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An experimentally validated neural-network potential energy surface for H atom on free-standing graphene in full dimensionality

Sebastian Wille[a,c], Hongyan Jiang[a], Oliver Bünermann[b,d], Alec M. Wodtke[a,b,d], Jörg Behler[c,d], and Alexander Kandratsenka[*a]

SUPPLEMENTARY INFORMATION

1 HDNNP details

The NNs for hydrogen and carbon atoms were constructed using symmetry functions of radial type

$$\rho_m = \sum_n f_c(r_{mn}) \exp\left[-\eta r_{mn}^2\right],$$

and angular type

$$\phi_m = \sum_{k,n\neq m} \frac{(1+\lambda\cos\theta_{kmn})^\zeta}{2^{\zeta-1}} f_c(r_{km}) f_c(r_{mn}) f_c(r_{kn}) e^{-\eta(r_{km}^2+r_{mn}^2+r_{kn}^2)}$$

centered on atom m. Here r_{mn} denotes the distance between atoms m and n, θ_{kmn} is the angle between vectors $\mathbf{r}_{mk}$ and $\mathbf{r}_{mn}$; f_c is a cutoff function, which gives zero if its argument is larger than $12a_0$ and 1 otherwise. Indices in sums run over all the neighboring atoms of central atom m. η, λ and ζ are the parameters defining a symmetry function, their values are listed in Table 1. We use 30 input neurons for an H-atom and 60 per C-atom.

The quality of the fit to the DFT data is shown for the energies in Fig. 3 of the main body of the paper. In this supplementary section, Fig. 1 shows in turn the correlation of the amplitudes of forces $|F_{\mathrm{DFT}}|$ extracted from the DFT data and forces $|F_{\mathrm{NN}}|$ obtained with HDNNP. Fig. 2 presents the same information in the form of the histogram providing a clearer representation of the fit errors. The RMSE associated with the forces is small, $\sim$90 meV/Å.

2 MD Trajectories

The most important performance feature of the HDNN-PES is its ability to accurately calculate the energy and forces for a system with many degrees of freedom with low computational costs. This is particularly important in the simulations of angle resolved atomic scattering experiments from surfaces. The experimental design detects only a small fraction of the scattered atoms due to its high angular resolution. Consequently, one needs hundreds of thousand trajectories to reduce statistical noise to the level of the experimental data. Table 2 shows the total number of MD trajectories calculated at the conditions used in the paper as well as the number of trajectories scattered into the cone with the apex angle of 3° corresponding to the geometry of the experimental setup.

Table 1 Parameters for the atom-centered symmetry functions for H- and C-atoms. Equations for the types used can be found in section 1.

no.	$\eta(a_0^{-2})$	λ	ζ
Radial			
1	0.000		
2	0.005		
3	0.013		
4	0.027		
5	0.060		
6	0.156		
Angular			
7	0.000	1	1
8	0.000	1	2
9	0.000	1	4
10	0.000	1	16
11	0.000	-1	1
12	0.000	-1	2
13	0.000	-1	4
14	0.000	-1	16
15	0.013	1	1
16	0.013	1	2
17	0.013	1	4
18	0.013	1	16
19	0.013	-1	1
20	0.013	-1	2
21	0.013	-1	4
22	0.013	-1	16
15	0.156	1	1
16	0.156	1	2
17	0.156	1	4
18	0.156	1	16
19	0.156	-1	1
20	0.156	-1	2
21	0.156	-1	4
22	0.156	-1	16

[a] Department of Dynamics at Surfaces, Max-Planck-Institute for Biophysical Chemistry, Am Faßberg 11, 37077 Göttingen, Germany. E-mail: akandra@mpibpc.mpg.de
[b] Institute for Physical Chemistry, Georg-August University of Göttingen, Tammannstraße 6, 37077 Göttingen, Germany
[c] Institute for Physical Chemistry, Theoretische Chemie, Georg-August University of Göttingen, Tammannstraße 6, 37077 Göttingen, Germany.
[d] International Center for Advanced Studies of Energy Conversion, Georg-August University of Göttingen, Tammannstraße 6, 37077 Göttingen, Germany.

