Phase diagram of $^4$He on graphene

Jodok Happacher  
Department of Physics, Arnold Sommerfeld Center for Theoretical Physics and Center for NanoScience,  
University of Munich, Theresienstrasse 37, 80333 Munich, Germany

Philippe Corboz  
Theoretische Physik, ETH Zurich, CH-8093 Zurich, Switzerland

Massimo Boninsegni  
Department of Physics, University of Alberta, Edmonton, Alberta, Canada, T6G 2G7

Lode Pollet*  
Department of Physics, Arnold Sommerfeld Center for Theoretical Physics and Center for NanoScience,  
University of Munich, Theresienstrasse 37, 80333 Munich, Germany

(Received 27 December 2012; revised manuscript received 29 January 2013; published 19 March 2013)

The low-temperature phase diagram of $^4$He adsorbed on a single graphene sheet is studied by computer simulations of a system consisting of nearly a thousand helium atoms. In the first layer, two commensurate solid phases are observed with fillings 1/3 and 7/16, respectively, separated by a domain wall phase, as well as an incommensurate crystal at a higher coverage. No evidence of a thermodynamically stable superfluid phase is found for the first adlayer. Second-layer promotion occurs at a coverage of 0.111(4) Å$^{-2}$. In the second layer, two phases are observed, namely a superfluid and an incommensurate solid, with no commensurate solid intervening between these two phases. The computed phase diagram closely resembles that predicted for helium on graphite.

DOI: 10.1103/PhysRevB.87.094514  
PACS number(s): 67.25.bh, 67.80.dm, 67.80.bd, 67.25.dj

I. INTRODUCTION

The study of films of highly quantal fluids, such as helium, is motivated by the search for novel phases of matter in confinement and/or reduced dimensions. Indeed, an experimentally controllable way of making quasi-2D interacting $^4$He systems is to adsorb a thin film of $^4$He on a substrate. On weakly attractive substrates, such as those of some alkali metals, $^4$He forms superfluid films (down to a monolayer$^1$ thin) whose thickness smoothly increases with chemical potential, with no evidence of layering.$^2,3$ On the other hand, on stronger substrates adsorption occurs through the formation of successive, well-defined layers (up to seven on graphite), with essentially no quantum-mechanical atomic exchanges taking place between the first few adjacent adlayers. The phase diagram on these substrates is richer, displaying a variety of phases, including crystalline ones, either commensurate or incommensurate with the underlying substrate.

Crowell and Reppy$^4$ raised the possibility of a “supersolid” phase,$^5$ characterized by simultaneous density and superfluid long-range order, in the vicinity of a possible crystalline phase of the second helium adlayer, registered with the underlying graphite substrate. This contention has recently been reiterated.$^6$ The most reliable, first-principle numerical studies of helium films on graphite have yielded no evidence of such a phase, as no registered crystal is observed in the second adlayer.$^7$

Graphene (a single sheet of graphite) has also been theoretically considered as a possible substrate for helium adsorption, and the phase diagram of the adsorbate in the low temperature (i.e., $T \to 0$) limit has been computed by means of different numerical techniques.$^8$–$^{11}$ A single sheet of carbon atoms is somewhat less attractive than a graphite substrate. Quantitatively, the atomic binding energy for the first $^4$He adlayer is reduced by approximately 10% (about 13.4 K) compared to graphite.$^8$ One might imagine that the energy offset could lead to different physical behavior, but first principle calculations suggest that a difference of that order of magnitude in the adsorption potential is likely to have little or no effect on the phase diagram of helium on graphite.$^7$ Thus, one may expect no qualitative differences in the phase diagram of $^4$He adsorbed on graphene versus that on graphite. Indeed, that is the conclusion at which most numerical studies carried out so far for this system have arrived, with an outstanding puzzle concerning a possible superfluid response in the first adsorbed layer, near and at commensurate filling, reported in Refs. $9$ and $11$.

We report in this article results of a theoretical study of the low-temperature phase diagram of $^4$He adsorbed on graphene, based on computer simulations. We consider here a system comprising at least twice as many $^4$He atoms than in previous studies by others, the goal being that of attempting a reliable extrapolation of the physics of the system in the thermodynamic limit. The main findings of our study are largely in line with most previous works on graphene, but with no evidence of any “supersolid” phase, neither in the second nor in the first adsorbed layer.

