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Effect of Graphene on Ice Polymorph

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Abstract: Recently, ice with the stacking disorder structure, consisting of random sequences of cubic ice (Ic) and hexagonal ice (Ih) layers, is reported to be more stable than pure Ih/Ic. While, due to a much lower free energy barrier of heterogeneous nucleation, in practice, the freezing process of water is usually controlled by heterogeneous nucleation which is triggered by an external medium. Herein, molecular dynamic simulations were carried out to explore the polymorph dependence of ice on the lattice structure of substrates. It turns out that, during the nucleation stage, the polymorph of ice nuclei can be severely altered by the graphene substrate, on which the Ih was found to occupy an absolute majority in new-formed ice. This can be attributed to the structure similarity between graphene and basal face of Ih. Besides the nucleation stage, our results suggest that the substrate can not affect the polymorph of ice which is far from the graphene surface. The polymorph selectivity of graphene to Ih will diminish with the growth of ice layer.

Keywords: Heterogeneous Nucleation; Ice Polymorph; Stacking Disorder; Phase Selectivity

1. Introduction

For a long time, hexagonal ice (Ih) was assumed to be the most stable ice phase at atmospheric pressure or below. However, this understanding has been questioned by a large number of computer simulations[1-4] and experiments[5-9] in recent years. In the report of Lupi et al,[1] the stacking-disordered[10] critical ice crystallites are about 14 kJ/mol of crystallite more stable than hexagonal ice crystallites (at 230 K). It's noticed that there was no substrate in the simulation systems. While, in practice, it is almost impossible to eliminate the influence of foreign matters on ice nucleation,[11, 12] which could severely alter the ice nucleation process. Due to a much lower free energy barrier of heterogeneous nucleation, in practice, the freezing process of water is usually controlled by heterogeneous nucleation which is triggered by an external medium. With the presence of foreign matters, ice nucleation is mainly dominated by heterogeneous nucleation rather than homogenous nucleation. This raise a question that whether substrates with different lattice structure can affect the ice polymorph during heterogeneous ice nucleation/growth process?

As the main component of atmospheric aerosols, carbon surfaces composed can greatly promote heterogeneous ice nucleation.[13-15] Crystallization temperature of ice on the graphite surface is about 12 K higher than the temperature of homogeneous ice nucleation.[16, 17] This stimulated both experimental and molecular dynamics (MD) simulations investigation of heterogeneous ice nucleation on graphene/graphite and other carbon surfaces.[16, 18-20]

Therefore, to address the question that whether substrates can alter the ice polymorph during heterogeneous ice nucleation/growth process, MD simulations were conducted to explore the heterogeneous ice nucleation/growth processes on different carbon surfaces. The cubicity with the nucleation and growth of ice was extracted from each MD trajectories. The freezing efficiency for each substrate was also calculated.

2. Methods

Modeling. As shown in Figure 1, ice nucleation were studied on three types of atomic flat carbon surfaces with different lattice structure: *Graphene* (composed by six ring carbon atom), *Oblique-Haeckelite* (*O-Haeckelite*, composed by 5-6-7 ring carbon atom) and *Rectangular-Haeckelite* (*R-Haeckelite*, composed by 5-7 ring carbon atom).[21] The homogenous ice nucleation (*Homo*) simulations without any substrate were also carried out as control. The size of the 3D periodic simulation boxes (contain 15029 mW[22] water molecules) are $16.3 \times 15.3 \times 15.0 \text{ nm}^3$ for *O-Haeckelite* system, $17.0 \times 15.5 \times 15.0 \text{ nm}^3$ for *R-Haeckelite* system, $15.0 \times 14.8 \times 15.0 \text{ nm}^3$ for *Graphene* system, and $15.0 \times 15.0 \times 15.0 \text{ nm}^3$ for *Homo* system, respectively.

