

Electronic Supplementary Information

Adsorption Dynamics of Polyatomic Molecules on Planar Surfaces

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In this document, we describe the details involved with the modeling of the adsorbates (as monomers, dimers and trimers) and their associated interactions with the surface and each other.

1. Modeling Methane – Monomers

We first consider the shortest alkane, methane (CH_4). Because methane spins at a great rate when it is in a gas state, it is both convenient, and mathematically simpler, to treat a methane molecule as a quasi-spherical particle. In our simulations, we neglect any shape of the methane molecule, treating it as a sphere that can adsorb to a surface and diffuse around it, but without any sense of the orientation of the particle. Because of this, there is only one binding energy between the monomer and the surface, and only one value of the interaction energy between neighboring monomers. Methane has an adsorption energy of about 1000 K (on graphene), and its characteristic particle-particle interaction energy (estimated from the energy Lennard-Jones parameter) is about 140 K (*Stan, G.; Bojan, M. J.; Curtarolo, S.; Gatica, S. M.; Cole, M. W., Phys. Rev. B, 2000, 62, 2173*). These values are too high for our simulation scheme, so we scale them down to 100 K and 14 K, respectively, keeping the same ratio of the molecular interaction to the binding energy to the surface (14 %). As explained in the main paper, we use this ratio as a reference point ($\alpha = 1$), and we explore the behavior of systems with increasingly stronger interactions ($\alpha > 1$). Thus, we can simulate the behavior of methane directly, or by varying the ratio between the adsorption and interaction energies, we can represent a completely different system.

2. Modeling Ethane – Dimers

The next chain molecule is ethane, which is very similar to methane, except that it is longer. This similarity is why alkanes were of interest to begin with. Its chemical formula is (C_2H_6), but we consider it to be two quasi-spherical methyl groups bound together as a dimer. It serves us well to model ethane as a dimer; not only is it a simple model that contains the key characteristics of the alkane, but also many other molecules can also be accurately represented as dimers, giving our work a greater reach.

Ideally, a dimer can take on any position with respect to a hypothetical surface. However, this is not conducive to our simulation scheme. It adds too many parameters to the system, and as we mentioned previously, we only want to include the parameters

that play the most important role in the kinetics of adsorption. Therefore, we limit the orientations of flat molecules to “completely flat” along the surface or “perfectly perpendicular” to it. When it lays flat on the surface, we assign it twice the binding energy of methane (200 K on graphene). However, when ethane stands upright on the surface, the bottom methyl group is bound as before, but the upper half of the molecule is significantly farther from the carbon surface. Because of this, the binding energy for an upright dimer is 140 K, 100 K for the bottom particle and 40 K for the top particle because of the drop off of potential with distance from the surface.

The different orientations of ethane also affect the particle-particle interactions. We mentioned for methane we were using a monomer-monomer interaction energy of 14 K. This energy is still valid in the case of two flat dimers laying end to end (since both are treated as monomers). In the case of a flat dimer interacting with an upright dimer, the flat dimer interacts with both units of the upright dimer, so we used a total interaction energy of 21 K, since the top unit of the upright dimer is slightly farther away from the flat dimer. If two upright dimers are interacting with each other, we used a particle-particle interaction energy of 42 K because each of the methyl groups in one upright dimer interacts with each of the methyl groups in the other, creating four total bonds. A similar situation happens for two flat dimers lying parallel to each other. These values of the interaction energy between two dimers are listed in Table 1.

	flat	up
flat	14 - 42	21
up		42

Table 1. Pair interaction energy (in K) between dimers in different orientations.

3. Modeling Propane – Trimers

The final admolecule that we consider in this study is propane (C_3H_8). We consider this molecule to be a chain of three units, with methyl groups on either end separated by a methylene group. Propane has a bend of about 109° in it, which is close enough to the 120° angle that the triangular lattice naturally provides.

Similarly to our treatment of dimers, trimers have many possible orientations with a surface. We select the flat and upright orientations to maintain the parallel with dimers. We also choose to include a state in which the trimer makes an L- shape with the surface (nicknamed the “ell” state), where two of the units are flat on the surface and the third is standing upright to it. Flat trimers are assigned an adsorption energy of 300 K, and an ell trimer is given an energy of 240 K, since it is essentially the combination of one monomer and one upright dimer. Upright trimers are a little more complicated; we begin with an upright dimer and add another methyl group quite far from the surface, giving it a total energy of 150 K. All these values for the binding

energies, together with the ones for monomers and dimers are summarized in Table 2.

	1 site	2 sites	3 sites
monomer	100		
dimer	140 (up)	200 (flat)	
trimer	150 (up)	240 (ell)	300 (flat)

Table 2. Binding energy (in K) of a single molecule to the lattice for the different orientations considered, according to the number of lattice sites occupied.

We assign the interaction energies between the different configurations based on the energy of 14 K between interacting units of flat trimers. When a flat trimer interacts with the upright end of an ell trimer, we use an interaction energy of 21 K, like we do with dimers. Because the third trimer is so far off the lattice, we neglect its interaction with a flat trimer, and so we use 21 K as the interaction energy between a flat trimer and an upright trimer as well. Returning to dimers again, we use 42K for the interaction energy between the upright ends of two ell trimers. Admittedly, the upright half of an ell trimer is not perfectly perpendicular to the substrate, as we discussed previously, but this is a minor assumption in order to simplify our computational scheme. Finally, we use an interaction energy of 49 K between the upright end of an ell trimer and an upright trimer, and a binding energy of 70 K between two upright trimers (see Table 3). These interaction energies become large quite quickly due to all of the interactions between the units making up these admolecules. There is a particular energetic bias towards trimers that are upright, a situation that arises as the system approaches monolayer.

	flat	ell	up
flat	14 - 42 -70	21	21
ell		42	49
up			70

Table 3. Pair interaction energy (in K) between trimers in different orientations.