Molecular Simulation of Polymers, Insights and Limitations

Michael Brunsteiner

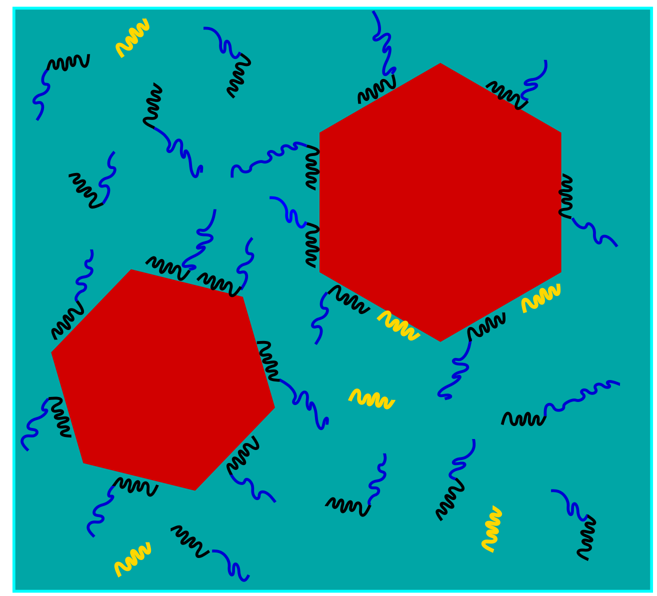
November 21$^{\mathrm{th}}$ 2004

Overview

- The problem
- Materials & methodologies
- Accurate results for simple materials
- Adsorption energies of polymers on pigment surfaces
- Meso-scale $\longrightarrow$ coarse graining
- Conclusions/outlook

The problem — Stability of Dispersions

- Pigment surface structure
- Solvent
- Additives
- Zeta potential
- Dispersant/surface affinity
- Dispersant/solvent interaction
- Temperature, etc ...

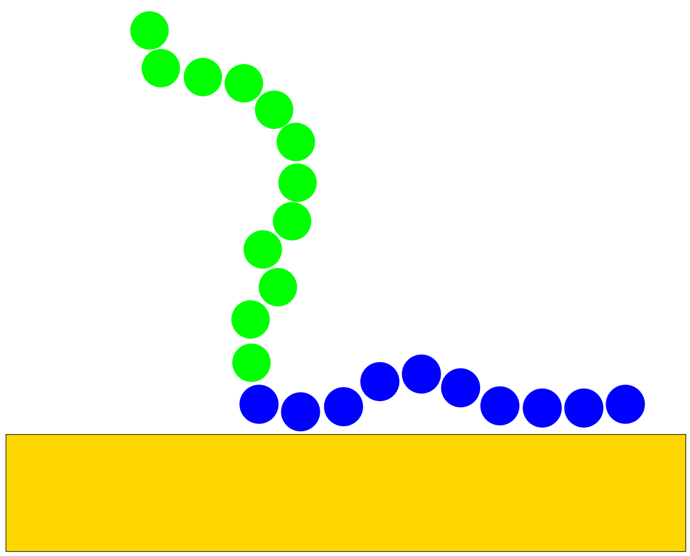


Many parameters $\longrightarrow$ complex optimisation
accelerate and focus development through **systematic** optimisation of one parameter (divide et impera).

The Dispersant

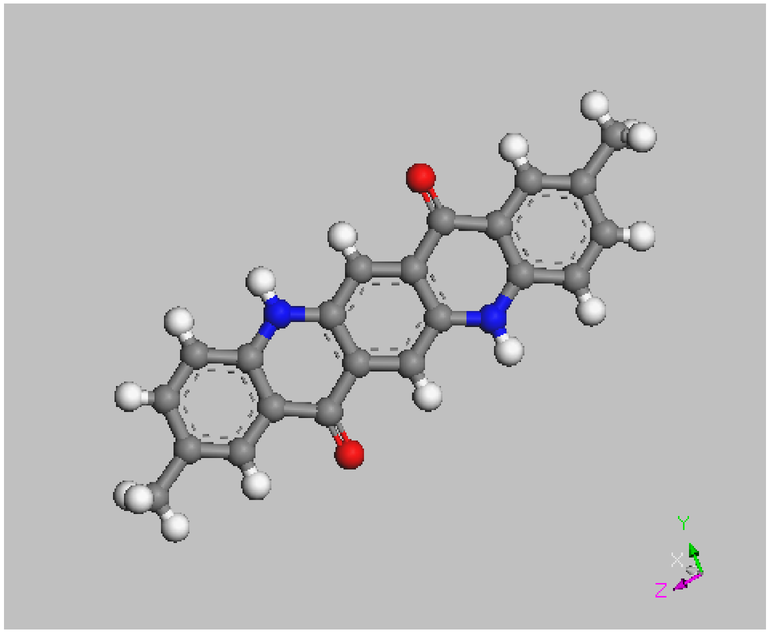
Synthetic (block-) Co-Polymers:

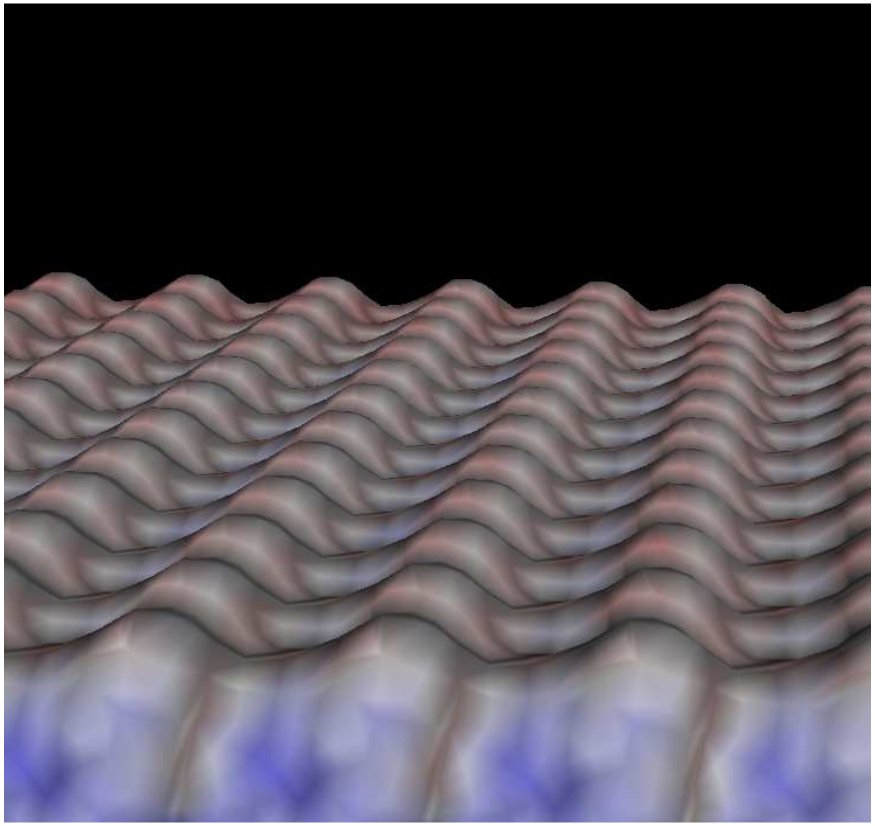
- high performance
- huge variety
- comaratively cheap



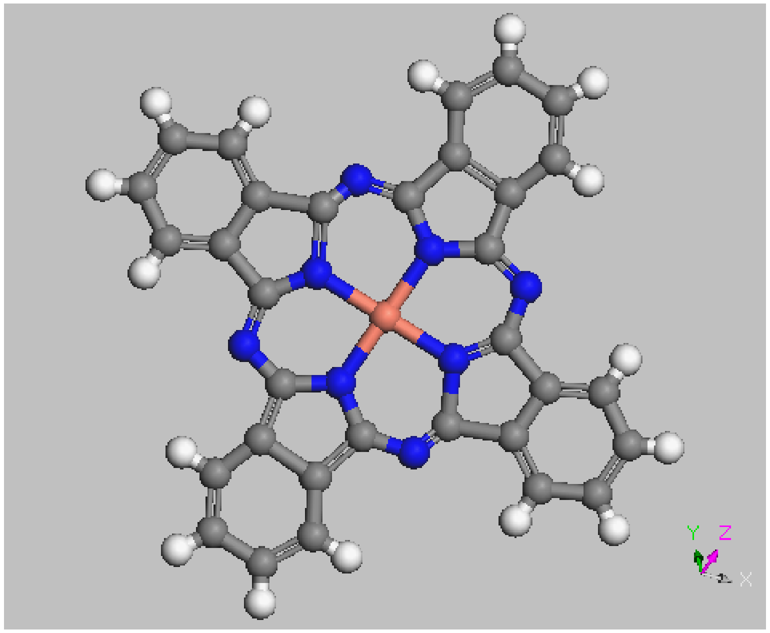
we concentrate on hydrophobic residues.

