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Understanding the growth and dynamics of graphene flakes on liquid Cu

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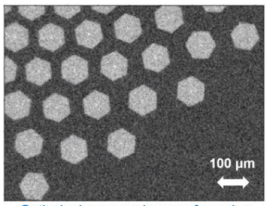
The use of liquid Cu as a catalyst for chemical vapor deposition of methane leads to high quality monolayer graphene sheets [1]. With our work we seek to develop an atomistic understanding of the role played by the liquid surface.

Interactions among flakes



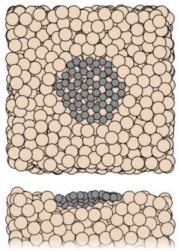
Optical microscope image of growing graphene flakes on liquid Cu at 1370 K
M. Jankowski et al., in preparation

Experimental observations have shown that growing graphene flakes self-align on liquid Cu.

In order to better understand the interaction between flakes and the liquid surface we carried out a series of molecular dynamics simulations using density functional theory and the COMB3 force field.

As seen to the right, a "sunken-in" state of the graphene flake was found in our studies. This behavior was observed in all of our simulations of flakes with radii ranging from 6 to 19 Å.

Calculations were carried out with FHI-aims, using light default settings for the basis set and integration grids, the PBE functional, gamma point k-point sampling, a dipole correction and the TS vdW correction.

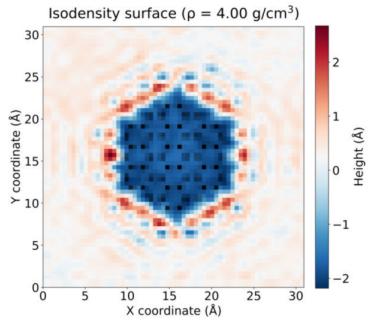


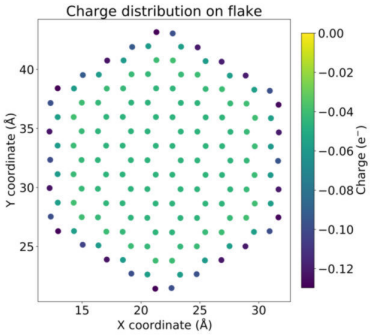
Top view and cross section of simulation cell

What can we learn from these atomistic simulations?

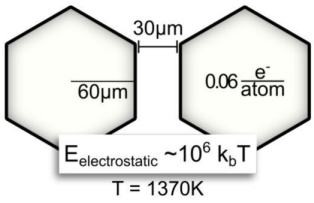
Aligning and averaging over multiple snapshots we obtain the shape of the liquid surface around the flake.

An interesting pattern emerges around the edges, which evidences a strong interaction of the edge carbon atoms with Cu.





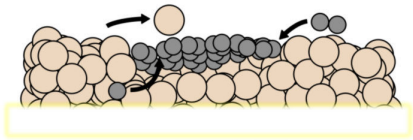
A big contribution to the interaction between flakes arises from electrostatic forces:



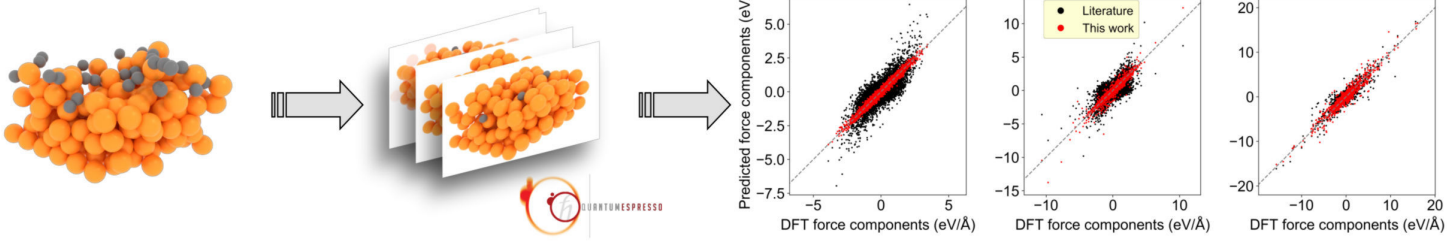
We are working towards bridging the gap between atomic scale simulations and experimental observations by coupling our calculations with capillary interaction theory [2].

Growth mechanism

The exact role of liquid Cu in carbon nucleation and defect healing is not yet well understood.
To study these processes we need chemical accuracy at a low cost.



We used a gaussian process regression to re-parameterize the semi-empirical method DFTB:



Run Molecular Dynamics simulations — **Calculate DFT forces in selected snapshots** — **Fit and evaluate new interatomic potential**

While the error on atomic forces improved after fitting a new DFTB repulsive potential, inaccuracies persist.

Machine learning to the rescue: Gaussian Approximation Potentials (GAPs) have surged in the last few years as a promising strategy to obtaining accurate but cheap interatomic potentials [3]. We are currently exploring the feasibility of such potentials to study nucleation reactions of carbon on liquid Cu.

Conclusions

With our simulations we shed some light into the atomic scale structure of graphene nano flakes on liquid Cu:

- We observe a noticeable influence of the flake in the surrounding Cu atoms.
- These disturbances could be explained by a strong interaction of the under-coordinated C atoms at the edge.
- We can calculate the electrostatic interaction between flakes on liquid Cu. While by itself, this interaction would be repulsive, in combination with a capillary interaction model it might explain the observed experimental phenomena of self-alignment.

Outlook

We are currently testing machine-learned interatomic potentials for carbon atoms on liquid Cu to aid in the understanding of the growth mechanism.

[1] Geng, Dechao, et al., Proc. Natl. Acad. Sci. U.S.A. , 109 (2012)
[2] Danov et al., J. Colloid Interface Sci. 287, 121 (2005)
[3] A. P. Bartók et al., Phys. Rev. Lett. 104, 136403 (2010)