Supplementary Information for

Equilibrium structure of dense trimesic acid monolayer on a homogeneous solid surface: from atomistic simulation to thermodynamics

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Porous structures of TMA layer on graphite and Au(111)

A decrease of tangential pressure in our model leads to the formation of the CW structure. This can be seen in Figure 8b. As the pressure in the fCW structure decreases, the density of the molecular layer drops sharply due to a release of the TMA molecules from the two-dimensional pores of the fCW layer. This process has the Langmuir-type adsorption/desorption mechanism.

We have additionally calculated the dependence of the chemical potential on the tangential pressure for the CW structure at several temperatures. Plotting these dependencies with the $\mu(p)$ graphs for the SF and fCW structures, we can find the stability regions of these phases by the intersection points (see figure below). Indeed, the CW structure becomes favorable as the tangential pressure decreases. The $\mu(p)$ lines for the fCW and CW structure intersect at pressures close to zero. We had also seen this transition in the direct FsMP/kMC simulations of the fCW structure with decreasing pressure (see Fig. 8(b)). The intersection points of the $\mu(p)$ lines for the SF and CW structures are located at slightly negative tangential pressures.

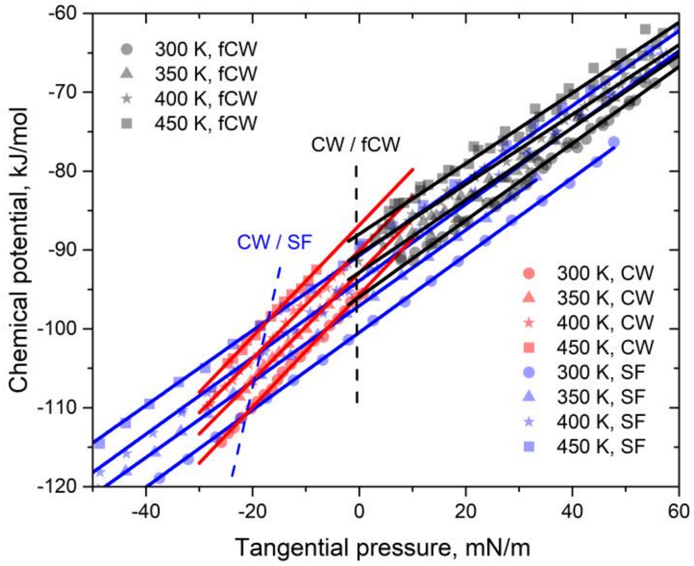

Fig. 1S. Pressure dependences of the chemical potentials of the CW, SF and fCW structures in monolayer of TMA molecules. The symbols are the results of the FsMP/kMC simulation at the indicated temperatures. The lines are linear approximations that satisfy the Gibbs-Duhem equation. The dashed lines are the phase transition lines: blue for CW/SF transition and black for CW/fCW transition.

It is difficult to imagine experimental conditions that could naturally create a negative tangential pressure in the molecular layer. Apparently, the matter is in the intermolecular potential and/or in the interactions of crystalline molecular layers of TMA with the substrate lattice. Here, the following comments can be made in this regard:

i) The lattice parameter of the CW structure on graphite is smaller than in vacuum (without considering the surface) [10.1021/la5048886]. Therefore, the CW structure on graphite is slightly “compressed” in terms of the intermolecular interactions. Thus, the tangential pressure in this structure on graphite may be positive or close to zero.

ii) We were unable to find accurate data on the lattice parameter of the CW structure on the Au(111) surface. However, the role of the “compressive” force can be attributed to the substrate-mediated interactions. This can also shift the region of existence of the CW phase to zero or positive pressures.

iii) The hexagonal pores of the CW structure in vacuum are larger than on the graphite surface [10.1021/la5048886]. Therefore, additional TMA molecules can easily adsorb into them and find a favorable position (either with zero or even negative interaction energy). The hexagonal pore of the CW structure on graphite is smaller in size. Apparently, this size is not enough for a TMA molecule to fill the 2D pore without overcoming some repulsive forces. This can also shift the region of existence of the CW structure towards positive or near zero pressures.

iv) We used the relatively short-ranged TMA-TMA potential. Considering the electrostatic and dispersion forces over longer distances may well lead to a change in pressure so that the region of existence of the CW structure will shift towards positive pressures.