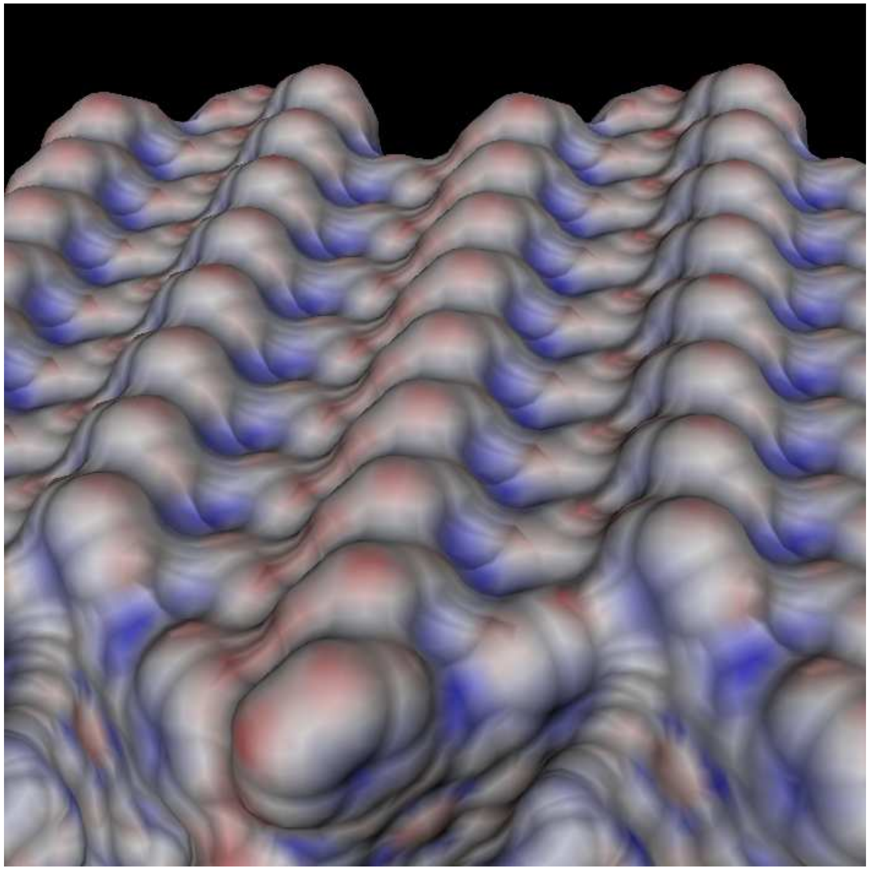
The Pigments I, PR122



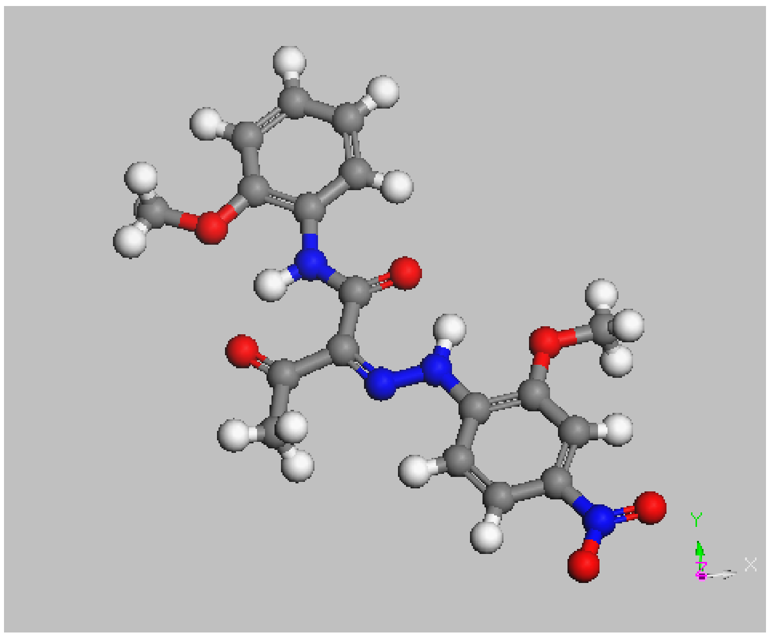


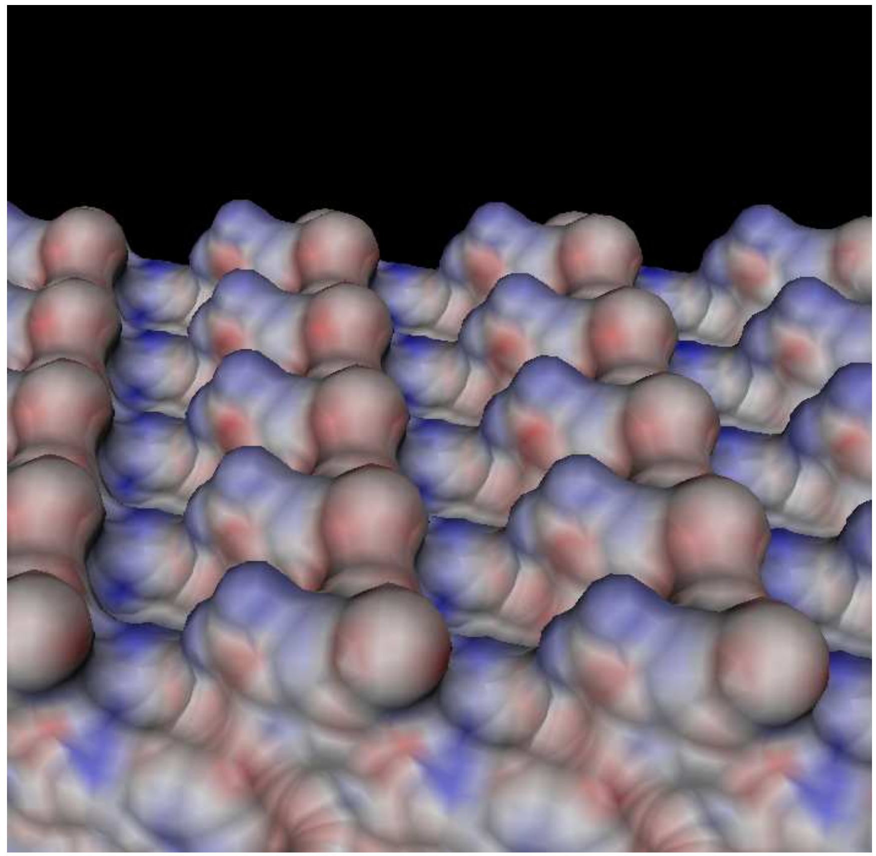
The Pigments II, PB15:3





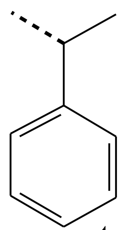
The Pigments III, PY74



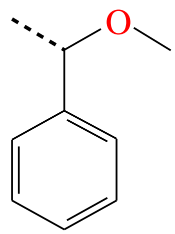


Monomers

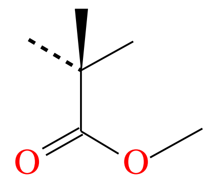
Hydrophobic residues of block-co-polymers



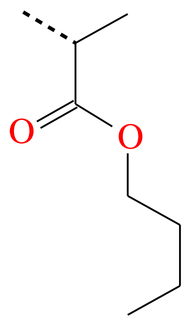
styrene
PSt



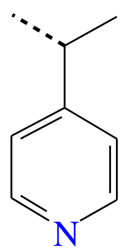
styrene–oxide
PStO



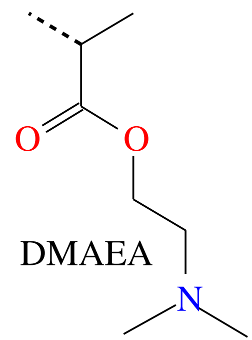
methyl methacrylat
PMMA



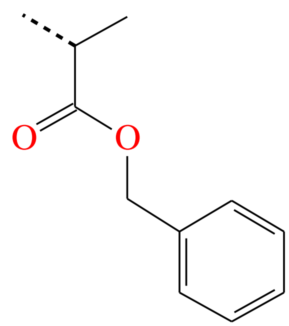
butyl–acrylat
PBA



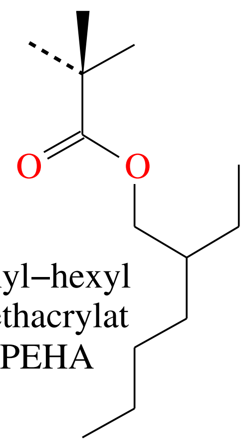
vinyl–pyridin
PVPyr



DMAEA



benzyl–acrylat
PBnA



ethyl–hexyl
methacrylat
PEHA

To Adsorbe or not to Adsorbe, Criteria

Concentration of adsorbed/solvated dispersant ([A]/[S])

Thermodynamics:	$\frac{[\mathrm{A}]}{[\mathrm{S}]} = \mathsf{K} = \text{const (in equilibriu m!)}$ $\mathsf{K} \propto \exp(-\Delta\mathrm{G}/RT)$
Kinetics:	$\frac{d[S]}{dt} \propto k[S]^n$ $k \propto \exp(-\Delta\mathrm{G}^{\ddagger}/RT)$

Which Method ?

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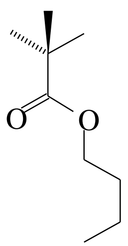
"low throughput screening" $\longrightarrow$ **Molecular dynamics**

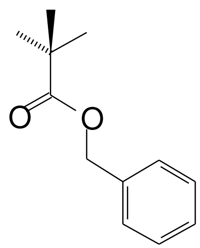
Molecular Dynamics — Software

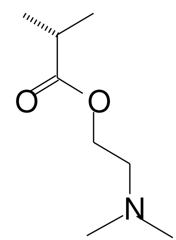
	Materials Studio	Gromacs
setup	+	−
preciseness	−	+
speed	4:47	0:18
analysis	−	+
documentation	+	+
cost	substantial	zero

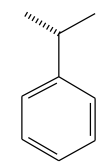
Forcefield I

Small clusters — DFT-LDA vs classical FF





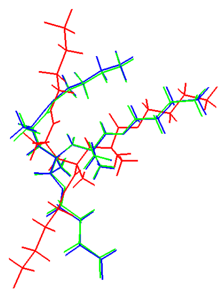
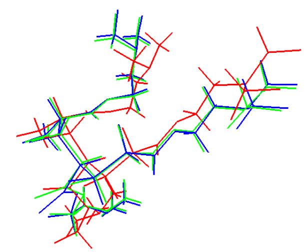
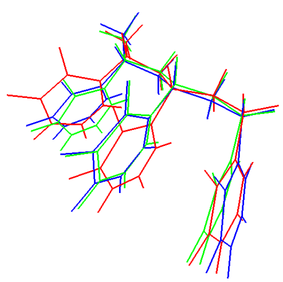
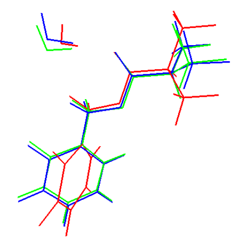




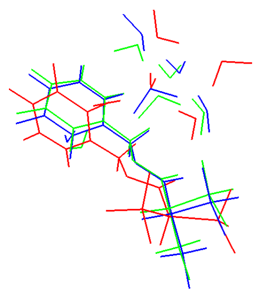
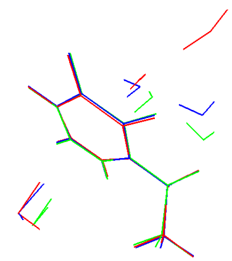
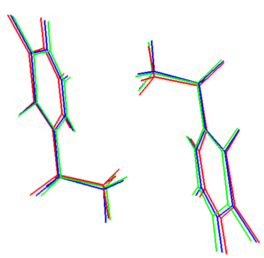
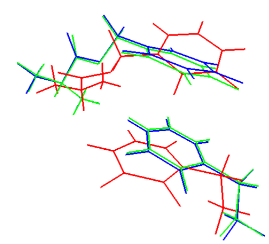
BMA BnMA MAD STY

label	monomer(s)	N_M	N_W	comment
BMA-3	butyl-methacrylate	3	0	trimer
MAD-3	2-dimethylamino ethylacrylate	3	0	trimer
STY-3	styrene	3	0	trimer
BnMA-1W	benzyl-methacrylate	1	1	monomer
BnMA-5W	benzyl-methacrylate	1	5	monomer
STY-3W	styrene	1	3	monomer
STY-2	styrene	2	0	two monomers
STY-BnMA	styrene + benzyl-methacrylate	1/1	0	two monomers

Forcefield II

align/comp	Compass	OPLSP	align/comp	Compass	OPLSP
BMA-3			MAD-3		
all/all	2.312	0.168	all/all	1.127	0.202
STY-3			BnMA-1W		
all/all	0.758	0.415	all/all	1.366	0.185
			BnMA/BnMA	1.118	0.106