Simulation Details. All MD simulations were performed by Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package.[23] The equations of water motion were integrated with the velocity Verlet algorithm with a time step 5 fs. All the simulations were conducted in the NVT ensemble. The temperature in the simulation systems was controlled by Nosé-Hoover thermostat. The same as previous report[16], ice nucleation were studied through cooling ramp of cooling rates of 1 K/ns with the temperatures ranging from 217 K to 207 K (for heterogeneous nucleation) and from 207 K to 197 K (for homogenous nucleation). To calculate the freezing efficiency $\Delta T_f = T_f - T_f^{homo}$, 20 independent trajectories were performed for each system. The interactions between water molecules and carbon atoms are taken from the previous report by Lupi' et al. [16], in which water-carbon interaction parameters are: $\sigma_{WC} = 0.32 \text{ nm}$, $\epsilon_{WC} = 0.13 \text{ kcal/mol}$ to reproduce water contact angle on graphene surface that observed in laboratory (namely 86°).[24].[25] All the carbon atoms in the substrates were fixed in all the MD simulations. Water molecules with Ih/Ic structure were identified by the method proposed by E. Maras et al.,[26] which is available in OVITO package.[27]

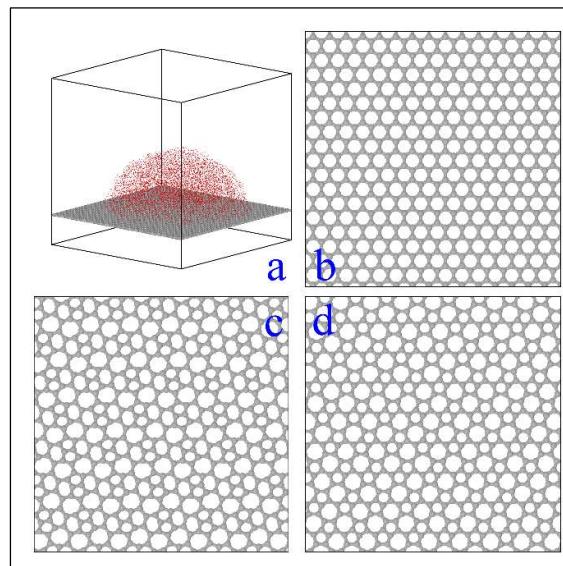


Figure 1. a) Example of a simulation box. b), c) and d) show top view (part) of substrates Graphene, O-Haeckelite and R-Haeckelite, respectively. Carbon atoms in substrate are portrayed as gray spheres. The water molecules are showed in red dots.

3. Results and Discussion

To investigate the effect of substrate lattice structure on the polymorph of ice, MD simulation was employed to study the ice formation process on different substrates: *Graphene*, *Oblique-Haeckelite* (*O-Haeckelite*) and *Rectangular-Haeckelite* (*R-Haeckelite*). As shown in Figure 2, consist with previous reports,[16, 28-30] the ice nuclei formed at the water-substrate interface for the systems of *Graphene*, *O-Haeckelite* and *R-Haeckelite*, which should

be due to the much lower heterogeneous nucleation barrier. For these heterogeneous nucleation systems, especially for the nucleation stage, the ice crystals exhibit a single-crystal-like structure with barely any grain boundary, which is due to the 1-dimentional structure match (in the direction perpendicular to the substrate surface) between a flat substrate and a flat crystalline face of ice. While for the *Homo* system, the new-formed ice exhibits a polycrystalline structure.

