Workshop on Understanding Quantum Phenomena with Path Integrals:
from Chemical Systems to Quantum Fluids and Solids
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Path-integral Monte Carlo Study of ^{4}He Adsorption on Carbon Allotropes

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Outline

I. Introduction

II. Our Theoretical Approach

III. ^4He on Graphite

IV. ^4He on Graphynes

V. Conclusion

I. Introduction

why ^{4}He on a substrate?

- a testbed to study quantum fluids in confined geometries
- effects of reduced dimensionality or finite size
- theoretical prediction of a supersolid phase in a Bose Hubbard model

  (1) cold bosons in optical lattices

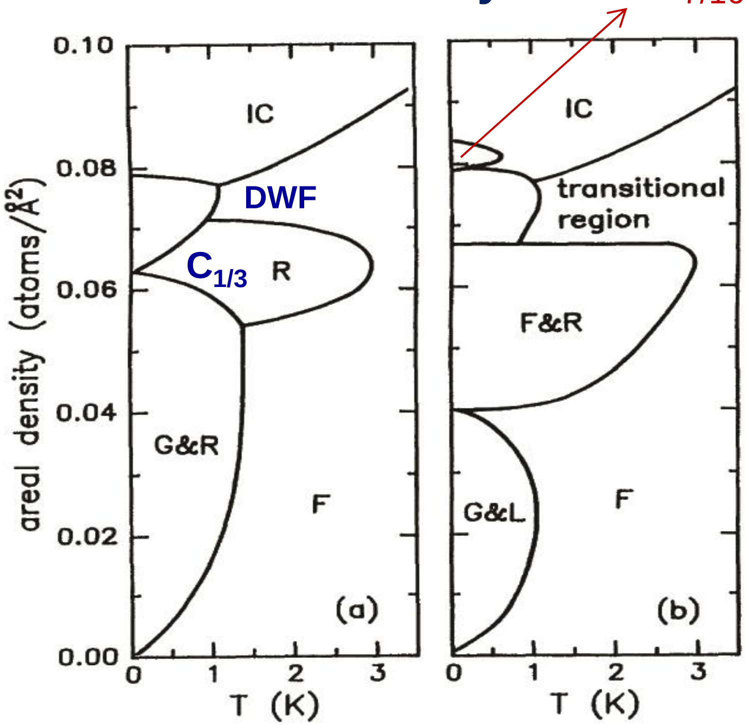
  (2) ^{4}He films on a substrate

^{4}He on graphite

- strong He-substrate interaction → layer-by-layer growth (~ 7 layers)
  each layer: a quasi-2D system
- interplay between He-He and He-substrate interaction
  → rich structural phase diagram (fluids, commensurate and IC solids, etc.)
- observation of superfluidity for the 2nd layer
  (*Crowell & Reppy, PRB 53, 2701 (1996)*)
  → speculated possible existence of supersolid phase

Experimental Phase Diagrams for ^{4}He on graphite

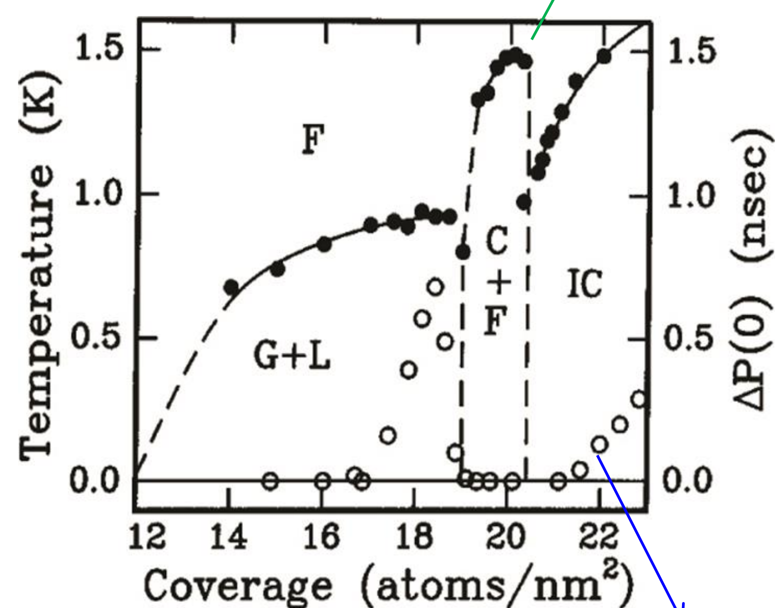
1st ^{4}He layer



Schick (1980)

Greywall and Busch (1991)

2nd ^{4}He layer



Crowell and Reppy (1996)

$C_{1/3}$ & IC : unambiguously observed

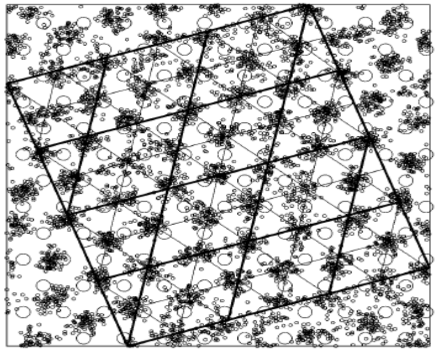
- speculation of supersolid phase ?
- but the existence of a C-phase has been in controversy

Previous calculations for the 2nd ^{4}He layer

(1) Pierce and Manousakis, PRL **81**, 156 (1998)

-. **over frozen incommensurate 1st layer**

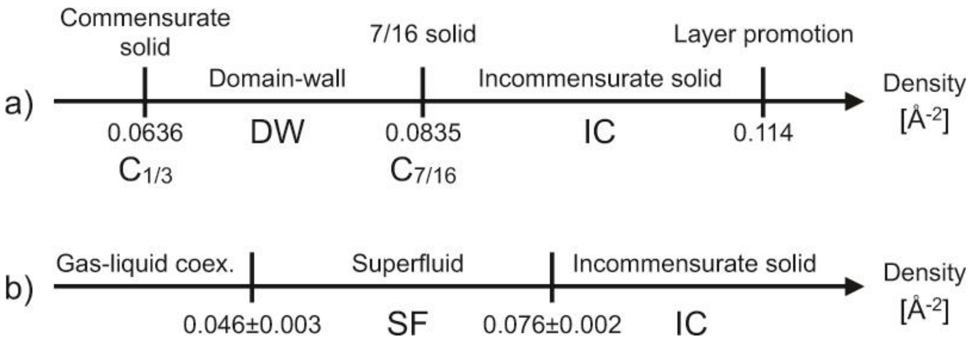
-. stable 2nd-layer $C_{4/7}$ structure



(2) Corboz *et al.*, PRB **78**, 245414 (2008)

-. incorporation of **zero-point motions of the 1st-layer ^{4}He atoms**

-. no stable 2nd-layer commensurate structure



1st layer

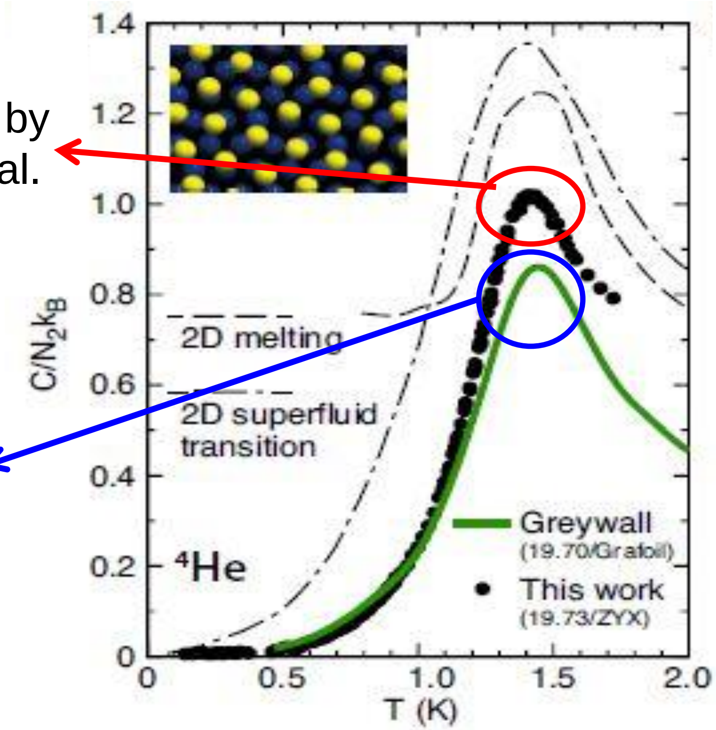
2nd layer

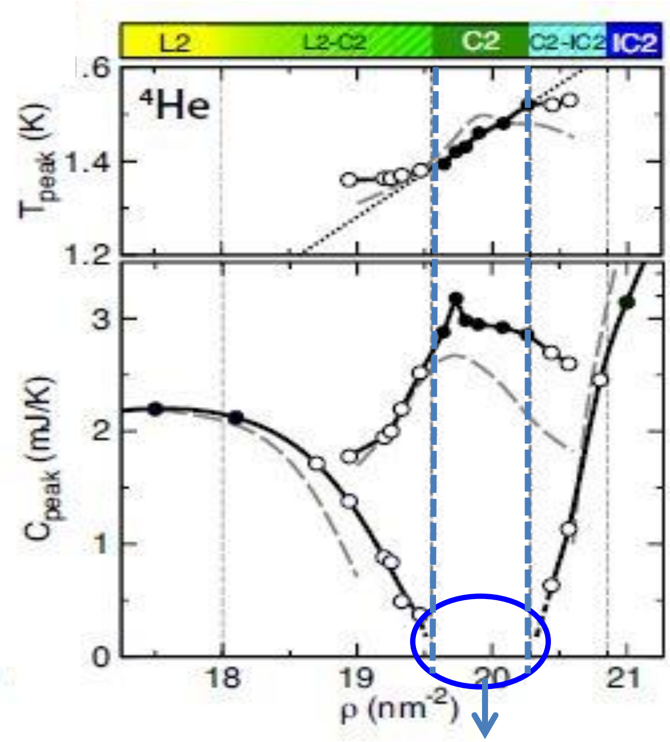
Recent heat capacity measurements for the 2nd ^{4}He layer

(1) S. Nakamura *et al*. , PRB **94**, 180501(R) (2016)

stronger peak by Nakamura et al.

