Molecular Simulation of Phosphonic Acid -Aluminum Oxide self-organization and their evolution into ordered monolayers

Supplementary Information

Hanno Dietrich[†], Thomas Schmaltz[‡], Marcus Halik[‡], Dirk Zahn[†]

- [†] Computer Chemie Centrum, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstr. 25, 91052 Erlangen
- [‡] Lehrstuhl für Werkstoffwissenschaften, Friedrich-Alexander-Universität Erlangen-Nürnberg, Martensstr. 7, 91052 Erlangen

1 Details on Methods

1.1 Simulation Conditions

All simulations were carried out using the DLPOLY Classics 1.9 codeⁱⁱⁱ with a 12 Å cutoff for long-range forces and an integration timestep of 1 fs. A Berendsen-type thermostatⁱⁱⁱ with a relaxation time of 0.5 ps was used to maintain a constant temperature of 300 K. All systems were simulated with 2D-periodic boundary conditions. To apply ambient pressure to the solvent layer, a mobile barrier was introduced to the corresponding systems by slight modification of the DLPOLY code, analogous to a pressure stamp in a previous work.^{iv} For geometric analyses snapshots of the trajectory were taken each picosecond.

1.2 Correction Term for Energies

Since the force field does not correctly reproduce the adsorption energies determined by Bauer *et al.*, we applied the following correction, where E_N is the original energy before correction of the surface with N adsorbed molecules, E_{empty} is the energy of the empty surface.

$$E_N = E_N - E_{empty} + N * E_{corr} - N * E_{ODPA-d}$$

The correction term E_{corr} is the difference between the adsorption energies E_{DFT}^{ads} from the DFT calculations carried out by Bauer *et al.* and the adsorption energy E_{FF}^{ads} calculated with the force field.

$$E_{corr} = E_{DFT}^{ads} - E_{FF}^{ads}$$

The adsorption energy E_{FF}^{ads} , was obtained from MD runs (1M steps, 50k steps equilibration, 1 fs integration time, 300 K, energies every 100 steps) of a deprotonated PA monodentately bound to the surface ($E_{PA-d \text{ on surf}}$) and of the deprotonated PA in vacuum ($E_{PA-d \text{ vac}}$).

$$E_{FF}^{ads} = E_{PA-d \text{ on surf}} - E_{PA-d \text{ vac}} - E_{empty}$$

In order to minimize the influence of the aliphatic chain, a methyl phosphonic acid (MPA) was chosen instead of ODPA for these simulations. The charges for the anchor atoms and the carbon atom were

taken from the deprotonated ODPA force field and the residual charge was divided by three and assigned to the hydrogen atoms of the methyl group.

1.3 Experimental methods

Grazing Incidence X-ray Diffraction (GIXD) experiments were carried out at beamline ID10 at the European Synchrotron Radiation Facility in Grenoble using 22 keV X-rays, as described before.^v The impinging angle α was set to 0.080°, which is just below the critical angle of silicon, $\alpha_c = 0.082$. The corresponding critical momentum transfer vector is qc = 0.032 Å⁻¹. The data was collected with a Pilatus 300K area detector with an illumination time of 10 s. Since the present self-assembled monolayers consist of crystallites, which are randomly oriented in the plane, any Bragg peak can be measured by mapping the (20, β)-space. The peak can be well described by a Lorentzian line shape.^{vi}

2 Results from Experiments

ODPA SAMs were investigated by means of X-ray reflectivity (XRR) and grazing incidence X-ray diffraction (GIXD) at the European Synchrotron Radiation Facility (ESRF). The results of XRR measurements are already published elsewhere^{vii} and reveal a thickness of the monolayer of 25.8 Å, which is in good agreement with theoretical values of the stretched out molecules. Hence the molecules feature an upright orientation, normal to the surface, with stretched alkyl chains. From the electron density in the alkyl chain region of 0.32 e/Å^3 and the determined thickness, the average molecular density could be calculated to 5.05 nm⁻².

GIXD measurements resulted in one Bragg rod at q = 1.485 Å⁻¹, which corresponds to a lattice spacing of 4.23 Å in a two dimensional hexagonal lattice, as it has been found before for alkyl-SAMs.^{vi} The nearest neighbor distance was calculated to 4.88 Å, which corresponds to a molecule density of 4.84 nm⁻² on the surface. The intensity line profile in q_z -direction exhibits a maximum of the diffracted intensity close to $q_z = 0$, revealing a perpendicular orientation of the molecules to the surface, without apparent tilt angle to the surface normal (Figure S1).