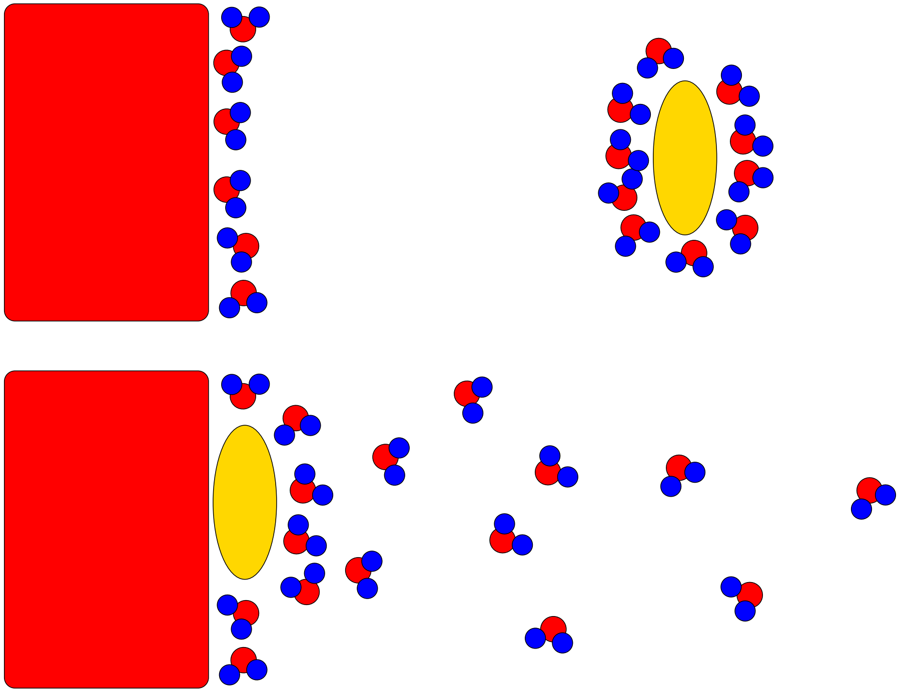
Forcefield III

align/comp	Compass	OPLSP	align/comp	Compass	OPLSP
BnMA-5W 			STY-3W 		
all/all	1.970	0.424	all/all	1.016	0.441
BnMA/BnMA	1.410	0.114	STY/STY	0.113	0.064
H_2O/H_2O	1.499	0.474	STY/H_2O	2.412	0.947
			H_2O/H_2O	1.386	0.527
STY-2 			STY-BnMA 		
all/all	0.257	0.107	all/all	1.677	0.134
STY1/STY2	0.067	0.055	STY/BnMA	0.143	0.051
STY2/STY1	0.220	0.072	BnMA/STY	0.595	0.113

ΔG_{ads} – Contributions

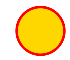
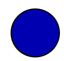
W: water X: pigment x-tal M: adsorbant

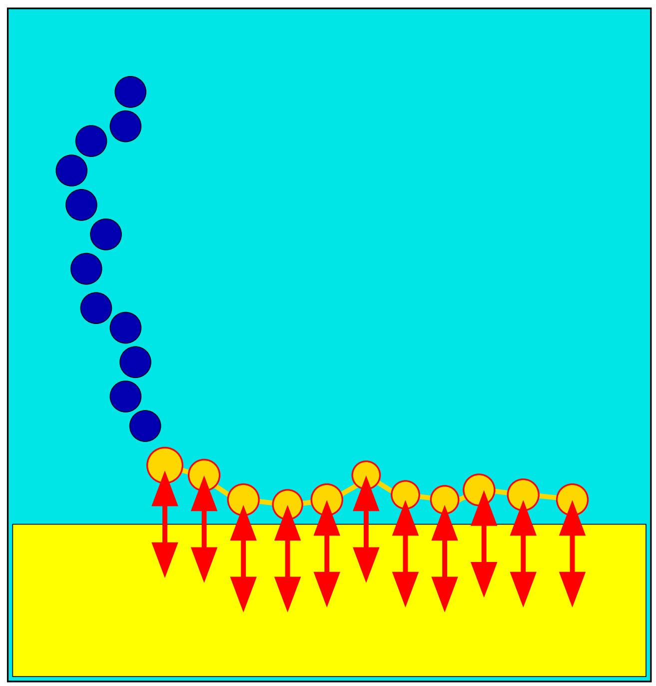
$$\Delta U_{MW} + \Delta U_{XM} + \Delta U_{XW} + \Delta U_{MM} + \Delta U_{XX} + \Delta U_{WW}$$



$$+ T\Delta S$$

Approximations I

We only consider the hydrophobic part  of dispersant. The hydrophilic part  is assumed to give a neglegible contribution to the binding affinity .



Approximations II

$$\Delta\hat{\mathrm{U}} = (\Delta\mathrm{U}_{\mathrm{XM}} + \Delta\mathrm{U}_{\mathrm{MW}} + \Delta\mathrm{U}_{\mathrm{MM}}) \times \frac{1}{\mathrm{A}_{\mathrm{ads}}}$$

We calculate and compare $\Delta\hat{\mathrm{U}}$

assumption:

The entropic contribution and $\Delta\mathrm{U}_{\mathrm{WW}}$ are compareable for similar dispersants on a given pigment surface/solvent.

Approximations III

In a first series of experiments we only look at ΔU_{XM}, the interactions between dispersant molecule and pigment surface.

NO SOLVENT — common approximatio

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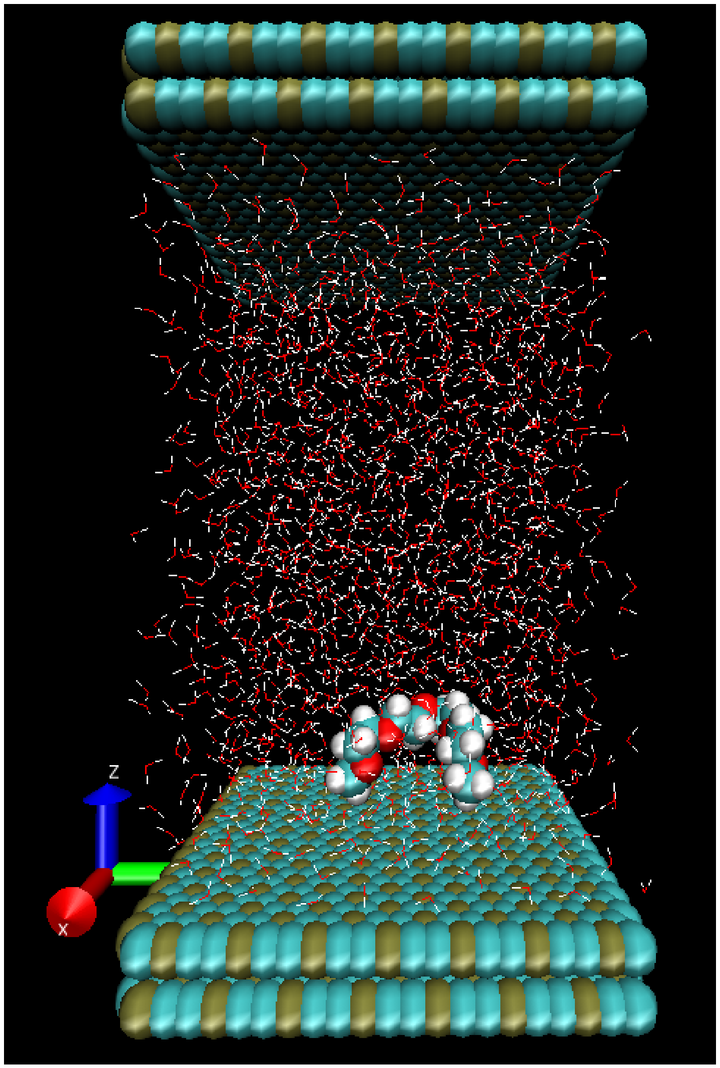
For the systems sudied here these interactions are probably not *specific* enough !

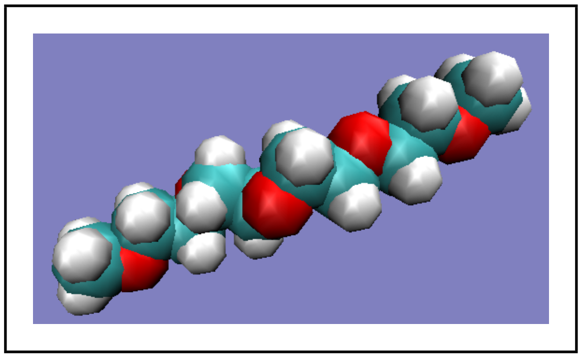
Free Energy, the Model System

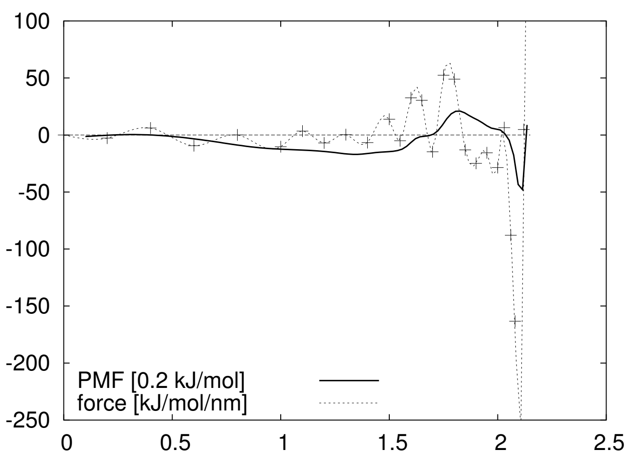


- Simple polymers in water between graphite-like surface
- calculate ΔA (ΔG) as potential of mean force (PMF)
- required simulation time: $\approx$ 100-fold

