

The microscopic mechanisms controlling heterogeneous ice nucleation are complex and remain poorly understood. Although good ice nucleators are generally believed to match ice lattice and to bind water, counter examples are often identified. Here we show, by advanced molecular simulations, that the heterogeneous nucleation of ice on graphitic surface is controlled by the coupling of surface crystallinity and surface hydrophilicity. Molecular level analysis reveals that the crystalline graphitic lattice with an appropriate hydrophilicity may indeed template ice basal plane by forming a strained ice layer, thus significantly enhancing its ice nucleation efficiency. Remarkably, the templating effect is found to transit from within the first contact layer of water to the second as the hydrophilicity increases, yielding an oscillating distinction between the crystalline and amorphous graphitic surfaces in their ice nucleation efficiencies. Our study sheds new light on the long-standing question of what constitutes a good ice nucleator.

Introduction

Although appearing common in daily life, controlling ice formation poses a significant challenge in various industries. The unfavorable crystallization of ice can easily cause hazardous road conditions, down power lines, damage crops, and stall aircraft engines.

Current anti-icing technologies employing deicing chemicals and heating coils are far from being perfect. The annual cost of corrosion damage to vehicles alone from road salt has been estimated to be around \$11.7 billion in the U.S.

Traditional wisdom [1] believes that a good ice nucleator should

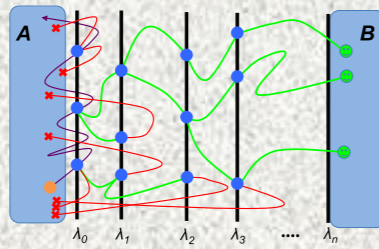
1. Match ice in their lattices
2. Bind water through an appropriate surface chemistry
3. Be insoluble in water

However, counter examples are often identified for every single criterion.

Q: What controls ice nucleation at the molecular level?

Method

We combine forward Flux Sampling (FFS) [2] with molecular dynamics (MD) simulation, to compute the rate of heterogeneous ice nucleation on both crystalline and amorphous graphene, with varied surface hydrophilicities.

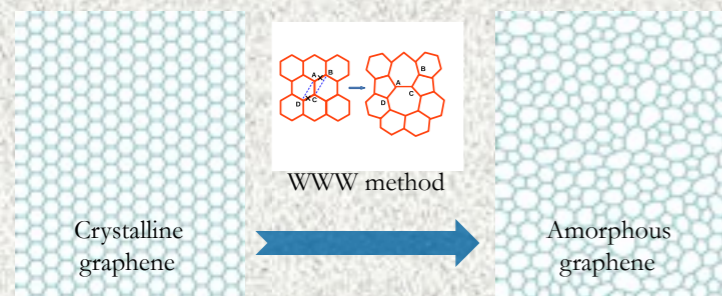


Water-carbon interaction is described by the mW [3] model. The hydrophilicity can be tuned by varying water-carbon interaction strength ϵ .

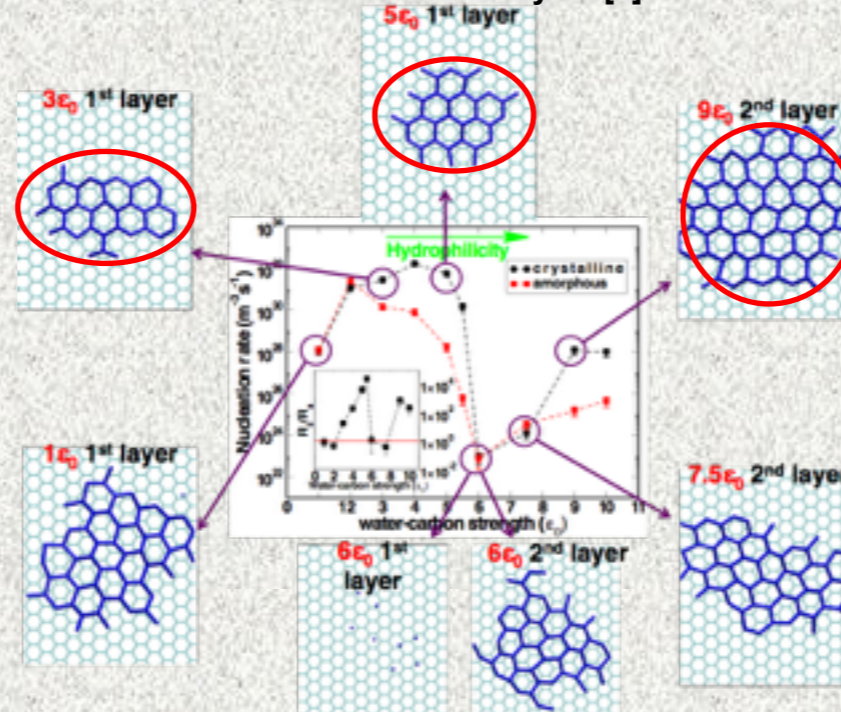
$$\phi_2(r) = A \epsilon \left[B \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \exp\left(-\frac{\sigma}{r - \delta} \right)$$

