

## ASSESSMENT OF THE CARBON-NICKEL INTERACTION FOR ATOMISTIC SIMULATION OF CARBON NANOFIBER GROWTH

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Investigating the dynamics of carbon nanofiber growth is necessary for probing further which role the Ni catalysts play. One could use classical molecular dynamics simulations to this purpose and we explore the possibilities of simple carbon-metal interaction models fitted to experimental and *ab initio* data.

Regarding the initial steps of the catalysis of nanotubes on metal nanostructures, DFT shows the importance of the stability of adsorbed C at 5-fold symmetric Ni metallic sites [1]. Using classical molecular statics with a Lennard Jones, we show that this is impossible in the frame of Van der Waals interactions, strongly supporting the carbidic nature of bonding. By parameterizing the LJ potential for carbidic bonding (DFT-LJ), we find an energetic order of favored C adsorption sites consistent with experimental findings [2] and migration energies by means of Nudged Elastic Band calculations consistent with DFT [1]. Moreover, the reliability of the DFT-LJ potential for Ni-C is validated for single carbon on (322) and (111) Ni surfaces, as well as inside bulk Ni.

The parameters ( $\epsilon, \sigma$ ) of the 12-6 Lennard Jones potential (DFT-LJ) were fitted to: (1) The energetic order of favored C adsorption sites obtained from DFT calculations [1, 3] and experimental findings [2]. (2) The migration energies from DFT calculations [1] by means of Nudged Elastic Band calculations. By fitting to (1), we got  $\sigma = 1.77 \text{ \AA}$ . By fitting to (2), we got  $\epsilon = 0.235 \text{ eV}$ . In fitting to (2), the migration energies were calculated also by the Nudged Elastic Band method. The nickel atoms are modeled by the second moment approximation to the tight-binding potential (TB-SMA). Three energy barriers,  $E_{diff}^1, E_{diff}^2, E_{diff}^3$ , of C diffusion steps on the Ni(322) surface in this work, compared with the points calculated by DFT calculations [1], are shown in Figure 1.  $E_{diff}^1, E_{diff}^2, E_{diff}^3$  correspond to “from step edge to clean surface”, “from clean surface to clean surface”, and “from clean surface to step edge”. It should be mentioned that fitting DFT-LJ parameters on  $E_{diff}^3$  is sufficient to predict  $E_{diff}^1$  and  $E_{diff}^2$  correctly.

Regarding the weak interaction for the whole graphene-Ni(111), we model the graphene on Ni(111) with a van der Waals potential (VDW-LJ) for the Ni-C, with parameters from the Ref. [4]. The VDW-LJ is very weak, and is only about 1/10 of the DFT-LJ for Ni-C interactions. We found that, in order to describe the growth of graphene on a Ni stepped surface it is necessary to couple the DFT-LJ with VDW-LJ for Ni-C, suggesting the role of both graphitic and carbidic bonding.

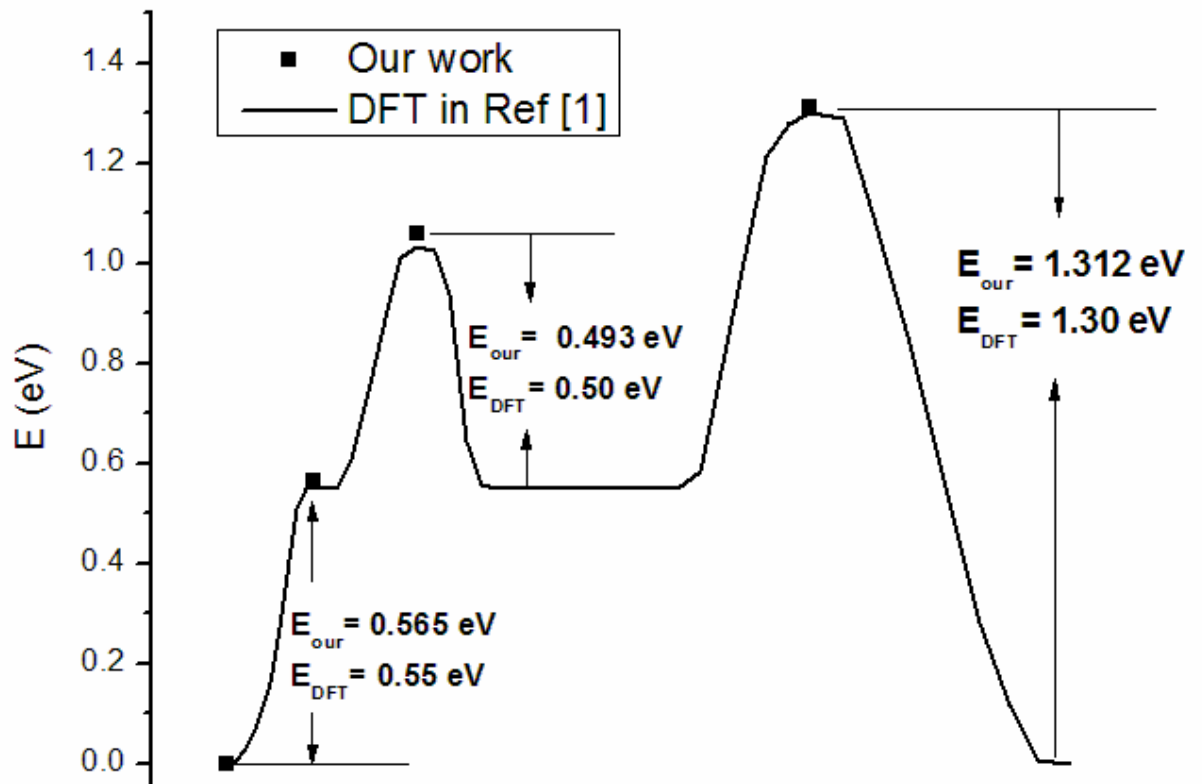
### References:

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**Figures:**



**Figure 1** Three energy barriers,  $E_{\text{diff}}^1$ ,  $E_{\text{diff}}^2$ ,  $E_{\text{diff}}^3$ , of C diffusion steps on the Ni(322) surface in this work, compared with the points calculated by DFT calculations [1].  $E_{\text{diff}}^1$ ,  $E_{\text{diff}}^2$ ,  $E_{\text{diff}}^3$  correspond to “from step edge to clean surface”, “from clean surface to clean surface”, and “from clean surface to step edge”.