The remainder of this paper is organized as follows: first, we briefly discuss the model of the system that is used, as well as the computational methodology; then, we proceed with the illustration of the results, focusing on the first and second adlayers. We summarize our main results in the Conclusions, where we also address issues that may be the subject of future work.
II. METHODOLOGY

In order to study numerically the physical properties of $^4$He on a graphene sheet, we performed equilibrium, large-scale computer simulations of a model of the system of interest, using the continuous-space Worm Algorithm.\textsuperscript{12,13} Graphene is modeled as an ideal, two-dimensional honeycomb lattice, with a carbon-carbon bond length $a = 1.42$ Å. Carbon atoms are treated as fixed particles in our simulation, an assumption justified by their relatively large mass, compared to that of the $^4$He atoms. The system is enclosed in a three-dimensional cell, shaped as a parallelepiped; the graphene sheet is aligned parallel to the $xy$ plane (at $z = 0$). Periodic boundary conditions are used in all directions, but the box is sufficiently elongated in the $z$ direction to make the boundary condition immaterial. The ensuing, quantum-mechanical many-body Hamiltonian is the following:

$$\hat{H} = -\frac{\hbar^2}{2m} \sum_i \nabla_i^2 + \sum_{i<j} v(r_{ij}) + \sum_{i \in L} u(|\mathbf{r}_i - \mathbf{R}_L|), \quad (1)$$

where $m$ is the mass of the $^4$He atoms, $v$ is a pairwise potential describing the interaction between two helium atoms, whereas $u$ describes the interaction of each helium-carbon pair, with $\mathbf{R}_L$ the position of a carbon atom. Both $u$ and $v$ are assumed to depend only on the relative distance between two particles. The interaction between helium atoms $v$ is taken to be the accepted Aziz pair potential,\textsuperscript{14} whereas for the carbon-helium potential $u$ a Lennard-Jones potential is used, with parameters $\epsilon = 16.2463$ K and $\sigma = 2.74$ Å, chosen following Ref.\textsuperscript{15}. The simulated systems comprise close to one thousand $^4$He atoms. The largest honeycomb lattice simulated here has size $49.19 \times 51.12$ Å and consists of 960 carbon atoms. All the simulations are performed in the grand canonical ensemble, at finite temperatures ranging from 0.5 to 1.0 K. The results at the two different temperatures differ very little, suggesting that they are essentially ground-state estimates, at least as far as energetics and structures are concerned. Finally, all the results presented here are independent of the initial atomic configuration utilized in the simulation.

III. RESULTS FOR THE FIRST LAYER

We start the discussion of our results with the first layer. Figure 1 shows the computed average equilibrium $^4$He coverage (two-dimensional density) as a function of chemical potential $\mu$.

As the chemical potential is increased above $\mu = -130$ K, the average $^4$He density jumps from zero to the value 0.0636 Å\textsuperscript{-2}, corresponding to the crystalline, commensurate $C1/3$ phase, wherein one of three equivalent adsorption sites of the lattice is occupied by a single $^4$He atom, as is shown in Fig. 2. In some simulations, a metastable liquid phase with a slightly higher value of the energy per atom was observed, which is typical for a first-order transition. Conceivably, such a phase might be seen in experiments.\textsuperscript{16} No evidence of a low-coverage thermodynamically stable superfluid (which exists on a smooth, flat substrate)\textsuperscript{1,17} is observed.