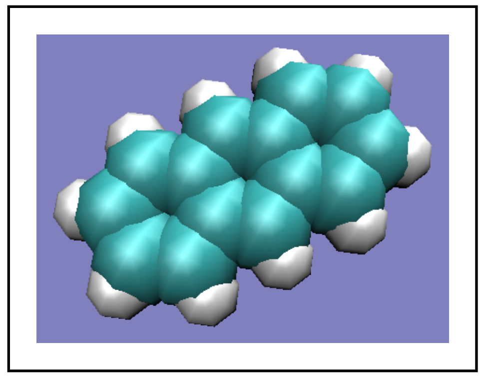
Free Energy, Molecules

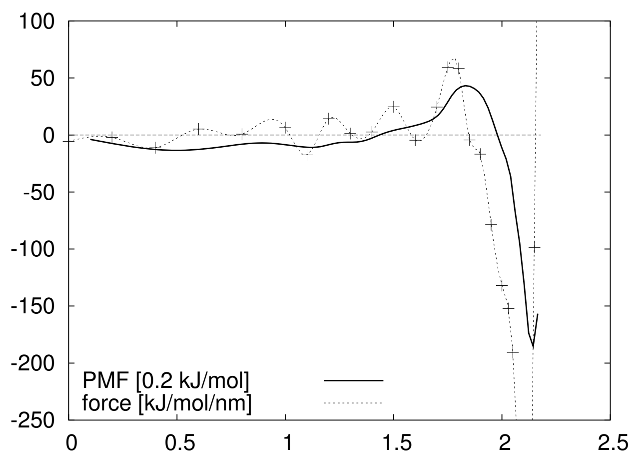
ethylene-oxide



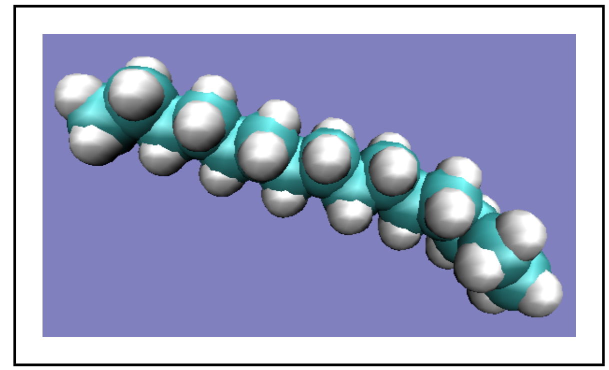


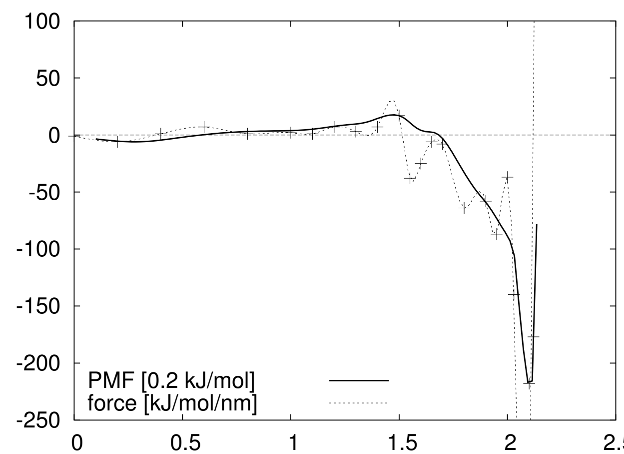
anthracene





pentadecane

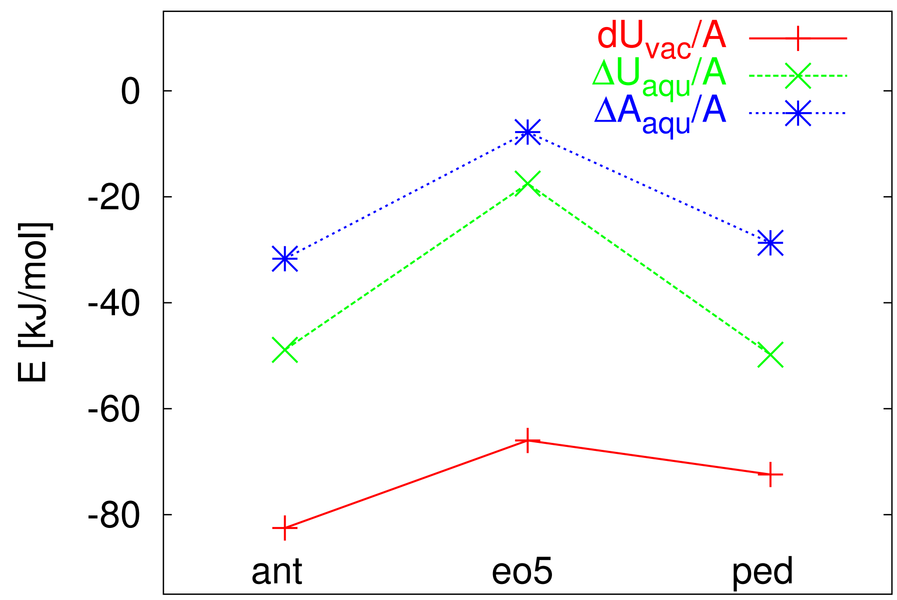




Free Energy, Results

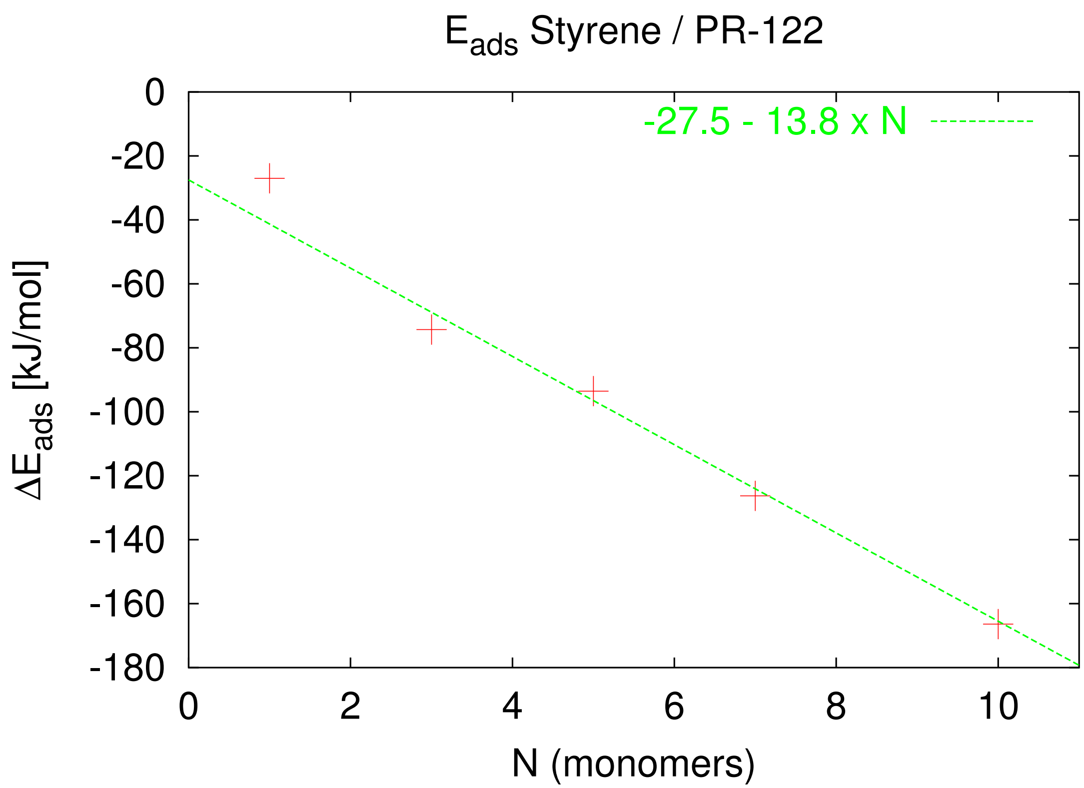
$$\Delta U = \Delta U_{XM} + \Delta U_{MM}$$
$$\Delta U_{aqu} = \Delta U_{XM} + \Delta U_{MM} + \Delta U_{MW}$$
$$\Delta A_{aqu} = \text{free energy of adsorption}$$

	ant	eox	ped
$\Delta U/A$	-82.5	-66.0	-72.4
$\Delta U_{aqu}/A$	-48.9	-17.5	-49.8
$\Delta A_{aqu}/A$	-37.3	-10.5	-45.7

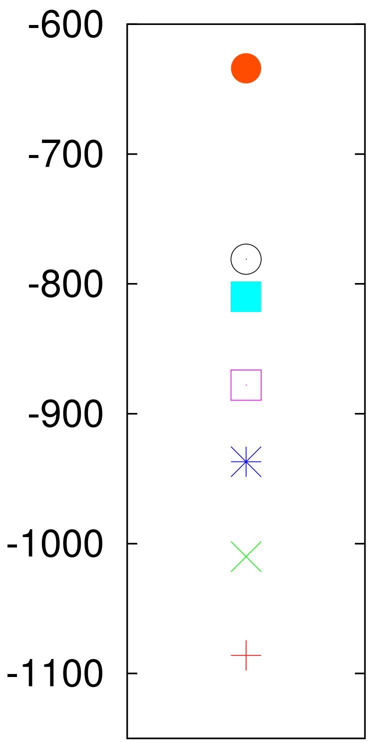


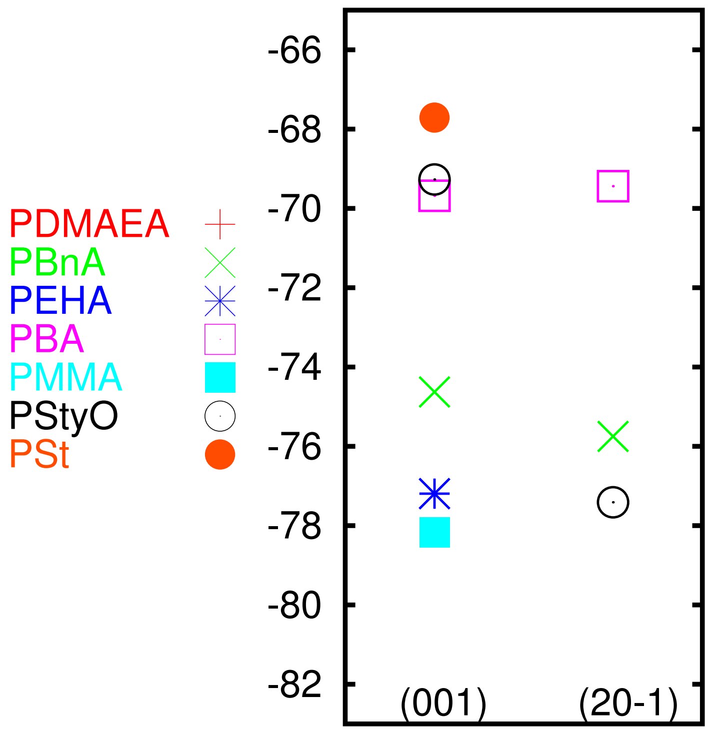
Vacuum Results I, $\Delta U(N)$

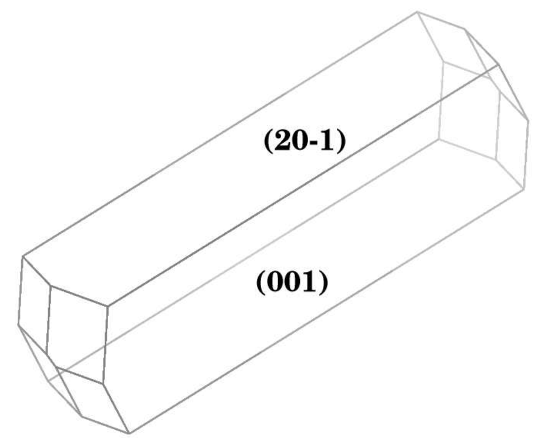
N_{mon} in commonly used dispersants: 10-150