Greywall's melting peak





commensurate phase

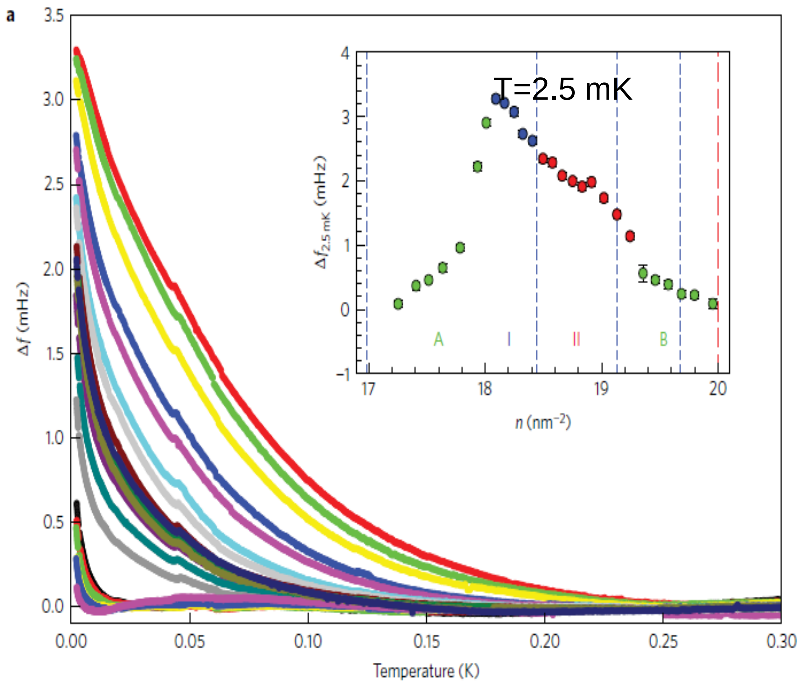
(2) M. Morishita, JLTP **187**, 453 (2017)

: no evidence for a 2nd-layer commensurate solid

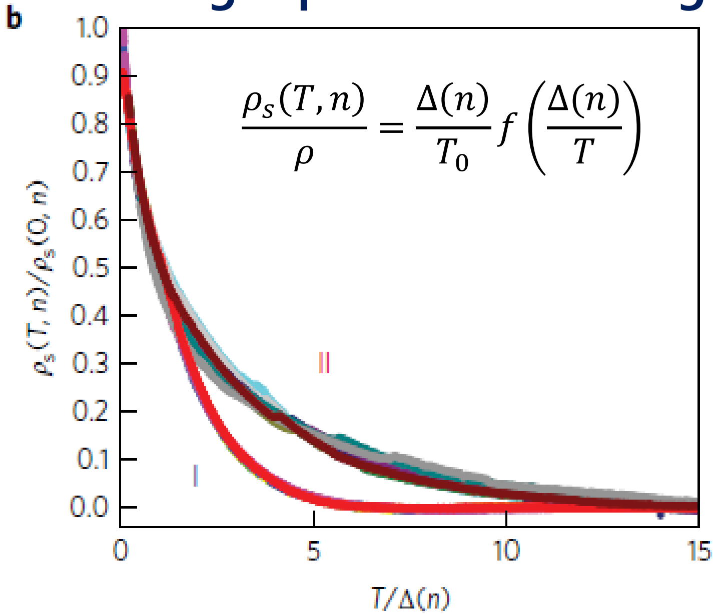
Recent torsional oscillator experiment

Nyéki *et al.*, Nature Physics **13**, 455 (2017)

freq. shift vs T



single-parameter scaling



"structural transition" at 18.45 nm^{-2}

➔ an excitation spectrum in region II : density wave ordering + superfluid order

II. Our Theoretical Approach

a more accurate description of quantum dynamics of the 1st-layer ^{4}He atoms

→ employ a ^{4}**He-graphite potential reflecting the corrugated surface.**

- System Hamiltonian:

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j} V_{He-He}(r_{ij}) + \sum_{i=1}^{N} V_{subs}(\vec{r}_i)$$

- He-substrate interaction:

$$V_{subs}(\vec{r}) = \sum_k U(\vec{r} - \vec{R}_k) + V_{1D}(z + 3.35)$$

topmost layer of graphite

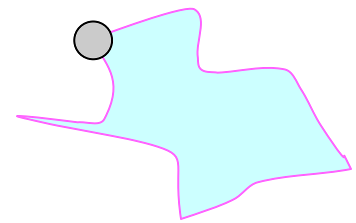
- anisotropic He-C pair potentials: *Carlos and Cole, Surf. Sci. 91, 339 (1980)*

$$U(\vec{r} - \vec{R}_k) = 4\varepsilon\left\{\left(\frac{\sigma}{|\vec{r} - \vec{R}_k|}\right)^{12}\left[1 + \gamma_R\left(1 - \frac{6}{5}\cos^2\theta\right)\right] - \left(\frac{\sigma}{|\vec{r} - \vec{R}_k|}\right)^{6}\left[1 + \gamma_A\left(1 - \frac{3}{2}\cos^2\theta\right)\right]\right\}$$

Path integral Monte Carlo (PIMC)

Thermal density matrix: $$\rho(R,R';\beta) = \langle R | e^{-\beta H} | R' \rangle$$

$$R = (\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$



For an diagonal observable in the coordinate space,

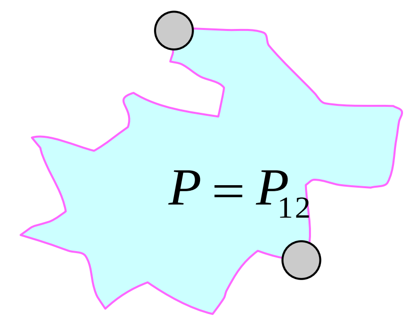
$$\langle O \rangle = Z^{-1} \int dR \rho\left(R,R;\beta\right) O(R)$$

$$\int \ldots \int dR_1 dR_2 \ldots dR_{L-1} \underline{\rho(R,R_1;\tau)} \ldots \rho(R_{L-1},R;\tau) \qquad \tau = \beta / L$$

$\Downarrow$

pair-product form of exact two-body density matrices

Bose symmetry: $$\rho_B(R,R;\beta) = \frac{1}{N!} \sum_P \rho(R,PR;\beta)$$



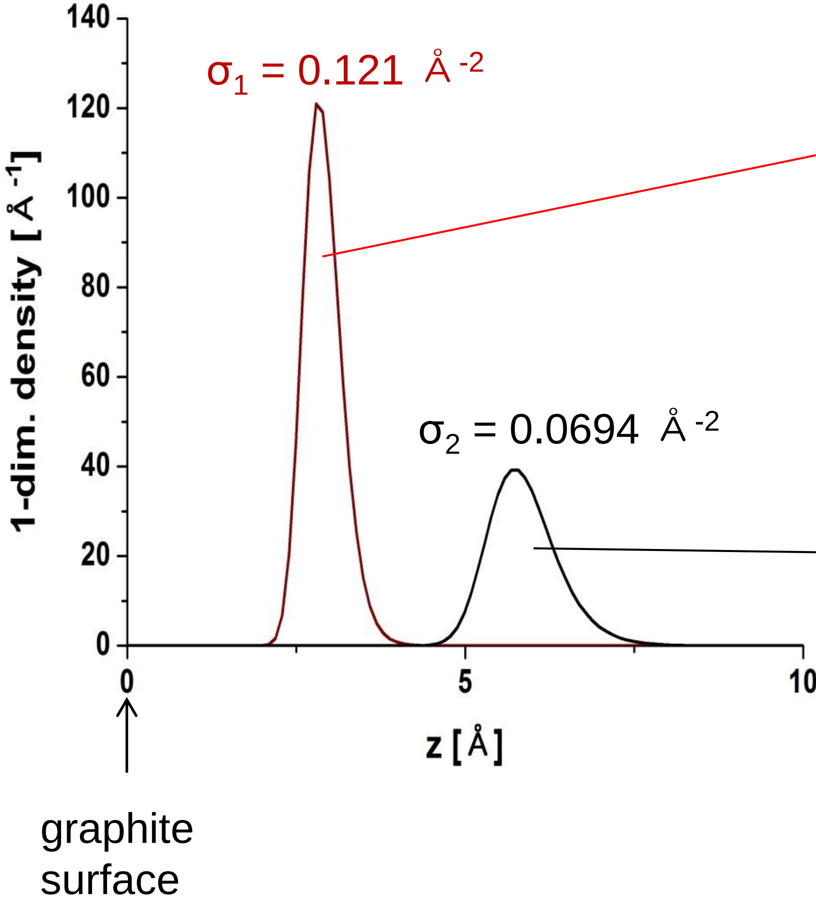
Multilevel Metropolis algorithm: sample permutations as well as discrete paths

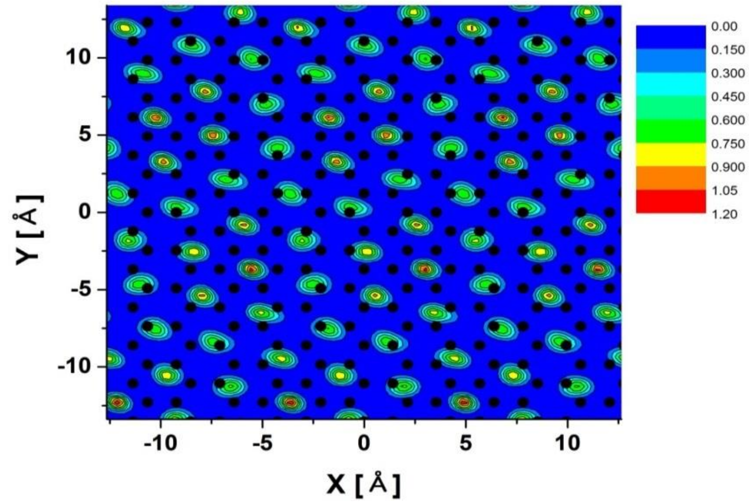
(For details, see D. M. Ceperley, Rev. Mod. Phys. **67**, 279 (1995))

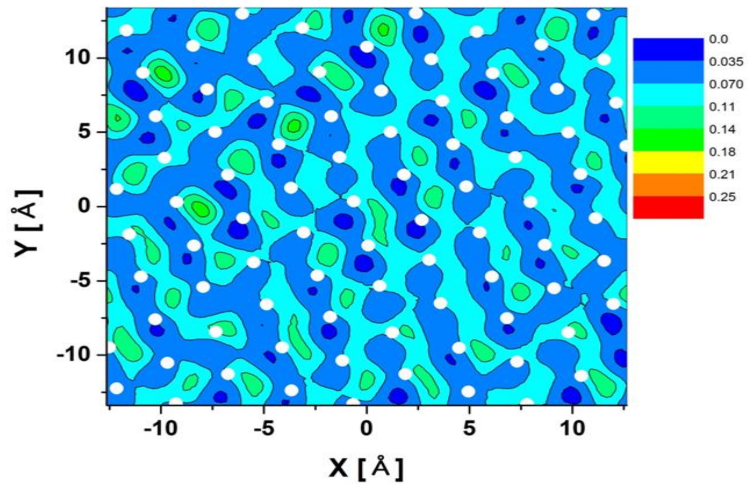
III. ^{4}He on Graphite

Ahn *et al.*, PRB **93**, 064511 (2016)