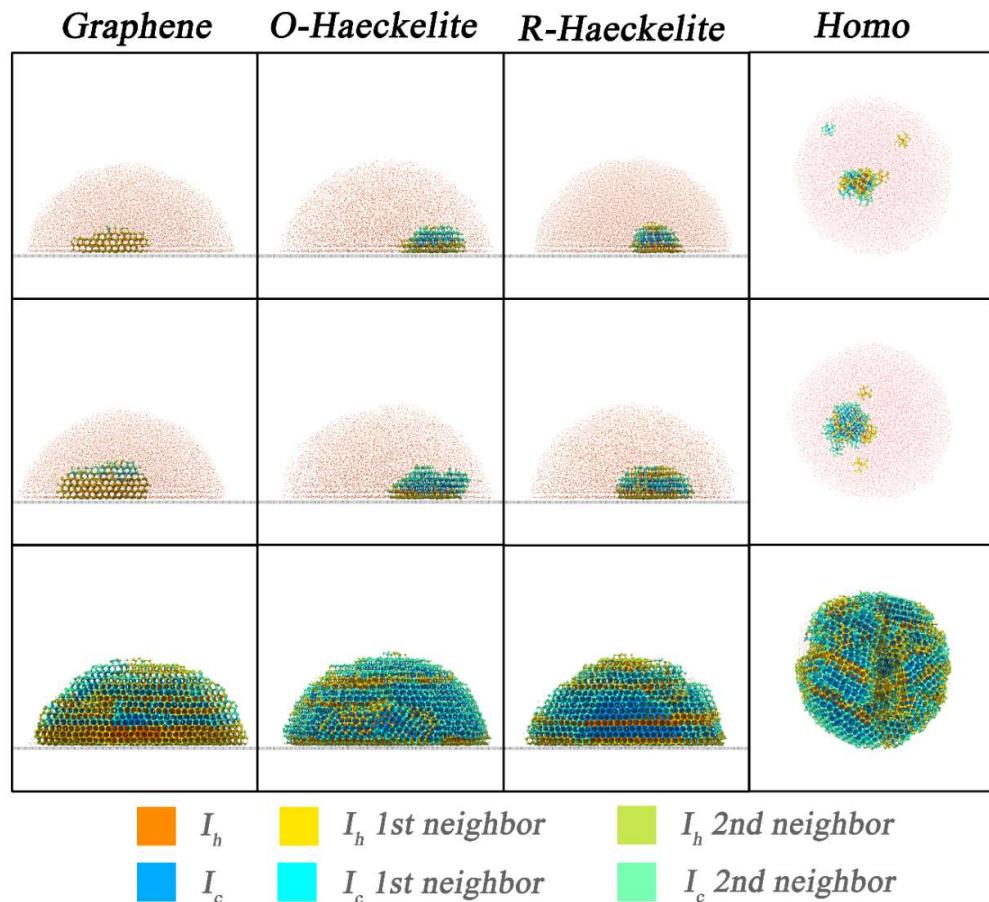


Figure 2. Lateral view of ice formation procedure from top to bottom: i) Ice nucleation; ii) Ice growth; iii) Water freezing completely. Liquid water is represented by red dots. Water molecules in ice crystallites are represented by colored ball-stick model. Carbon atoms in substrate are colored gray.

Intriguingly, for the system of *Graphene*, the I_h structure occupies an absolute majority in ice nuclei during the stage of nucleation. With the growth of ice (after about 5-6 layers of I_h formed), the I_c turns up, which is consist with the previous report that the I_c will growth on I_h embryos to form a more stable stacking disorder structure[1]. When almost all the liquid water freezing to ice, the percentage of I_c is not much different from that of I_h . While for the systems of *O-Haeckelite*, *R-Haeckelite* and *Homo*, in all stage of ice formation, the number of water molecules in I_c ice is always comparable with molecular number of water in I_h ice.

To reveal the phase change process of ice during heterogeneous nucleation processes, the molecular numbers of I_c and I_h as a fuction of system temperature (namely simulation time) were extracted from the ice formation MD trajectories (shown Figure 3). The snapshots in Figure 2 shared the same trajectories with results of Figure 3 for each system. As shown in Figure 3a (*Graphene* system), with the decreasing of temperature, the nucleation

process was observed in the Ih ice before the steady growth of Ic. In the growth stage, the Ic exhibited a larger growth rate than Ih, leading to an equivalent molecular number of Ih and Ic at the stage of water freezing completely. While for each of the systems in Figure 3 b, c and d, the Ic and Ih growth simultaneously as the system temperature decreasing, indicating that these systems have no selectivity to ice polymorph.

