Multiscale modelling of surfaces and interfaces

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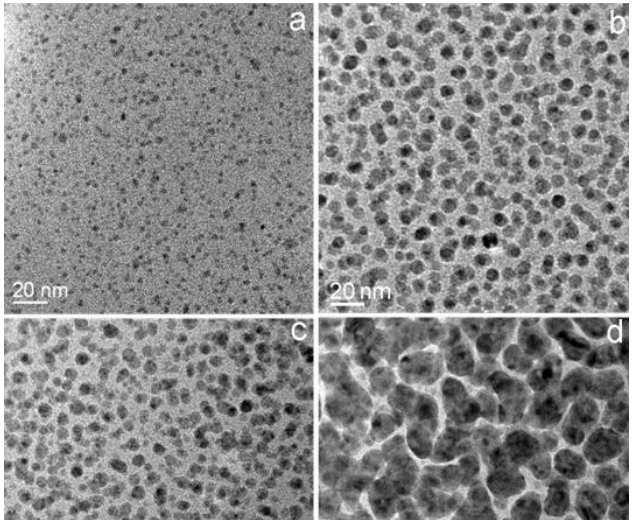
Surfaces and Interfaces

Two examples

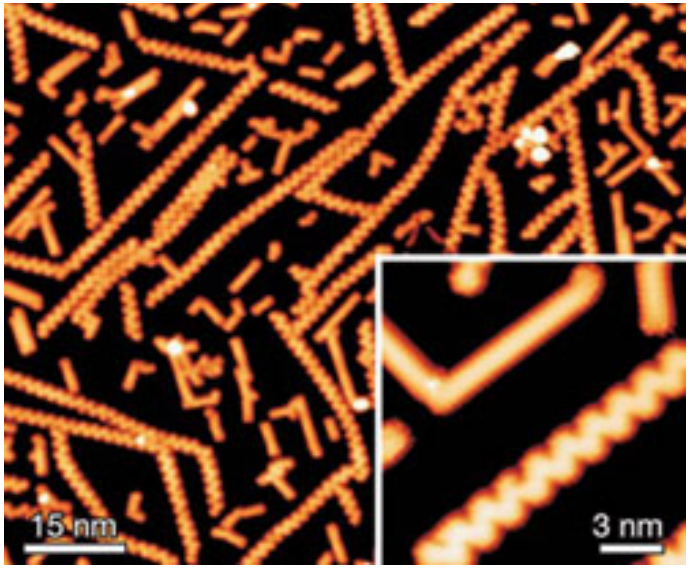
1) Polymer nanocomposites

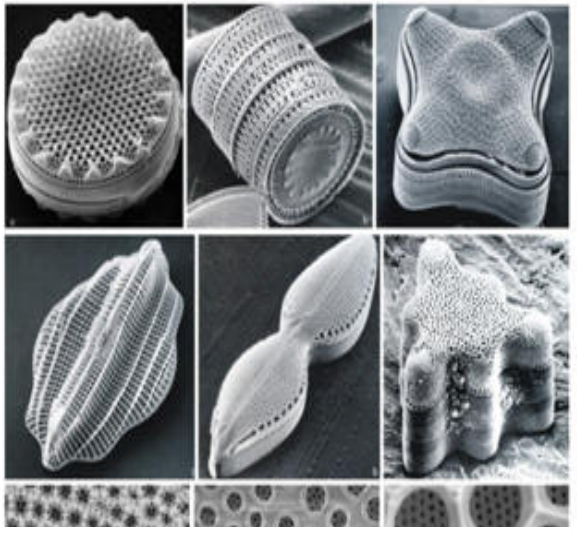
2) Self-assembled monolayers



Ag/Nylon composites
www.tf.uni-kiel.de/matwis/matv/img/fpnc1.jpg

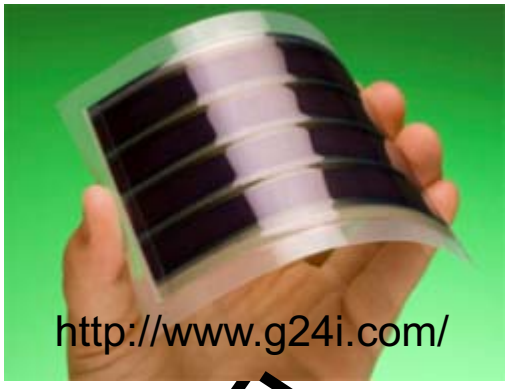
Graphene nanoribbons
Cai et al. Nature **466**, 470 (2010)

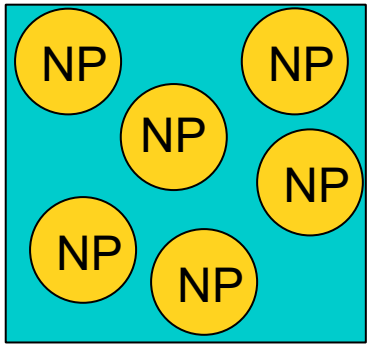




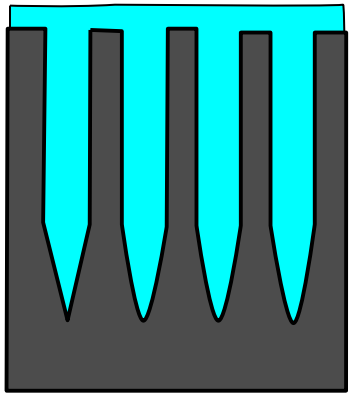
Biomineralisation
ww2.chemistry.gatech.edu/~kroeger/Kroeger/biomineralization.html

1) Polymer nanocomposites

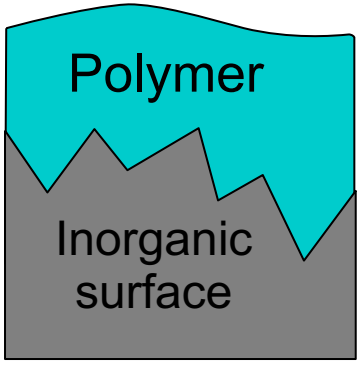




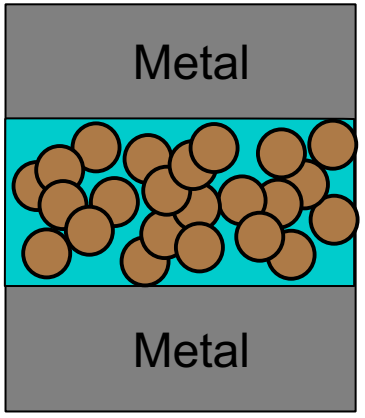
Biosensors
Drug delivery



Li-polymer batteries



Flexible electronics
Biomedical implants



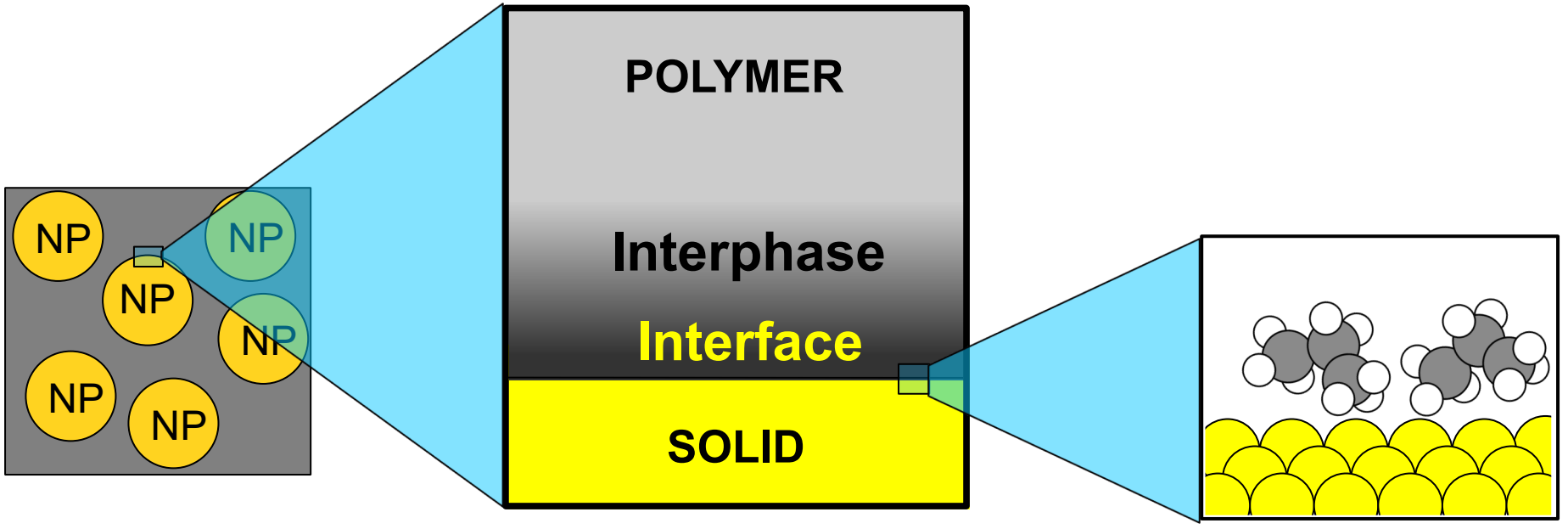
Dye-sensitized solar cells

Properties determined by soft-hard matter interfaces
Challenging for simulation and experiment

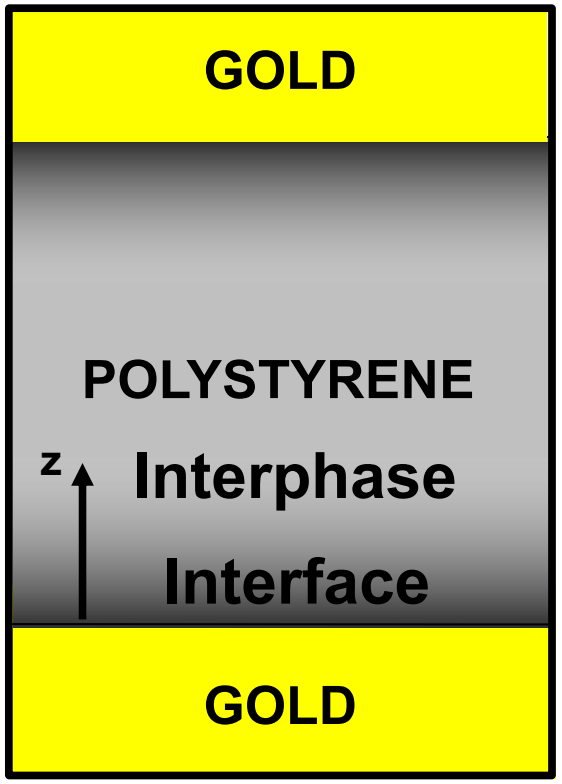
Key Questions

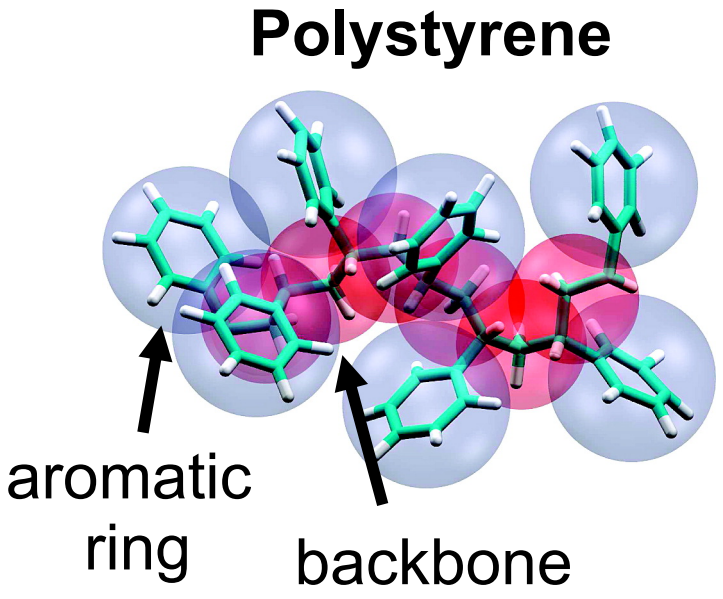
How does the surface affect the polymer
- structure
- dynamics

What is the interphase width?