With an 1st-layer IC solid





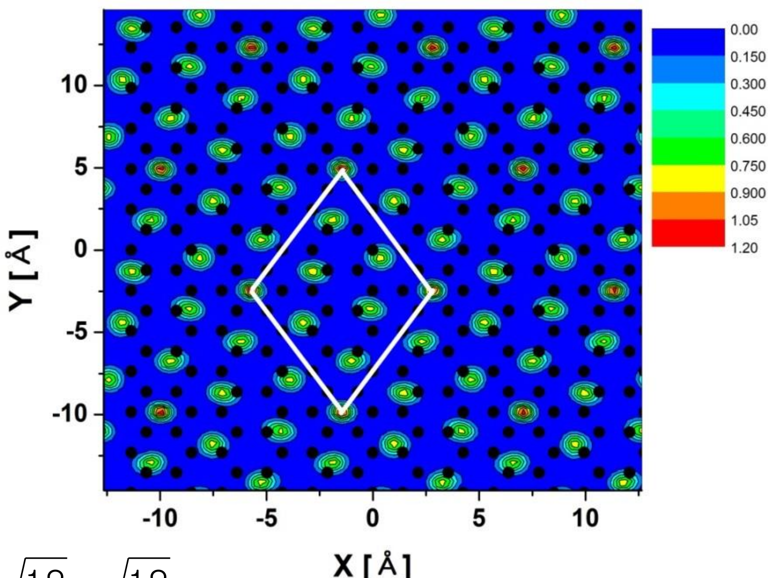


even with the corrugated substrate potential,

"no stable 2nd-layer comm. structure on an 1st-layer incomm. solid"

New 1st-layer commensurate solid

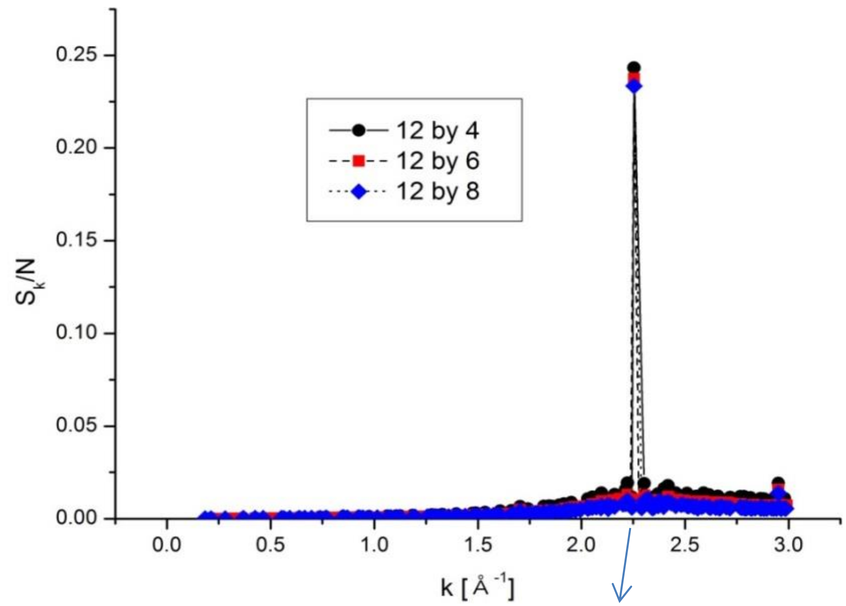
2D density plot at 0.111 Å $^{-2}$



$\sqrt{12} \times \sqrt{12}$

"a $C_{7/12}$ commensurate solid"
simulated from an random initial conf.

Static structure factor for $C_{7/12}$

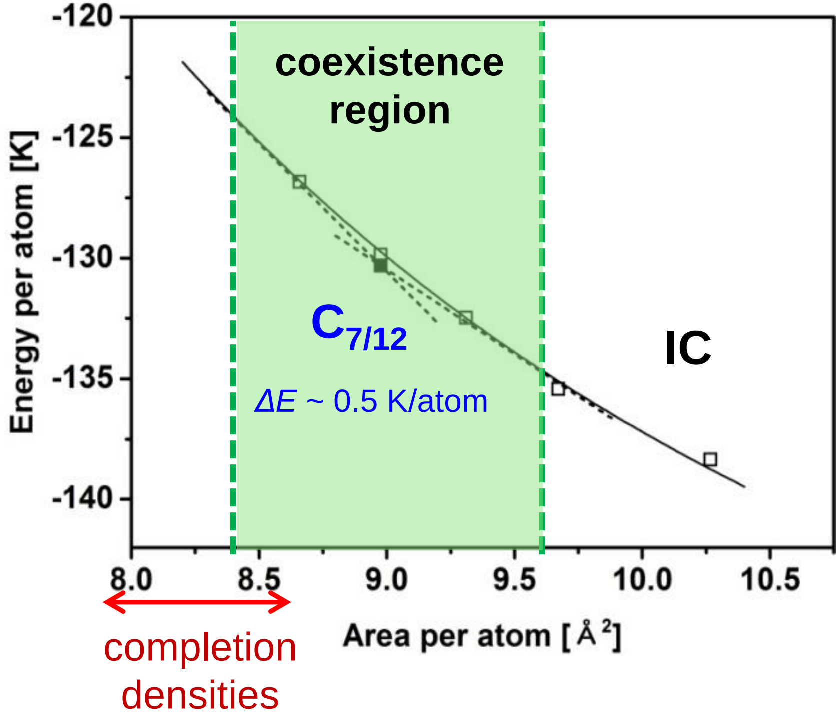


k = 2.253 Å^{-1}

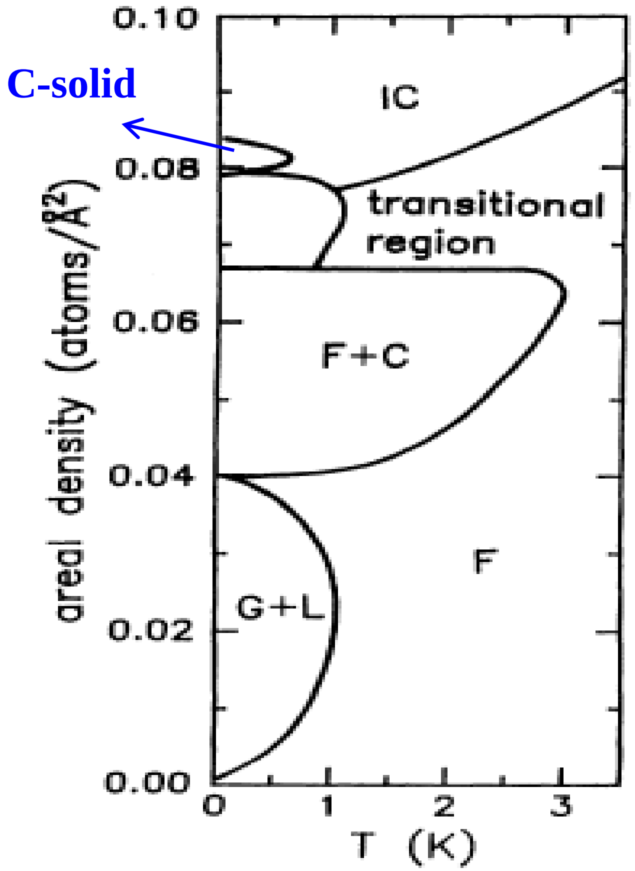
$C_{7/12}$ is not affected by finite size effects

New 1st-layer commensurate solid

high-density phases



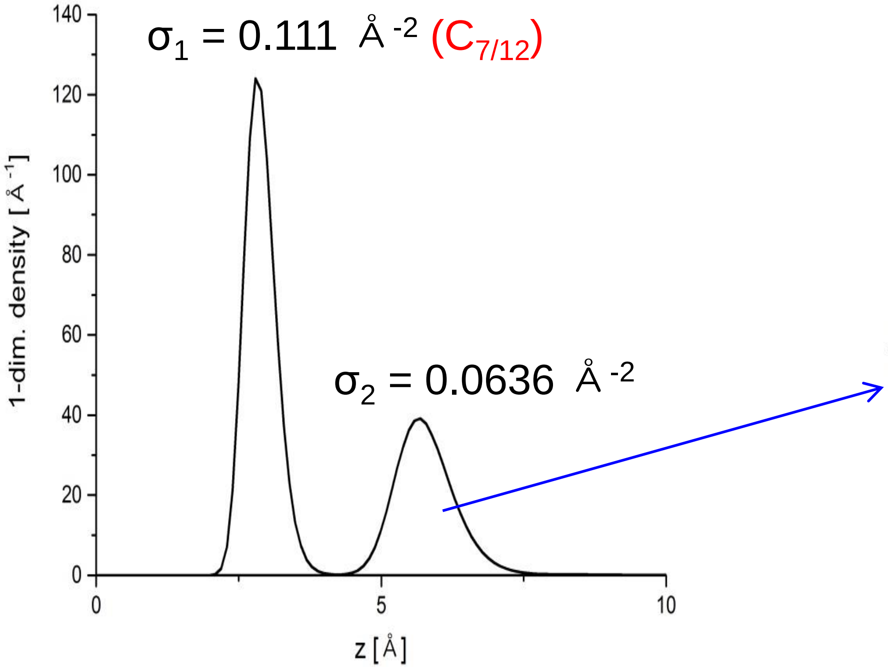
Experimental phase diagram



Greywall , PRB (1993)

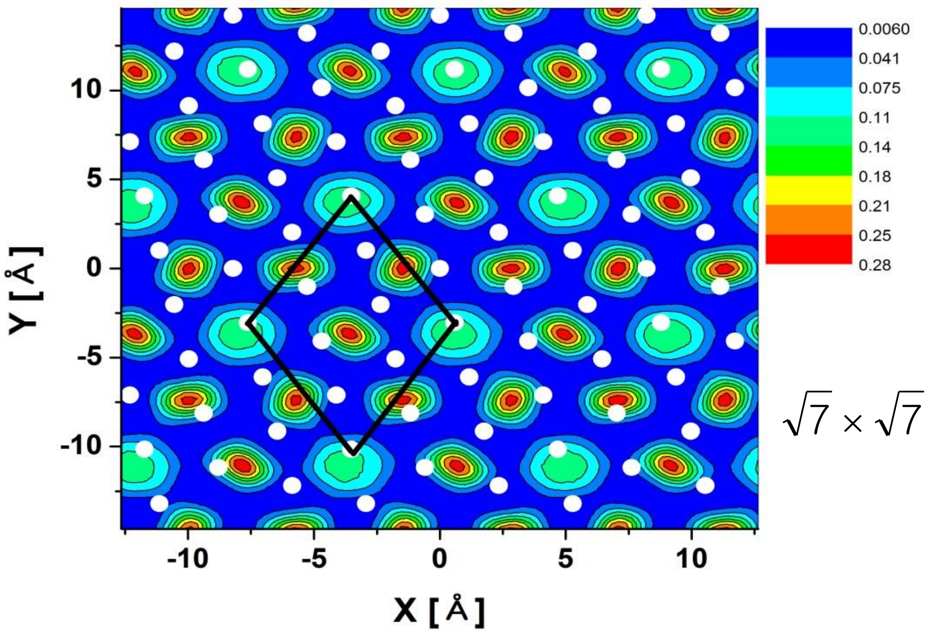
Both IC and $C_{7/12}$ phases coexist near the 1st-layer completion density.