Vacuum Results IIa, PB15:3 + M_{10}

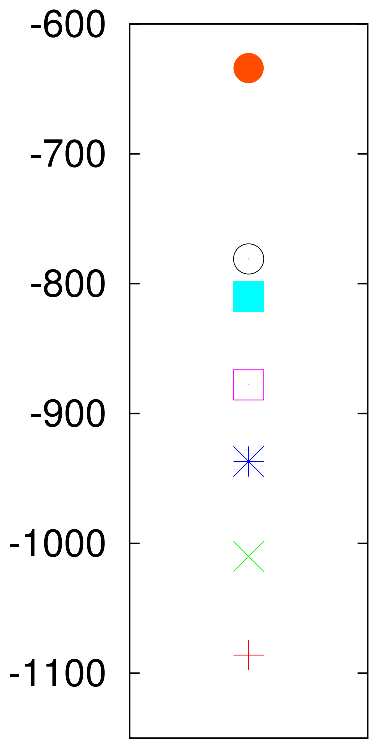


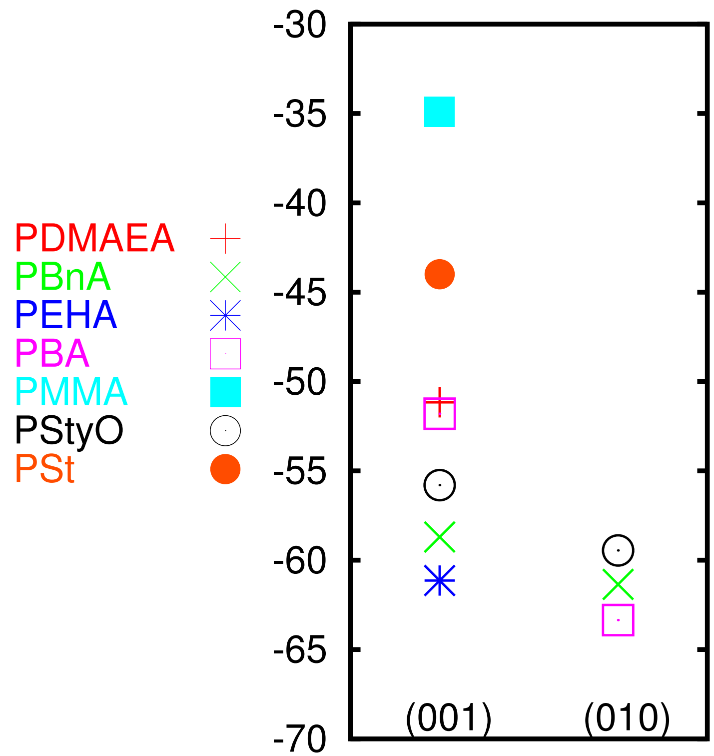


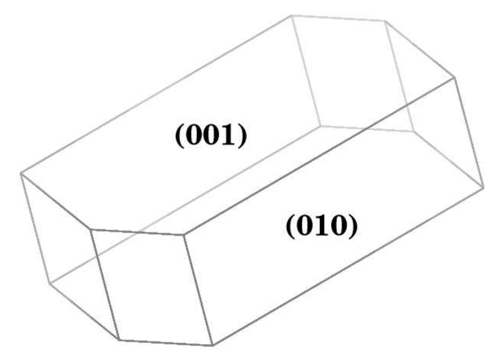


E_{solv} [kJ/mol] E_{ads} [kJ/mol/nm^2] morp hology

Vacuum Results IIb, PR122 + M_{10}

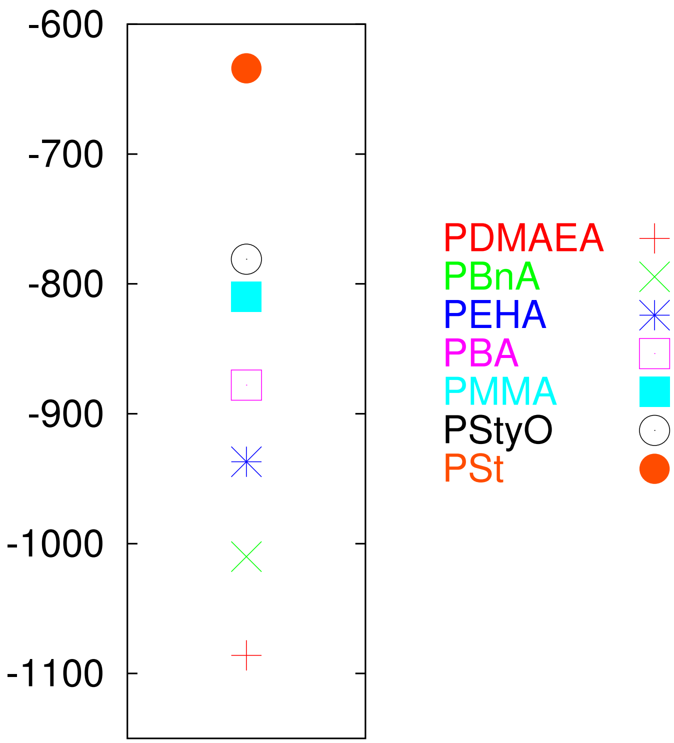


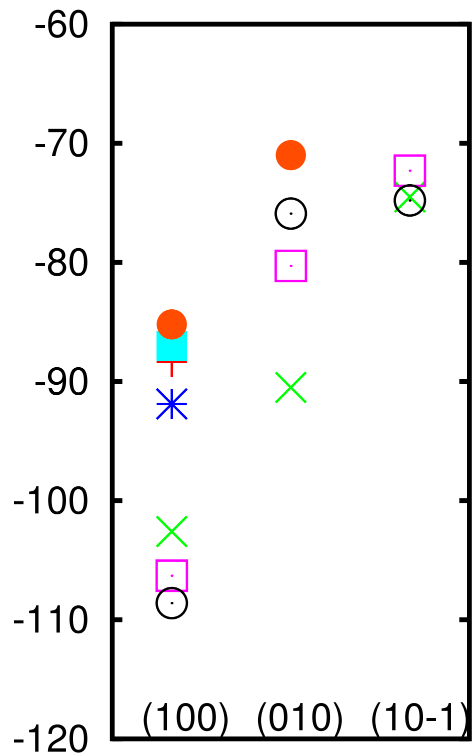


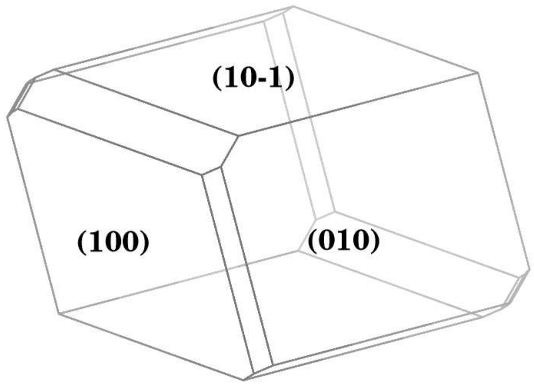


E_{solv} [kJ/mol] E_{ads} [kJ/mol/nm^2] morp hology

Vacuum Results IIc, PY74 + M_{10}







E_{solv} [kJ/mol] E_{ads} [kJ/mol/nm^2] morp hology

Vacuum Results – Conclusions

We get only qualitative results, but we can exclude a number of candidates.

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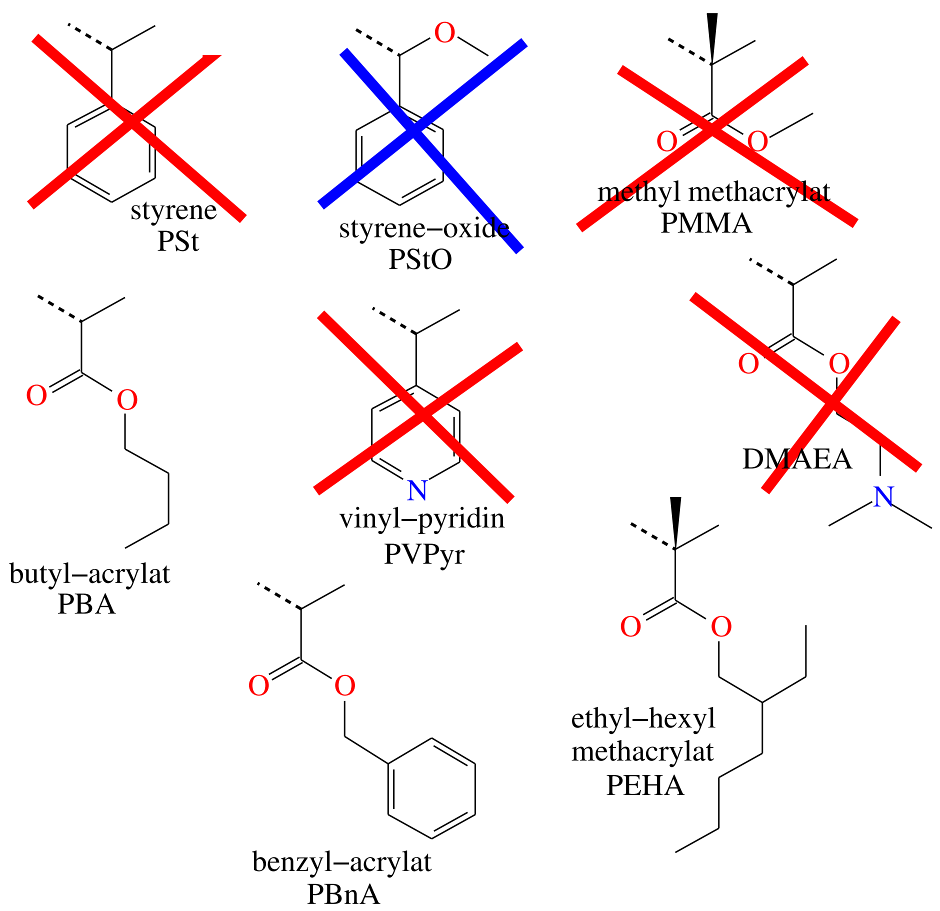
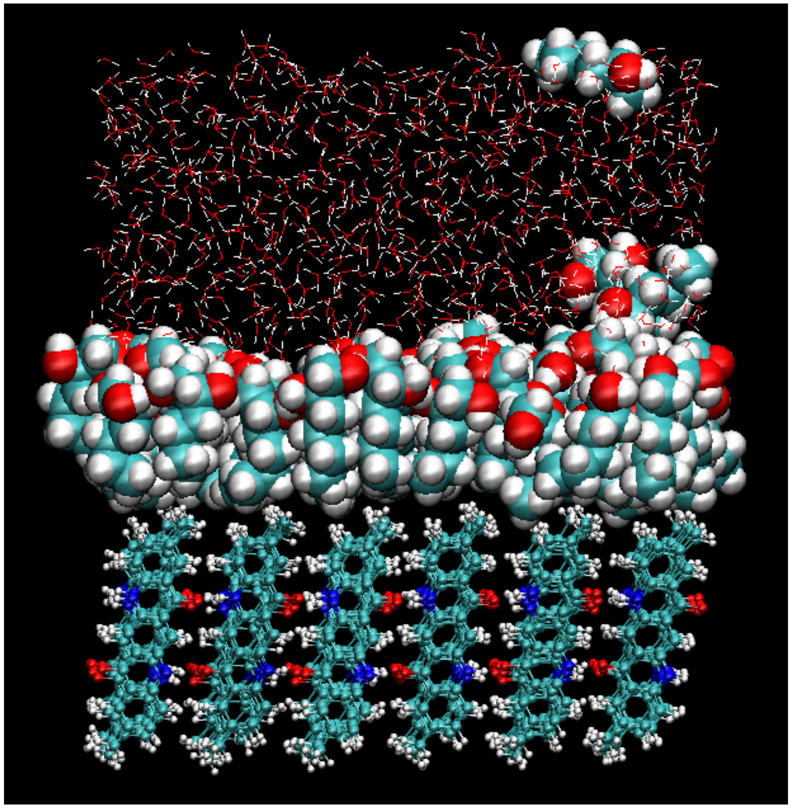
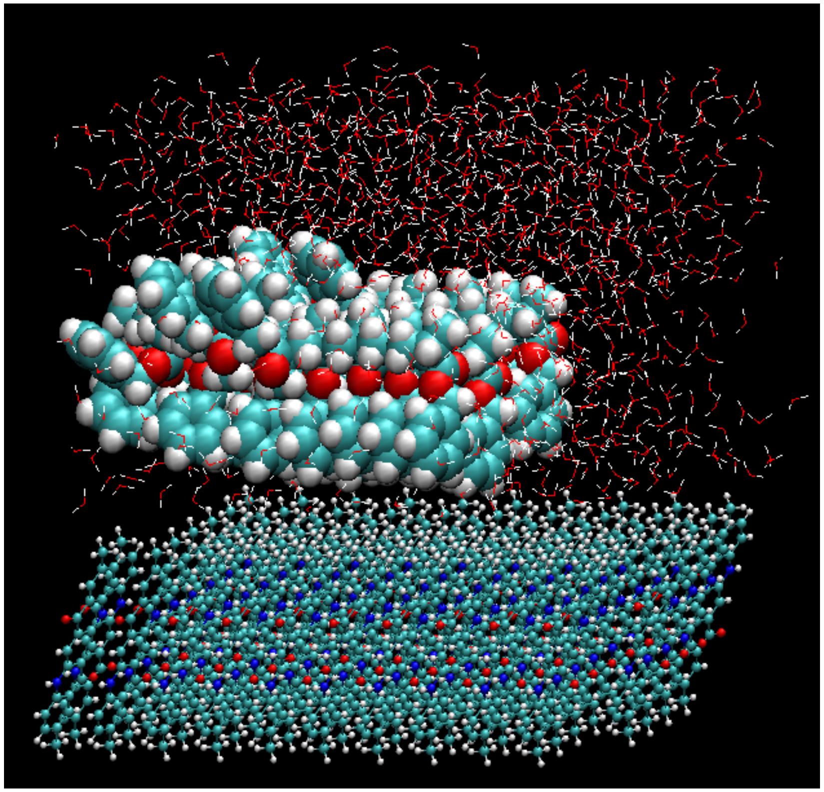


