Path-integral Monte Carlo calculations were performed to study the adsorption of $^4$He atoms on $\alpha$-graphyne. We find that one $^4$He atom can be embedded onto the in-plane center of each hexagon of the graphyne. In the first $^4$He layer above the $^4$He-embedded graphyne surface, a Mott insulating state was observed at the areal density of 0.0706 Å$^{-2}$ with three $^4$He atoms occupying each hexagonal cell while the helium atoms form a commensurate triangular solid at a density of 0.0941 Å$^{-2}$. Here we show that the Ising pseudo-spin symmetry introduced for two degenerate configurations of three $^4$He atoms in a hexagonal cell can be broken by additional $^4$He atoms placed at the hexagon vertices and the Mott-insulator to commensurate-solid transition is a transition from a nonmagnetic spin liquid of frustrated antiferromagnets to a spin-aligned ferromagnet under a particle-induced pseudo-magnetic field.

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Graphyne is a two-dimensional network of $sp^2$-bonded carbon atoms that possess some intriguing electronic properties. In particular, highly-asymmetric Dirac cones predicted for some graphynes would cause electrons to conduct only in a preferred direction, leading to electron collimation transport without any external field \[13\]. Graphyne also has a very large surface area, with its hexagon being much larger than that of graphene, which could allow various potential applications as new energy materials, including as a Li-ion battery anode \[14, 15\] and high-capacity hydrogen storage \[16, 17\]. Because of its large hexagon size, a single sheet of graphyne, unlike a graphene sheet, is predicted to be permeable to $^4$He atoms. This could result in more complex phase diagrams for the $^4$He adlayers on graphyne than those of the corresponding helium layers on graphene or graphite.

Here we performed path-integral Monte Carlo (PIMC) calculations to study $^4$He adsorption on $\alpha$-graphyne, a honeycomb structure with a hexagon side consisting of one $sp^2$-bonded carbon atom and two $sp$-bonded carbon atoms \[18\]. Unlike the case of graphene, in-plane adsorption of $^4$He atoms is observed on the graphyne surface 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 graphyne surface exhibits various quantum phases depending on the helium coverage; this helium layer is in a Mott insulating state at the areal density of 0.0706 Å$^{-2}$ with each hexagonal unit cell accommodating three $^4$He atoms and the helium atoms form a commensurate triangular solid at 0.0941 Å$^{-2}$.

In this study, 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 pair potential, we use an isotropic six-twelve Lennard-Jones potential, which was proposed by Carlos and Cole to fit helium scattering data from graphite surfaces \[19, 20\]. This empirical pair potential has been widely used to study helium adsorptions on various carbon isomers. A well-known Aziz potential \[21\] is used for the $^4$He-$^4$He interaction. In the path-integral representation, the thermal density matrix at a low temperature $T$ is expressed as a convolution of $M$ high-temperature density matrices with an imaginary time step $\tau = (Mk_B T)^{-1}$. Both $^4$He-
leads to the development of distinct layered structures, we can observe that increase in the number of 4He atoms on the graphyne surface, for different numbers of 4He adsatoms per 3 \times 2 rectangular simulation cell, which have dimensions of 21.01 \times 24.26 \text{Å}^2 and the computations were done at a temperature of 0.5 K. Here the upper graphyne layer is positioned at \( z = 0 \) and the lower layer at \( z = -3.35 \text{Å} \). One can observe that increase in the number of 4He adatoms leads to the development of distinct layered structures, similar to those observed on a graphite or graphene surface. The sharp peak located at \( z \sim -0.3 \text{Å} \) is completed with 12 4He atoms. This corresponds to the areal density of 0.0235 \text{Å}^{-2}, or to one helium atom per the hexagonal cell, which leads us to a conjecture that each hexagonal cell on the graphyne surface can accommodate one 3He atom at its in-plane center. This has been confirmed by the two-dimensional density distribution of 12 4He atoms in Fig. 1(b), which shows clear density peaks located at the centers of the hexagons. The black and brown dots of the honeycomb structures represent the two-dimensional positions of the carbon atoms in the upper and the lower graphyne layer, respectively. The layer of 4He atoms embedded onto the hexagon centers of the graphyne surface is called the zeroth helium layer, which is located slightly below the upper graphyne layer because of the attractive interaction with the lower graphyne layer. With the growth of the next helium layer (the first layer) located at \( z \sim 2.7 \text{Å} \), there was little change in the zeroth layer except for a slight tightening due to the compression from the first-layer 4He atoms.