Polystyrene thin film on Au(111)



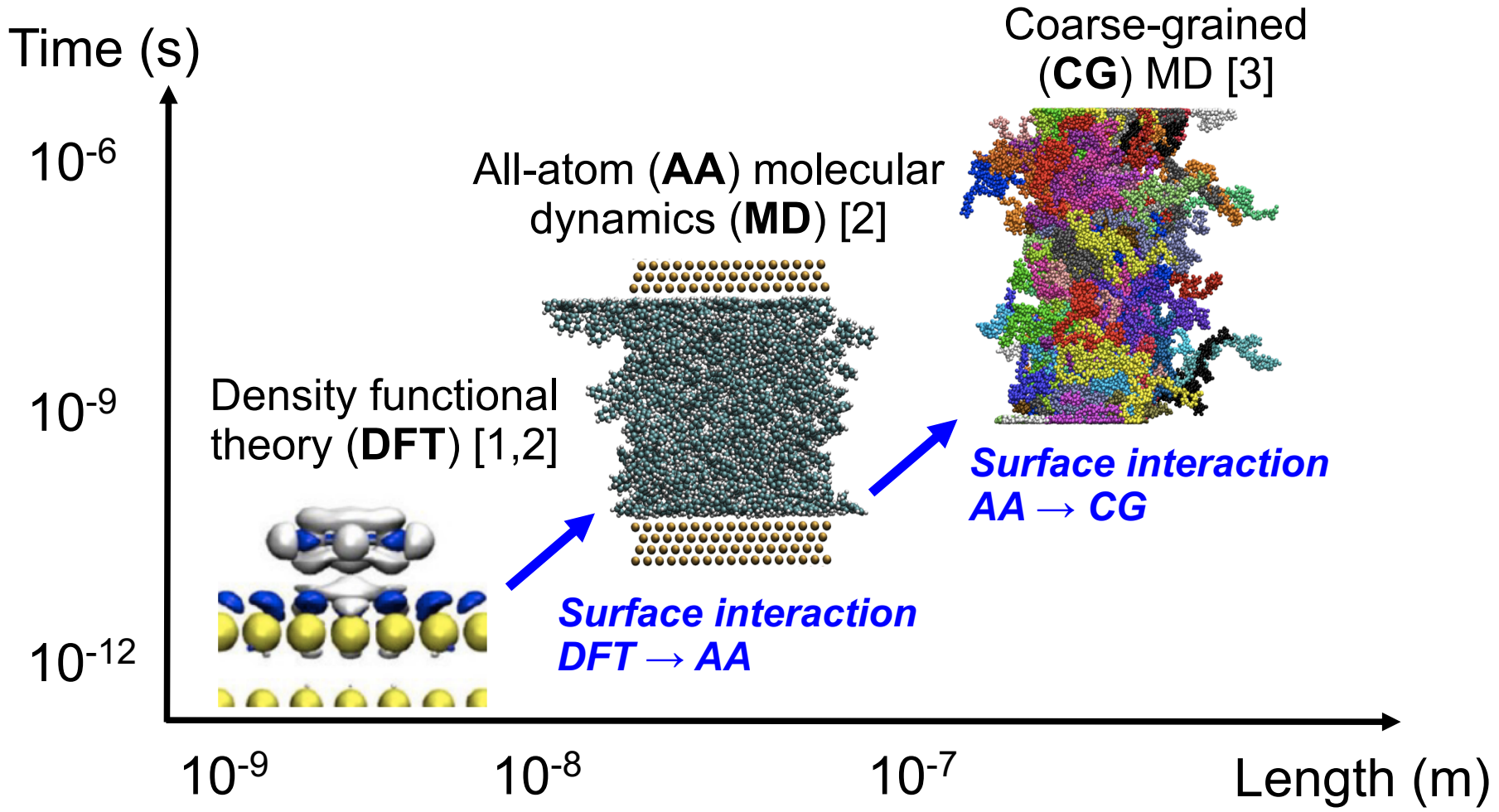


Fritz et al. Macromol. **42** 7579 (2009)

What is the effect of the surface on polymer properties?
What is the interphase width?

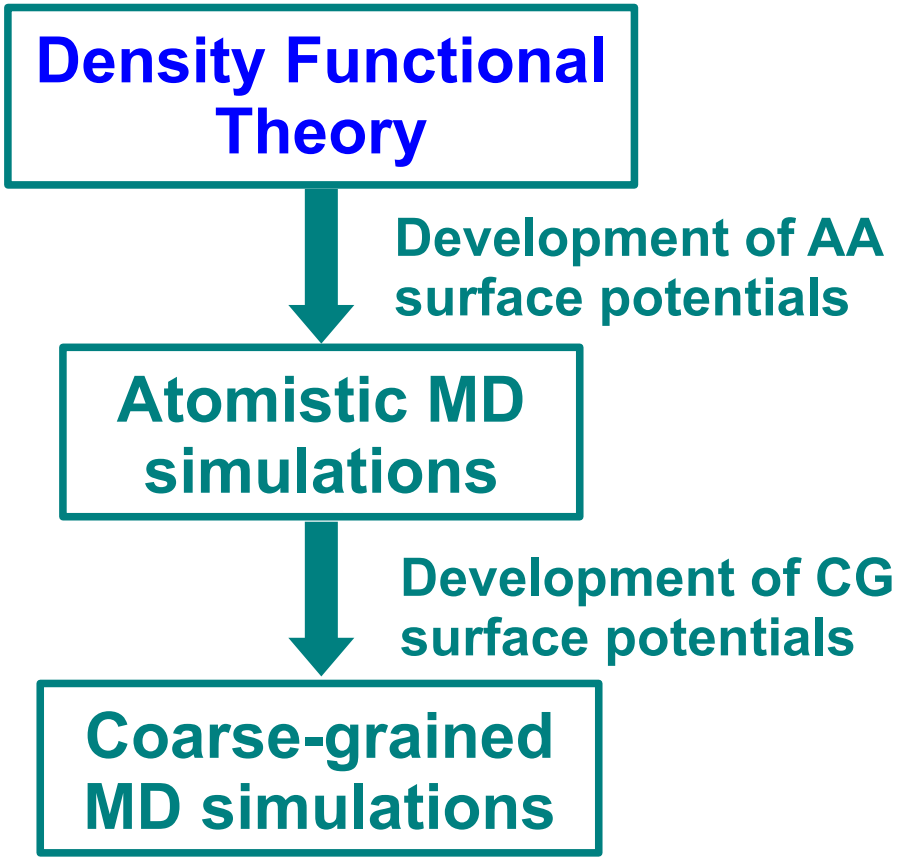
Multiscale modelling - DFT to MD

GOAL: Bridge time and length scales



[1] Johnston, JPCC **115** 14707 (2011)
[2] Johnston, Soft Matter **8** 6320 (2012)
[3] Johnston, Macromolecules **46** 5741 (2013)

Hierarchical multiscale approach



Building block approach

We want accurate polymer-surface interactions but quantum calculations of polymer chain on surface not feasible.

Divide and conquer!

Assumption: polystyrene = benzene + ethane

Polystyrene (PS)

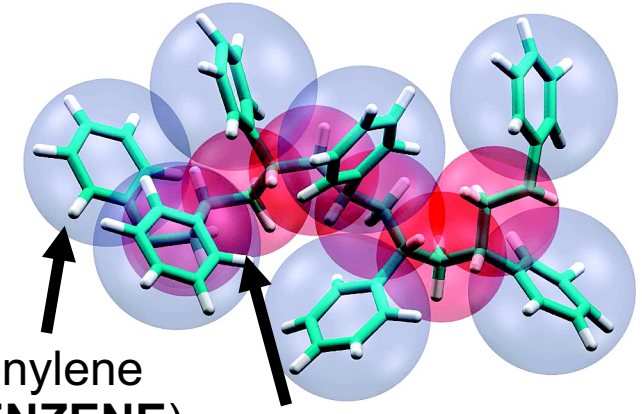
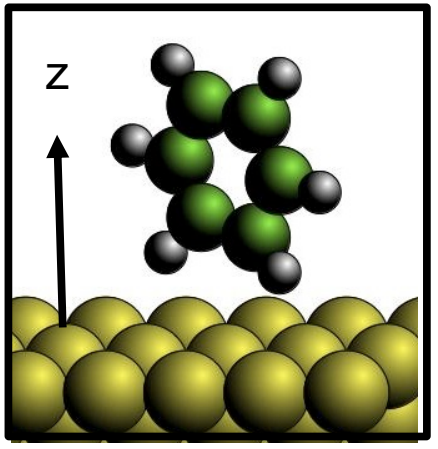


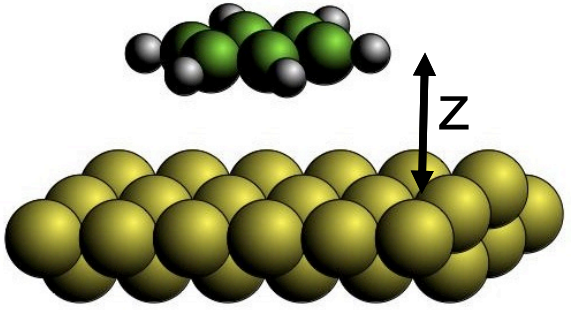
Image from Macromol. **42** 7579 (2009)



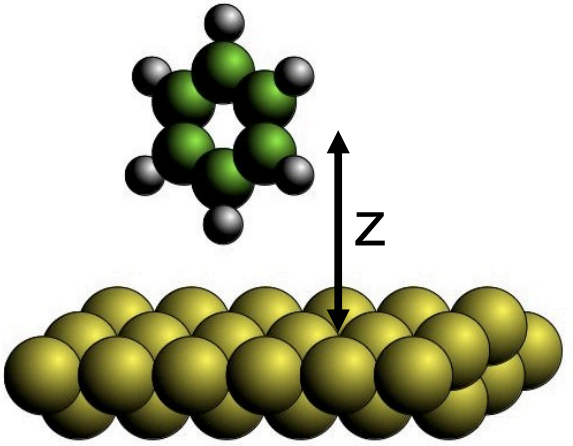
Classical surface interaction should reproduce the **quantum adsorption energy** for a **variety of molecular orientations.**

Density functional theory results

- Customised VASP 4.6 code
- DFT + vdW-DF using PBE exchange [1,2]
- Obtain adsorption energies $E_{\mathrm{ads}}(z)$ for different orientations

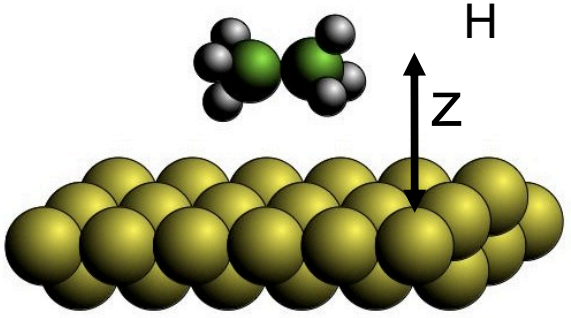


Benzene flat

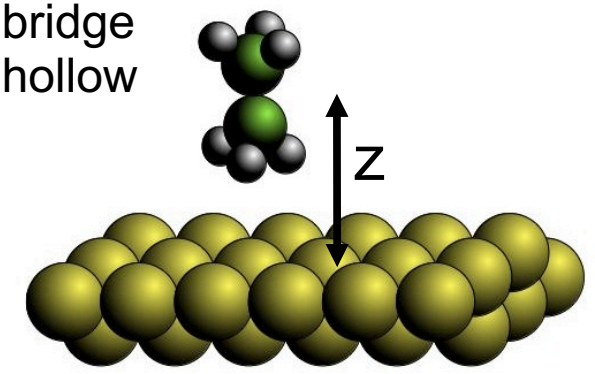


Benzene vertical

Sites:
T top
B bridge
H hollow



Ethane flat



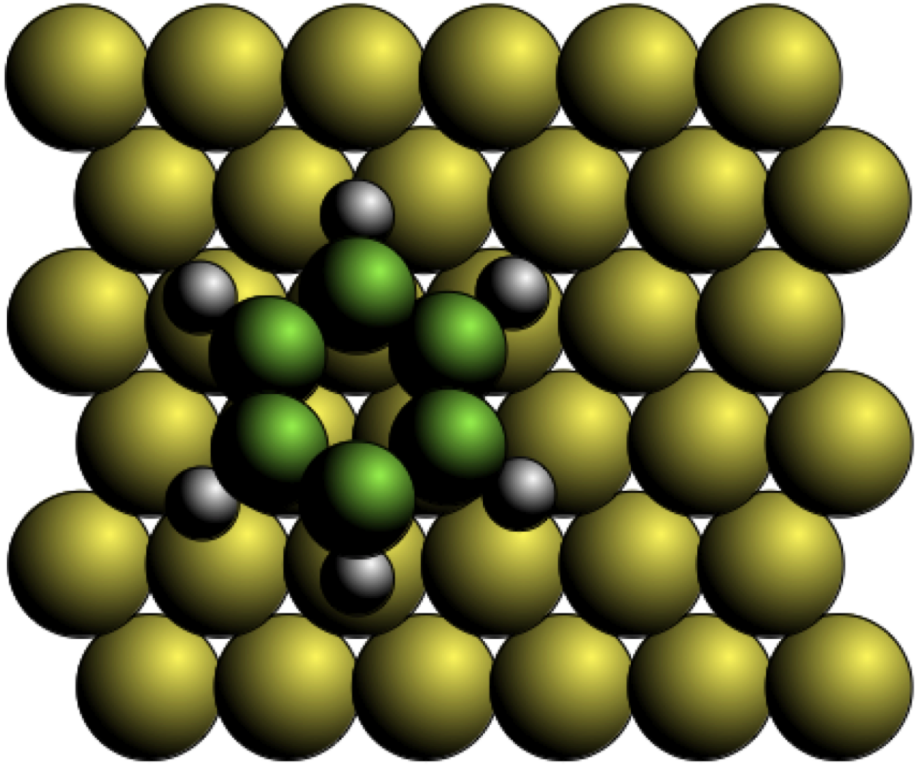
Ethane vertical

[1] Dion PRL **92** (2004)
[2] Gulans PRB **79** (2009)