Polymers on PR122

Asorption energies of BnMA, EHMA, STY, BMA and hexane-diol.



70 hexane-diol

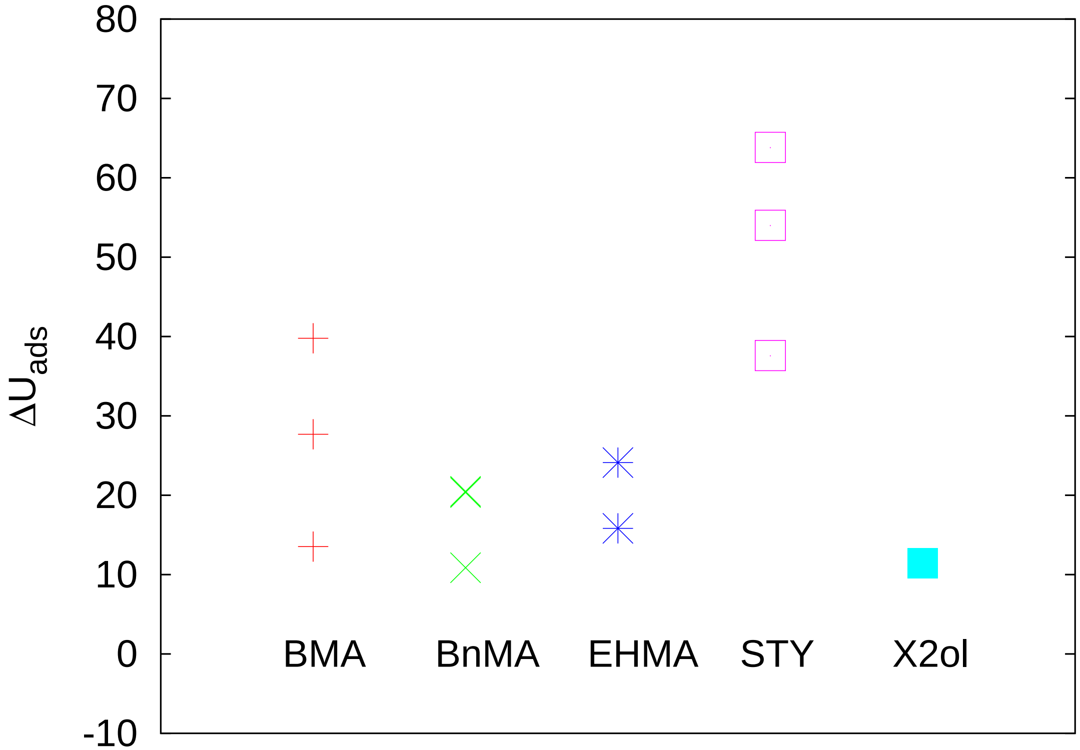


PBeMA 3 decamers

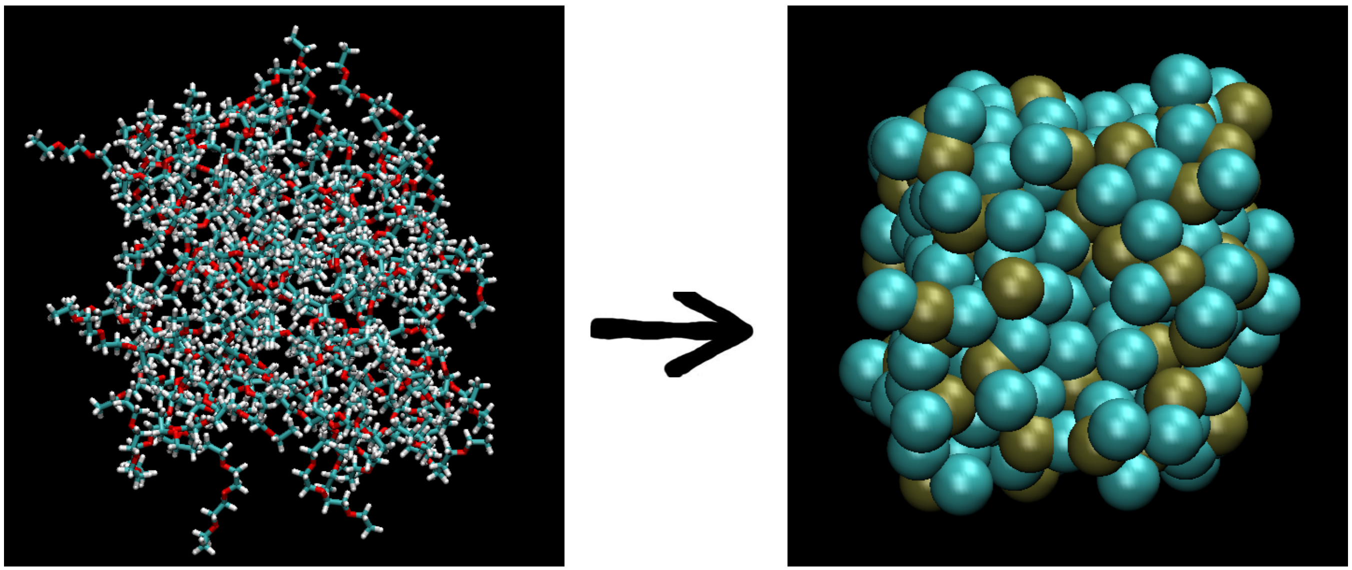
Polymers on PR122, Results I

Uii	Uij	Uiw	Uix	U14	sum	acov	NM	ΔU/(A/NM)	avg
				BMA					
-0.82	-234.12	369.56	-105.16	13.82	43.28	9.59	3	13.53	
-10.80	-151.45	349.88	-110.53	18.44	95.55	10.35	3	27.69	
-32.01	-135.22	403.96	-115.95	18.76	139.54	14.03	4	39.78	27.0
				BnMA					
-7.24	-166.58	340.94	-104.27	4.26	67.10	9.83	3	20.49	
-9.40	-199.65	339.61	-106.07	10.29	34.77	9.60	3	10.87	
42.89	-308.04	397.94	-75.46	-4.14	53.19	10.46	4	20.34	17.2
				STY					
2.00	-177.04	372.49	-56.12	-0.78	140.55	13.01	5	54.01	
4.76	-156.08	330.72	-65.00	-2.90	111.50	11.86	4	37.60	
-0.84	-147.32	356.85	-63.74	-2.47	142.48	8.93	4	63.84	51.0
				EHMA					
-23.56	-211.51	339.62	-84.20	32.82	53.16	10.08	3	15.82	
-2.62	-198.56	419.04	-129.61	12.39	100.64	12.52	3	24.12	20.0
				X2ol					
9.65	-91.83	94.25	-7.45	-2.27	2.34	14.35	70	11.43	
43.04	-60.28	78.05	-15.18	7.18	52.81	12.37	32	136.65	