On the 1st-layer $C_{7/12}$ solid



the 2nd-layer 2D density

(white dots : 1st-layer ^{4}He density peaks)



additional ^{4}He atoms:
not squeezed into the 1st layer at T=0.5 K

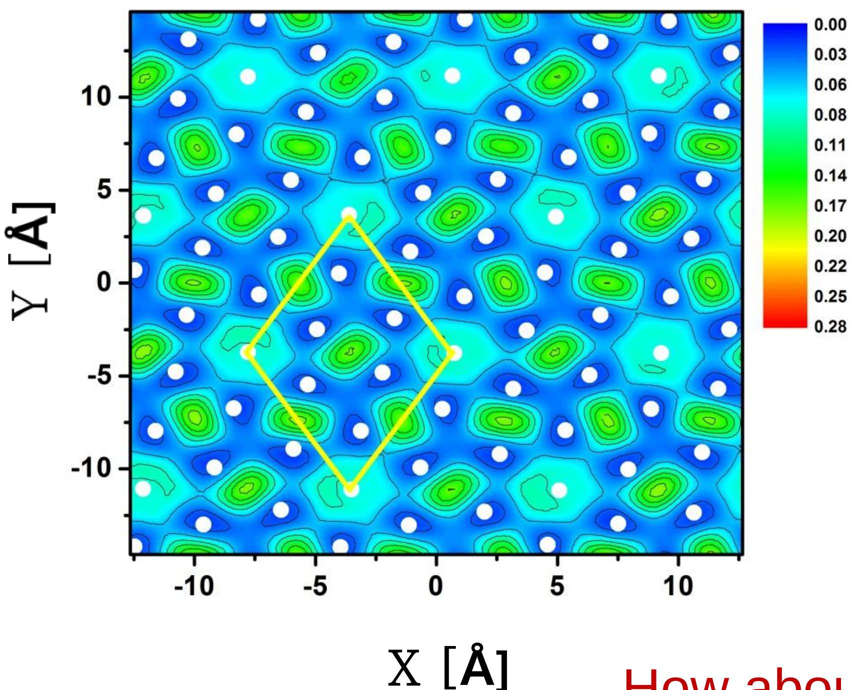
- the $C_{4/7}$ structure proposed by Elser (PRL 1989)
- This $C_{4/7}$+$C_{7/12}$ configuration could be metastable.

Vacancy formation in the $C_{4/7}$ - ^{4}He 2nd layer

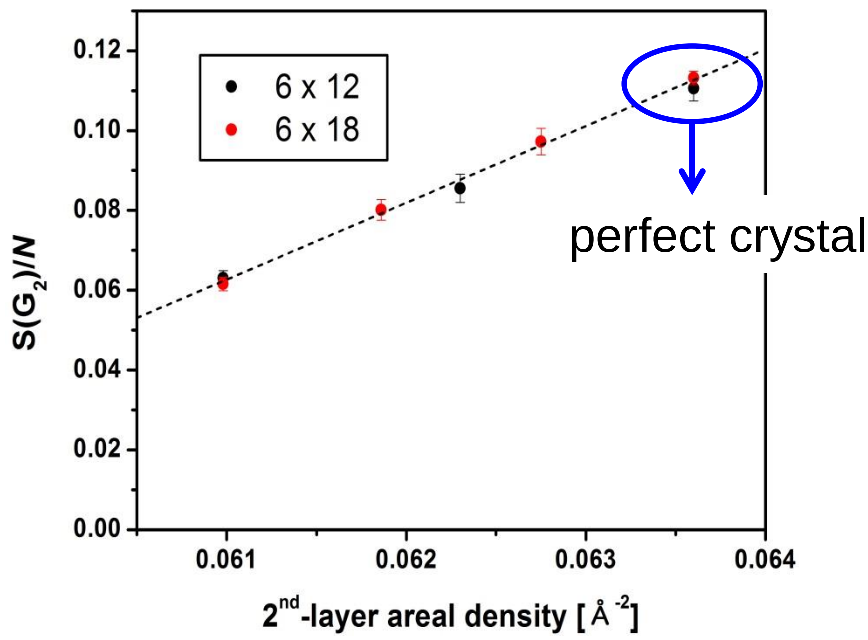
-. mobile vacancies are created while preserving the 4/7 order

-. frequent hoppings to the neighboring lattice sites

the second ^{4}He layer
with 2% vacancies



structure-factor peak values

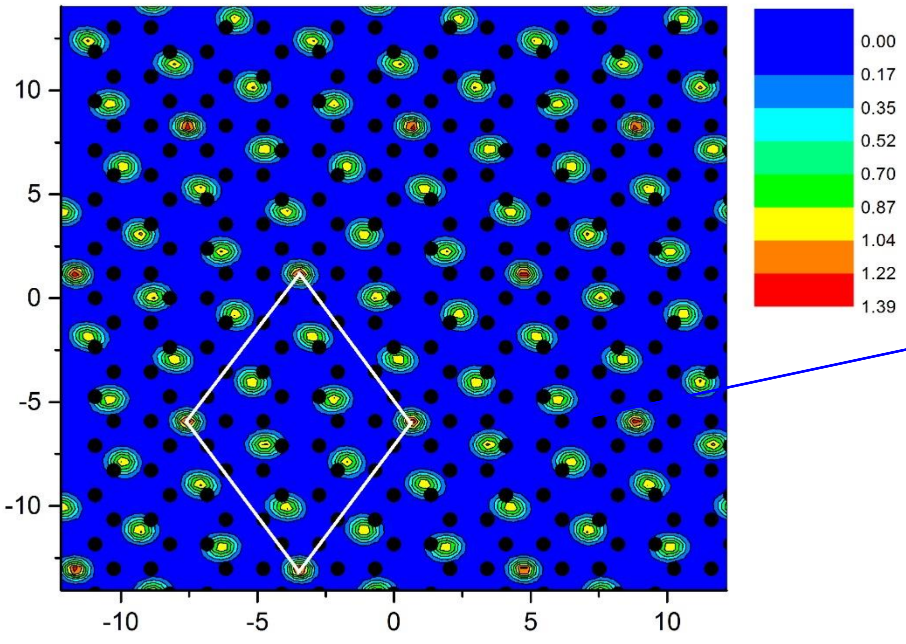


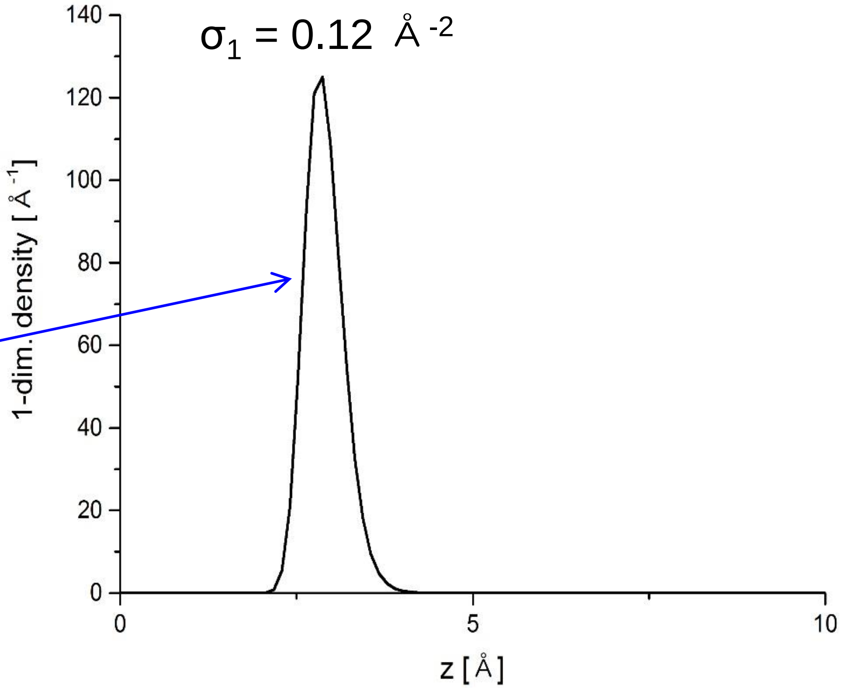
How about superfluidity?

^{4}He on strained graphene

The 1st layer on graphene under compressive strain could be completed at the $C_{7/12}$ density .

the 1st-layer 2D density

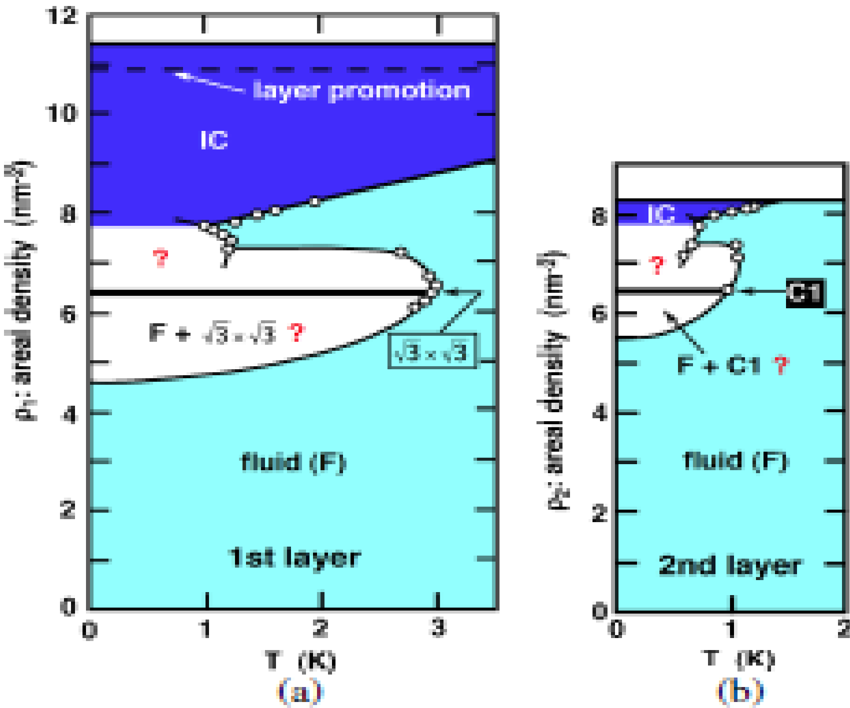




$C_{7/12}$ structure on graphene
under biaxial compressive strain ~ 3.6%

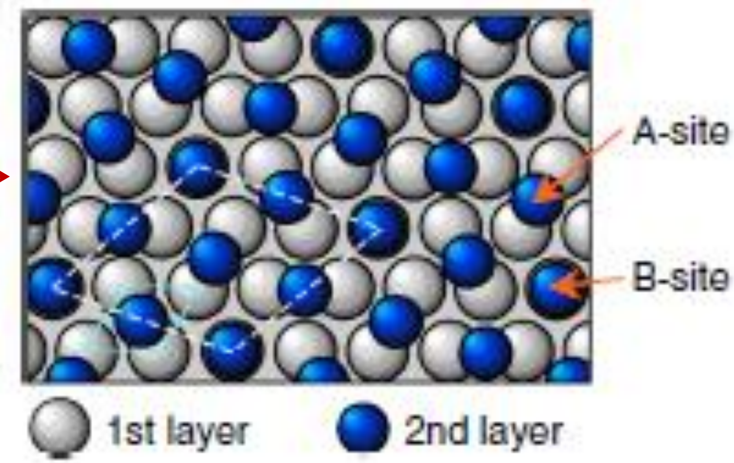
^{3}He on graphite

Phase diagram of ^{3}He layers



from H. Fukuyama, JPSJ 77, 111013 (2008)