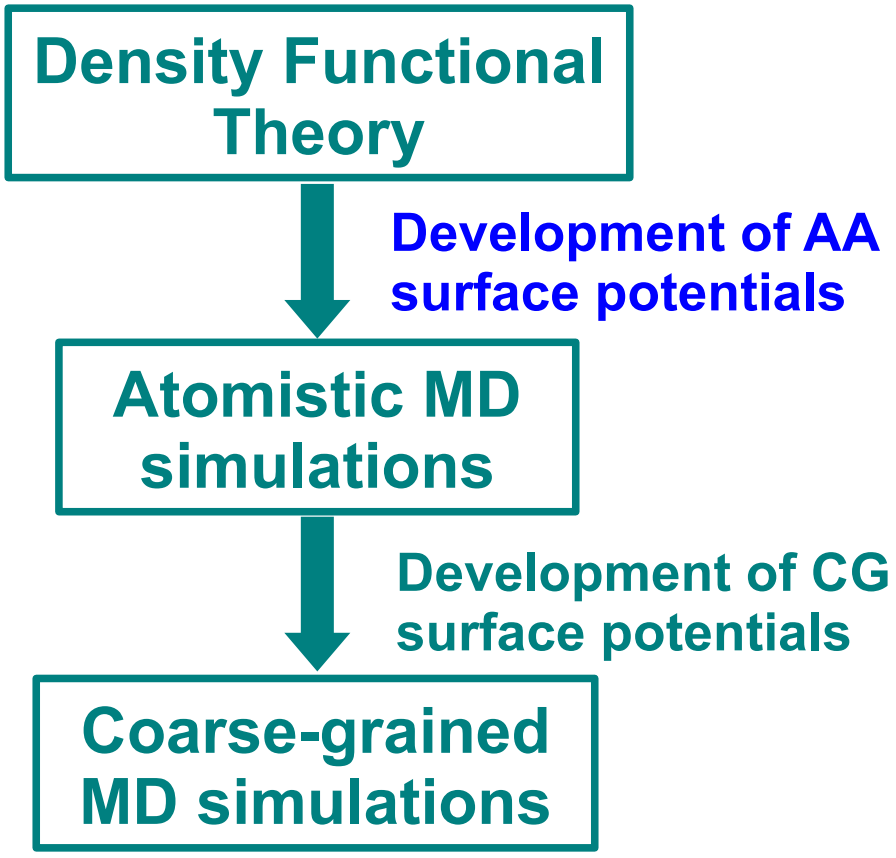
- Ground state configuration of benzene is flat on hollow site
- Weak site dependence
- Adsorption is due to vdW forces
- Ethane adsorbs much more weakly than benzene

$E_{ads,gs}$ (kJ/mol)	
Present [1]	**82.1**
Ref [2]	77.2
DFT+D [3]	73.3
Expt TDS [4]	61.8

[1] Johnston JPCC **115** (2011)
[2] McNellis PRB **80** (2009)
[3] Tonigold JCP **132** (2010)
[4] Syomin JPC 105 (2001)



Hierarchical multiscale approach



Develop AA pair potentials for surface

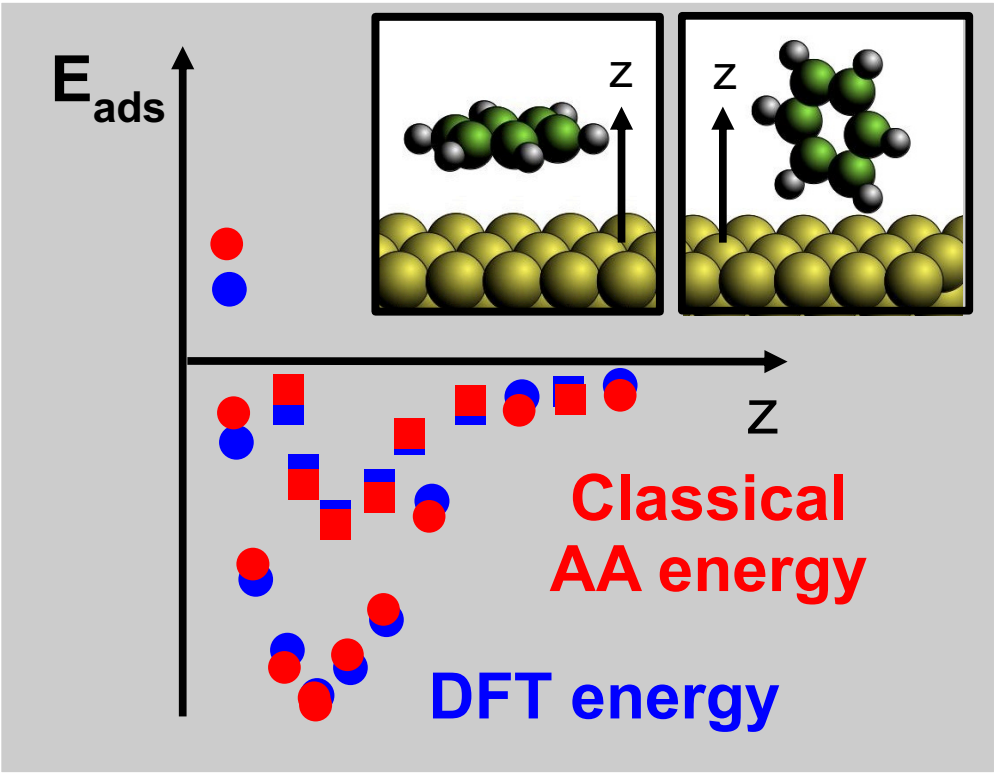
Obtain DFT and AA adsorption energy $E_{\text{ads}}(z)$ for configuration, k

$$E^{\text{AA}}_{\text{ads}\,k} = \sum_{i=1}^{N}\sum_{j=1}^{M} V\left(r_{ij}, \varepsilon_{ij}, \mathrm{r}_{0\,ij} \cdots\right)$$

Adjust pair potential parameters to minimise energy difference between DFT and AA for all configurations:

$$\Delta E = \sum_{k} w_k \left(E^{\text{AA}}_{\text{ads}\,k} - E^{\text{DFT}}_{\text{ads}\,k}\right)^2$$

Repeat for all "building blocks" e.g. ethane



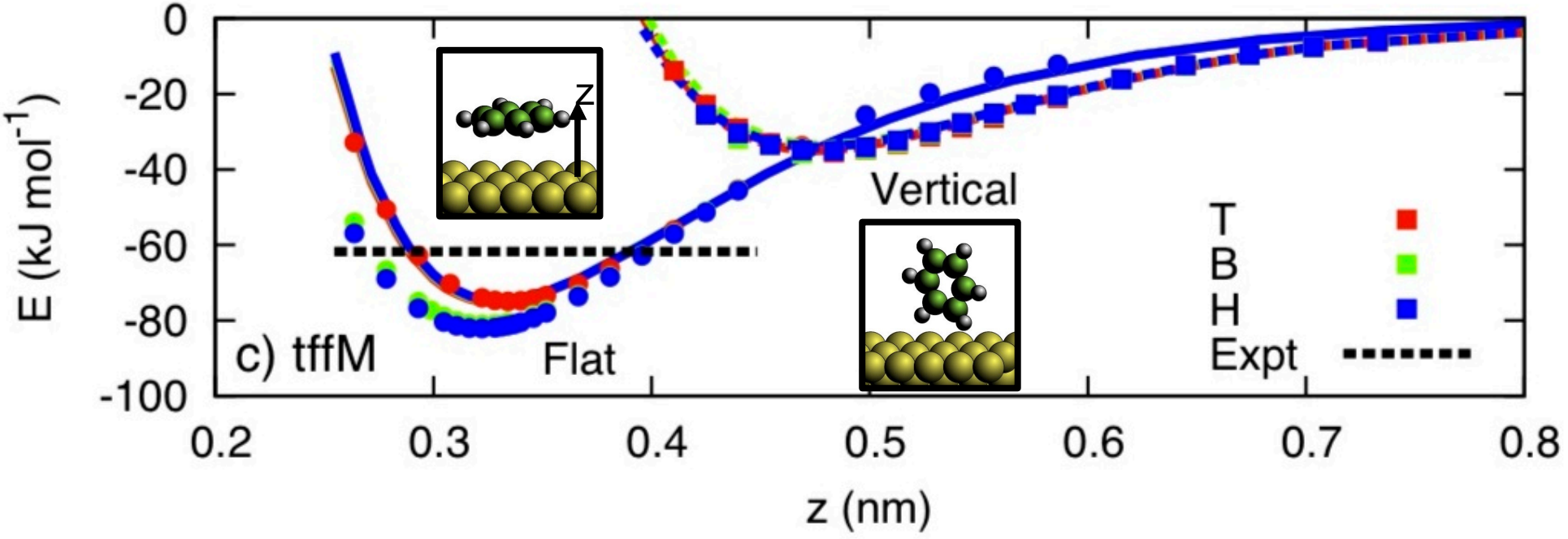
$V(r_{ij})$ is classical AA pair potential
e.g. LJ or Morse
N molecule and M surface atoms
k configuration (orientation, distance)

AA potentials for benzene on Au

Morse potential for benzene/Au

2 atom pairs, C-Au, H-Au → 6 parameters

$$V_{\mathrm{M}}\left(r_{ij}\right)=\varepsilon_{ij}\left[\exp\left(-2\alpha_{ij}\left(r_{ij}-r_{0\,ij}\right)\right)-2\exp\left(-\alpha_{ij}\left(r_{ij}-r_{0\,ij}\right)\right)\right]$$