The $C1/3$ crystal forms at a distance $z = 2.864(7)$ Å, with a full width at half maximum $\Delta z = 0.65(2)$ Å (these numbers hold for the entire first layer), only slightly greater than that for graphite. The thermodynamic stability of the $C1/3$ phase is signaled by an extended plateau of the density as a function of $\mu$, hinting at a large gap of about 6.0(5) K in the spectrum and implying a zero superfluid response and zero compressibility. All of this is very similar to hardcore bosons on a lattice with long-range interactions and also to what is observed on graphite.\textsuperscript{7} However, Ref.\textsuperscript{9} reports a very small (less than 1%) but finite value of the superfluid fraction at $T = 0$, increasing to approximately 14% upon doping such phase with vacancies. Assuming a Kosterlitz-Thouless scenario for the U(1) transition for the $C1/3$ phase, the transition temperature corresponding to the data of Ref.\textsuperscript{9} corresponds to $T \approx 5$ mK. In Tables I and II, we computed the superfluid properties of the $C1/3$ phase down to $T = 10$ mK for a system consisting of $8 \times 6$ and $8 \times 8$ $^4$He atoms, respectively. We used 200 times slices per inverse Kelvin, except for the $T = 10$ mK case on the $8 \times 8$ system where 160 slices per inverse Kelvin were used because of limitations of computer memory. This led to a reduction of less than one percent on the kinetic energy. Simulations were started with an initial superfluid. In Tables I and II, we see that all data are consistent with insulating behavior and a large gap of a few K in the $C1/3$ phase, which is consistent with the results of Ref.\textsuperscript{11}. Nonzero winding numbers are possible on our small system sizes (ruining out ergodicity problems) but are a result of finite-size effects and disappear exponentially with system size. In particular, at $T = 10$ mK, a Kosterlitz-Thouless scenario would have predicted a strong superfluid response of the order of 50% of the value reported in Ref.\textsuperscript{9} (at $T = 0$ K). This is clearly not the case, and we conclude that the diffusion Monte Carlo results of Ref.\textsuperscript{9} are irreproducible, prompting a critical and systematic
appearance of domain walls, as is seen in Fig. 2, which first
find phase separation.
employed here offers distinct advantages over other ensembles
which is the maximum first-layer coverage. The temperature is
the incommensurate crystalline phase, at a coverage of 0.111 Å
this work (see also Fig. 3). Bottom row, right: 4He density profile
phase labeled as C7
principal axes. In the thermodynamic limit, it has no superfluid
proliferation of domain walls is observed, along more and more
akin to striped phases, but with increasing chemical potential a
occur along one principal axis of the C1
over 16 absorption sites. For this commensurate structure,
formation and which can be seen as every unit cell of the
unit cells are shown with dashed lines.
comparing the actual potentials felt at locations inside the unit
large-scale simulations. Surprisingly, the helium atoms are in
our case distributed more uniformly over the unit cell than in
previous works. Moreover, the structure is slightly rotated
(a comparison with the commensurate phases seen by others is
shown in Fig. 3). We performed the simulation with a smaller
system size (the same as the one used in Ref. 11), and we
also used as initial configuration one corresponding to the
the density profile obtained in Ref. 11, but our Monte Carlo
simulation still stabilized, after a sufficiently long time, to
the same structure of higher symmetry inside the unit cell,
shown in Fig. 3. Thus, we conclude that the difference is not
attributable to system size, nor is it a result of a specific choice
of initial atomic configuration.

The most likely reason for the difference between
our and previous results is the modeling of the helium-carbon
interaction. While we use here a two-body potential [μ in Eq. (1)] with fixed carbon positions, thereby retaining
full rotational symmetry, previous studies made use of an
external one-body potential obtained by summing anisotropic
Lennard-Jones potentials proposed to fit helium scattering
from graphite. The slightly different ways of accounting for
correlation may well be at the root of the lower symmetry
structure found in previous studies, and this is supported by
comparing the actual potentials felt at locations inside the unit
cell, which differ between the two methods.

On increasing μ even further, the C7/16 phase is replaced
by an incommensurate, compressible solid phase, sketched
in Fig. 2 (panel on the left in the bottom row). The density
increases linearly with chemical potential until a density
too, no finite superfluid signal is computed. Figure 2 shows
the 4He density profile for the C7/16 phase observed in our
large-scale simulations. Surprisingly, the helium atoms are in
our case distributed more uniformly over the unit cell than in
previous works. Moreover, the structure is slightly rotated
(a comparison with the commensurate phases seen by others is
shown in Fig. 3). We performed the simulation with a smaller
system size (the same as the one used in Ref. 11), and we
also used as initial configuration one corresponding to the
the density profile obtained in Ref. 11, but our Monte Carlo
simulation still stabilized, after a sufficiently long time, to
the same structure of higher symmetry inside the unit cell,
shown in Fig. 3. Thus, we conclude that the difference is not
attributable to system size, nor is it a result of a specific choice
of initial atomic configuration.

