Commensurate-incommensurate solid transition in the $^4$He monolayer on $\gamma$-graphyne

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(Dated: May 19, 2014)

Path-integral Monte Carlo calculations have been performed to study the $^4$He adsorption on $\gamma$-graphyne, a planar network of benzene rings connected by acetylene bonds. Assuming the $^4$He-substrate interaction described by a pairwise sum of empirical $^4$He-carbon interatomic potentials, we find that unlike $\alpha$-graphyne, a single sheet of $\gamma$-graphyne is not permeable to $^4$He atoms in spite of its large surface area. One-dimensional density distributions computed as a function of the distance from the graphyne surface reveal a layer-by-layer growth of $^4$He atoms. A partially-filled $^4$He monolayer is found to exhibit different commensurate solid structures depending on the helium coverage; it shows a $C_{2/3}$ commensurate structure at an areal density of 0.0491 Å$^{-2}$, a $C_{3/3}$ structure at 0.0736 Å$^{-2}$, and a $C_{4/3}$ structure at 0.0982 Å$^{-2}$. While the promotion to the second layer starts beyond the $C_{4/3}$ helium coverage, the first $^4$He layer is found to form an incommensurate triangular solid when compressed with the development of the second layer.

PACS numbers: 67.25.bd, 67.25.bh, 67.80.B-, 75.10.-b

For the past few decades, a system of $^4$He atoms adsorbed on a substrate has been intensively studied to investigate physical properties of low-dimensional quantum fluids. Carbon allotropes have often been chosen as substrates for this purpose because they provide strong enough interactions for $^4$He adsorbates to show multiple distinct layered structures [1]. As a result of the interplay between $^4$He-$^4$He and $^4$He-substrate interaction, these helium adlayers are known to exhibit rich phase diagrams including various commensurate and incommensurate solids. On the surface of graphite, a monolayer of $^4$He atoms is crystallized to a $C_{1/3}$ commensurate solid at an areal density of 0.0636 Å$^{-2}$ and goes through various domain structures before freezing into an incommensurate triangular solid as the helium coverage increases [2,3]. Similar quantum phase transitions were predicted for the $^4$He monolayer on a single graphene sheet [4,5]. While no superfluidity has been observed in the first $^4$He layer, the second layer on graphite does show finite superfluid response at intermediate helium coverages as first revealed by torsional oscillator measurements of Crowell and Reppy [6]. Whether this second-layer superfluid phenomenon is related to two-dimensional super-solidity is still an ongoing issue pursued heavily by some experimentalists.

The $^4$He adsorption on the surface of a carbon allotrope other than graphite or graphene has recently been investigated. While $^4$He atoms adsorbed on the interstitials or the groves of carbon nanotube bundles showed characteristics of one-dimensional quantum fluid [7,8], a series of theoretical calculations predicted well-distinct layered structures for $^4$He atoms adsorbed on the outer surfaces of fullerene molecules with each near-spherical helium layer exhibiting various quantum states depending on the number of $^4$He adatoms [9,10]. More recently, graphynes, $sp-sp^2$ hybridized two-dimensional networks of carbon atoms [11,12], have attracted much interest because of their intriguing electronic features such as both symmetric and asymmetric Dirac cones [13,14] and high carrier mobility [15]. Furthermore, they have much larger surface area than graphene, which has prompted extensive investigation of their possible applications as high-capacity hydrogen storage [19, 20] and Li-ion battery anode materials [21]. Using the path-integral Monte Carlo (PIMC) method, one of us recently studied the $^4$He adsorption on $\alpha$-graphyne [22], a honeycomb structure of both $sp^2$-bonded carbon atoms and $sp$-bonded ones. Due to the presence of much larger hexagons than those of graphene, in-plane adsorption of $^4$He atoms was observed on $\alpha$-graphyne with a single $^4$He atom being embedded to the center of each hexagon. The first layer of $^4$He atoms adsorbed on the $^4$He-embedded $\alpha$-graphyne was found to undergo a Mott-insulator to commensurate-solid transition which was interpreted as a transition from a spin liquid of frustrated antiferromagnets to a ferromagnetic phase with the introduction of Ising pseudospins based on the sublattice symmetry of the honeycomb structure [22].