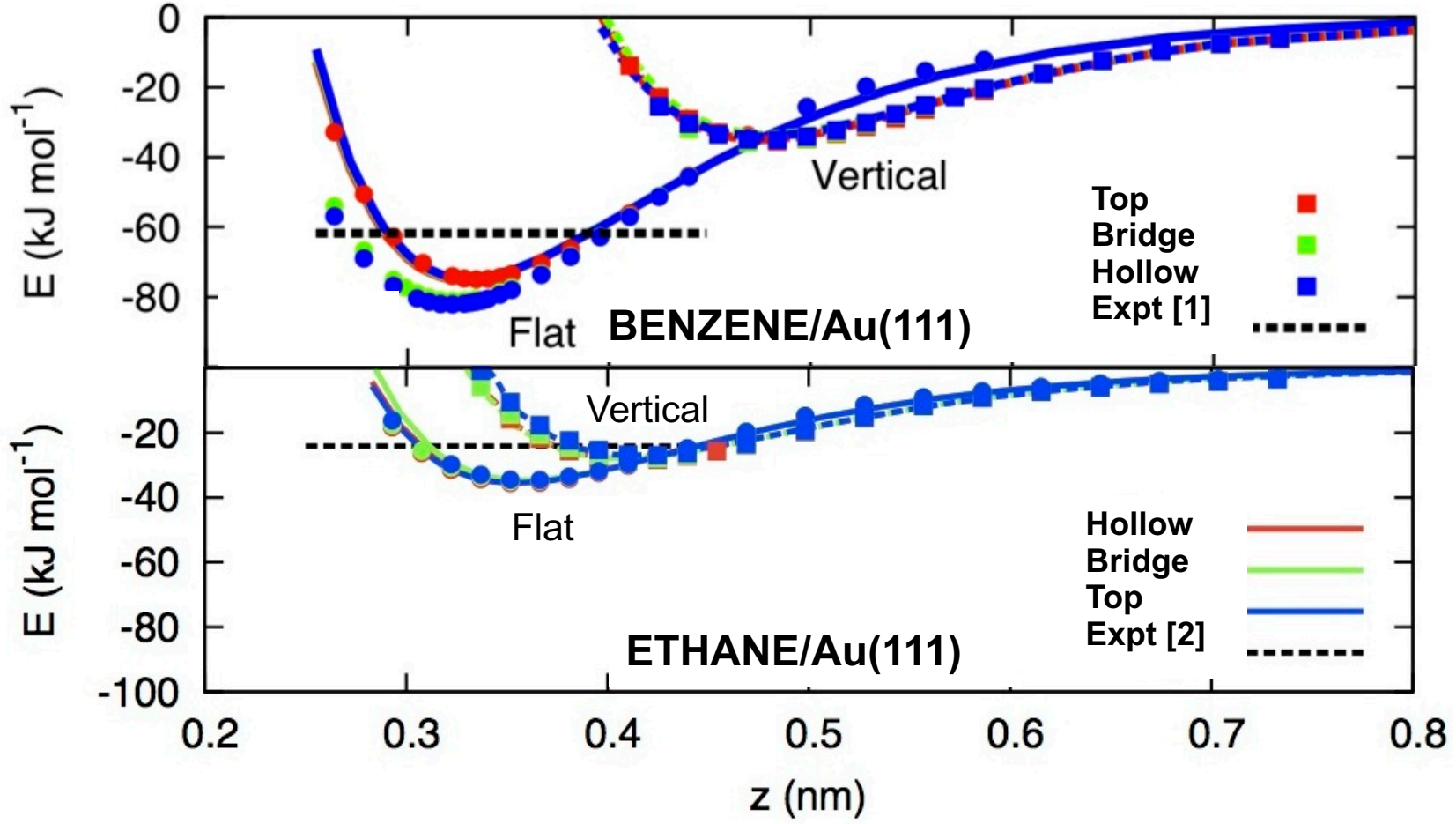


Morse potential is good fit for both flat and vertical orientations

Does not describe site dependence but this is a small effect

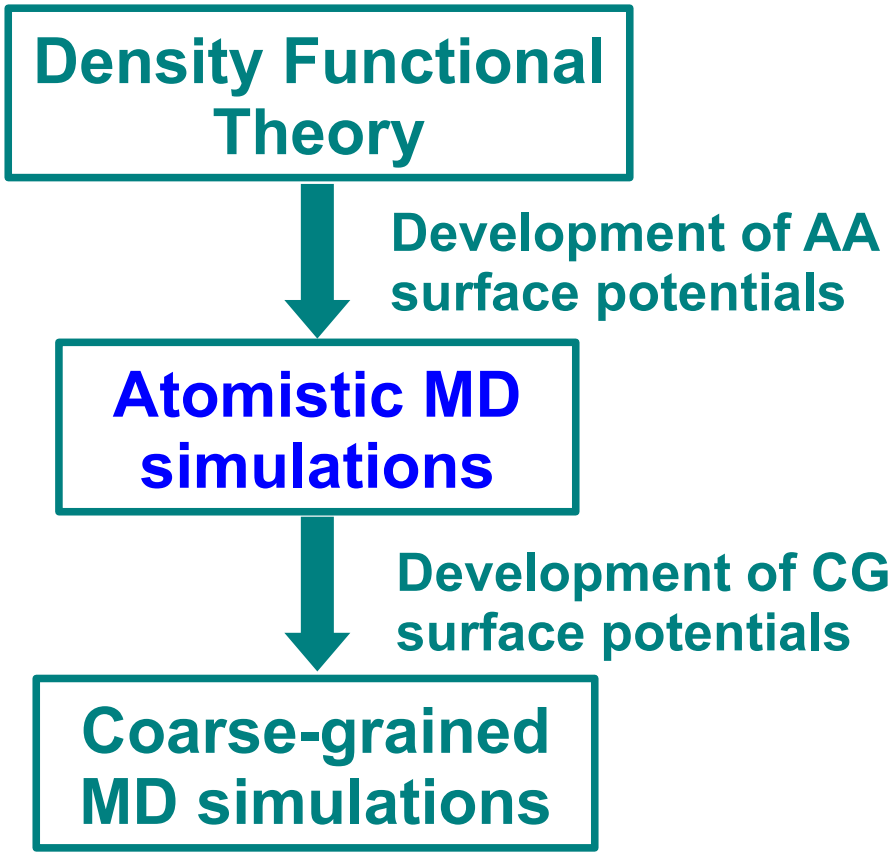
Morse potentials for benzene and ethane

Benzene more strongly adsorbed than ethane



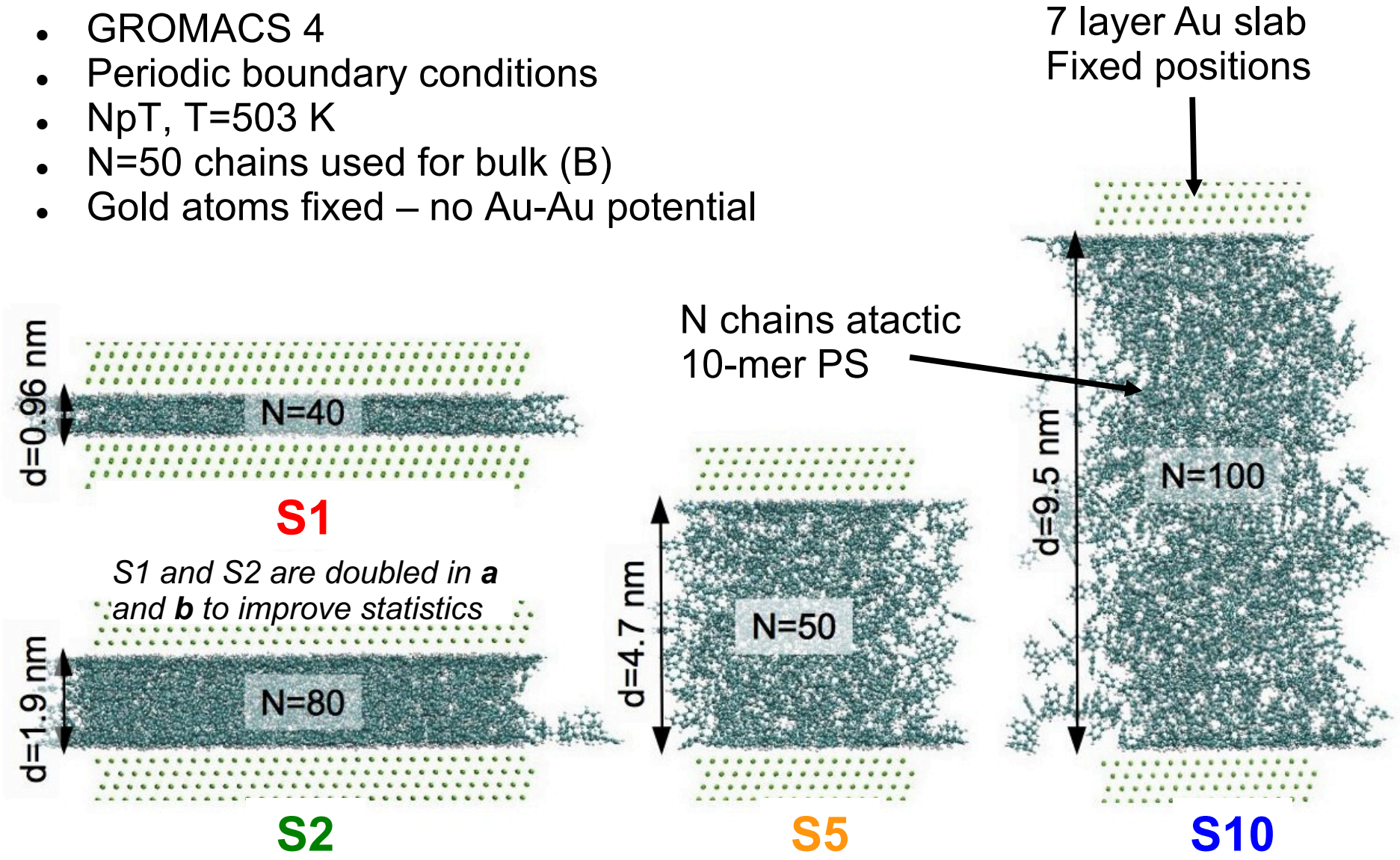
[1] Syomin JPC **105** (2001)
[2] Wetterer JPCB **102** (1998)
[3] Johnston JPCC **115** (2011)
[4] Johnston SM **8** (2012)

Hierarchical multiscale approach

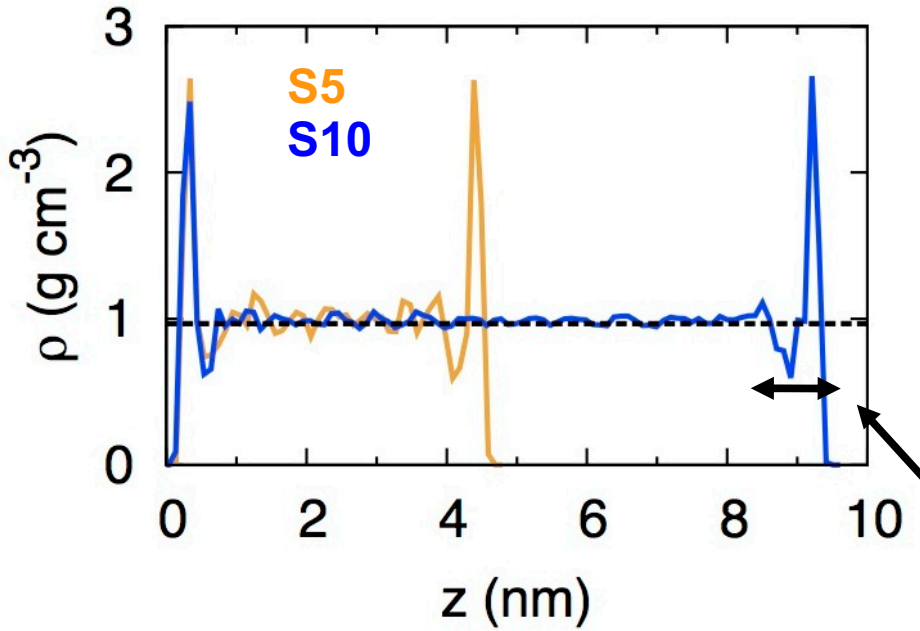


Classical atomistic molecular dynamics

- GROMACS 4
- Periodic boundary conditions
- NpT, T=503 K
- N=50 chains used for bulk (B)
- Gold atoms fixed – no Au-Au potential

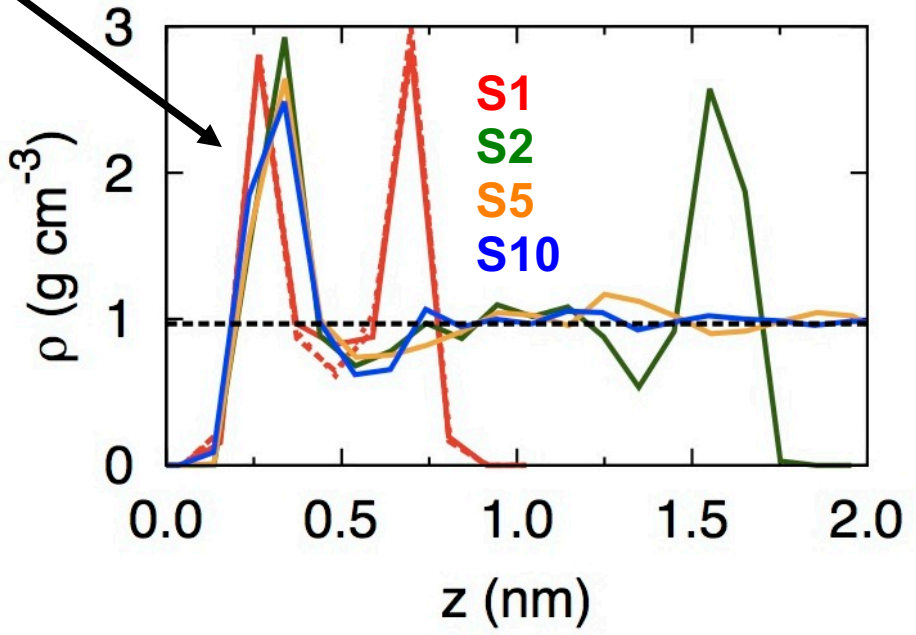


Density profiles



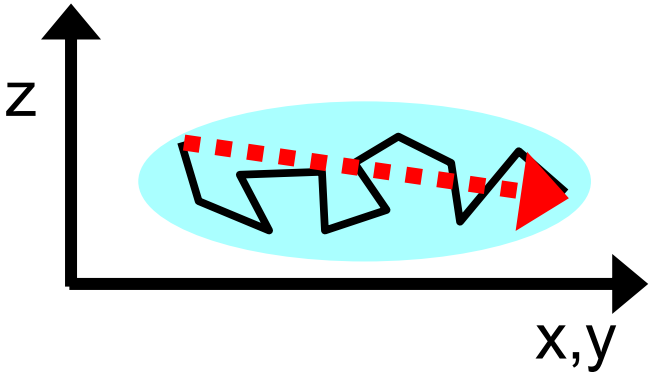
Film reaches bulk density ≈1.5 nm from surface

Single peak at surface (adsorption layer)