Figure S1: Result of a grazing incidence X-ray diffraction measurement of a pure C18-PA SAM with a diffraction map in (q_r,q_z) -space (a), the extracted and background-corrected profile in q_r -space (circles) with the corresponding Lorentzian fit (line) (b), a schematic representation of the two-dimensional hexagonal lattice with corresponding lattice parameters (c), and the extracted and background-corrected profile in q_z -space (d).

3 Additional Results and Figures from Simulations



Figure S2 Flowchart of the algorithm used for adsorption of new molecules



Figure S3 Distribution of phosphonic acid molecules for growth simulation A without enforced superlattice at coverage of 0.61 nm⁻² (top left), 2.43 nm⁻² (top right), 3.27 nm⁻² (bottom left) and 3.60 nm⁻² (bottom right). Coordinating oxygen atoms of PAs shown in blue, Oxygen atoms of surface hydroxides are shown in green if they match the lattice and in red otherwise.



Figure S4 Distribution of phosphonic acid molecules for growth simulation B with $(2/\sqrt{3} \times 2/\sqrt{3})R30^\circ$ superlattice at coverage of 0.61 nm⁻² (top left), 2.43 nm⁻² (top right), 3.27 nm⁻² (bottom left) and 3.76 nm⁻² (bottom right). Coordinating oxygen atoms of PAs shown in blue, Oxygen atoms of surface hydroxides are shown in green if they match the lattice and in red otherwise.



Figure S5 Distribution of phosphonic acid molecules for growth simulation C with (1×1) superlattice at coverage of 0.61 nm⁻² (top left), 2.43 nm⁻² (top right), 3.27 nm⁻² (bottom left) and 5.07 nm⁻² (bottom right). Coordinating oxygen atoms of PAs shown in blue, Oxygen atoms of surface hydroxides are shown in green if they match the lattice and in red otherwise.



Figure S6 Orientation of PA-anchors in systems derived from growth run A without target lattice in vacuum (top row), in hexane (middle row) or in 2-propanol (bottom row) at coverage of 0.61 nm⁻² (left column), 2.43 nm⁻² (right column), respectively. Hydrogen bonds are displayed in blue. Each image is an average over 1000 frames, thus deep blue indicates stable hydrogen bonds, whilst light blue represents bonds that occur only occasionally. Molecules that rotate easily appear blurred whereas sharp contours denote a low degree of rotational freedom.



Figure S7 Orientation of PA-anchors in systems derived from growth run B with $(2/\sqrt{3} \times 2/\sqrt{3})R30^{\circ}$ superlattice in vacuum (top row), in hexane (middle row) or in 2-propanol (bottom row) at coverage of 0.61 nm⁻² (left column), 2.43 nm⁻² (right column), respectively. Hydrogen bonds are displayed in blue. Each image is an average over 1000 frames, thus deep blue indicates stable hydrogen bonds, whilst light blue represents bonds that occur only occasionally. Molecules that rotate easily appear blurred whereas sharp contours denote a low degree of rotational freedom.



Figure S8 Orientation of PA-anchors in systems derived from growth run C with (1×1) superlattice in vacuum (top row), in hexane (middle row) or in 2-propanol (bottom row) at coverage of 0.61 nm⁻² (left column), 2.43 nm⁻² (right column), respectively. Hydrogen bonds are displayed in blue. Each image is an average over 1000 frames, thus deep blue indicates stable hydrogen bonds, whilst light blue represents bonds that occur only occasionally. Molecules that rotate easily appear blurred whereas sharp contours denote a low degree of rotational freedom.

3.1 Hydrogen Bonding Network

Table S1 lists the average number of hydrogen bonds in all system derived from the growth simulations. The data shows that hydrogen bonds between two phosphonic acids are favored by the (1×1) superlattice (C) and hindered by the $(2/\sqrt{3} \times 2/\sqrt{3})R30^\circ$ lattice (B), where the anchors are too far apart to form stable hydrogen bonds. The number of hydrogen bonds between phosphonic acids in systems derived from run A lie in between the two values from B and C, since domains with both lattices are present (c.f. Figure S3-5). The deep blue of most hydrogen bonds in Figure S8 also indicates that the H-bonds in the (1×1) lattice are much more stable than that in the $(2/\sqrt{3} \times 2/\sqrt{3})R30^\circ$ lattice shown as light blue lines in Figure S7).

No significant trend for the influence of either hexane or 2-propanol on the hydrogen bonding network could be derived from the data, as the differences are within the margins of error and can be attributed to the rotation of a few PA anchors, which can be seen in Figure S6-8. Thus, it appears that 2-propanol only forms additional hydrogen bonds with the PA anchors rather than weakening or strengthening the existing network. Surprisingly, the 2-propanol hardly forms H-bonds towards the surface in the simulations at higher coverage (c.f. Table S1), although the surface is accessible in places. Instead H-bonds to nearby anchors are preferred, since these are more exposed and less stabilized than the surface hydroxides.

