Determining the Contact Angle of a Frozen SAM via Pressure-Tensor and Droplet Method

In the following the contact angels of a hydrophobic SAM (0% OH) and a hydrophilic SAM (100% OH) are compared, based on two different methods, the pressure-tensor-method and the droplet-method. (see Felix's Paper for more details on both methods; F. Sedlmeier et al. Biointerphases (3) 2008,FC23)

1 Pressure Tensor

The solid-liquid-surface tension of SPC-water on a 'frozen' SAM is obtained via the pressure-tensor (see Fig. 1 for a snapshot of the simulation box). Subsequently the contact angle is calculated from Young's equation. The SAMs are completely 'frozen', meaning that the atoms cannot move, they do not interact with each other, but only with water. The SAMs are placed in the middle of the simulation box. I do not see any movements of the SAM during the simulation.
Young's equation for a 'frozen' surface:

$$\cos(\theta) = -\frac{\gamma_{sl}}{\gamma_{lv}} \tag{1}$$

For $\gamma_{lv} = 57\text{mN/m}$, I took the value obtained by Alexander Herz in his diploma thesis.
The surface tension is obtained for the pressure-tensor as:

$$\gamma_{sl} = \frac{L_{box} - L_{SAM}}{2}\left(P_{zz} - \frac{P_{xx} + P_{yy}}{2}\right) \tag{2}$$

The result ion contact angels are:
$\theta_{0pc} = 116.8°$
$\theta_{100pc} = 0°$

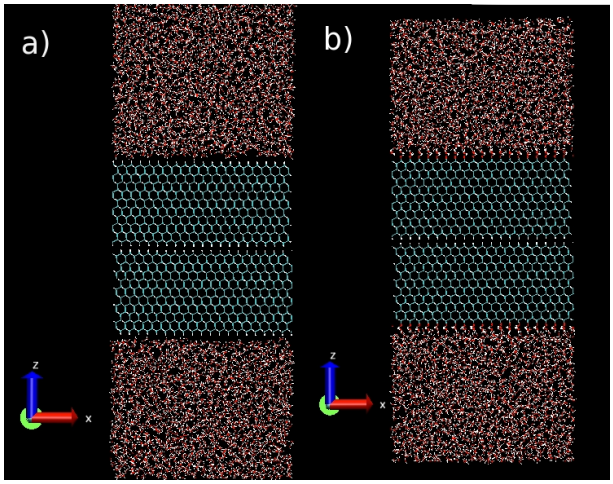

Abbildung 1: Snapshot of the simulation box for the pressure-tensor-method. (a) hydrophobic SAM (b) hydrophilic SAM

2 Droplet-Method

For the droplet-method the exact same 'frozen" SAMs are used. Simulations with drops containing approximately 1000, 2000 and 3000 water molecules are performed. The resulting contact angeles are extrapolated to large drops (Fig. 2).

$\theta_{0pc} = 117°$
$\theta_{100pc} = 0°$
Laila did similar simulations with more drop-sizes (see the summery she sended around for more details). These simulations result in (see Fig.3):
$\theta_{0pc} \approx 145°$
$\theta_{100pc} = 0°$

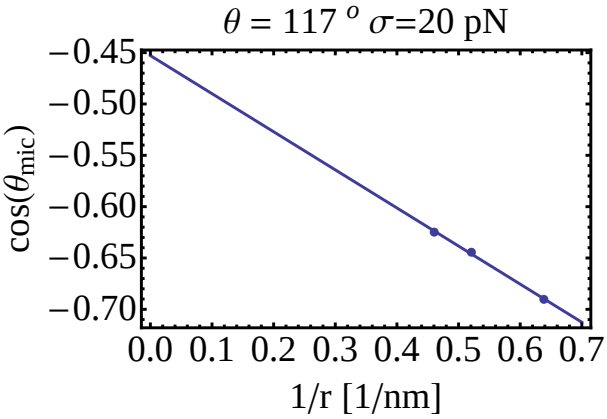

Abbildung 2: contact angle in dependence of the inverse drop-radius

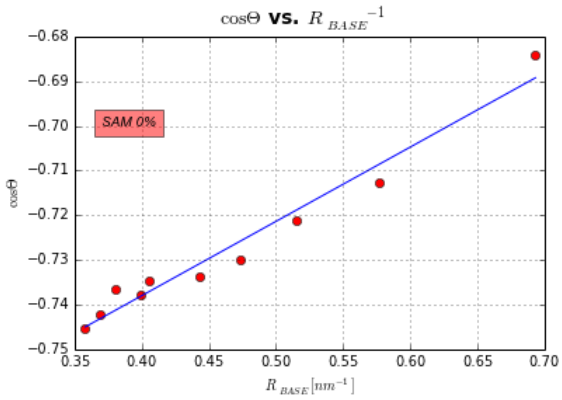

Abbildung 3: contact angle in dependence of the inverse drop-radius

3 simulation

Equilibration the frozen SAMs with pressure-coupling is very tricky. It turned out that with two runs (4000 steps+96000 steps) with semi-isotropic (P_z=1bar) Parrinello-Rahman-pressure-coupling, the correct pressure is obtained. In the subsequent Berendsen-pressure-coupling-simulation the pressure in z-directions remains constant.