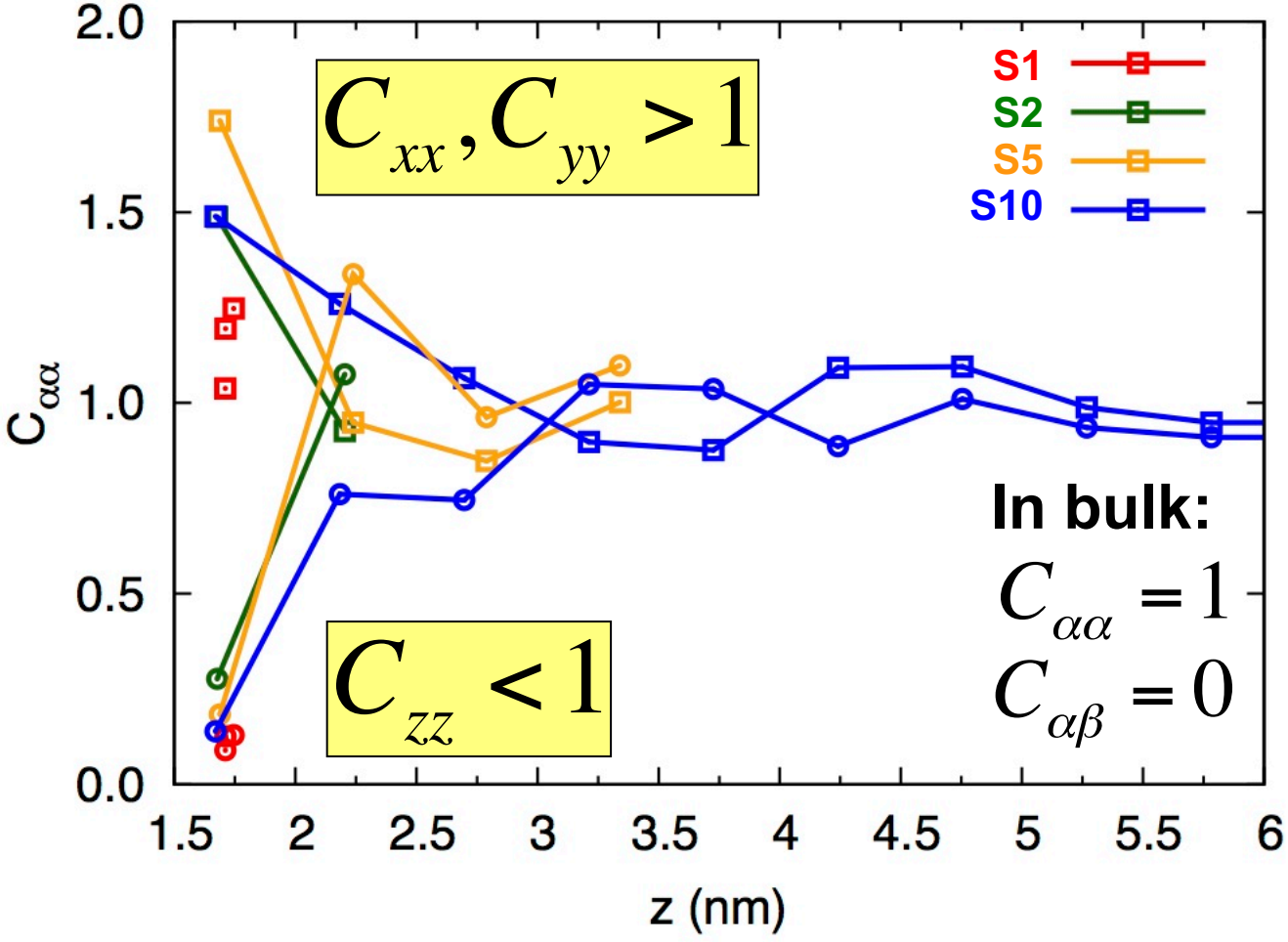
Structure - chain conformation

$\boldsymbol{R}_e$ = end-to-end vector



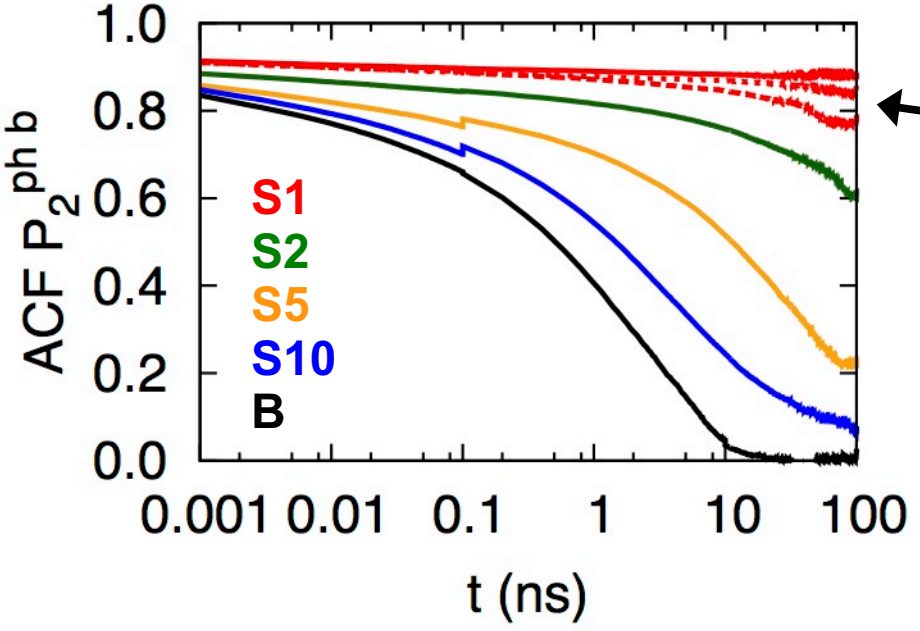
Conformation tensor:

$$C_{\alpha\beta} = 3\left\langle \frac{R_{e\,\alpha}.R_{e\,\beta}}{\left\langle R_e^2 \right\rangle_{bulk}} \right\rangle$$



- Near surface, tensor components are:
  - extended in x and y
  - compressed in z
- Chains oriented parallel to surface

Time autocorrelation function



S1 films almost frozen

Confinement increases time to decorrelate

Small discontinuity is a result of separate analysis over short and long time scales.

K. Johnston and V. Harmandaris
Soft Matter 8 6320 - 6332 (2012)

Comparison with experiment

Positron Annihilation Lifetime Spectroscopy (PALS)

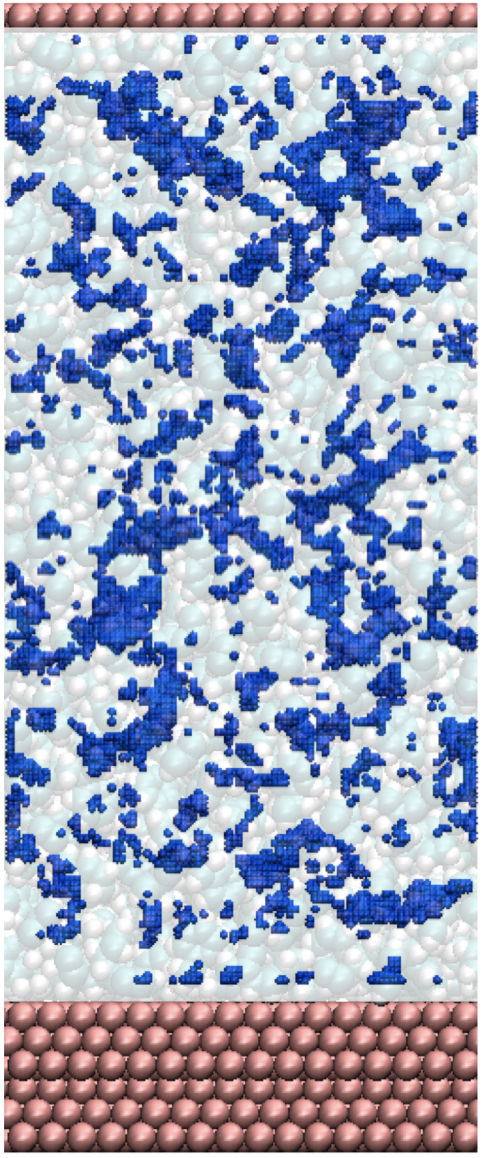
- Positron lifetimes measure the free volume
- **Similar system**: 18-mer PS on Au(111)
- Observed a **decrease in positron lifetime** for PS near Au surface, corresponding to an **increase in density**
- PALS estimate an interphase ~ 10 nm

A free volume analysis of the simulations show that the free volume in the bulk is higher than the free volume in the film.

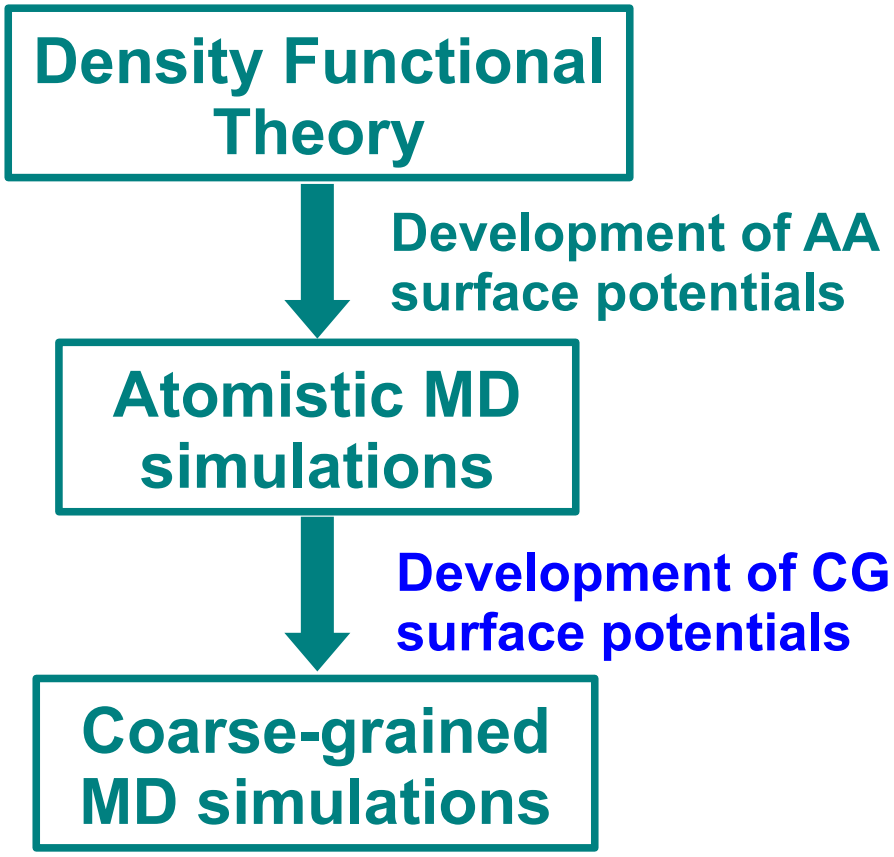
Qualitative agreement between simulation and experiment.

[Butt *et al*, Macromol**. 47** 8459 (2014)]

Free volume in 10 nm PS film



Hierarchical multiscale approach



CG Model for Polystyrene

Model developed by Fritz *et al* Macromol. **42** 7579 (2009)

Each monomer represented by 2 beads

Explicitly accounts for **tacticity** of chain

Reproduces well the density and chain conformations for the polystyrene melt.

Polystyrene (PS)

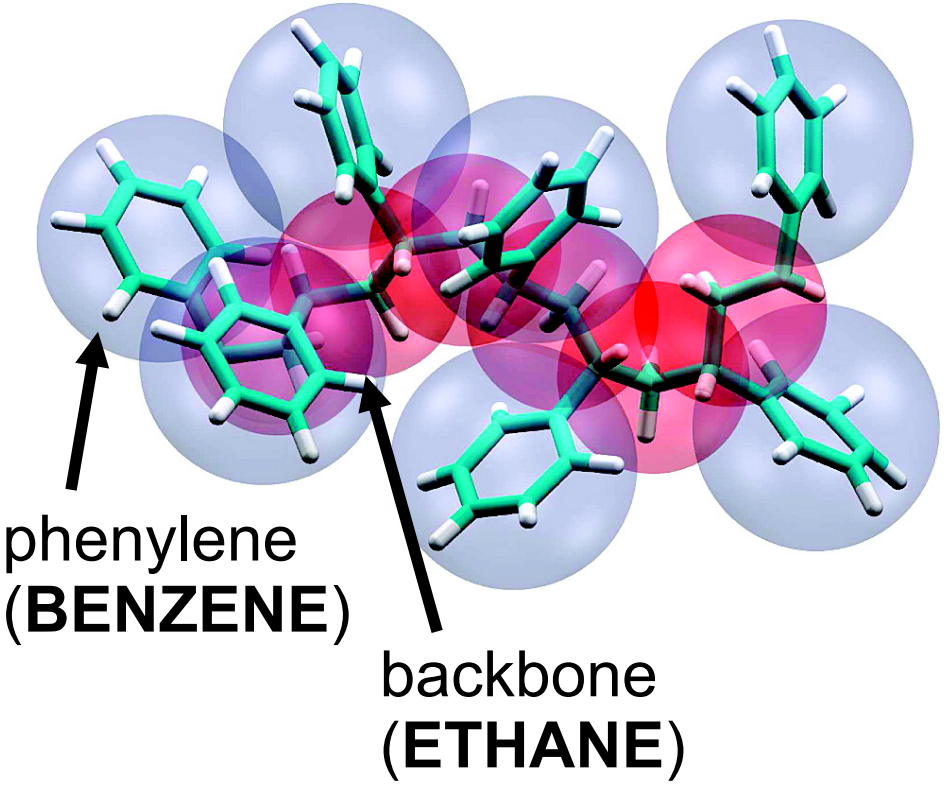
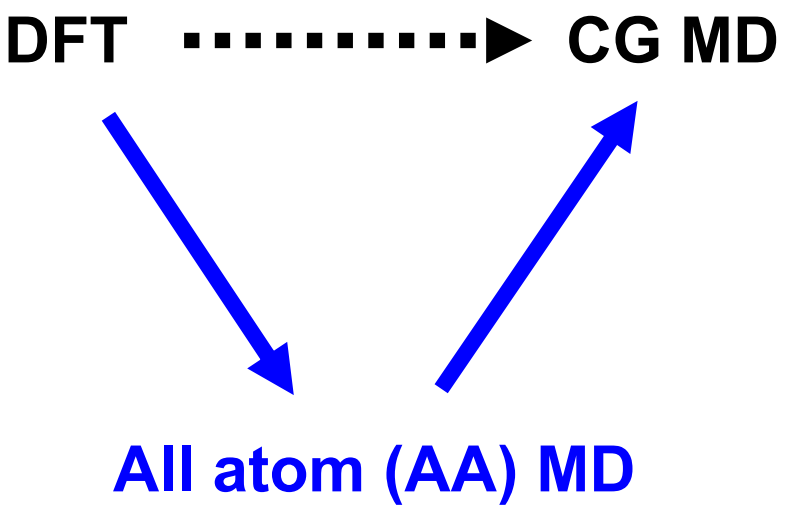
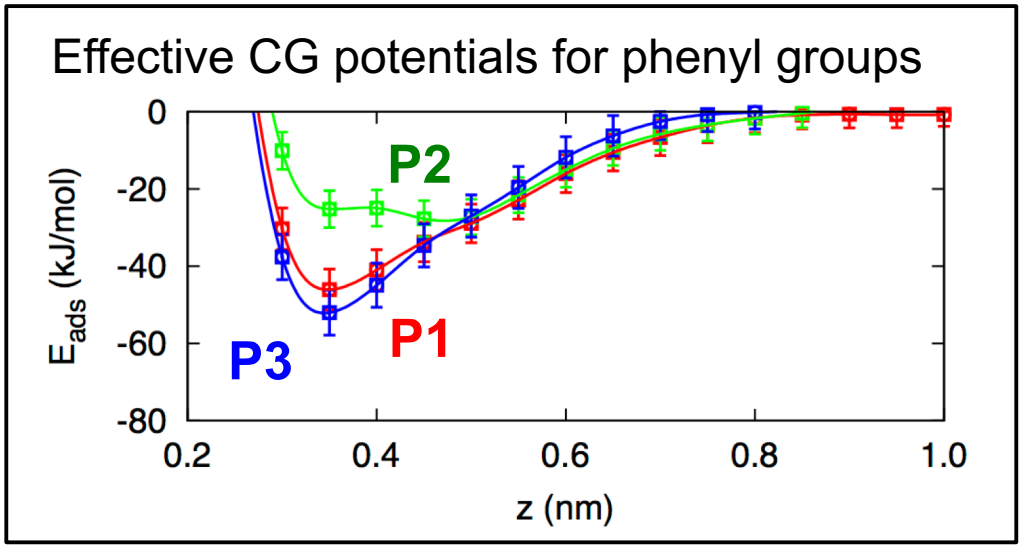
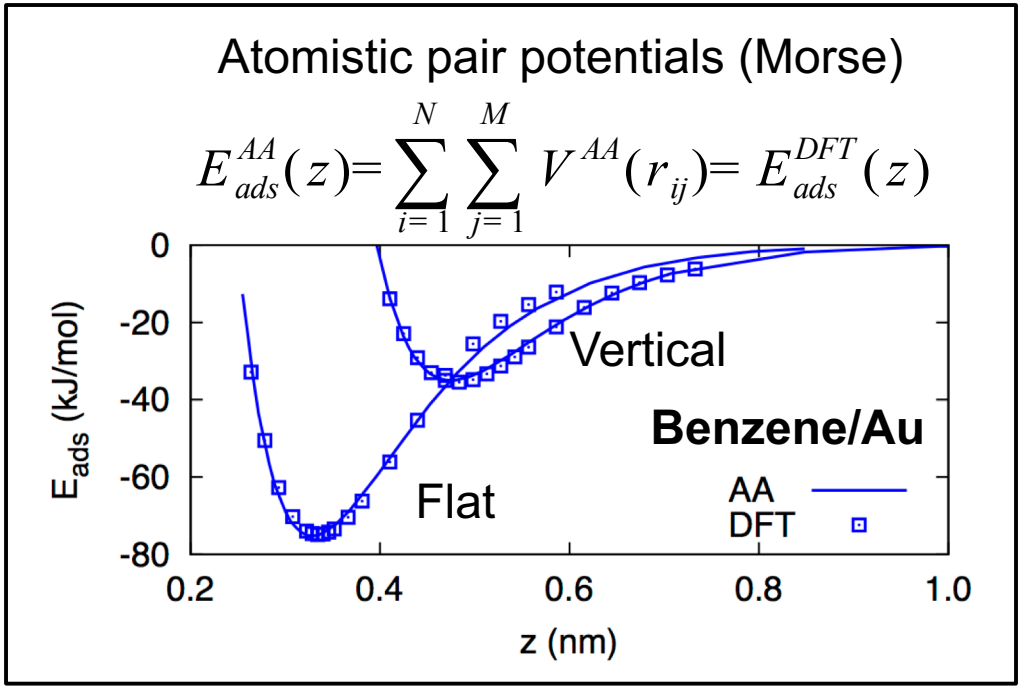