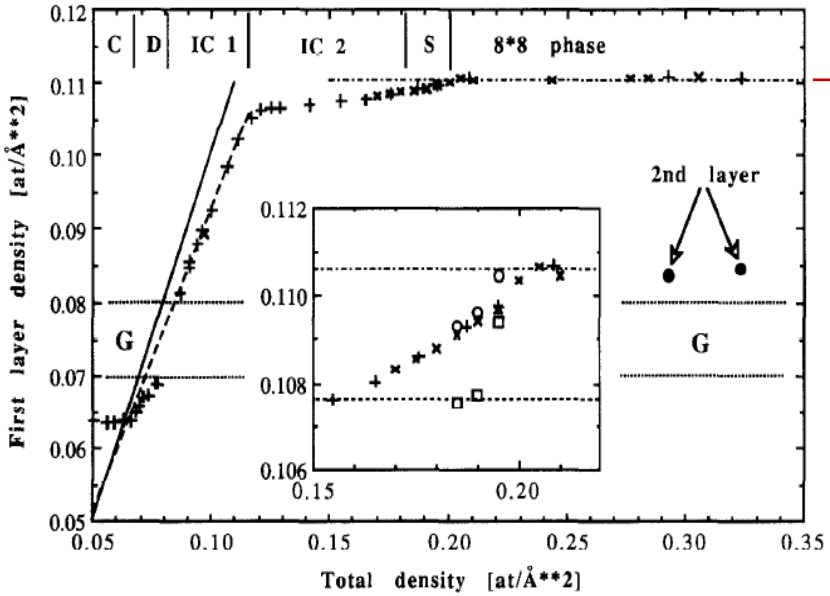
the 2nd-layer $C_{4/7}$ structure



- the melting peak
- the magnetization measurement
- mK heat-capacity peak
  : gapless spin liquid of frustrated antiferromagnets
  (Ishida et al., PRL 79, 3451 (1997))

Why is a ^{3}He $C_{4/7}$ structure stable?

- neutron scattering data for ^{3}He on graphite



→ ~ 0.111 Å^{-2} : the $C_{7/12}$ density

Lauter *et al.*, Physica B **165-166**, 597 (1990)

- the completed ^{3}He 1st layer: a $C_{7/12}$ solid?
- If so, is this the reason why the 4/7 structure is stable in the 2nd ^{3}He layer?

Summary – ^{4}He on graphite

- no stable 2nd-layer commensurate structure on top of a first-layer incommensurate solid even with the corrugated ^{4}He-graphite potential.

- a new commensurate solid of $C_{7/12}$ in the 1st ^{4}He layer at a high areal density of 0.111 Å^{-2}.

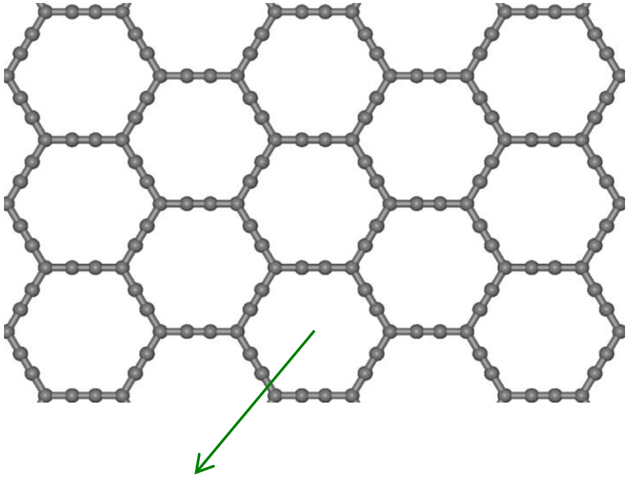
- The 2nd-layer $C_{4/7}$ solid is found to be metastable on top of the 1st-layer $C_{7/12}$ solid.

- ^{4}He on strained graphene could show a stable 2nd-layer $C_{4/7}$ structure.

III. ^{4}He on Graphynes

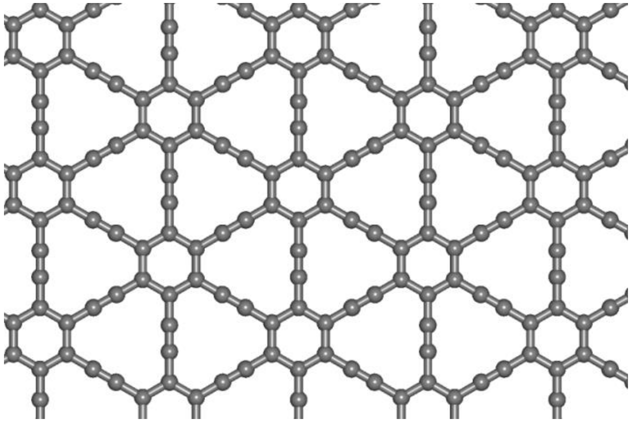
Graphyne : a 2D network of *sp*- and *sp*^{2}-bonded carbon atoms

α-graphyne



~ 8 times larger than
the hexagon of graphene

γ-graphyne



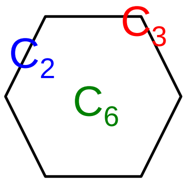
large surface area

- high-capacity hydrogen storage materials
- Li-ion battery anodes

^{4}He on α-graphyne

Kwon *et al.*, PRB **88**, 201403(R) (2013)

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \sum_{i<j} V_{He-He}(r_{ij}) + \sum_{i=1}^{N} V_{subs}(\vec{r}_i)$$

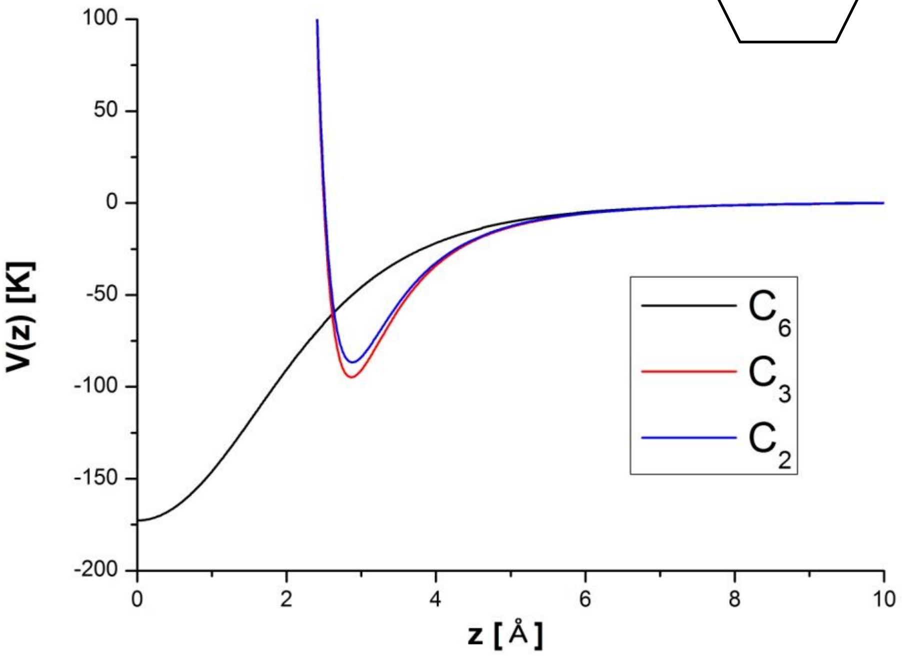


He-substrate interaction:

$$V_{subs}(\vec{r}) = \sum_{k:\,\mathrm{carbon}} V_{He-C}(|\vec{r} - \vec{R}_k|)$$

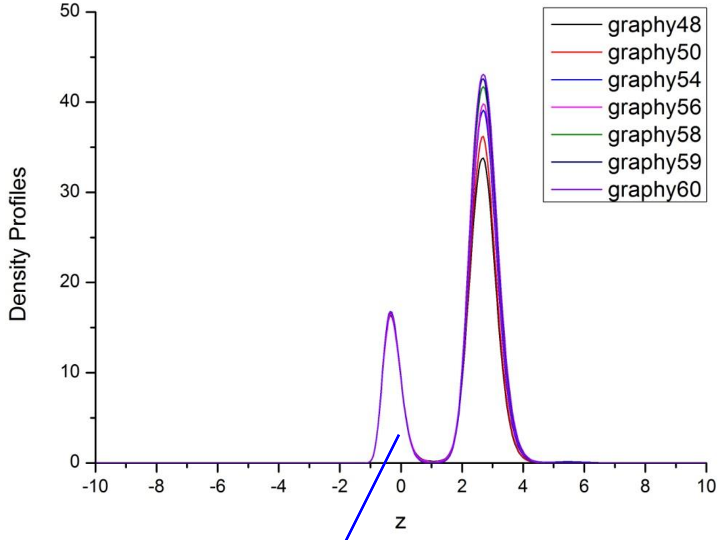
LJ 6-12 inter-atomic pair potential

Stan and Cole, Surf. Sci. **395**, 280 (1998)



