction and takes effect in the short range, while the r^{-6} and r^{-3} terms take effect in the long range. Comparing r^{-6} term and r^{-3} term, the r^{-6} term can be neglected if $Cu^2r^3 \gg 4\varepsilon_{O\text{-}O}\sigma_{O\text{-}O}^{6}$, i.e. $r \gg 1.99$ Å, which can be approximately fulfilled around the equilibrium position ($r_{eq} \sim 3$ Å > 1.99 Å). Through statistics of the orientations of water molecules, we calculate the evolution of the interaction energy V with respect to q with and without

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considering the r^{-6} term, respectively, as shown in Fig. S3. Despite the minor difference in the values of V, the trend for the variation of V with q is consistent in Fig. S3(a) and Fig. S3(b), which is the key for the ice-liquid-ice transitions. Therefore, we omit the r^{-6} term in our theoretical model for simplicity as shown in equation (3).

SI 3: Evaluation of the Maxwellian relaxation time

Maxwellian relaxation time τ is a concept in rheology. For the elastically deformed viscoelastic material having the properties of both elasticity and viscosity, there remained shear stresses in them when the deformation ceases. After a sufficiently long time, the internal stresses in the material almost disappear. Maxwellian relaxation time is of the order of the time required for damping the stress[2]. In our work, we applied the concept of the Maxwellian relaxation time to the confined water film on graphene, which is solid-like.

There are three parameters determining the properties of water: the size of a water molecule l_{water}, the viscosity η and the surface tension γ. Thus, the Maxwellian relaxation time of water should be $\tau = l_{water}\eta/\gamma$. For liquid water at 300 K, values of these three parameters are l_{water} = 2.75 Å, η = 0.88×10^{-3} Pa·s and γ = 0.072 N/m, respectively, deriving τ_{liquid} = 3.33 ps. However, the Maxwellian relaxation time of ice should be much larger than τ_{liquid}. Therefore, we assume that τ_{ice} = 33.3 ps for q = 0.00 – 0.06 e, τ_{liquid} = 3.33 ps for q = 0.07 – 0.12 e, and τ_{ice} = 33.3 ps for q = 0.13 – 0.18 e.

SI 4: Diffusion coefficient calculated from molecular dynamics (MD) simulations

Lateral diffusion coefficient D is related to the mean square displacement (MSD) by Einstein equation[3]

$$D = \frac{1}{4}\lim_{t\to\infty}\frac{\left\langle\left|\vec{r}(t)-\vec{r}(0)\right|^2\right\rangle}{\Delta t} \qquad \text{\\* MERGEFORMAT (S2)}$$

where $\left|\vec{r}(t)-\vec{r}(0)\right|$ is the distance traveled by a molecule over the time interval of length Δt. We should mention that center motion of the water overlayer is removed when MSD is calculated. As shown in Fig. S4, MSD increases linearly with time at equilibrium.
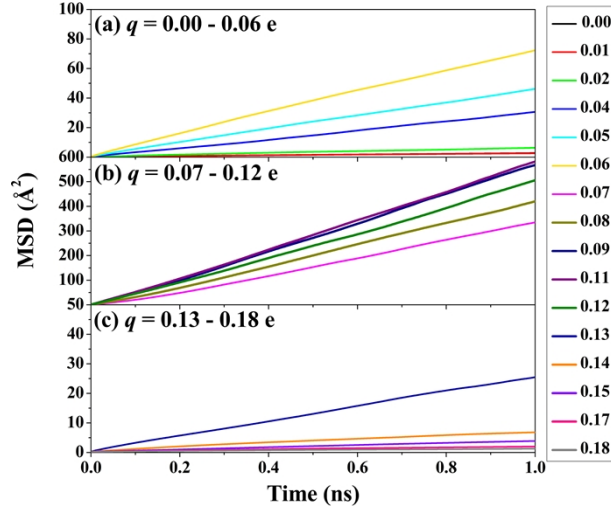
Fig. S4 MSD of water molecules in the first layer water.