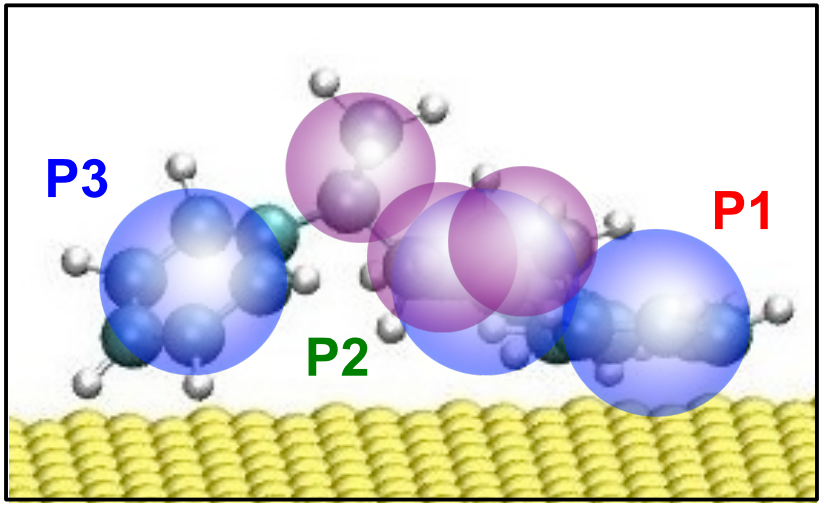
Image from Macromol. **42** 7579 (2009)

Development of CG surface potentials



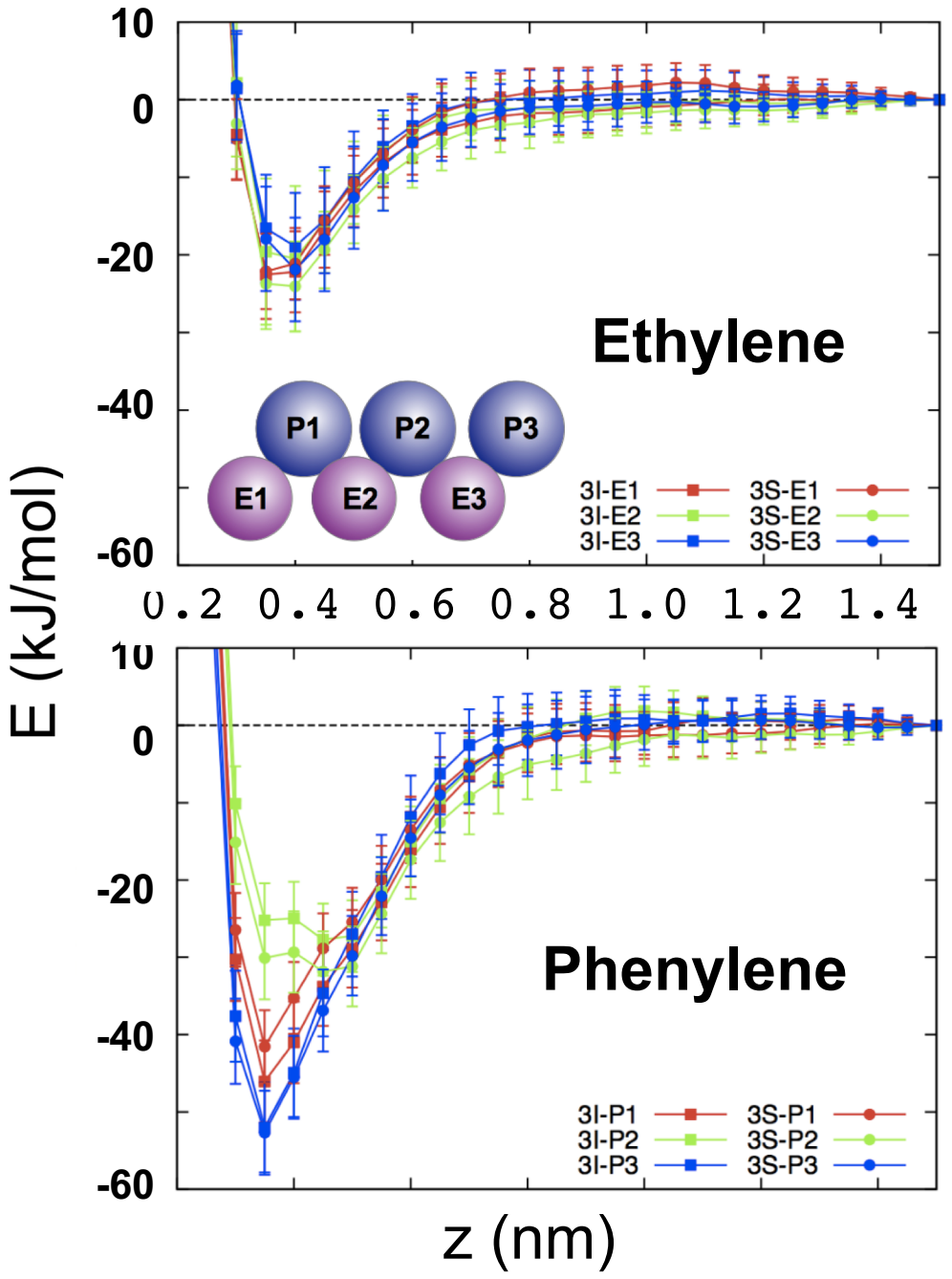






AA MD constraint dynamics of short chain on surface

Effective potentials



Calculated for:

- iso- and syndiotactic chains
- bead positions along chain

Phenylene beads

- exhibit stronger interaction than backbone
- end beads more attractive than central beads