Here we have performed the PIMC simulations to study the $^4$He adsorption on $\gamma$-graphyne, the most stable structure among graphynes [23]. With the increasing number of $^4$He adatoms, multiple distinct helium layers are observed on $\gamma$-graphyne. Because of larger hexagons of graphyne, these $^4$He adsorbates show a richer phase diagram than the corresponding ones on graphite or graphene. Unlike $\alpha$-graphyne, however, even a single sheet of $\gamma$-graphyne is found to be impermeable to $^4$He atoms. It is found that the $^4$He monolayer exhibits various commensurate solid structures at different areal densities before crystallizing into an incommensurate triangular solid at its completion.

In this study, a single $\gamma$-graphyne sheet is fixed at $z = 0$ and the helium-graphyne interaction is described by a sum of pair potentials between the carbon atoms and a $^4$He atom. For the $^4$He-C interatomic potential, we use...
FIG. 1: (Color online) (a) A contour plot of the minimum $V_{\text{min}}(x, y)$, above each point $(x, y)$ on $\gamma$-graphyne and (b) the $^4\text{He}$-graphyne potential as a function of the distance $z$ from the graphyne surface along different symmetry directions. The black dots in (a) represent the positions of carbon atoms on the $\gamma$-graphyne surface. In (b), the blue, the red, and the black line correspond to the 3-fold symmetry direction, the 6-fold direction, and the direction of a saddle point (see white numbers and alphabet S in (a)), respectively. The length unit is Å and the potential energies are in units of Kelvin.

an isotropic 6-12 Lennard-Jones potential proposed by Carlos and Cole [24] to fit helium scattering data from graphite surfaces. While Fig. 1(a) shows a contour plot of the minimum potential energy, $V_{\text{min}}(x, y)$, above each point $(x, y)$ on $\gamma$-graphyne, Fig. 1(b) presents our $^4\text{He}$-graphyne potential as a function of the distance $z$ from graphyne along three different symmetry directions perpendicular to the graphyne surface. As seen in Fig. 1(a), there are three adsorption sites per graphyne unit cell, two global minima of the $^4\text{He}$-graphyne potential located at the centers of big irregular hexagons and one local minimum located at the center of a small regular hexagon (or a benzene ring). A bigger hexagon, which has much larger area than a smaller one, is expected to accommodate more than one $^4\text{He}$ atom. Figure 1(b) shows that the global minima in the three-fold symmetry directions are located closer to the graphyne surface by $\sim 0.5$ Å than the local minima in the six-fold symmetry directions and the potential energy difference between them is as large as $\sim 30$ K. From this we conjecture that the $^4\text{He}$ adatoms predominantly occupy the global minimum sites at low helium coverages, rather than the local minima. We here note that there is strong repulsive potential barrier for $^4\text{He}$ atoms as they approach the graphyne surface, i.e., $z \to 0$, suggesting that $^4\text{He}$ adatoms cannot penetrate through a $\gamma$-graphyne sheet from one side to the other.

This approach of modeling $^4\text{He}$-substrate potential with a pairwise sum of empirical interatomic potentials has been widely used to study the $^4\text{He}$ adsorptions on various carbon-based substrates, including $\alpha$-graphyne [22]. For the $^4\text{He}-^4\text{He}$ interaction, we use a well-known Aziz potential [25]. Since the exact form of thermal many-body density matrix is not known at a low temperature $T$, one can resort to the path-integral representation where the low-temperature density matrix is expressed by a convolution of $M$ high-temperature density matrices with an imaginary time step as large as $40$ K. We employ the multilevel Metropolis algorithm described in Ref. [26] to sample the imaginary time paths as well as the permutations among $^4\text{He}$ atoms. To minimize finite size effects, periodic boundary conditions are applied to a fixed $3 \times 2$ rectangular simulation cell with dimensions of $20.58 \times 23.76$ Å$^2$. All PIMC simulations presented here started from random initial configurations of $^4\text{He}$ atoms.

Here we consider the $^4\text{He}$ adsorption only on one side of the graphyne sheet, i.e., $z > 0$. Figure 2 presents one dimensional $^4\text{He}$ density distributions as a function of distance $z$ from the graphyne surface for different numbers of $^4\text{He}$ adatoms $N$ per $3 \times 2$ rectangular simulation cell. These density distributions confirm the above assertion that $^4\text{He}$ adatoms cannot penetrate to the other side of $z < 0$ through a single graphyne sheet because of the presence of the strong repulsive potential barrier. As more $^4\text{He}$ atoms are adsorbed, one can see the development of layered structures as evidenced by well-distinct density peaks in Fig. 2. The first sharp peak is located at $z \sim 2.7$ Å and the second peak at $z \sim 5.8$ Å, similar to the case of $^4\text{He}$ on graphene [3]. We observe the emergence of the second layer when the number of $^4\text{He}$ adatoms per $3 \times 2$ simulation cell increases beyond $N = 48$ (an areal density of $0.0982$ Å$^{-2}$). With further development of the second helium layer, more $^4\text{He}$ atoms are found to be squeezed into the first layer. From this we conjecture that the completed first layer would be a compressible incommensurate solid like the corresponding layer on graphene [3] or graphite [2, 28].
cell with dimensions of 20.58 $\times$ 23.76 Å$^2$ and the computations were done at a temperature of 0.5 K.