Polymers on PR122, Results II



Coarse Grained Molecular Dynamics

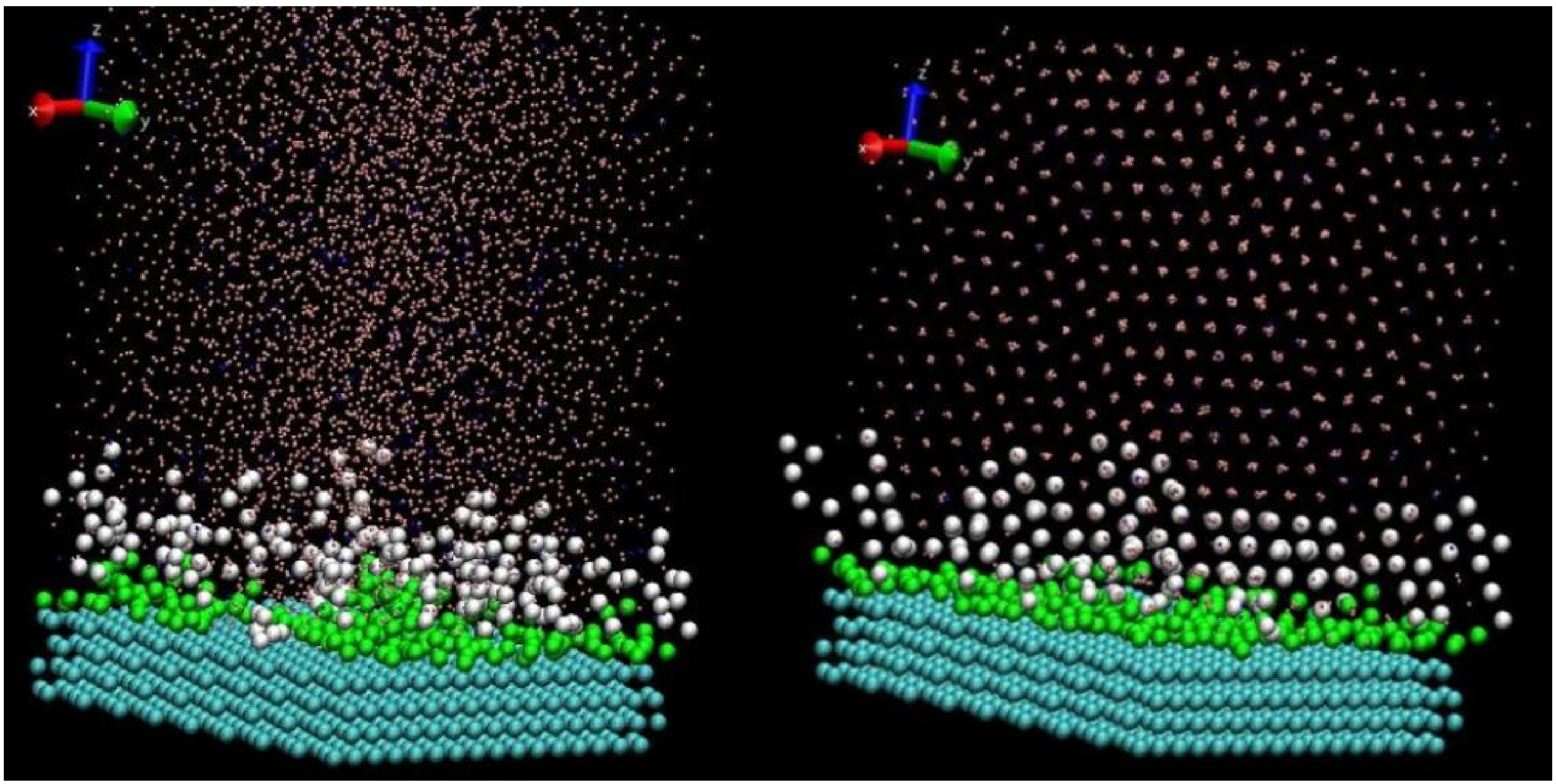


• less detail • longer timescales • larger systems

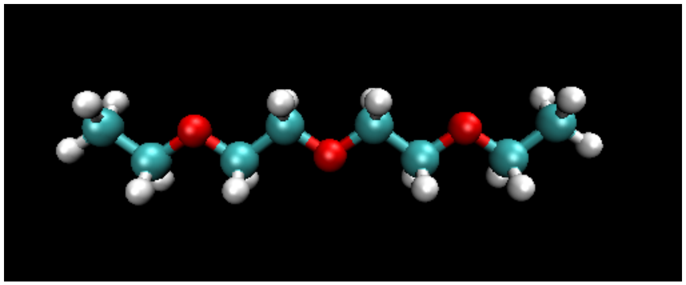
Does it Work ?

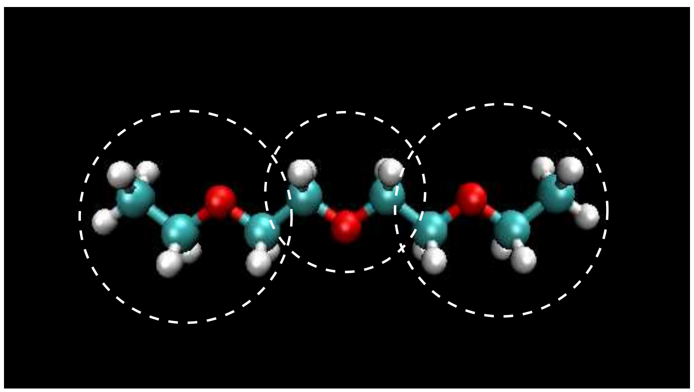
Does it Work ?

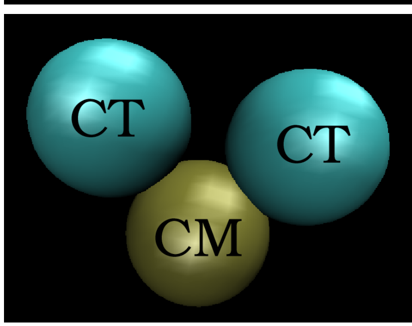
Water is a Complex Material



Fitting a CG Potential





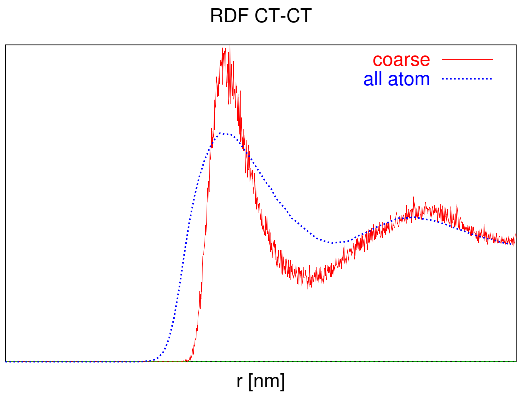


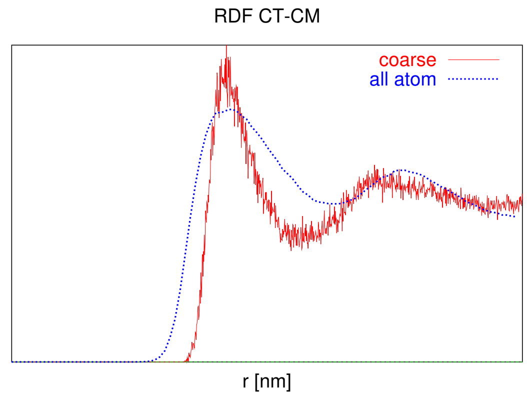
diethyl carbitol

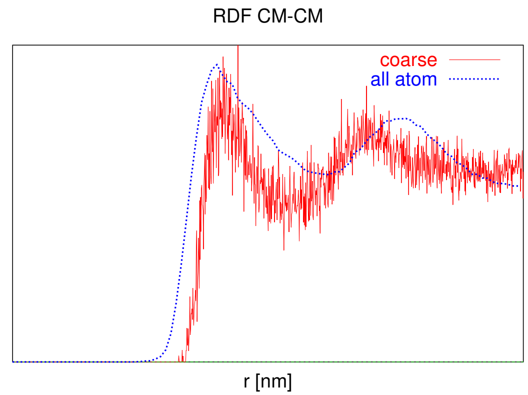
- identify “united atoms”
- declare new atom types
- fit interaction parameters

to reproduce properties of the all atom system

Diethyl Carbitol





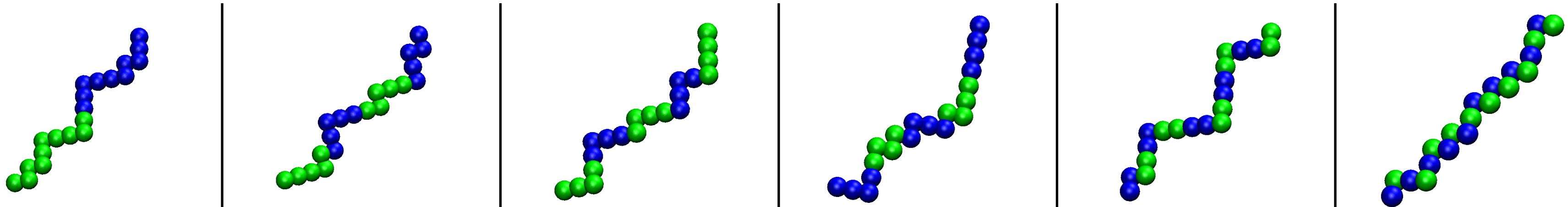


Neat Solvent at 1 atm/300 K

	E_{CT}/E_{CM}	E_{tot}	Lx	angle	bond	R_{gyr}
aa	-40.8/-27.5	-5455.0	31.33	105.8	3.79	6.07
cg	-41.0/-27.6	-5490.0	31.29	106.9	3.85	6.08