ϵ : water-carbon interaction strength

The amorphous graphene was obtained by introducing the Stone-Wales defects successively into crystalline graphene through combing Wooten-Weaire-Winer (WWW) method [4] with Metropolis Monte Carlo.

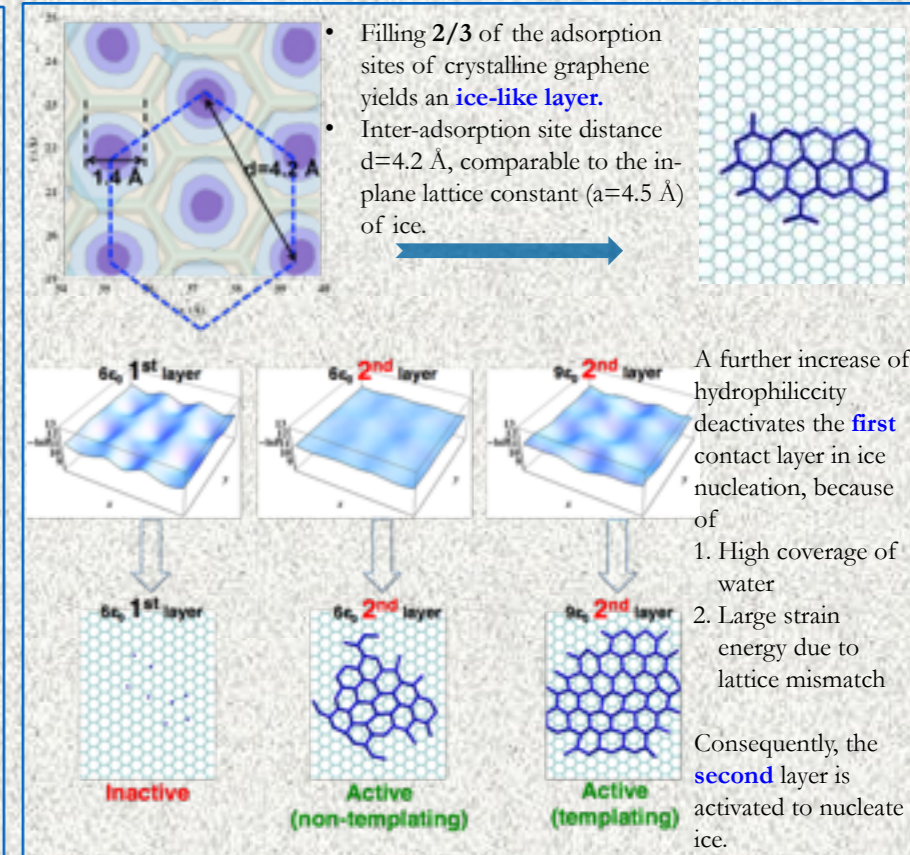
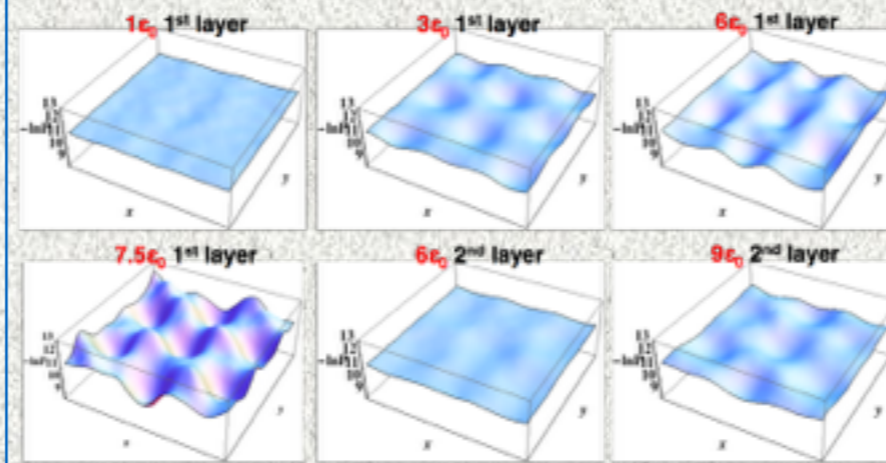