The most likely reason for the difference between
our and previous results is the modeling of the helium-carbon
interaction. While we use here a two-body potential [μ in Eq. (1)] with fixed carbon positions, thereby retaining
full rotational symmetry, previous studies made use of an
external one-body potential obtained by summing anisotropic
Lennard-Jones potentials proposed to fit helium scattering
from graphite. The slightly different ways of accounting for
correlation may well be at the root of the lower symmetry
structure found in previous studies, and this is supported by
comparing the actual potentials felt at locations inside the unit
cell, which differ between the two methods.

On increasing μ even further, the C7/16 phase is replaced
by an incommensurate, compressible solid phase, sketched
in Fig. 2 (panel on the left in the bottom row). The density
increases linearly with chemical potential until a density

TABLE II. Winding number squared along x and y axis for 8 × 8
4He atoms in the C1/3 phase.

<table>
<thead>
<tr>
<th>T[K]</th>
<th>(W^2_x)</th>
<th>(W^2_y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2(2) × 10^{-5}</td>
<td>0(0)</td>
</tr>
<tr>
<td>0.1</td>
<td>0(0)</td>
<td>2(2) × 10^{-4}</td>
</tr>
<tr>
<td>0.05</td>
<td>3(3) × 10^{-4}</td>
<td>0(0)</td>
</tr>
<tr>
<td>0.02</td>
<td>0(0)</td>
<td>0(0)</td>
</tr>
<tr>
<td>0.01</td>
<td>0(0)</td>
<td>0(0)</td>
</tr>
</tbody>
</table>

FIG. 2. (Color online) Top row, left: the commensurate C1/3 phase. Top row, right: domain wall structure at a coverage of 0.072 Å^-2. Bottom row, left: C7/16 commensurate phase as found in this work (see also Fig. 3). Bottom row, right: 4He density profile for the incommensurate crystalline phase, at a coverage of 0.111 Å^-2, which is the maximum first-layer coverage. The temperature is T = 0.5 K in all cases.

Further increasing the chemical potential leads to the
appearance of domain walls, as is seen in Fig. 2, which first
occur along one principal axis of the C1/3 phase. This phase is
akin to striped phases, but with increasing chemical potential a
proliferation of domain walls is observed, along more and more
principal axes. In the thermodynamic limit, it has no superfluid
response. This process stops when a commensurate crystalline
phase labeled as C7/16 with a coverage of 0.0835 Å^-2 is
formed and which can be seen as every unit cell of the
C1/3 phase being surrounded by domain walls. The C7/16
structure has a rhombic unit cell, with 4He atoms distributed
over 16 absorption sites. For this commensurate structure,
TABLE I. Winding number squared along x and y axis for 8 × 6
4He atoms in the C1/3 phase.

<table>
<thead>
<tr>
<th>T[K]</th>
<th>(W^2_x)</th>
<th>(W^2_y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>6(5) × 10^{-5}</td>
<td>6(4) × 10^{-5}</td>
</tr>
<tr>
<td>0.1</td>
<td>4(3) × 10^{-4}</td>
<td>8(3) × 10^{-5}</td>
</tr>
<tr>
<td>0.05</td>
<td>3(3) × 10^{-4}</td>
<td>4(3) × 10^{-5}</td>
</tr>
<tr>
<td>0.02</td>
<td>9(6) × 10^{-5}</td>
<td>6(4) × 10^{-5}</td>
</tr>
<tr>
<td>0.01</td>
<td>0.028(12)</td>
<td>0.036(13)</td>
</tr>
</tbody>
</table>

FIG. 3. (Color online) Left: 4He density profile for the C7/16 phase as seen in Ref. 11. The unit cells are shown with dashed lines. The small (white) dots represent the underlying graphene lattice. The large (red) dots are maxima of the density. Right: 4He density profile for the C7/16 phase obtained in this study.
The equilibrium coverage is roughly 0.150 Å⁻². No evidence of any supersolid phase is found. For higher density was also seen when the second layer is strongly occupied. For density in the first layer before layer promotion starts; this first-layer density was also seen when the second layer is strongly occupied. For higher μ, a first-order phase transition to an incommensurate solid occurs. No evidence of any supersolid phase is found.