We now analyze the structure of the first 4He layer above the 4He-embedded graphyne surface. Two-dimensional density distributions of the first 4He layer, at a temperature of \( T = 0.5 \text{K} \), are shown in Fig. 2. We note that an adsorption site for 4He (or a hexagonal unit cell) determined by the substrate potential is large enough to accommodate multiple 4He atoms. In fact, each hexagonal cell is found to be able to accommodate up to 3 4He atoms. At the first-layer areal density of \( \sigma_1 = 0.0235 \text{Å}^{-2} \), which corresponds to one 4He atom per hexagonal cell, the average helium occupancies of some hexagonal cells are higher than one while the others have the helium occupancies lower than one (see Fig. 2(a)). This irregularity can be understood by the fact that attractive on-site interaction between two 4He atoms accommodated by a single hexagonal cell, along with the substrate-potential barrier, results in low probability for a 4He atom to hop to a neighboring cell. When the helium density is doubled to \( \sigma_1 = 0.0471 \text{Å}^{-2} \), every hexagonal cell seen in Fig. 2(b) contains two 4He atoms. As the helium coverage increases further, shown in Fig. 2(c), all hexagonal cells show fractional occupancies close to \(~ 2.5 \), which suggests frequent hopping of the third 4He atom in a cell to its neighbor. Figure 2(d) shows that each hexagon involves the maximum number of 4He atoms, namely 3 4He atoms, at the areal density of 0.0706 \text{Å}^{-2}. This is concluded to be a Mott insulating state \( \text{He}^3 \) where a strong repulsive on-site interaction prohibits a 4He atom from hopping from one adsorption site (a hexagonal cell) to the neighboring ones. The winding number estimator of Ref. [22] was used to compute the superfluidity of the 4He layer on the 4He-embedded graphyne surface, from which significant superfluid fractions were observed only at the areal densities corresponding to fractional 4He occupancies as in

![Image of graph showing density distributions](image-url)
FIG. 2: (Color online) Two-dimensional density distributions of the first-layer $^4$He atoms adsorbed on the $^4$He-embedded $\alpha$-graphene surface at areal densities of (a) 0.0235, (b) 0.0471, (c) 0.0588, and (d) 0.0706 Å$^{-2}$. The black dots represent the positions of the carbon atoms in the upper graphyne layer. The length unit is Å and all contour plots are in the same color scale denoted by the color table in the upper right hand corner.

FIG. 3: (Color online) Ising pseudo-spin states ((a) spin up and (b) spin down) assigned to two degenerate ground-state configurations for three first-layer $^4$He atoms accommodated in a hexagonal unit cell on the $\alpha$-graphyne surface. The black and the blue dots correspond to the positions of the carbon atoms and the $^4$He atoms, respectively. The characters A and B represent two different triangular sublattice sites of the honeycomb structure of $\alpha$-graphyne.

the case of Fig. 2(c). In particular, the superfluidity was found to be completely quenched at the Mott insulating density of $\sigma_1 = 0.0706$ Å$^{-2}$, where the $^4$He layer undergoes a superfluid to Mott-insulator transition.

As shown in Fig. 3 there are two degenerate ground-state configurations for 3 first-layer $^4$He atoms in a hexagonal unit cell on the graphyne surface. This allows us to introduce Ising pseudo-spins; (a) spin up for one configuration and (b) spin down for the other. It is found that the inter-cell interaction between $^4$He atoms in two neighboring cells energetically favors anti-aligned pseudo-spin configurations and results in a weak antiferromagnetic interaction between the neighboring spins. The helium density distribution for the Mott insulating state, shown in Fig. 2(d), shows that each pseudo-spin fluctuates between the up- and the down-state with a tendency of being anti-aligned with its neighbors. These fluctuations are understood to be due to the geometrical frustration at the triangular lattice. Another PIMC simulation starting from an initial spin-aligned configuration also produced a $^4$He density distribution consistent with the pseudo-spin state of Fig. 2(d) which was obtained from a random initial $^4$He configuration. This suggests that the Mott insulating state corresponds to a nonmagnetic spin liquid of frustrated antiferromagnets [25] in terms of the pseudo-spin degrees of freedom.