Table S1 average number of hydrogen bonds μ and standard deviation σ for all systems derived from the growth simulations calculated from histograms or average over 1000 frames for vacuum simulations and 2000 frames for . Fit errors are usually below 1% except for the PA-PA histograms at 0.61 nm⁻² coverage, where the number of bins is very small. Here, the errors range up to 11%.

ρ	run	solvent	PA-PA		PA-alumina		PA-solvent		solvent-alumina	
$[nm^{-2}]$			μ	σ	μ	σ	μ	σ	μ	σ
0.61	А	None	1.48	0.61	21.62	3.46				
		Hexane	1.44	0.63	22.36	3.47				
		2-propanol	3.04	0.85	27.17	3.70	50.53	2.65	30.02	3.43
	В	None	1.42	1.06	18.68	3.47				
		Hexane	1.81	1.08	21.42	3.49				
		2-propanol	0.76	0.88	23.86	3.58	48.49	2.35	29.12	3.35
	С	None	6.95	1.14	17.95	3.34				
		Hexane	7.32	1.05	17.24	3.22				
		2-propanol	6.47	1.17	24.23	3.47	45.44	2.48	33.87	3.67
2.43	Α	None	50.6	2.61	72.9	6.13				
		Hexane	49.1	2.68	74.5	6.03				
		2-propanol	50.7	2.66	74.9	6.06	33.4	2.16	0.01 a	0.12 ª
	В	None	27.1	3.70	69.3	6.16				
		Hexane	25.5	3.75	66.5	6.02				
		2-propanol	21.1	3.26	66.7	6.09	38.0	0.25	0.49 a	0.25 a
	С	None	73.1	2.76	79.5	5.76				
		Hexane	72.1	2.79	81.0	5.91				
		2-propanol	69.8	2.92	82.0	5.82	42.3	0.63	0.50 a	0.63 a

^a value has been calculated by averaging instead of fitting the histogram, since the histograms only contained two or three bins



3.2 Radial Pair Distribution Functions

Figure S9 Histograms of the tilt angle. Coverage is color coded according to the scale in the first graph.

Figure S10 Histograms of the dihedral angles in the alkyl chain. Coverage is color coded according to the scale in the first graph of Figure S9.

Figure S11a shows plots of the radial pair distribution function (RDF) of the terminal carbon atoms of the chains in system A at various densities. This RDF is an excellent measure for the long-range order in the system as peaks will only emerge if the chains arrange in regular patterns. A first maximum evolves at about 2.8 nm⁻² when the formation of domains begins. As the domains grow larger, a second broad peak emerges at about 10 Å. By comparison with snapshot iv) of figure 3A it is obvious that the order of the domains does not reach much further than that. In Figure S11b, by contrast, which shows the RDF series for system C, the domains grow further and start to coalesce, which leads to a much more long-ranged order. A third peak develops at a coverage of about 3.3 nm⁻² and upon further addition of PAs more and more peaks arise until the final RDF for a coverage of 5.07 nm⁻² is well structured up to the cutoff of 30 Å. The gray dashed curve shows a calculated RDF for an ideal (1 × 1) superlattice, *i. e.* a hexagonal lattice with a spacing of 4.77 Å, with a standard deviation of 1 Å. The curve nicely matches the final RDF from run C which corresponds to the well-ordered structure shown in snapshot iv of figure 3C. By comparison of the RDFs among each other, a peak shift for the maxima towards lower distances can be observed. This shift is caused by the decrease in tilt angle within the domains that implies a reduction of the cross-section of the chains.



Figure S11 Radial distribution function of the CH_3 carbon atoms at various states during growth from simulations A (top) and B(bottom). The red and green curves represent the systems solvated in hexane and 2-propanol, respectively. The gray reflexes mark the ideal positions and relative intensities of the ideal (1×1) superlattice. The gray dashed line is a curve calculated from these reflexes with a standard deviation of 1 Å.



Figure S12 Left: Snapshot of system A with a coverage of 2.44 nm⁻² before solvation. Center: Snapshots of the final configurations for the simulations derived from system A with added 2-propanol (blue, top) and hexane (yellow, bottom). Excess solvent is omitted for clarity. Right: Same as center after removal of the solvent.



Figure S13 Left: Snapshot of system B with a coverage of 2.44 nm⁻² before solvation. Center: Snapshots of the final configurations for the simulations derived from system B with added 2-propanol (blue, top) and hexane (yellow, bottom). Excess solvent is omitted for clarity. Right: Same as center after removal of the solvent.

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