^{4}He on an AB-stacked bilayer α-graphyne

1D density distribution

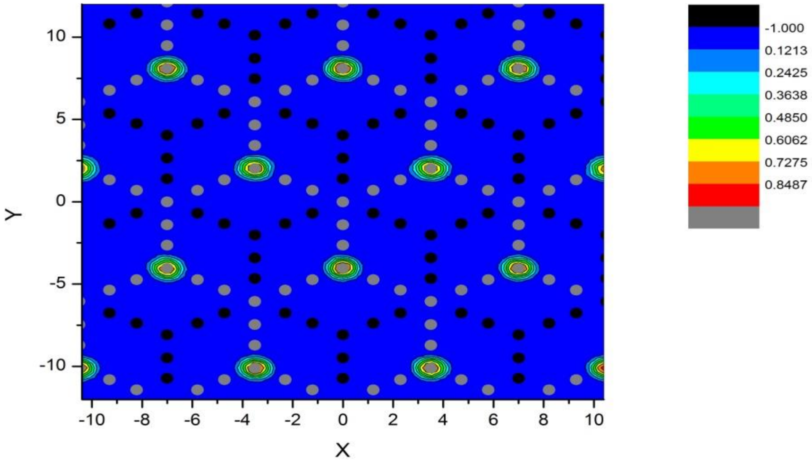


of ^{4}He atoms per 3x2 rectangular simulation cell

upper graphyne layer: z=0
lower graphyne layer : z=-3.35 Å

zeroth-layer areal density: σ=0.0235 Å^{-2}

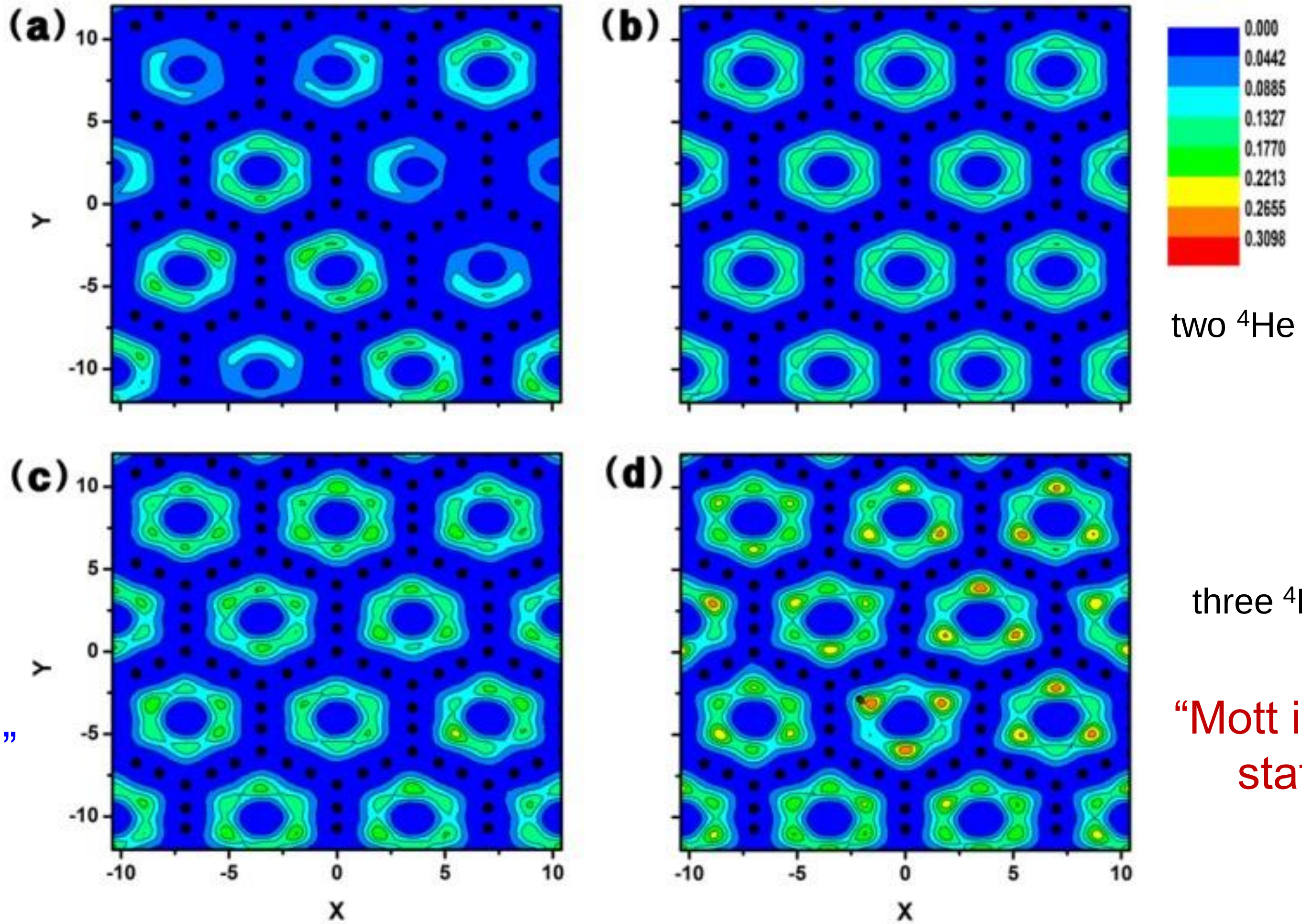
2D plot of the zeroth layer



2D density plots of the 1st ^{4}He layer

σ=0.0235 Å^{-2}

σ=0.0471 Å^{-2}



two ^{4}He

three ^{4}He

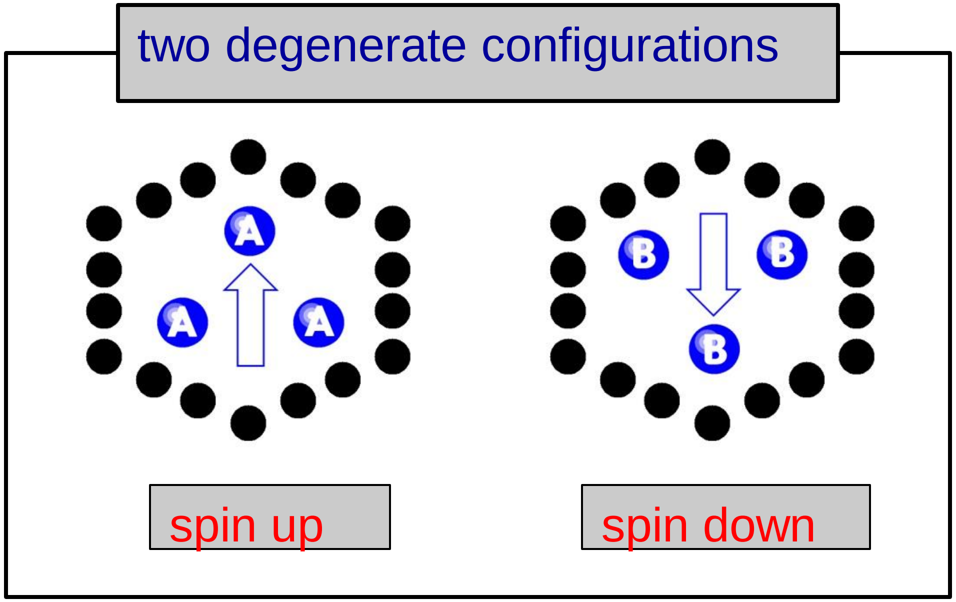
~2.5 ^{4}He atoms

“superfluid”

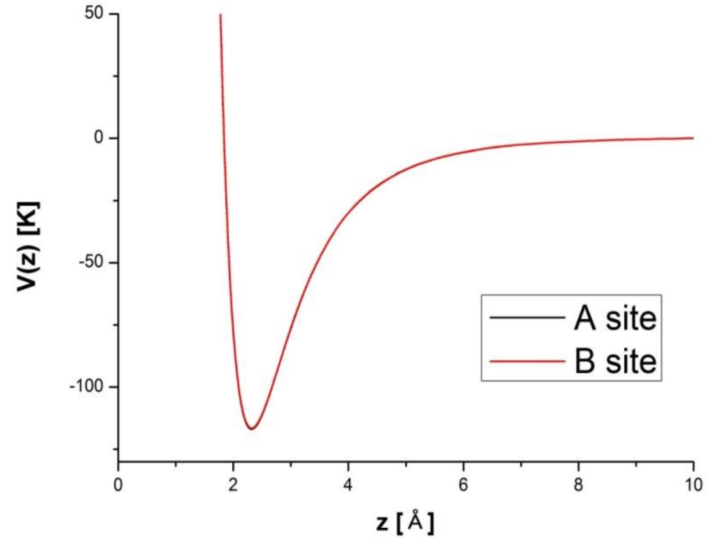
“Mott insulating state”

σ=0.0588 Å^{-2}

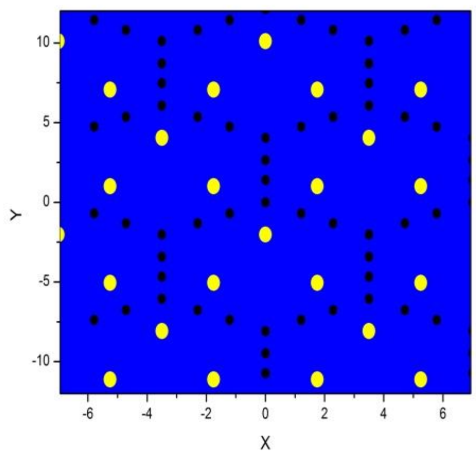
σ=0.0706 Å^{-2}

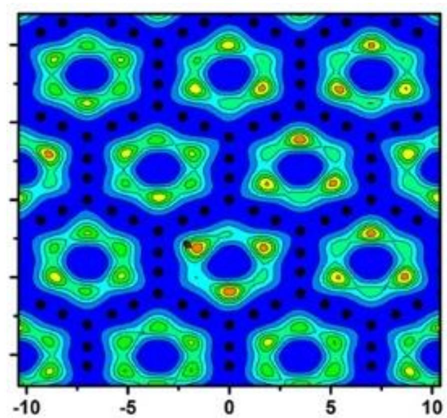


He-substrate potential



initial configuration

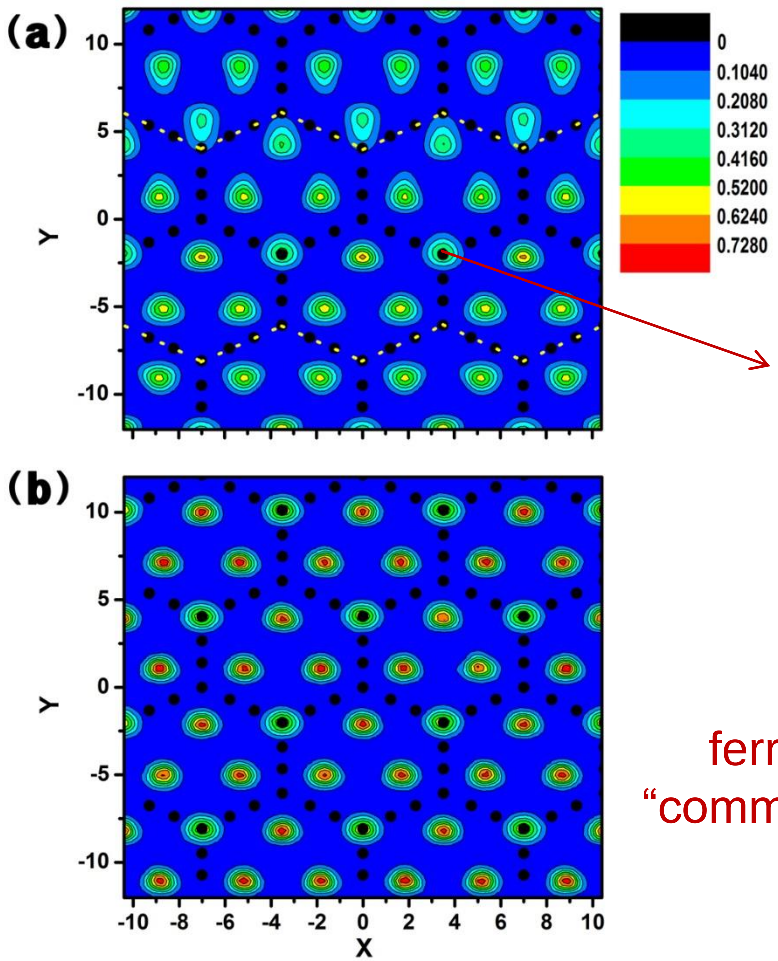




“ frustrated antiferromagnet”