We now turn to the second layer. The first stable phase that we observe is a uniform liquid, which is superfluid. The horizontal line denotes the maximum first layer density, that we observe is a uniform liquid, which is superfluid. The horizontal line denotes the maximum density in the first layer before layer promotion starts; this first-layer density was also seen when the second layer is strongly occupied. For higher μ, a first-order phase transition to an incommensurate solid occurs. No evidence of any supersolid phase is found.

IV. RESULTS FOR THE SECOND LAYER

We now turn to the second layer. The first stable phase that we observe is a uniform liquid, which is superfluid. The horizontal line denotes the maximum density in the first layer before layer promotion starts; this first-layer density was also seen when the second layer is strongly occupied. For higher μ, a first-order phase transition to an incommensurate solid occurs. No evidence of any supersolid phase is found.

of 0.107(3) Å⁻² is reached where the first atoms in the second layer are found. This value is slightly higher than the one reported in Ref. 11, but lower than the one from Gordillo et al., namely 0.115 Å⁻². It is also lower than the corresponding one for a graphite substrate, either from theoretical calculations, namely 0.114 Å⁻², or inferred from specific heat measurements, i.e., 0.127 Å⁻², something that can be attributed to the weaker substrate attraction.

V. CONCLUSION

We studied the phase diagram of the first and second layer of ⁴He adsorbed on graphene. In the first layer, we find a very stable C1/3 phase, followed by a domain wall phase, a C7/16 phase, and an incommensurate solid. This is the same as for graphite, and in line with previous studies. The only difference we observed consisted of the density distribution of the helium atoms inside the C7/16 unit cell, where we observed a small rotation (and more symmetric) distribution. We attribute this difference to the modeling of the carbon-helium interaction, which was done slightly differently than in previous studies: We used a fully rotationally symmetric two-body potential between carbon and helium atoms and kept a (classical) hexagonal carbon lattice in the simulation, while previous studies used a one-body potential that could be isotropic or anisotropic. We neglected defects, disorder, and other lattice imperfections in the graphene. For the second layer, our results are also in line with the ones found on graphite and previous studies showing a superfluid and an incommensurate solid at higher coverages. No commensurate structures are found, nor any supersolids. Layer promotion occurs at a slightly lower chemical potential than for graphite because of the slightly weaker helium-substrate potential.

In future work, we will study more realistic descriptions of graphene, which is not entirely flat but has intrinsic microscopic roughening. Suspended graphene sheets under a transmission electron microscope were seen to have a surface normal varying by several degrees and the out-of-plane deformations reach 1 nm. This roughened structure...
is thought to suppress and stabilize thermal vibrations and to
influence the behavior as an adsorbent. Our setup can also be
modified to study helium inside carbon nanotubes: instead of
using periodic boundary conditions in both \(x\) and \(y\) directions
on the graphene substrate, one could use periodic boundary
conditions only in the \(x\) direction.

ACKNOWLEDGMENTS

We thank A. B. Kuklov for fruitful discussions. M.B.
thanks the Arnold Sommerfeld Center at the LMU Munich
for hospitality during the early stages of this work. L.P.
acknowledges support from Marie Curie CIG “FDIAGMC,”
Grant No. PCIG11-GA-2012-321918.

(1999).
150, 1 (2008).
5The denomination “supersolid” is in any case fundamentally
incorrect for a system of this type. See, for instance, M. Boninsegni
and N. V. Prokof’ev, Rev. Mod. Phys. 84, 759 (2012).
150, 032096 (2009).
7P. Corboz, M. Boninsegni, L. Pollet, and M. Troyer, Phys. Rev. B
78, 245414 (2008).
9M. C. Gordillo, C. Cazorla, and J. Boronat, Phys. Rev. B 83, 121406
(2011).
10M. C. Gordillo and J. Boronat, Phys. Rev. B 85, 195457
(2012).
74, 036701 (2006).
14R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T.
16D. S. Greywall and P. A. Busch, Phys. Rev. Lett. 67, 3535
20J. C. Meyer, A. K. Geim, M. I. Katsnelson, K. S. Novoselov, T. J.