Block vs Random

polymers on hydrophobic surface



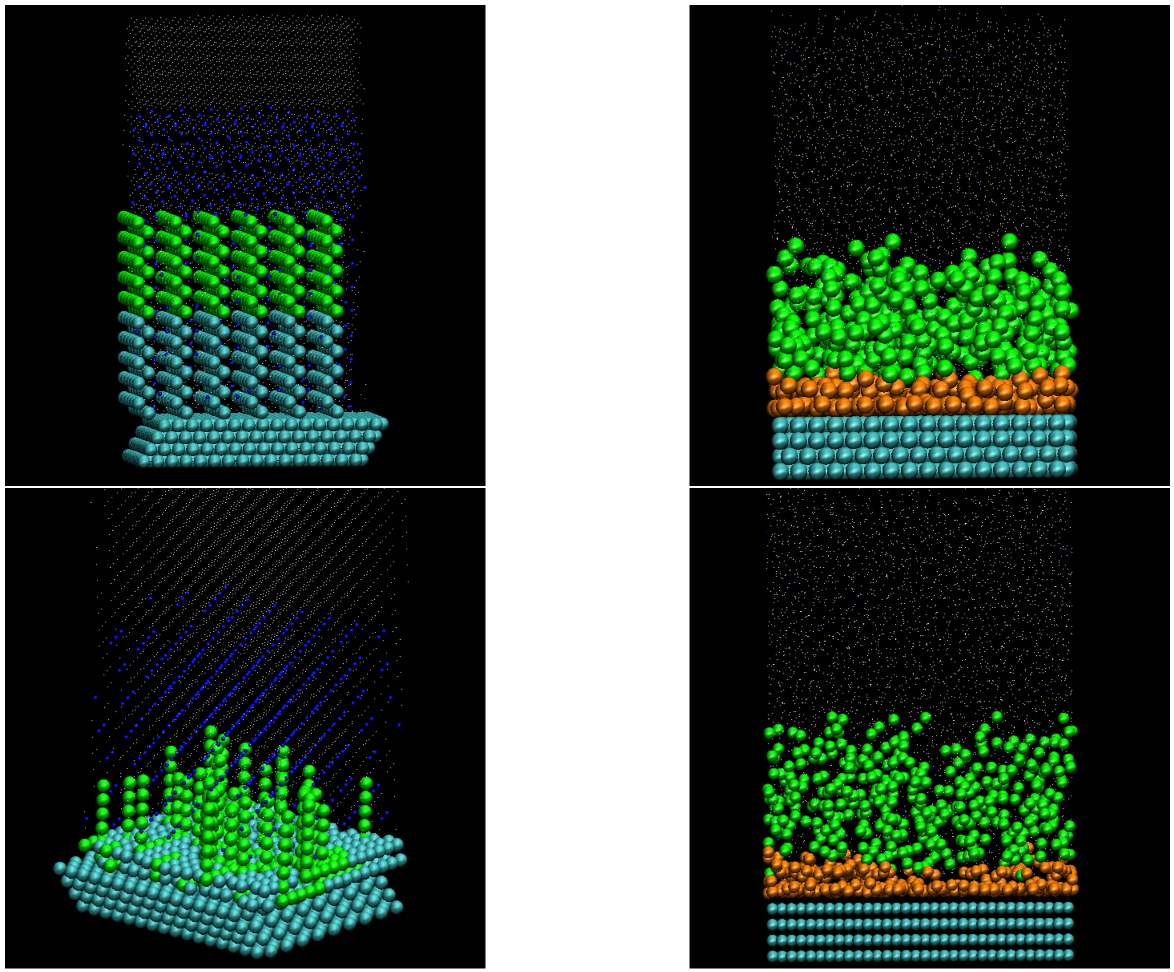
2×10	4×5	5×4	5×4	10×2	20×1

ΔU_{ads}

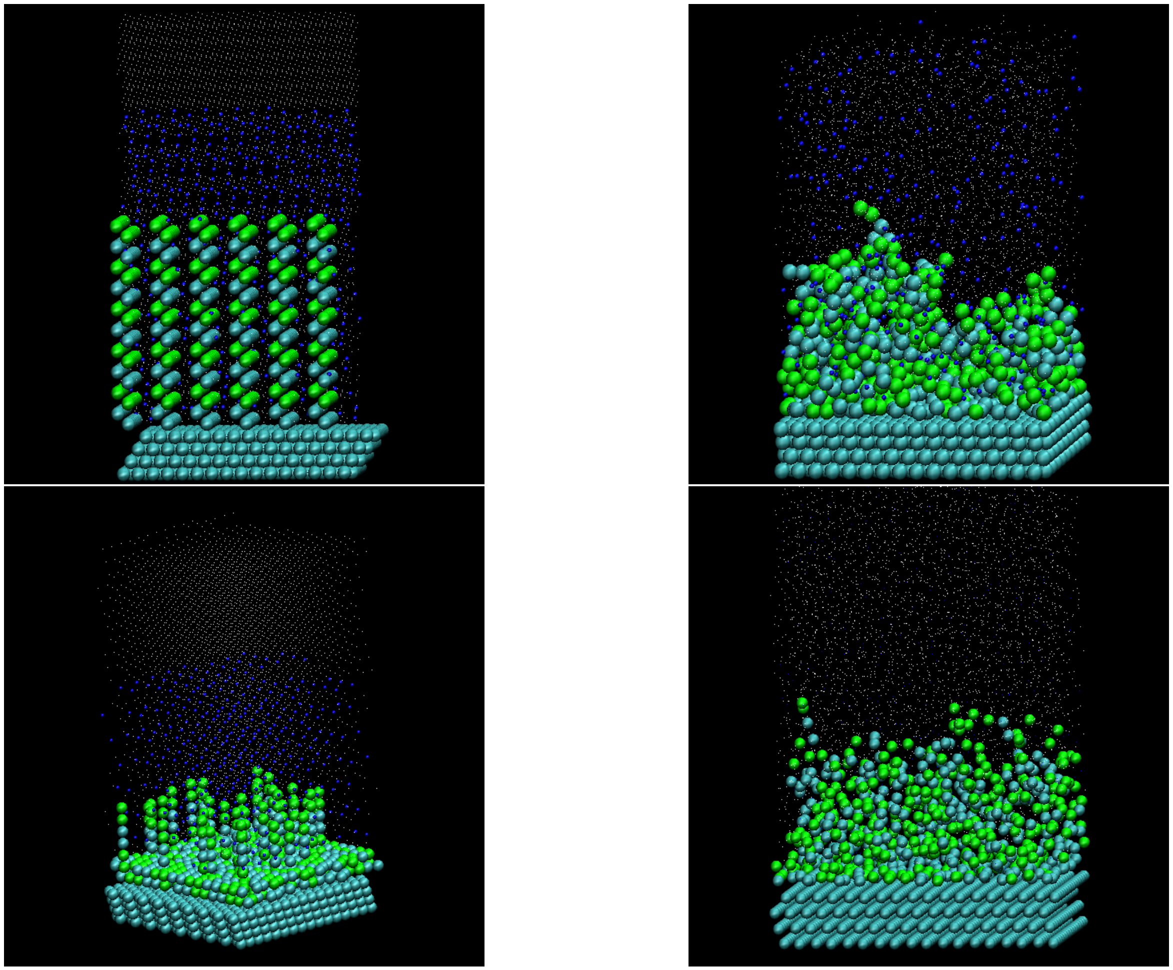
-525	-508	-496	-502	-475	-473

ΔS will enchance this trend !

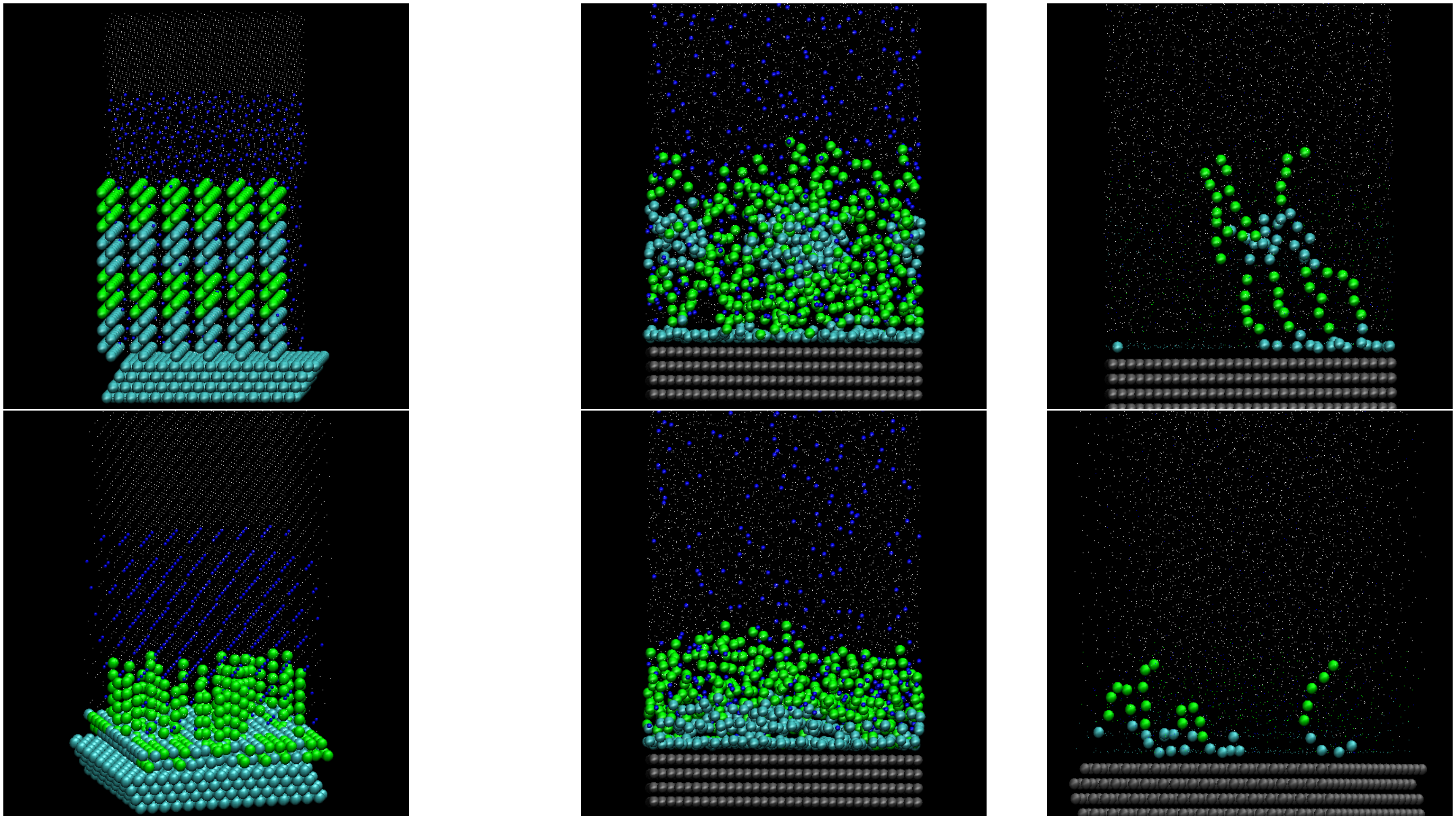
Covered Surfaces, 10-10 BCPs



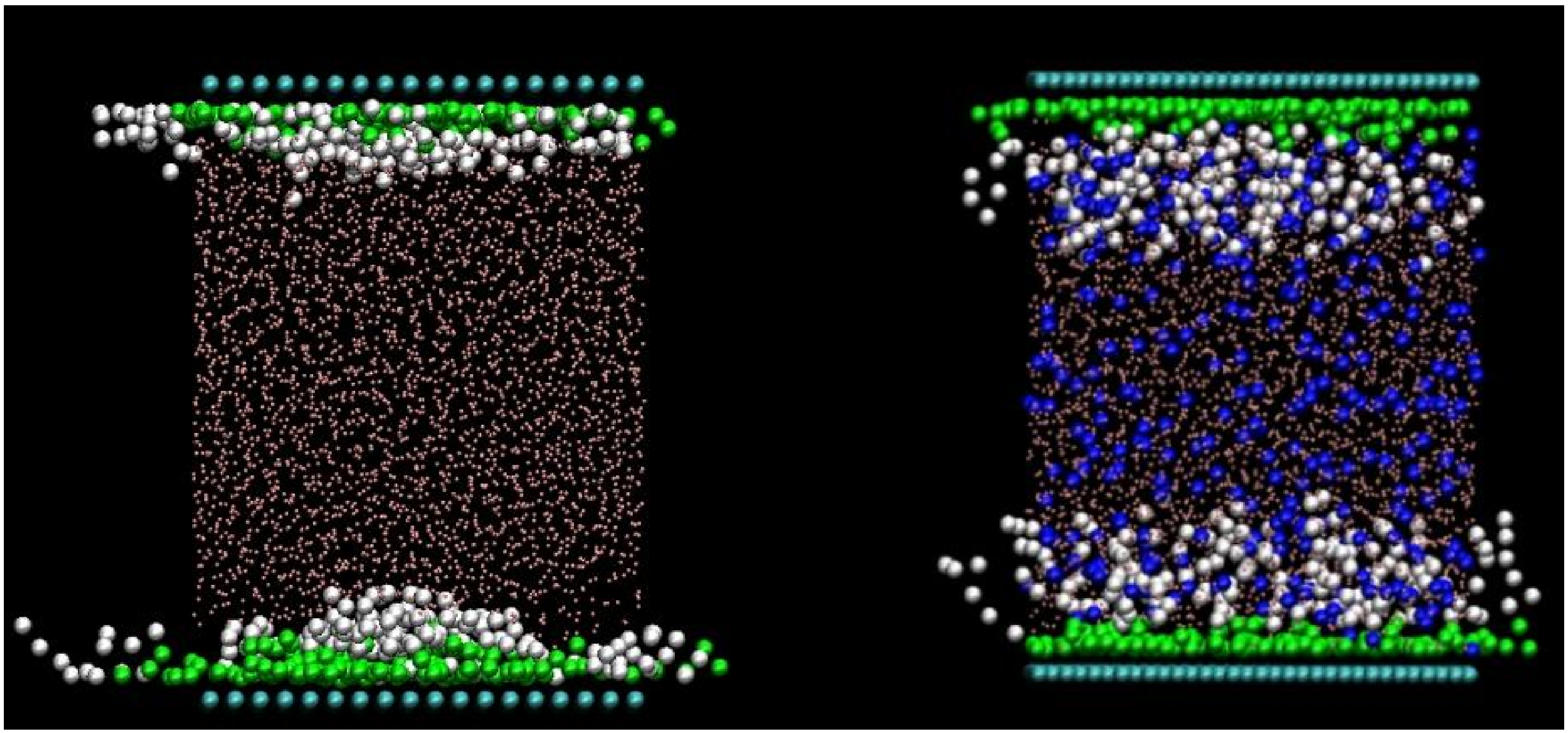
Covered Surfaces, 10×2 CPs



Covered Surfaces, 4×5 CPs



Hydrophilic Monomer: Charged vs Polar



Charge also enhances steric/entropic repulsion.

Conclusions and Outlook

- We can give a semi-quantitive ranking of different polymers with respect to their binding affinity to pigment surfaces.

- To confirm our results we need to use meso-scale methods.

- We develop a coarse grained model for our materials to assess longer time-scales and system size effects.