2D density plots at high densities

$\sigma=0.0824$ Å^{-2}



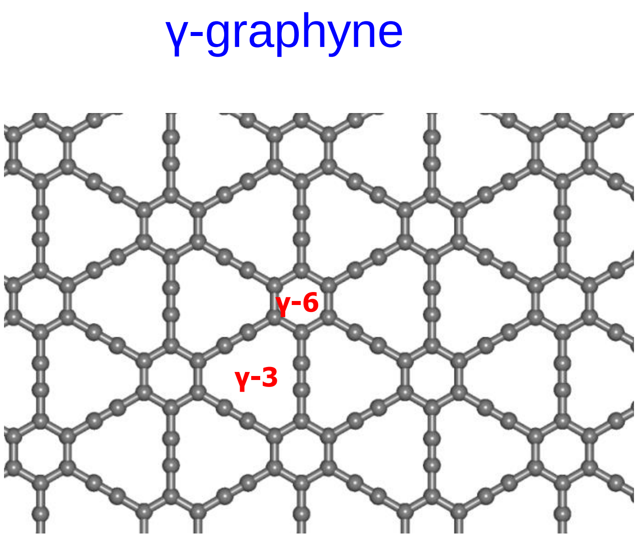
local “pseudo-magnetic” field

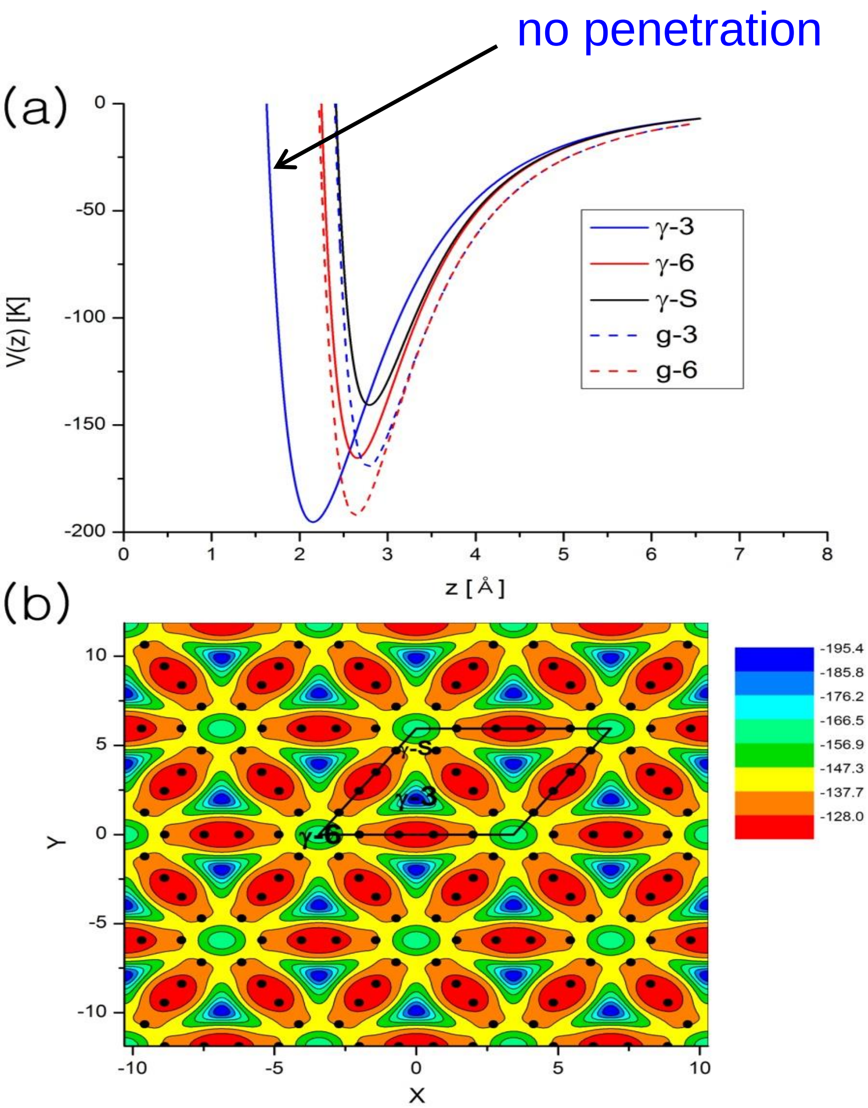
$\sigma=0.0941$ Å^{-2}

ferromagnetic ordering
“commensurate triangular solid”

^{4}He on γ-graphyne

Ahn *et al.*, PRB **90**, 075433 (2014)

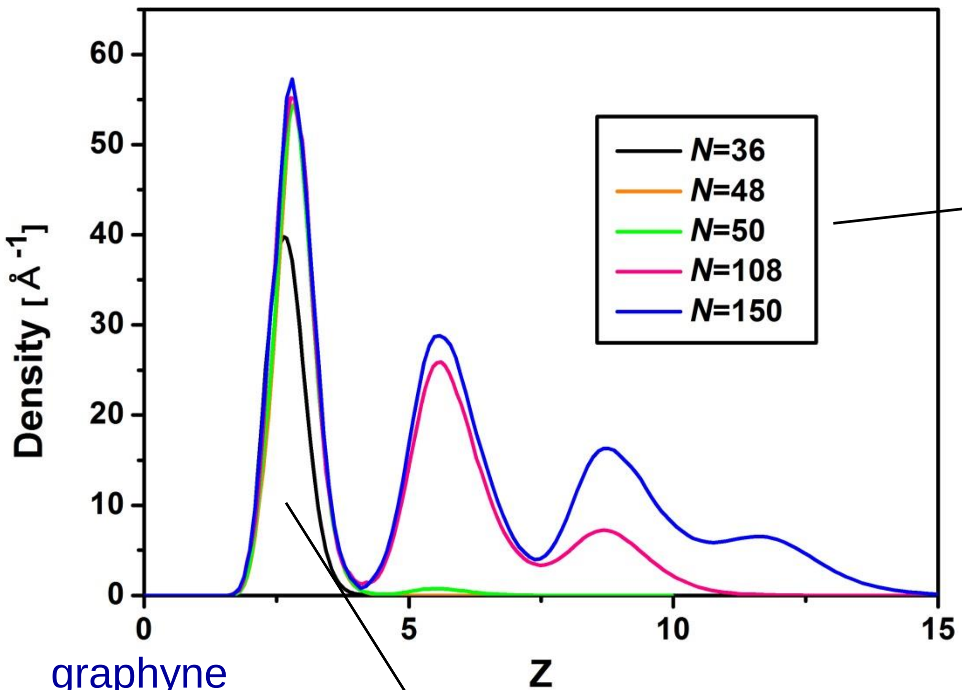




3 ^{4}He adsorption sites per unit cell

^{4}He on a single γ-graphyne sheet

1D density distribution



graphyne
at z=0

of ^{4}He atoms
per 3x2 rectangular simulation cell

“layer-by-layer growth”

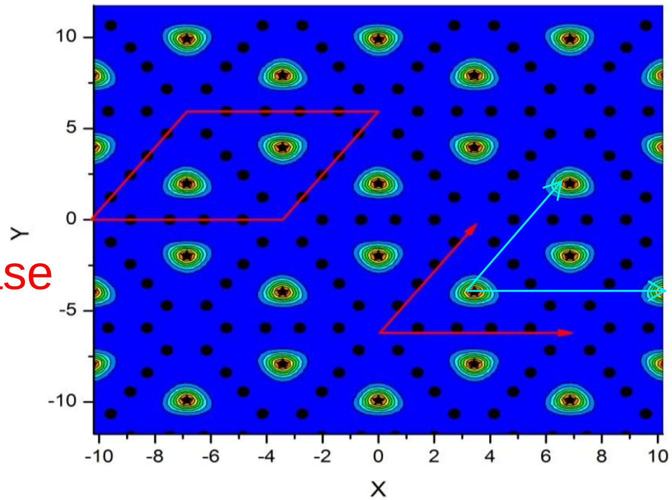
The first layer completed at areal density of σ ~ 0.115 Å^{-2}