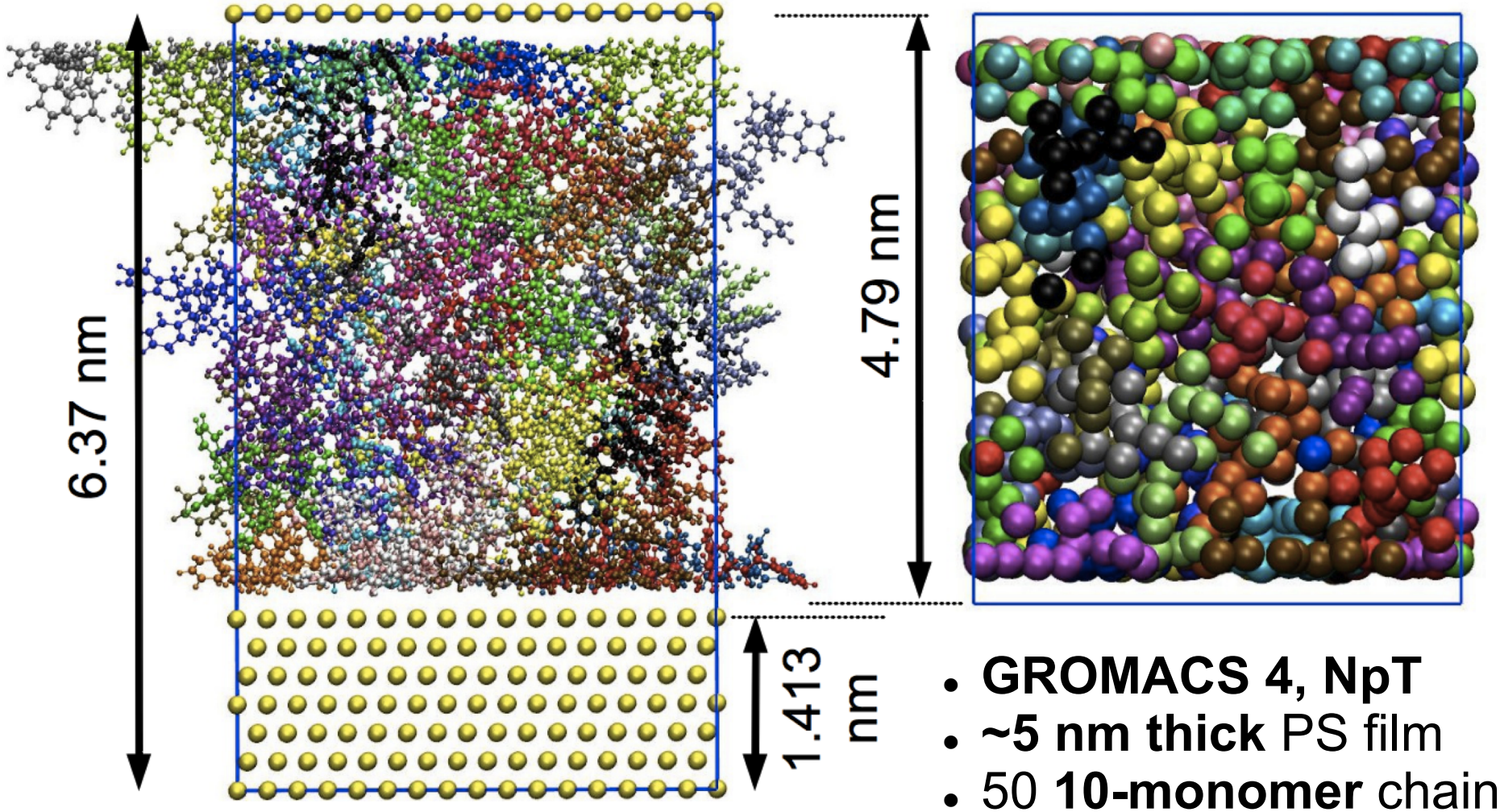
Backbone (ethylene) beads

- no strong position dependence

Tacticity has only a weak influence

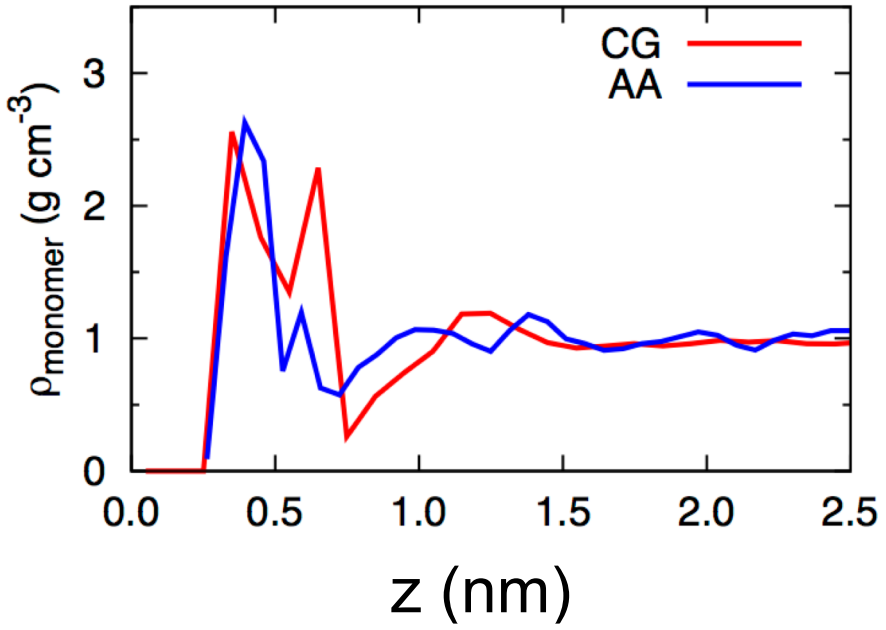
Validation of CG potentials

Compare AA and CG results



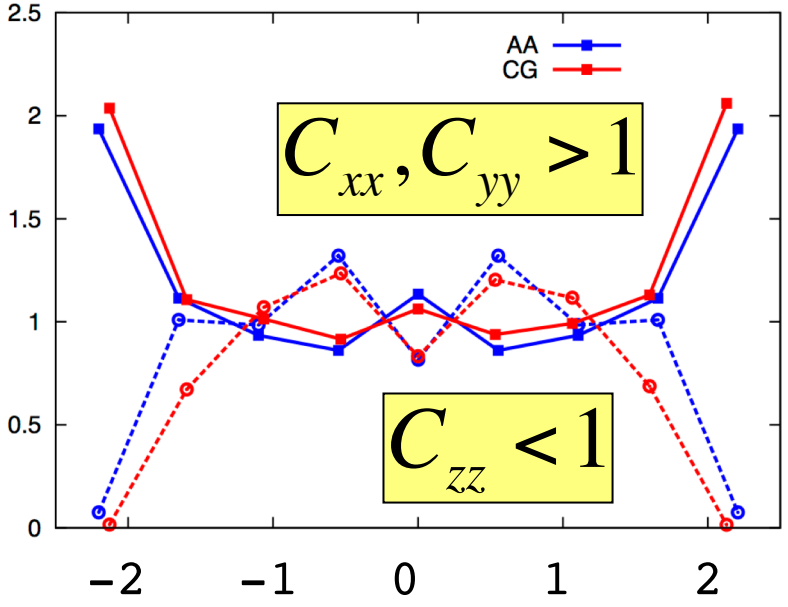
- **GROMACS 4, NpT**
- **~5 nm thick** PS film
- 50 **10-monomer** chains

Structural properties



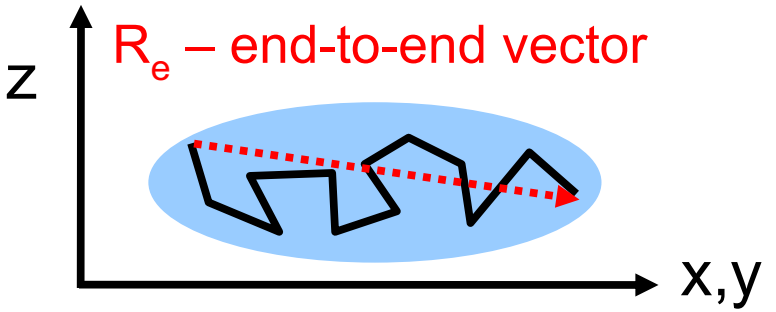
Bead density

- First density peak in good agreement with AA results
- Unlike AA, CG has high second peak, due to central P beads
- Discrepancy due to spherical approximation

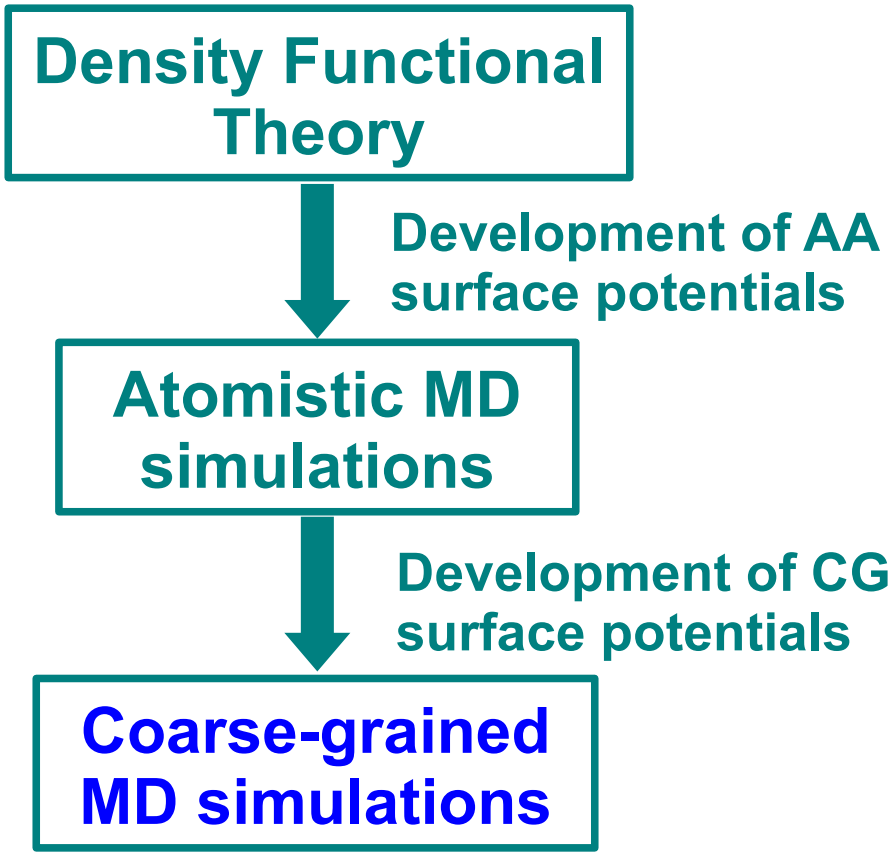


Conformation tensor

- Chains orient along the surface
- Excellent agreement between AA (symmetrized) and CG results



Hierarchical multiscale approach



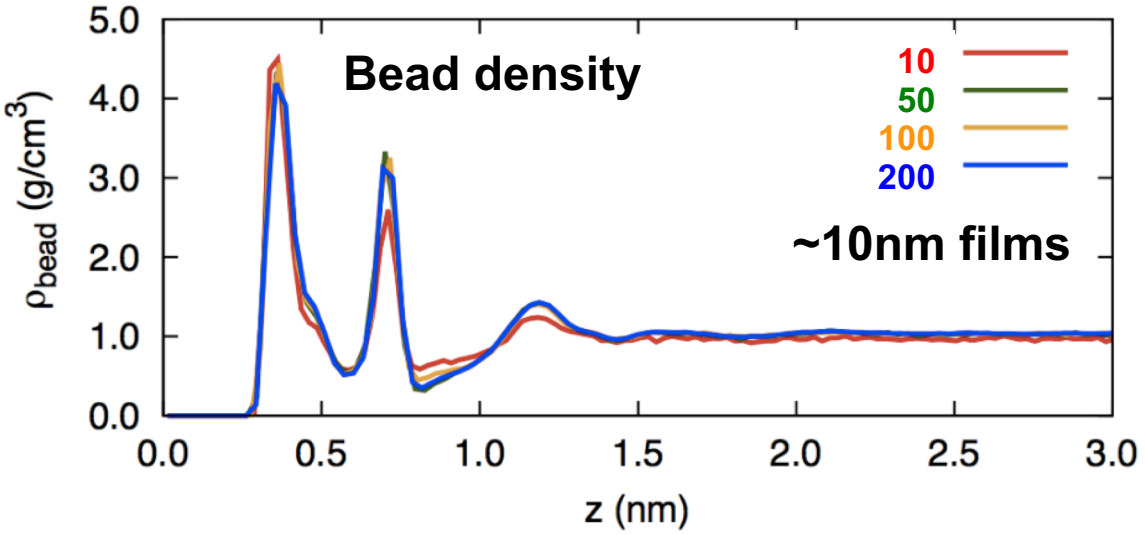
Long chain polystyrene films

For **10 monomer** chains the

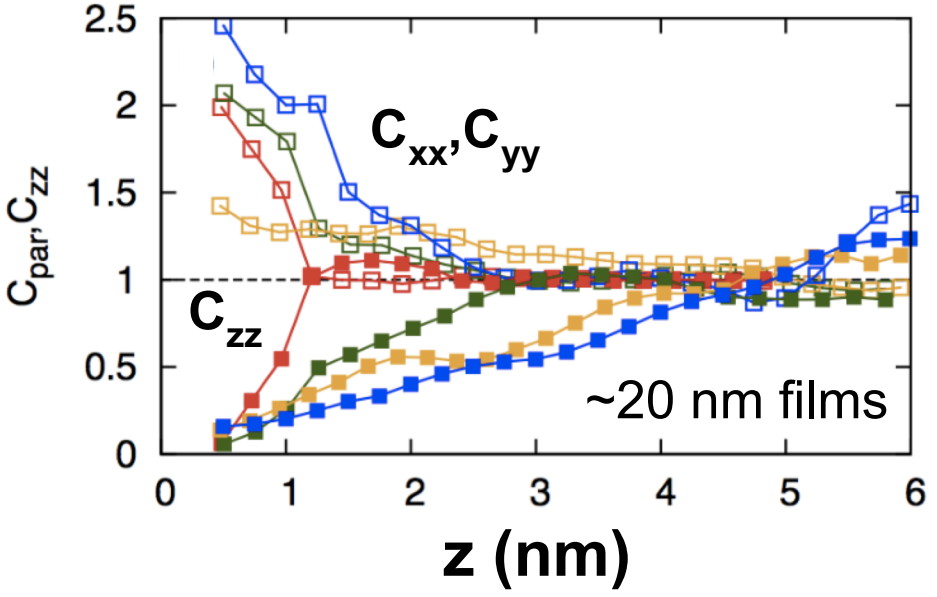
- density reaches its bulk value after 1-2 nm
- conformation tensor becomes bulk-like after 1-2 nm.

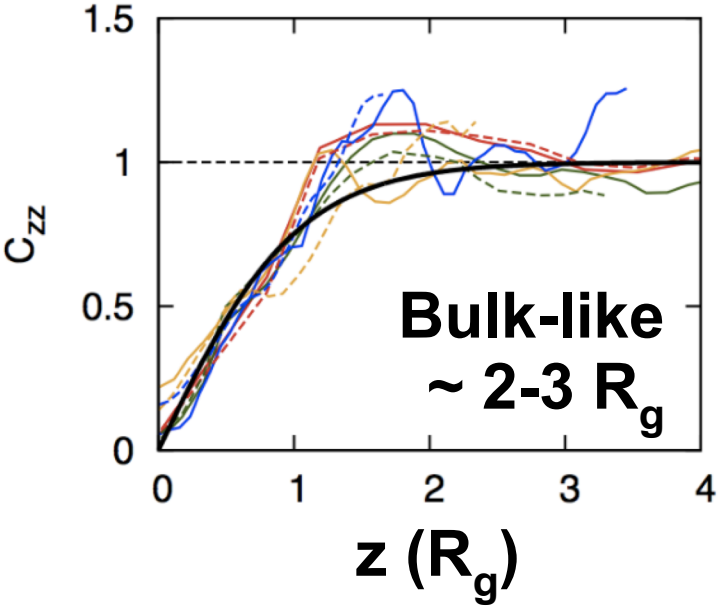
What about longer chain systems?

Density reaches bulk after ~1.5 nm, independent of chain length



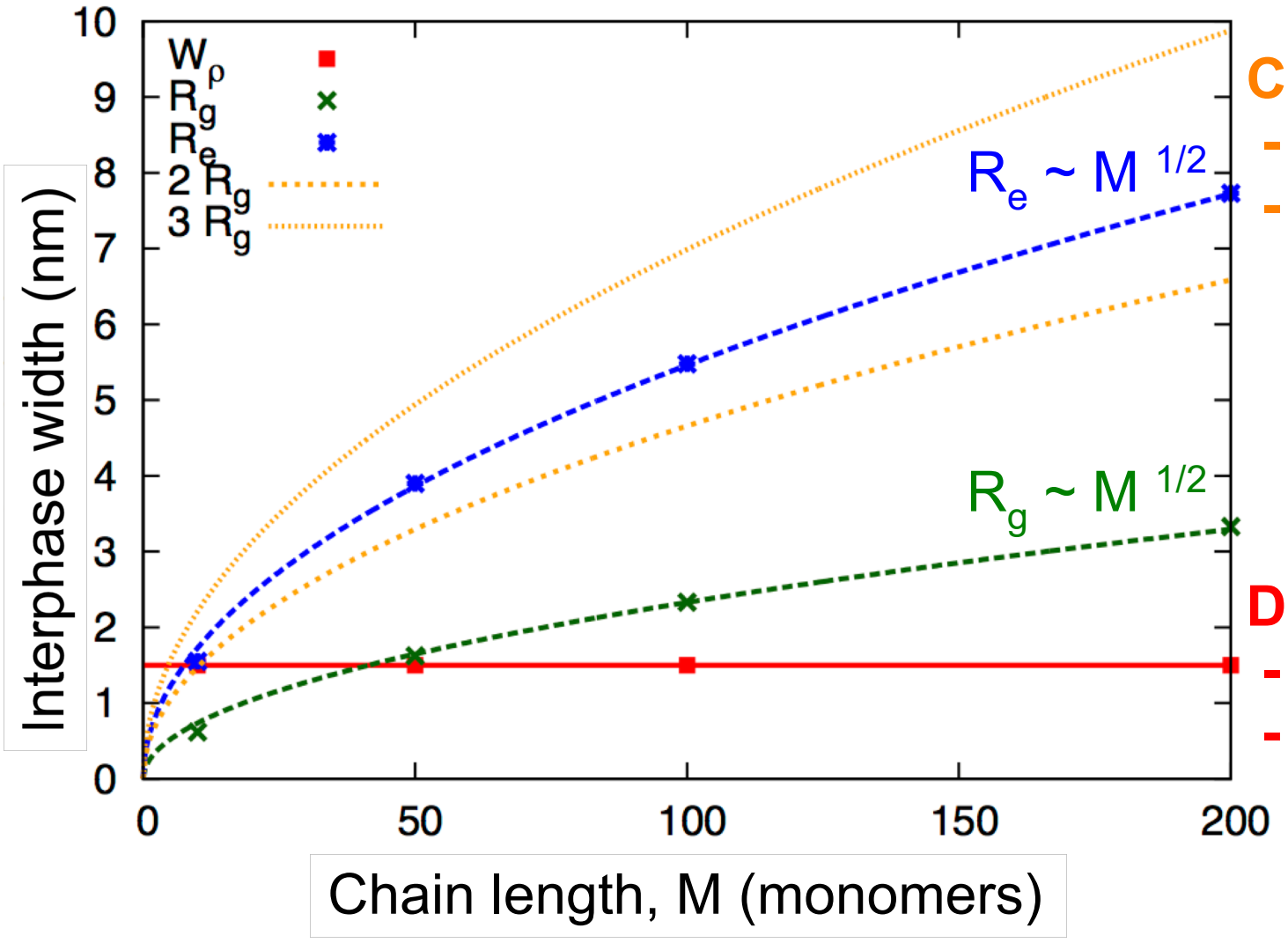
Conformations profile depends on chain length