SI 5: Phase transitions of water overlayer on negatively charged graphene

We plot the lateral oxygen-oxygen radial distribution function (RDF) parallel to the graphene surface in Fig. S5. For q = -0.00 − -0.05 e, the RDF shows long-ranged order, indicating ice phase, the structure of which is hexagonal as visualized in Fig. S6(a). For this range of q, the diffusion coefficient D (Fig. S7) is of the order of 10^{-12} − 10^{-10} m^2/s, further confirming the solid state. When q is varied across q_{c1} between -0.05 e and -0.06 e, the long-ranged character of the RDF changes to short-ranged abruptly accompanied by the increase of D to 10^{-9} m^2/s, suggesting the first-order solid to liquid (Fig. S6(b)) phase transition. For q = -0.06 − -0.12 e, the first peak of the RDF (r = 2.65 Å) becomes lower with the increase of q, indicating the evolution to more disordered structure. Simultaneously, the second peak increases, the position of which decreases from r = 4.45 Å to r = 3.75 Å. When q is increased to -0.12 e, the second peak outstrips the first peak. Further increase of q leads to the gradual disappearance of the peak at r = 2.75 Å and the increase of the new first peak, the position of which decreases from r = 3.75 Å to r = 3.55 Å, indicating the evolution to less disordered structure (Fig. S6(c)). Although the RDFs of q = -0.06 − -0.18 e all exhibit short-ranged character corresponding to disordered state, D decreases from the order of 10^{-9} m^2/s to 10^{-8} m^2/s continuously, suggesting the second-order liquid to solid phase transition. The lack of long-ranged order of the solid corresponds to amorphous solid. From the above discussions, we conclude that the water overlayer

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on the negatively charged graphene experiences ice-liquid-amorphous phase transitions in the course of increasing q.
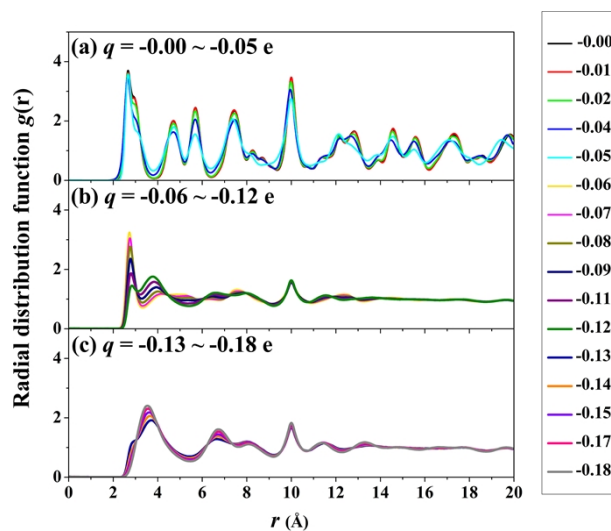

Fig. S5 Lateral oxygen-oxygen radial distribution function for water overlayer on negatively charged graphene.
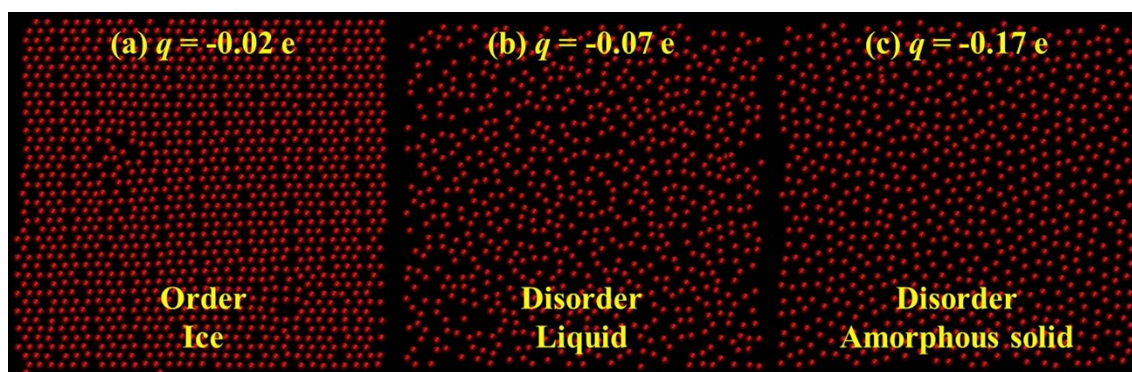

Fig. S6 Snapshot of the first layer water on negatively charged graphene with different charge values q with showing the oxygen atoms only.
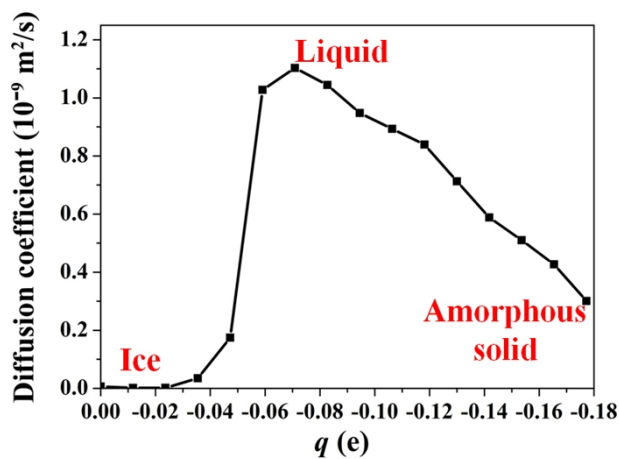

Fig. S7 Diffusion coefficient of the first layer water on negatively charged graphene.