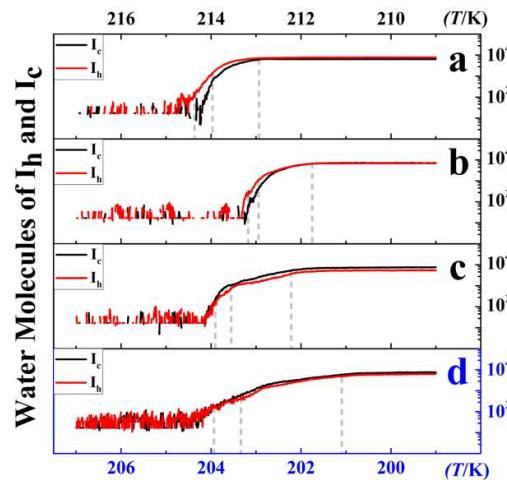


Figure 3. Molecular numbers of water molecules in Ic and Ih during a cooling ramp for the systems of a) *Graphene*, b) *O-Haeckelite*, c) *R-Haeckelite* and d) *Homo*. The dashed vertical lines indicate position of snapshots of the ice nucleation, ice growth and water freezing completely in Figure 2. The blue borders are for panel d).

To quantitatively reveal the polymorph of ice formed on different substrates, cubicity[2] (proportion of Ic) of the new-formed ices were calculated from the 20 independent MD trajectories for each system (refer to Table 1 and Table S1). As shown in Table 1, the cubicity of ice in *Homo* system are $52.4 \pm 6.9\%$, $56.1 \pm 6.5\%$ and $58.8 \pm 4.4\%$ for the stage of ice nucleation, ice growth and water freezing completely, respectively, which is consist with the previous report (about 55 %).[1-3, 31] While for the system of *Graphene*, the cubicity at nucleation stage is only $30.2 \pm 18.1\%$, which is significantly lower than that of the *Homo* system. The results suggest that the graphene substrate has a preferential selectivity to Ih over Ic, which could attribute to the fact that Ih (basal face) and graphene share the same hexagonal structure and have a similar lattice structure. The distance between the center of two hexagon rings on graphene surface is 2.46 \AA ,[20, 32] and the distance of water molecules in the basal face of Ih is 2.76 \AA .[33, 34] According to previous reports[20, 35, 36], in the water-graphene system, the center of a hexagon formed by carbon atoms correspond to the adsorption energy minima positions of water molecules. Due to the similarity of lattice structure between basal plane of Ih and graphene, slight adjustment of the position of interface water molecules can match the lattice structure of graphene. The calculated mismatch[37] between the substrate and the ice is 10.9 %. The Ice-Nucleating protein, with a mismatch of 10% to ice, was found to be able to dramatically promote the nucleation of ice.[38] In the report of Bi et al.,[20] it was found that the first layer ice on graphene substrate was mainly composed by Ih, while the first layer on amorphous graphene substrate (similar to the *O-Haeckelite* substrate in this paper), the structure of the ice was somewhat messy. It also suggests that, the similarity between the graphene and the basal face of Ih results in the selective promotion to Ih over Ic. Therefore, it can be concluded that, on the surface of graphene, the formation of Ih was selectively promoted.

Table 1. Average cubicity of each simulation system. From top to bottom is the stages of ice nucleation, ice growth and water freezing completely, respectively.