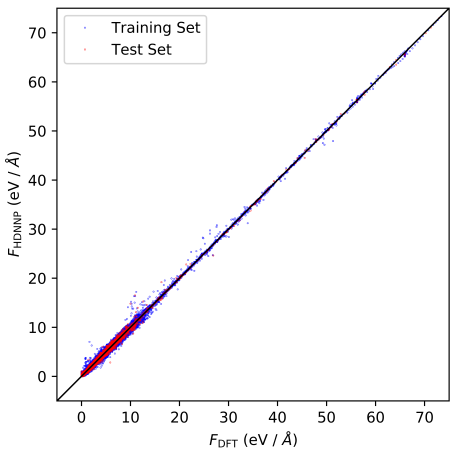

Fig. 1 Correlation plot of HDNNP $|F_{\mathrm{HDNN\text{-}PES}}|$ and DFT forces $|F_{\mathrm{DFT}}|$ for the training set in blue and test set in red, respectively. The HDNNP represents the DFT forces over the whole range quite well or at least reasonable.

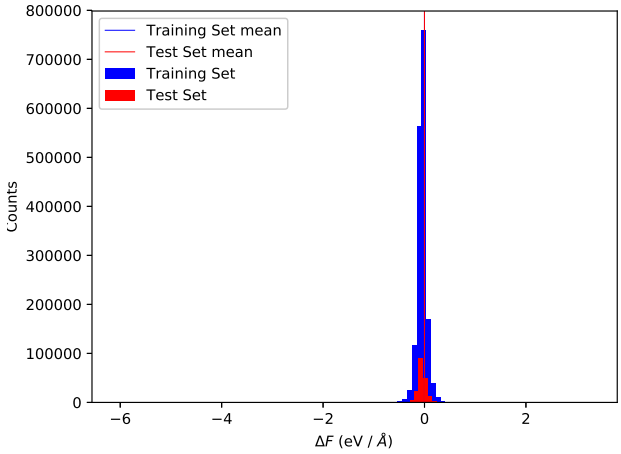

Fig. 2 Histogram of differences of the forces $F_{\mathrm{DFT}} - F_{\mathrm{HDNN\text{-}PES}}$ for the training set in blue and test set in red, respectively. The mean values for the training and test set are also shown in the corresponding colour.

Table 2 Showing the total number of simulated trajectories N_{total}, scattered trajectories within detection limit compared to experimental setup N_{3°, the normal component of incidence energy and sticking probability S_0 for H/D at incidence polar angle θ_i.

	θ_i	N_{total}	N_{3°	$E_i \cos^2 \theta_i$/eV	S_0
H	40	354,911	22,630	1.13	0.21
	50	291,238	22,533	0.79	0.39
	59.5	322,691	122,205	0.49	0.22
D	43	189,577	7,021	1.03	0.52
	51	183,837	10,452	0.76	0.68
	59.5	221,861	73,607	0.49	0.39

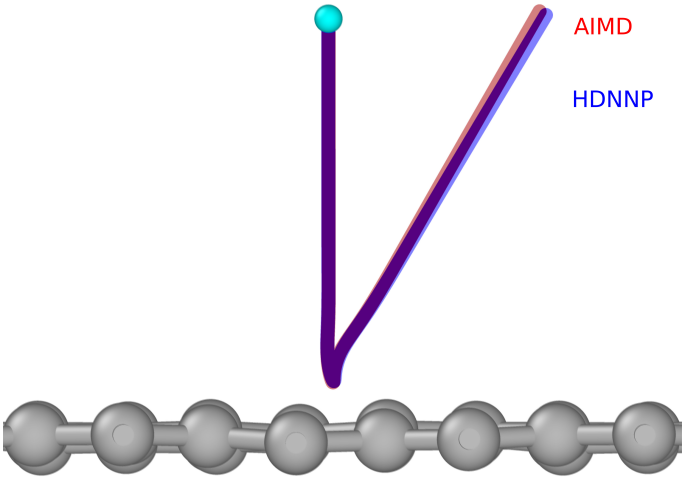

Fig. 3 Side view of Fig. 5 of the main text.

When simulating hydrogen scattering from graphene, the trajectories were interrupted after a 200 fs simulation time. H atoms which had not left the surface after this time were considered to have adsorbed. The sticking probabilities for the incidence conditions used in the main paper are collected in Table 2.

3 Trajectories visualized

To get a feeling how the scattering happens it is often useful to visualize trajectory as shown in Fig. 5 on the main body of the paper. Fig. 3 provides a side view additional to the top view shown in Fig. 5 of the main text. We also created several movies, where one can follow the trajectories in more detail. We added a top and a side view for the AIMD and HDNNP trajectory. Furthermore, we added three movies showing an example of the quasi-elastic energy loss channel (fast channel), the high energy loss channel (slow channel) and adsorption of the projectile on the surface, which is not possible to see in the experiment. All the movies included in the SI are created using OVITO version 2.9.0.