We now discuss the high-density structures of the first helium layer above the $^4$He-embedded $\alpha$-graphyne. Figure 4 shows the two-dimensional density distributions of the first-layer $^4$He atoms at two high areal densities. When the areal density increases beyond the Mott-insulating density of $\sigma_1 = 0.0706$ Å$^{-2}$, the additional helium atoms are found to be placed at the vertices of the hexagons, that is, above the $sp^2$-bonded carbon atoms. In Fig. 4(a), one can see 6 $^4$He atoms located at the hexagon vertices. The presence of a $^4$He atom at a hexagon vertex affects the pseudo-spin states of the surrounding hexagonal cells. There are two different triangular sublattice points in the honeycomb structure of $\alpha$-graphyne, which are denoted by A and B in Fig. 4. The additional helium atoms placed at A sites favor the surrounding three pseudo-spins to be in the spin-up state.
to minimize the $^4\text{He}-^4\text{He}$ interaction, while those at $B$ sites prefer the spin-down state in the neighboring cells. Hence the $^4\text{He}$ atoms at the $A$ and $B$ sites play the role of a local pseudo-magnetic field that forces the surrounding spins to be aligned in a certain direction. As the helium coverage increases beyond the Mott insulating density, we observed the formation of some local ordering of the pseudo-spins due to some additional helium atoms occupying the vertex carbon sites. In Fig. 4(a) for the areal density of 0.0824 Å$^{-2}$, two well-defined ferromagnetic domains with each of them consisting of the pseudo-spins aligned in the same direction, are seen to be separated by the yellow dotted lines. A homogeneous ferromagnetic phase is observed at the areal density of 0.0941 Å$^{-2}$. In Fig. 4(b), every $A$ site, one of two triangular sublattices of the honeycomb structure, is occupied by a single $^4\text{He}$ atom while every $B$ site, the other sublattice, is vacant without any $^4\text{He}$ atom. This sublattice symmetry breaking causes all pseudo-spins to be aligned in the same direction. One can also see in Fig. 4(b) that the first-layer $^4\text{He}$ atoms in the spin-aligned ferromagnetic phase constitute a triangular solid whose crystalline structure is commensurate with the underlying honeycomb structure of the graphyne surface. We note that all lattice points of this triangular solid are not the adsorption sites predetermined by the substrate potential and that the interaction potential between a first-layer $^4\text{He}$ atom and the $^4\text{He}$-embedded graphyne surface has the highest value at the hexagon vertices. From this we understand that the $^4\text{He}$-$^4\text{He}$ interaction as well as the $^4\text{He}$-substrate interaction is crucial in the manifestation of the triangular crystalline structure shown in Fig. 4(b). We observe that $^4\text{He}$ atoms are promoted to the second layer when the first-layer helium coverage increases beyond $\sigma_1 = 0.0941$ Å$^{-2}$.

Our PIMC calculations reveal that the in-plane $^4\text{He}$ adsorption takes place on $\alpha$-graphyne and a single helium atom is embedded to its in-plane hexagon center. The first layer of $^4\text{He}$ atoms adsorbed on the $^4\text{He}$-embedded graphyne surface is found to exhibit various quantum phases depending on the helium coverage. The Mott insulating state where each hexagonal unit cell accommodates three $^4\text{He}$ atoms is considered to be a spin liquid of frustrated antiferromagnets at a triangular lattice in terms of the Ising pseudo-spins assigned to two degenerate helium configurations. The pseudo-spin symmetry can be broken by the presence of additional $^4\text{He}$ atoms occupying the hexagon vertices, which causes a ferromagnetic domain to be developed at higher helium densities. The pseudo-magnetic field induced by the additional particles is similar to the strain-induced pseudo-magnetic field proposed recently to engineer graphene electronic structures [26, 27], in a sense that it breaks the sublattice symmetry of a honeycomb structure. At the helium coverage of $\sigma_1 = 0.0941$ Å$^{-2}$, the first $^4\text{He}$ layer is in a ferromagnetic phase with all Ising pseudo-spins being aligned in the same direction under a particle-induced pseudo-magnetic field, where the $^4\text{He}$ adatoms are found to constitute a commensurate triangular solid. The formation of vacancy defects in this two-dimensional solid and their possible contribution to superfluidity is now under investigation.

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