2D density plots of the 1st ^{4}He layer

σ=0.0491 Å^{-2}

$C_{2/3}$

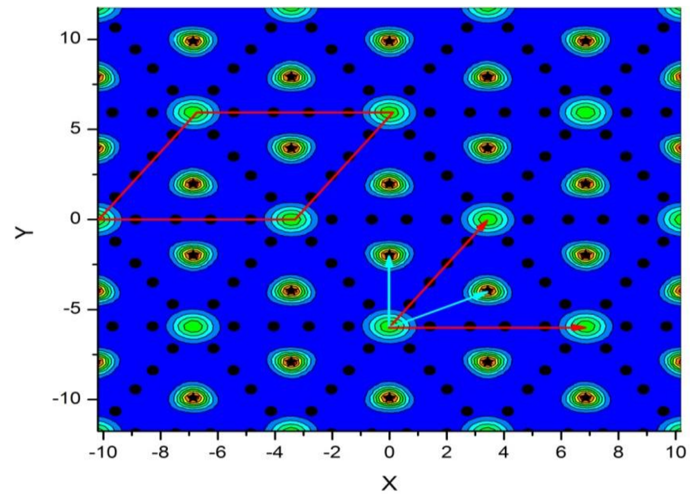
1x1 phase



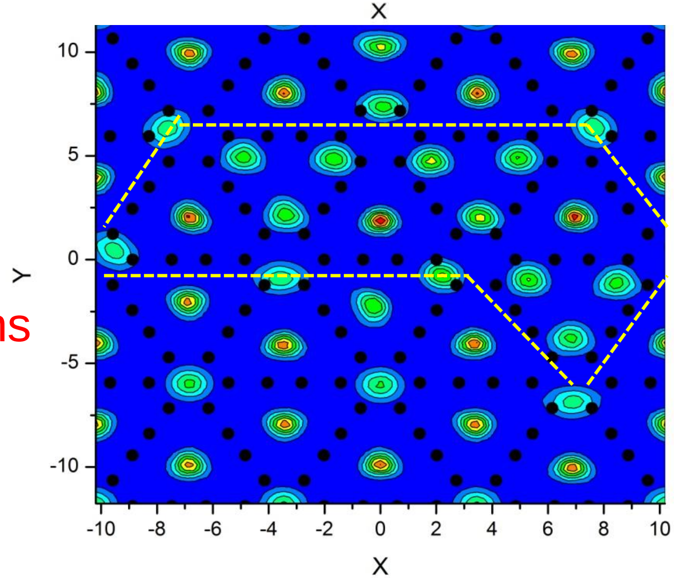
σ=0.0736 Å^{-2}

$C_{3/3}$

$\frac{1}{\sqrt{3}}$x$\frac{1}{\sqrt{3}}$ phase



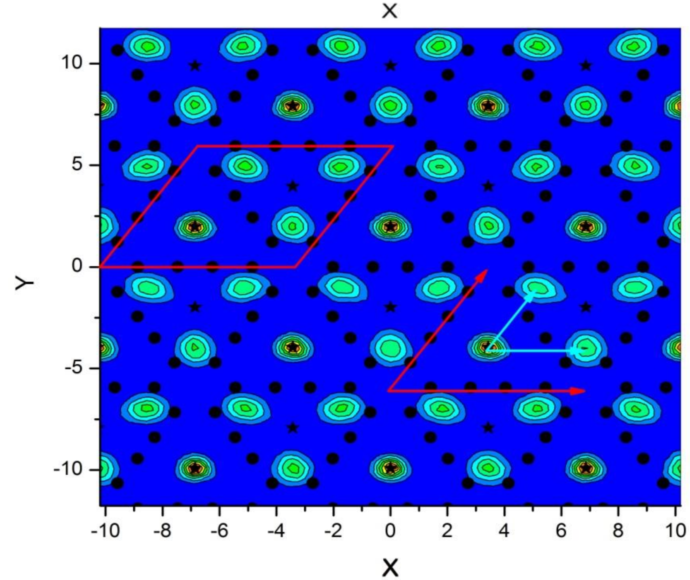
two domains



σ=0.0859 Å^{-2}

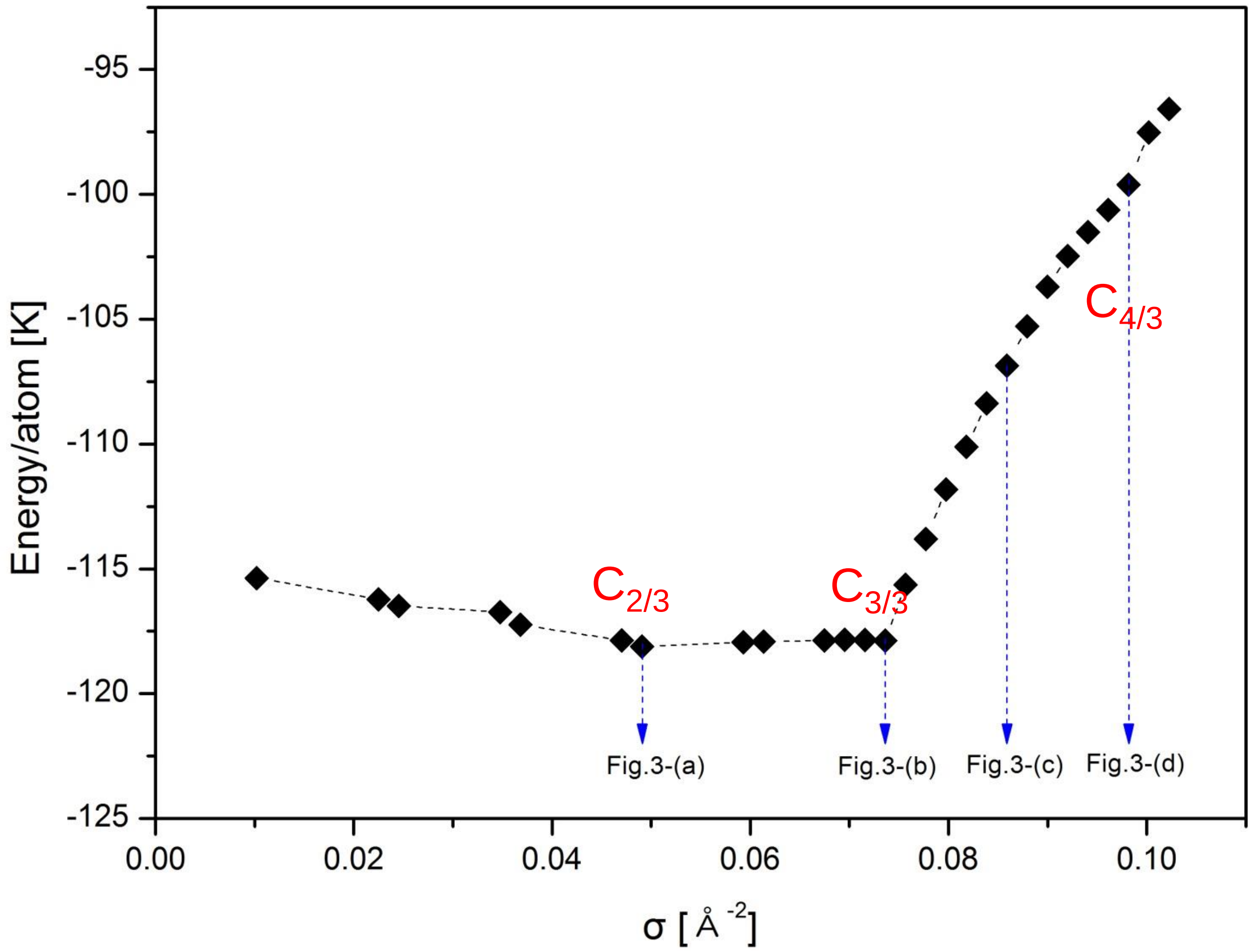
$C_{4/3}$

$\frac{1}{2}$x$\frac{1}{2}$ phase



σ=0.0982 Å^{-2}

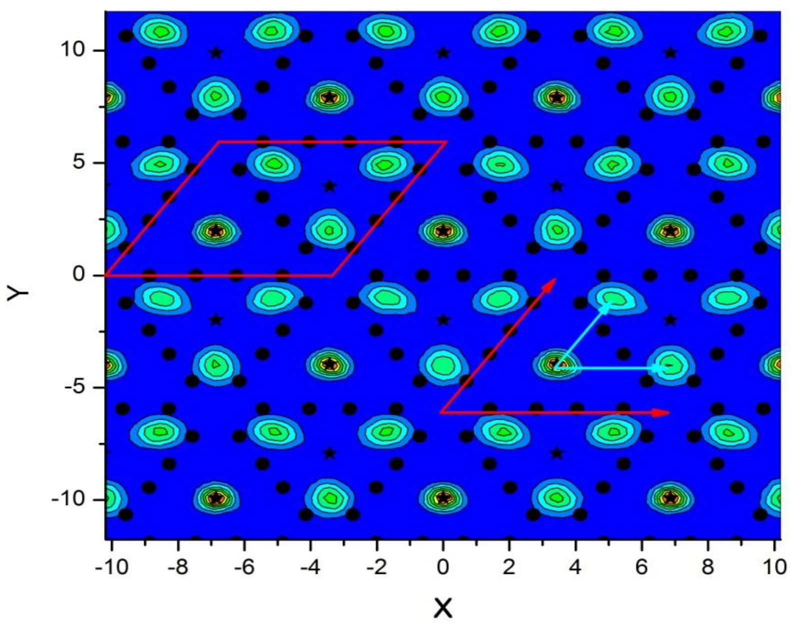
Energy per ^{4}He adatom



$C_{2/3}$: the lowest-energy state
$C_{4/3}$: beyond this coverage, the promotion to the second layer starts.

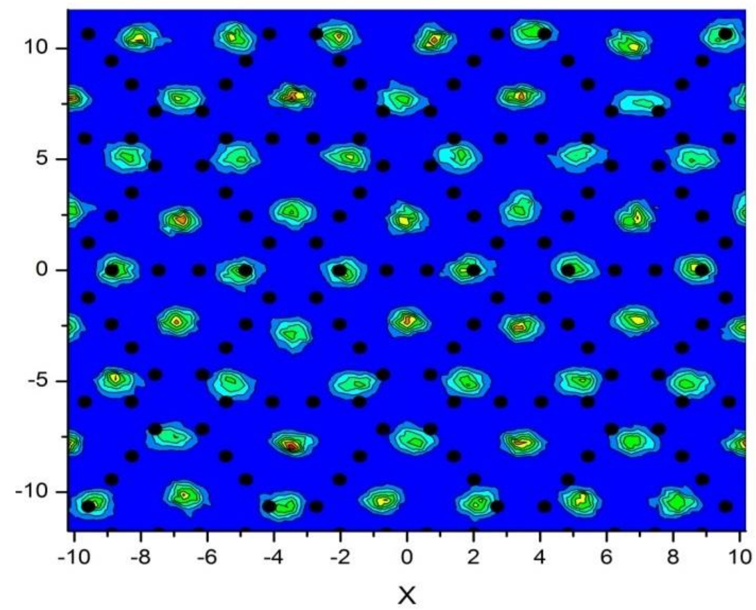
2D density plots at high densities

σ=0.0982 Å^{-2}



$C_{4/3}$ commensurate solid

σ=0.115 Å^{-2}



incommensurate solid
at the completion of the 1st layer

commensurate-incommensurate transition

Summary - ^{4}He on graphynes

α-graphyne

- large hexagon area → in-plane ^{4}He adsorption

- the 1st layer on the ^{4}He-embedded graphyne surface
  -. observe a transition from superfluid to Mott insulator between σ=0.0471 Å^{-2} and 0.0706 Å^{-2}
  -. Mott insulating state: frustrated antiferromagnet
  -. commensurate triangular solid at σ=0.0941Å^{-2}
  : ferromagnetic ordering under particle-induced “pseudo-magnetic” field

γ-graphyne

- no penetration through a single graphyne sheet

- the ^{4}He monolayer
  -. various commensurate solid structures: $C_{2/3}$, $C_{3/3}$, $C_{4/3}$
  -. the lowest-energy state : $C_{2/3}$ at an areal density of σ=0.0491 Å^{-2}
  -. the 1st layer completed to an incommensurate triangular solid at σ ~ 0.115 Å^{-2}

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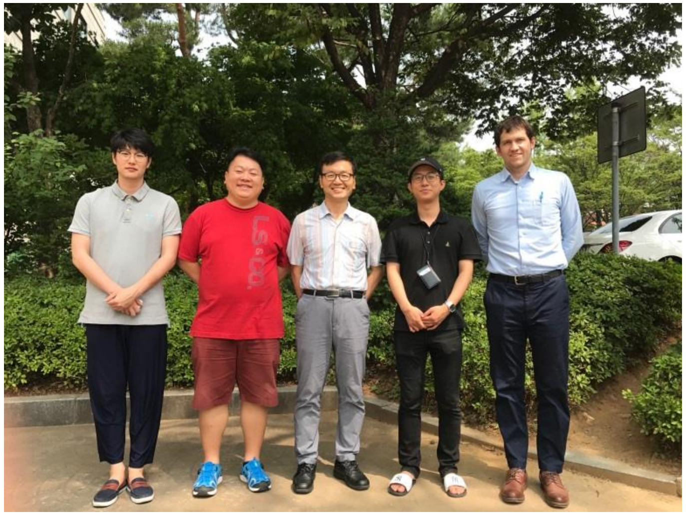

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