![Density vs Z](image)

**FIG. 2:** (Color online) One-dimensional density of $^4$He atoms adsorbed on a single $\gamma$-graphyne sheet as a function of the distance $z$ (in Å) from the graphyne surface. Here $N$ represents the number of $^4$He adatoms per $3 \times 2$ rectangular simulation cell with dimensions of 20.58 $\times$ 23.76 Å$^2$ and the computations were done at a temperature of 0.5 K.

![Energy vs density](image)

**FIG. 3:** (Color online) Energy per $^4$He atom of the first $^4$He layer on $\gamma$-graphyne as a function of the helium coverage. The alphabets (a), (b), (c), and (d) correspond to the areal densities of 0.0491, 0.0736, 0.0859, and 0.0982 Å$^{-2}$, respectively, for which two-dimensional $^4$He density plots are shown in Fig. 4. The energies were computed at a temperature of 0.5 K.

that the first layer is completed at an areal density of $\sim 0.115$ Å$^{-2}$ while the corresponding value on graphene was predicted to be $\sim 0.12$ Å$^{-2}$. This small (about 4 %) difference suggests that the $^4$He-graphene potential is more attractive than the $^4$He-graphyne potential and graphene may accommodate more $^4$He atoms in its immediate vicinity than graphyne.

Now we discuss the energetics of the $^4$He-graphyne system, which provides some insight into the growth of the $^4$He adlayers on $\gamma$-graphyne and their different quantum phases. Figure 3 shows the energy per $^4$He atom as a function of an areal density $\sigma$. At low densities of $\sigma < 0.0736$ Å$^{-2}$, the energy per $^4$He atom changes very little, indicating that each $^4$He atom occupies one of the adsorption sites, i.e., the $^4$He-graphyne potential minima. It is found that the energy per atom has the lowest value at $\sigma = 0.0491$ Å$^{-2}$ which corresponds to two $^4$He atoms per the graphyne unit cell. Noting that there are two global minima of the $^4$He-graphyne potential per the unit cell (see Fig. 1(a)), we conjecture that in the lowest energy state at $\sigma = 0.0491$ Å$^{-2}$ each global minimum is occupied by a single $^4$He atom. After filling all global minima, additional $^4$He atoms are expected to occupy the local minima located above the centers of the small hexagons, which is consistent with slight increase in the energy per atom for $0.0491$ Å$^{-2} < \sigma < 0.0736$ Å$^{-2}$.

Since the distances between the adsorption sites on the graphyne surface are long enough ($\sim 4$ Å), the $^4$He-$^4$He interaction is understood to have minimal effects while $^4$He atoms are filling these adsorption sites. Each adsorption site, whether it is a global minimum or a local minimum, is occupied by a single $^4$He atom at an areal density of $\sigma = 0.0736$ Å$^{-2}$, three $^4$He atoms per the graphyne unit cell, beyond which one can observe a sudden increase in the energy per atom in Fig. 3. The continuous increase of the energy per atom for $\sigma > 0.0736$ Å$^{-2}$ suggests that the $^4$He-$^4$He interaction as well as the $^4$He-substrate interaction plays a critical role in determining quantum states of the $^4$He monolayer at high helium coverages. One can observe a significant jump in the energy per atom at an areal density of $\sigma = 0.0982$ Å$^{-2}$, which reflects the start of the second-layer promotion concluded in the analysis of the one-dimensional density distributions of Fig. 2.