Results and Analysis [5]



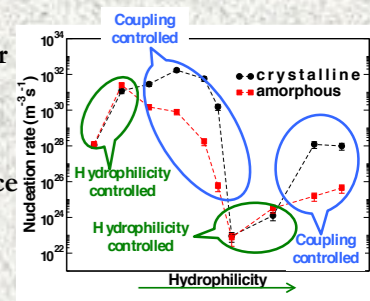
- In the low ($\epsilon_0 \leq \epsilon \leq 2\epsilon_0$) and mid-high ($6\epsilon_0 \leq \epsilon \leq 7.5\epsilon_0$) range of hydrophilicity: Crystallinity of graphene is found to play an **inactive** role.
- In the mid-low ($2\epsilon_0 \leq \epsilon \leq 2\epsilon_0$) and high ($\epsilon \geq 7.5\epsilon_0$) range of hydrophilicity: Crystalline graphene yields significantly higher ice nucleation rates than the amorphous.
- The higher ice nucleation efficiency of crystalline graphene in ($2\epsilon_0 \leq \epsilon \leq 2\epsilon_0$) and ($\epsilon \geq 7.5\epsilon_0$) is closely related to the templating effect.
- **Q: Why does this templating effect only occur at certain hydrophilicity?**

The answer can be obtained through examining the **in-plane density of water in the contact layers varies with hydrophilicity**



Conclusions

- Neither surface crystallinity nor crystallinity alone is a good indicator for an ice nucleator.
- Ice nucleation can be surprisingly complex at the molecular level.
- At the thermodynamic level, however, ice nucleation can be “simple” [6].
- There must exist a unified description bridging both thermodynamic and molecular views.



References

1. Pruppacher, H.; Klett, J. Microphysics of Clouds and Precipitation; Kluwer Academic Publisher, 2007.
2. Allen, R. J.; Frenkel, D.; Wolde, P. R. T. Simulating Rare Events in Equilibrium or Nonequilibrium Stochastic Systems. *J. Chem. Phys.* 2006, 124, 04102 1-16.
3. Lupi, L.; Hudait, A.; Molinero, V. Heterogeneous Nucleation of Ice on Carbon Surfaces. *J. Am. Chem. Soc.* 2014, 136, 3156–3164.
4. Wooten, F.; Winer, K.; Weaire, D. Computer Generation of Structural Models of Amorphous Si and Ge. *Phys. Rev. Lett.* 1985, 54, 1392–1395.
5. Yuanfei Bi, Raffaella Cabriolu, Tianshu Li, Heterogeneous Ice Nucleation Controlled by the Coupling of Surface Crystallinity and Surface Hydrophilicity, *J. Phys. Chem. C*, 2016, 120 (3), 1507–1514
6. Raffaella Cabriolu; Tianshu Li Ice nucleation on carbon surface supports the classical theory for heterogeneous nucleation. *Phys. Rev. E* 2015, 91, 052402.