Electronic supplementary material for "Coarse-graining the structure of polycyclic aromatic hydrocarbons clusters"

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1 Dimer energy curves

The parameters of the PY potential were adjusted to reproduce reference energy curves obtained at the all-atom (AA) level, using frozen molecular geometries taken from density-functional theory calculations at the standard B3LYP/aug-cc-pVDZ level. In the AA description all atoms carry a partial charge taken from the electronic density obtained at the DFT level through the RESP electrostatic potential fitting procedure, and a Lennard-Jones center. The AA model is thus pairwise, with LJ parameters taken as our earlier work¹ from van de Waal.²

From the potential energy curves as a function of intermolecular distance and at various relative orientations, four geometric parameters of the ellipsoids (assuming axial symmetry) and the two LJ parameters of the PY model were adjusted by least-square fitting.

The following Figure 1 and Figure 2 depict the variations of the potential energy with intermolecular distance for the coronene and circumcoronene dimers, respectively, within the AA model and after adjusting the PY parameters:

The corresponding parameters are given in Table 1.

For the binary clusters we simplify the problem by keeping the shape matrices associated with the individual molecules, only optimising the LJ parameters ε and σ for the heterogeneous interaction. The adjustment on the all-atom reference data was again performed for the four possible symmetric orientations between coronene and circumcoronene, leading to $\varepsilon = 162.8$ kJ/mol and $\sigma = 3.61$ Å (see Figure 3).



Figure 1: Potential energy curves of the coronene dimer in the face-to-face, side-by-side, and T-shape configurations. The dashed and solid lines refer to the coarse-grained and all-atom results, respectively.

Table 1: Parameters of the coarse-grained potentials obtained by fitting the all-atom results for coronene and circumcoronene. PY and PY+Q refer to the pure Paramonov-Yaliraki potential and to its correction with linear quadrupole moments.

	σ	ε	a_{\parallel}^r	a_{\perp}^{r}	a^a_{\parallel}	a^a_\perp	Q_0
Molecule	Å	kJ/mol	Å	Å	Å	Å	$e Å^2$
coronene (PY)	3.67	93.4	4.88	1.56	4.28	1.56	0
coronene (PY+Q)	3.83	107.5	4.74	1.54	3.99	1.54	1.48
circumcoronene (PY)	3.92	241.0	7.01	1.53	6.05	1.54	0

2 Potential energy function for the interaction with graphite

The extension of the PY potential to ellipsoids interacting with infinite crystalline substrates was inspired from the 10-4-3 Steele potential,³ in which the global interaction of an atom deposited on a layered material was exactly integrated over all layers assuming individual atom-atom interactions of the Lennard-Jones type. Owing to translational symmetry, and in absence of substrate corrugation the potential must only depend on the distance of the molecule to the surface, assumed to lie at z = 0 with the substrate located at z < 0. In order to capture the dependence on orientation we initially used a straightforward extension of the Steele potential, replacing the distance to the



Figure 2: Potential energy curves of the circumcoronene dimer in the face-to-face, side-by-side, and T-shape configurations. The dashed and solid lines refer to the coarse-grained and all-atom results, respectively.

surface by the distance z_{\min} from the ellipsoid to the z = 0 surface:

$$U_{k}^{\text{sub}}(\vec{r}, \mathbf{A}_{k}^{r}, \mathbf{A}_{k}^{a}) = 2\pi\rho_{\text{S}}\Delta\sigma_{g}^{2}\varepsilon_{g}\left[\alpha\left(\frac{\sigma_{g}}{z_{\min}^{r}}\right)^{10} - \beta\left(\frac{\sigma_{g}}{z_{\min}^{a}}\right)^{4}\right]$$
(1)

where the superscripts *r* and *a* after z_{min} refer to the repulsive and attractive shape matrices \mathbf{A}^r and \mathbf{A}^a . In the equation above, all parameters ρ_S , Δ , σ_g and ε_g have the same meaning as in the original Steele potential, only did we drop the last term in power -3 which was not found necessary to reproduce the all-atom reference data.

The distances z_{\min} from the ellipsoid and the surface are obtained by locating the two points of the ellipsoid where the gradient is aligned along the *z* axis. Denoting z_i the center of the ellipsoid, $A_{\alpha\beta}$ the components of the shape matrix with $\alpha, \beta = \{x, y, z\}$ it is straightforward to calculate

$$z_{\min} = z_i - \frac{1}{\sqrt{\rho_i}},\tag{2}$$

with

$$\rho_{i} = \frac{A_{zz}A_{xy}^{2} + A_{yy}A_{xz}^{2} + A_{xx}A_{yz}^{2} - A_{xx}A_{yy}A_{zz} - 2A_{xy}A_{yz}A_{xz}}{A_{xy}^{2} - A_{xx}A_{yy}}.$$
(3)

Those expressions can be differentiated to yield the forces and torques that are required to carry



Figure 3: Potential energy curves of the coronene-circumcoronene cluster in the face-to-face, sideby-side, and the two possible T-shape configurations. Coronene and circumcoronene are depicted by yellow and orange disks, and the dashed and solid lines refer to the coarse-grained and all-atom results, respectively.

the minimizations.

The reference energy curves with the all-atom model where obtained by summing the 10-4-3 Steele potential, using the existing LJ parameters for carbon-graphite interactions and the Lorentz-Berthelot combination rules for the hydrogen-graphite interactions. In the case of coronene, the best fit for the coarse-grained potential was obtained for $\sigma_g = 1.8$ Å and $\varepsilon_g = 52$, leading to a well depth of approximately 213 kJ/mol at 3.42 Å from the surface in the parallel configuration (see Figure 4).



Figure 4: Potential energy curves for coronene physisorbed on graphite, as a function of the distance z of the molecular center to the surface at z = 0. The dashed and solid lines refer to the all-atom and coarse-grained potentials, respectively.

3 Structures and energetics of circumcoronene clusters

The total binding energy per molecule in circumcoronene clusters $(C_{54}H_{18})_N$ are represented in Figure 5 for both the all-atom reference description and the coarse-grained PY model.



Figure 5: Binding energy per molecule of circumcoronene clusters, as obtained from the most stable structures described at the all-atom (AA) level or using the coarse-grained (CG) PY model. The vertical dashed lines separate the regions where the global minimum structure changes, the labels C, HS, and HM being defined in the text.

As was the case for coronene, the structures obtained with the two methods are again very similar with the same competing topologies that belong to the HS, HM, and MS motifs. Differences arise above size 15, with the single handshake structure predicted by the CG model being less favored at the level of all-atom descriptions: for $15 \le N \le 17$ multiple stacks (MS) are found, while for N = 18 and 19 the HM topology is prefered.

4 Structures of binary coronene/circumcoronene clusters



Figure 6: Coarse-grained minima of $(C_{24}H_{12})_N(C_{54}H_{18})_N$ clusters denoted, with the coronene and circumcoronene molecules depicted as yellow and orange ellipsoids, respectively. The clusters are denoted as N : N for N = 1-10.



Figure 7: Coarse-grained minima of $(C_{24}H_{12})_N(C_{54}H_{18})_{16-N}$ clusters, with the coronene and circumcoronene molecules depicted as yellow and orange ellipsoids, respectively. The clusters are denoted as N : 16 - N for N = 1-10. Some minima already depicted in the main article have been omitted.

References

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