For further analysis of different phases of the $^4$He monolayer, we computed two-dimensional density distributions of $^4$He adatoms on $\gamma$-graphyne at various areal densities. In all four density plots presented in Fig. 4 a distinct density peak represents the occupancy of a single first-layer $^4$He atom. At an areal density of 0.0491 Å$^{-2}$, which corresponds to the lowest energy state, each of the irregular hexagons is seen in Fig. 4(a) to accommodate one $^4$He atom at its center, confirming our conjecture made from the energetic analysis. These $^4$He atoms form a honeycomb structure with the same primitive vectors as those of the underlying graphene triangular lattice, which is therefore a 1 x 1 registered phase in the Wood’s notation. It is also a C$_{2/3}$ commensurate solid with two out of every three adsorption sites being occupied by $^4$He atoms. The lowest-energy state for the $^4$He monolayer on graphene is a C$_{1/3}$ commensurate solid. We note that the C$_{2/3}$ commensurate solid on graphene is realized at an areal density significantly lower than the C$_{1/3}$ commensurate helium coverage of 0.0636 Å$^{-2}$ on graphene. Furthermore, vacancies created in this C$_{2/3}$ solid on graphene are found to be immobile and very weakly, if ever, interacting with each other, which could be understood
by high potential barrier and long distances between the neighboring adsorption sites.

As conjectured above, the local minima located at the centers of the small regular hexagons accommodate additional $^4$He atoms beyond the $C_{2/3}$ commensurate coverage. Figure 4(b) shows another commensurate structure at an areal density of $\sigma = 0.0736$ Å$^{-2}$, where each of the adsorption sites, both global minima and local minima, is occupied by a single $^4$He atom. In this $C_{3/3}$ commensurate structure, the $^4$He adatoms form a triangular solid structure registered by $1\sqrt{3} \times 1\sqrt{3}$ to the graphyne triangular lattice. With further increase of the helium coverage beyond the $C_{3/3}$ solid, where the energy per $^4$He atom increases monotonically as shown in Fig. 3, the $^4$He monolayer enters a regime of various domain structures. At higher $^4$He coverages, the $^4$He-$^4$He interaction as well as the $^4$He-substrate interaction is expected to affect the structure of the $^4$He monolayer. At an areal density of 0.0859 Å$^{-2}$, one can observe two different domains separated by the yellow dotted lines in Fig. 4(c); one domain involves some irregular hexagons accommodating three $^4$He atoms while the other consists of the $^4$He atoms in the $C_{3/3}$ commensurate order. Another homogeneous phase of the $^4$He monolayer is observed at an areal density of 0.0982 Å$^{-2}$, where all $^4$He atoms are accommodated by irregular hexagons and no small hexagon includes a $^4$He atom. In this phase, some irregular hexagons accommodate three $^4$He atoms and the neighboring ones include only one $^4$He atom. With an alternating order of the three-atom and the single-atom irregular hexagons, the $^4$He atoms constitute another perfect triangular solid whose primitive vectors are one half of those of the underlying graphyne structure. This $1\sqrt{2} \times 1\sqrt{2}$ registered phase is a $C_{4/3}$ commensurate solid with 4 $^4$He atoms being accommodated by a graphyne unit cell. We note that Li atoms attached to $\gamma$-graphyne could constitute an in-plane structure similar to this $C_{4/3}$ solid as reported in Ref. [21]. As discussed above, the $^4$He adatoms start to get promoted to the second layer beyond the $C_{4/3}$ commensurate coverage of 0.0982 Å$^{-2}$. With further development of the second $^4$He layer, more $^4$He atoms are found to be squeezed into the first layer. The fully-compressed first layer shows an incommensurate triangular lattice structure like the corresponding layer on graphite.

Our PIMC calculations have showed multiple distinct $^4$He layers on a single sheet of $\gamma$-graphyne which is not permeable to $^4$He atoms unlike $\alpha$-graphyne. The $^4$He
monolayer on γ-graphyne is found to exhibit various commensurate structures depending on the helium coverage, including the $1 \times 1$, the $\sqrt{3}\times\sqrt{3}$, and the $\frac{1}{2}\times\frac{1}{2}$ registered phases. While some theoretical calculations predicted that zero-point vacancies would not be thermodynamically stable in bulk solid $^4$He \cite{29-31}, a substrate potential could stabilize the vacancy formation in a commensurate $^4$He solid on a substrate. Therefore the existence of a stable commensurate structure is understood to be critical in realizing the vacancy-based supersolidity proposed originally by Andreev and Lifshitz \cite{32}. One of several commensurate structures we found in the $^4$He monolayer on γ-graphyne could manifest the superfluid response induced by vacancies, which is now under our investigation.

This work was supported by the Basic Science Research Program (2012R1A1A2006887) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology. We also acknowledge the support from the Supercomputing Center/Korea Institute of Science and Technology Information with supercomputing resources including technical support (KSC-2013-C3-033).

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