Substrate	Graphene	O-Haeckelite	R-Haeckelite	Homo
Cubicity / %	30.2 ± 18.1	42.5 ± 13.7	46.4 ± 12.3	52.4 ± 6.9
	42.3 ± 14.6	48.2 ± 13.9	48.7 ± 11.7	56.1 ± 6.5
	52.0 ± 9.7	53.8 ± 8.8	55.5 ± 7.0	58.8 ± 4.4

To further investigate the effect of substrate lattice structure on heterogeneous ice nucleation, freezing efficiency of the substrates, based on the method of Lupi et al.,[16] were calculated (shown in Figure 4). It follows that the calculated freezing efficiency for graphene, O-Haeckelite and R-Haeckelite substrates are 12.4 ± 0.4 K, 10.7 ± 1.0 K and 12.4 ± 0.9 K, respectively, which are consist with the previous reports that crystallization temperature of ice on the graphite surface is about 12 ± 3 K higher than the temperature of homogeneous ice nucleation.[16, 17] The freezing efficiency of different substrates has no significant difference, indicating that, although the substrates exhibit different polymorph selectivity of ice, the heterogenous nucleation premotion effect of the substrates on ice are similar. While, it should be pointed out that the heterogenous nucleation premotion effect changes with the system temperature.[20] To calculate the freezing efficiency, the system temperature is steady decreased. The freezing processes are driven by a very high supercooling, which can reduce the difference of heterogenous nucleation premotion effect. For instance, the heterogeneous ice nucleation rates on different substrates exhibit significant difference only when the system temperature increased as high as 235 K.[20] Thus, a systematic study, e.g. heterogeneous nucleation barrier and heterogeneous nucleation rate, is necessary to gain more accurate results by taking into the influence of temperature. Another thing that need to be specified is that, in our results, the calculated homogeneous nucleation temperature of ice is 1.9 K higher than that in previous report,[16] which could attribute to the number difference of water molecules between this work and the previous report (5241 water molecules in previous report, and 15029 water molecules in this work). According to classic nucleation theory (CNT), the greater number of water molecules in the system, the greater nucleation probability of ice is. Therefore, the homogenous nucleation temperature of ice in this work is slightly higher than the previous reported result.

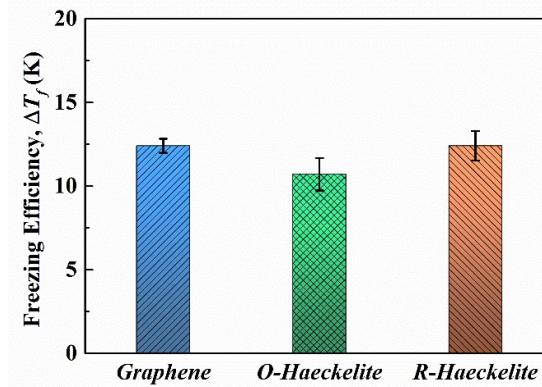


Figure 4. Freezing efficiency ΔT_f of substrates in *Graphene*, *O-Haeckelite* and *R-Haeckelite* systems.

4. Conclusions

To summarize, MD simulations were carried out to explore the impact of substrates lattice structure on the polymorph of ice formed by heterogeneous nucleation. It turns out that the graphene substrate has a preferential selectivity to Ih over Ic during the nucleation

stage, which is resulted by the same hexagonal structure and similar lattice structure between graphene and Ih. While, after the stage of nucleation, the cubicity of new-formed ice increased up to about 52%, due to the more stable property of stacking disorder ice. When water freezing completely, the cubicity of ice were range from 52% to 58%, which is in good agreement with Homo system and the previous results. It suggests that the graphene substrate can only affect the polymorph of interfacial ice during the nucleation stage.

Supplementary Materials: Table S1: Cubicity of the nucleation stage in each simulation trajectory. Figure S1: Surface morphology of 2-dimentional carbon substrate with all the carbon atoms randomly distributed, the *Random* system. Figure S2: Snapshots of ice nucleation on different substrates (include *Random*). Figure S3. Freezing efficiency ΔT_f of different lattice structure substrates (include *Random*).

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