SI 6: Determination of the upper bound for the charge value

In this paper, we gradually increase the charge value of each carbon atom from 0.00 − 0.18 e to investigate phase transitions of water overlayer responding to the external electric field. The upper bound for the charge value is very important because it determines whether the system would break down.

The breakdown voltage of suspended graphene from the experiments[4, 5] is on the order of 1 V. According to the linear approximation for the low energy electronic dispersion relationship in graphene, the relationship between the excess charge density n on graphene and voltage V at temperature T is expressed by[6, 7]

$$n = -q_e \int_0^\infty d\varepsilon f(\varepsilon, V, T) g(\varepsilon), \text{ \\* MERGEFORMAT (S3)}$$

in which, $f(\varepsilon, V, T) = \text{sign}(V) \left\{ \exp\left[(\varepsilon - q_e |V|) / (k_B T) \right] + 1 \right\}^{-1}$ is the Fermi occupation factor, where $V > 0$ for electrons, $V < 0$ for holes, and k_B is the Boltzmann constant. $g(\varepsilon) = 8\pi |\varepsilon| / (h v_F)^2$ is the density of states per unit area, in which h is Planck constant and $v_F = 10^6$ m/s the Fermi velocity in graphene. From equation * MERGEFORMAT (S3), we estimate the upper bound for the charge density on graphene to be of the order of $10^{14} - 10^{15}$ electron/cm^2 according to the breakdown voltage of graphene. In this paper, the upper bound for the charge value is 0.18 e, which corresponds to the charge density of 6.87×10^{14} electron/cm^2. Thus, the range of the charge value (0.00 − 0.18 e) used in our simulations is feasible.

SI 7: Structure of water monolayer on graphene predicted by SPC/E and TIP4P

Although the TIP4P water model can qualitatively model phase transitions of bulk water as a response to the variation of temperature or pressure, it does not indicate that it can model the structure and phase transitions of water overlayer as a response to the variation of external electric field more accurately. We have compared the structure of water overlayer on graphene predicted by SPC/E and TIP4P, respectively, with that from experiments[8] as shown in Fig. S8. The results show that

the structure predicted by SPC/E is closer to the experimental results than that by TIP4P. So we chose SPC/E to model the water molecules in our simulations.
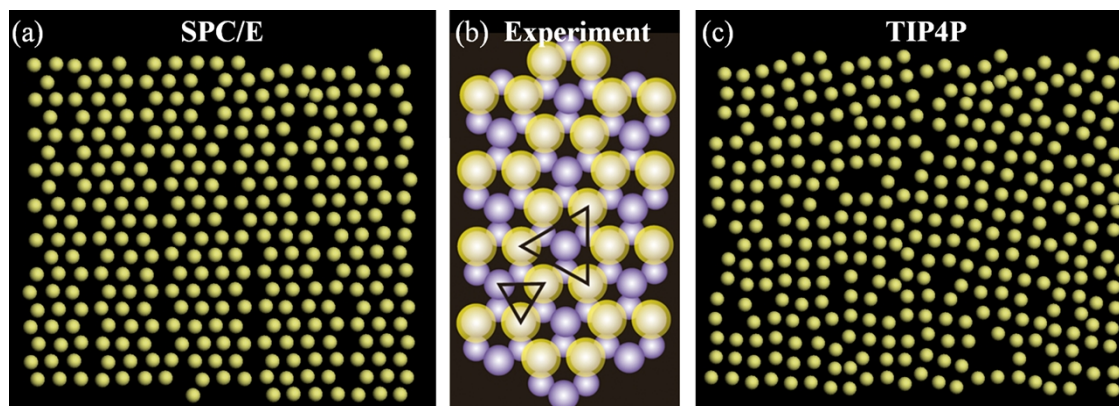

Fig. S8 Structure of water overlayer on graphene with displaying oxygen atoms (yellow atoms) only. (a) Water structure on graphene predicted by SPC/E. (b) A schematic representation of the water molecules adsorbed on highly oriented pyrolytic graphite as observed from experiments by atomic force microscopy[8]. (c) Water structure on graphene predicted by TIP4P.

References

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