10
50
100
200

Interphase width vs chain length



Conformation:
- **bulk after ~2-3 R_g**
- **depends on M**

Density:
- **bulk after ~1.5 nm**
- **independent of M**

Interphase width is "property-dependent"

[Johnston and Harmandaris, Macromol, **46** 5741-5750 (2013)]

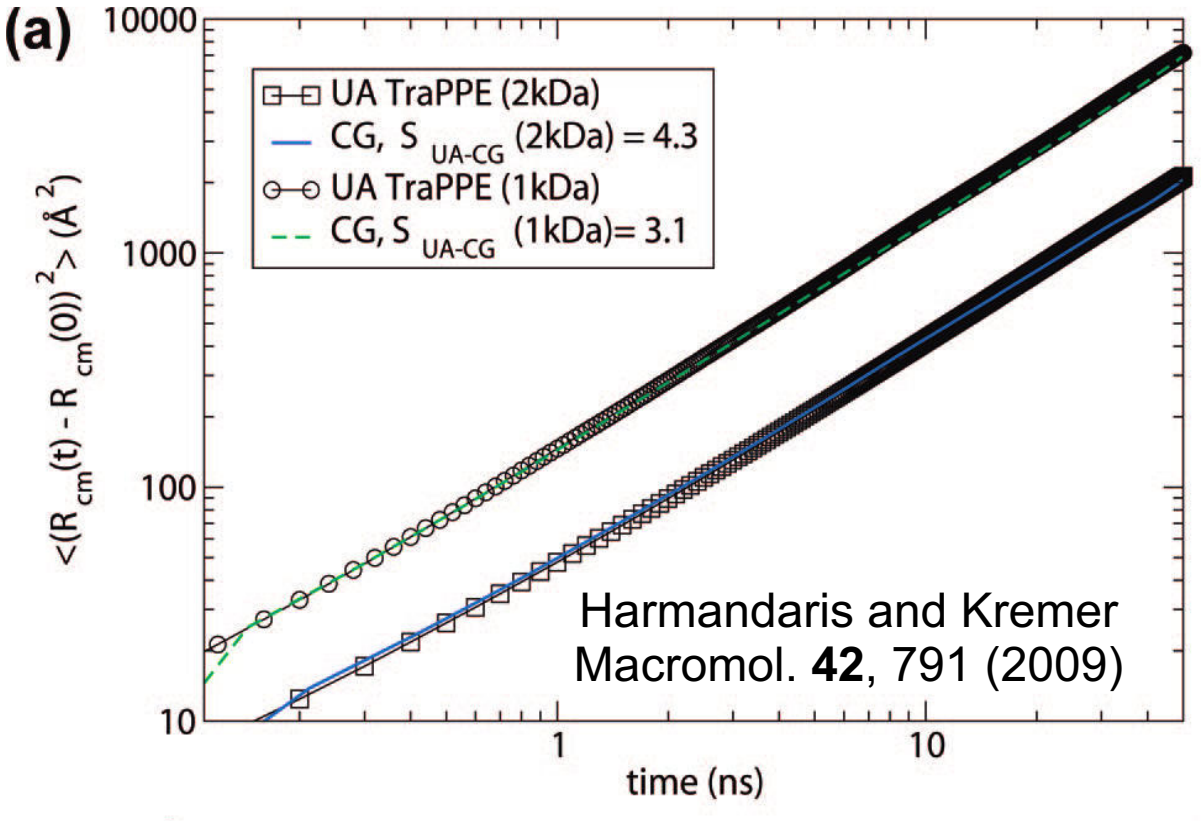
What about the CG dynamics?

Compare AA and CG mean square displacements (msds)

CG time faster than AA time

For **bulk** CG msds map to AA msds via a **scaling factor**

Scaling factor is **model-dependent**



Dynamics of CG model

CG dynamics are faster at the surface
Fast equilibration for structural properties

Problem: Time scaling not possible for this case

Solution: Add corrugation/site-dependence to surface

Approach
Optimise CG pair potentials in an analogous way to the AA case

Work in progress...

Summary for polystyrene thin films

Hierarchical multiscale approach: DFT to AA to CG

AA results:

- relaxation times for bulk in agreement with experiment
- structurally qualitative agreement with PALS

CG model:

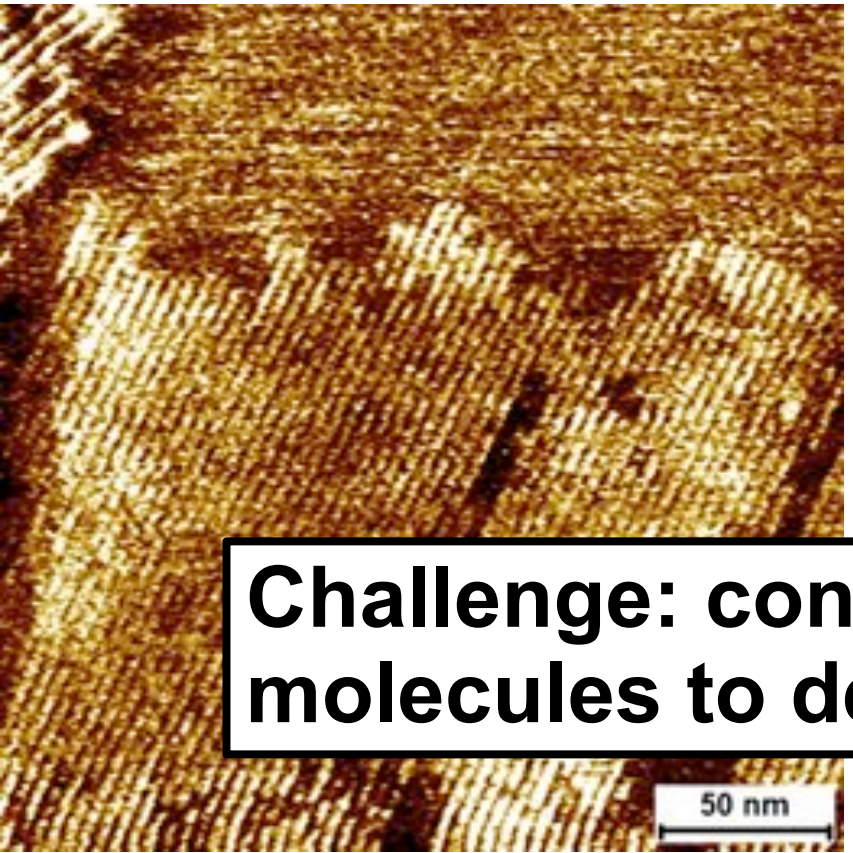
- can simulate longer chains and thicker films
- in excellent structural agreement with AA model

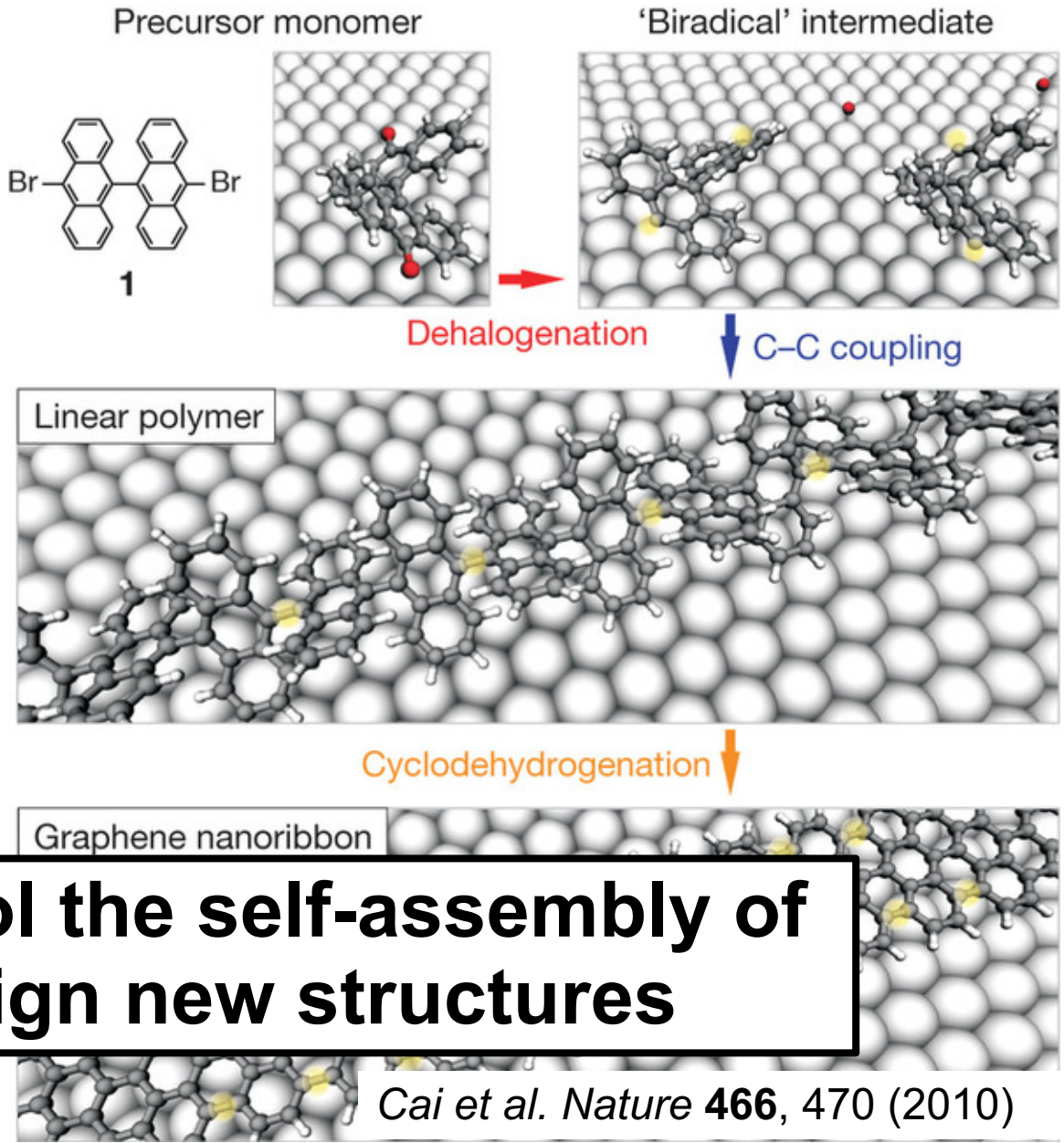
Future work:

- Calculate dielectric spectra/relaxation times for thin film
- Develop an improved model for CG surface potential

2) Self-assembled monolayers

Bottom up synthesis of graphene nanoribbons





Challenge: control the self-assembly of molecules to design new structures

Cai et al. Nature **466**, 470 (2010)

Adsorption of halogenated molecules

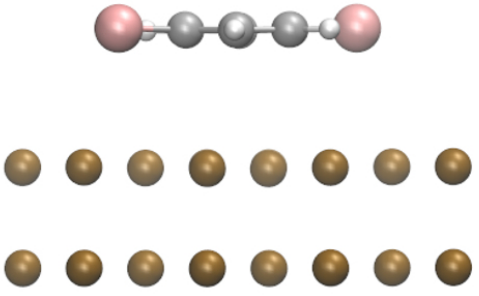
What is the effect of the surface?

On Au(111) physisorption only

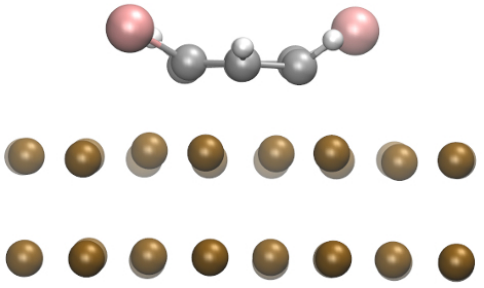
On Pt(111) aromatic molecules have two adsorption states:

- physisorbed
- chemisorbed

This system is bistable and the stability of each state can be **tuned via type and number of halogen atoms**

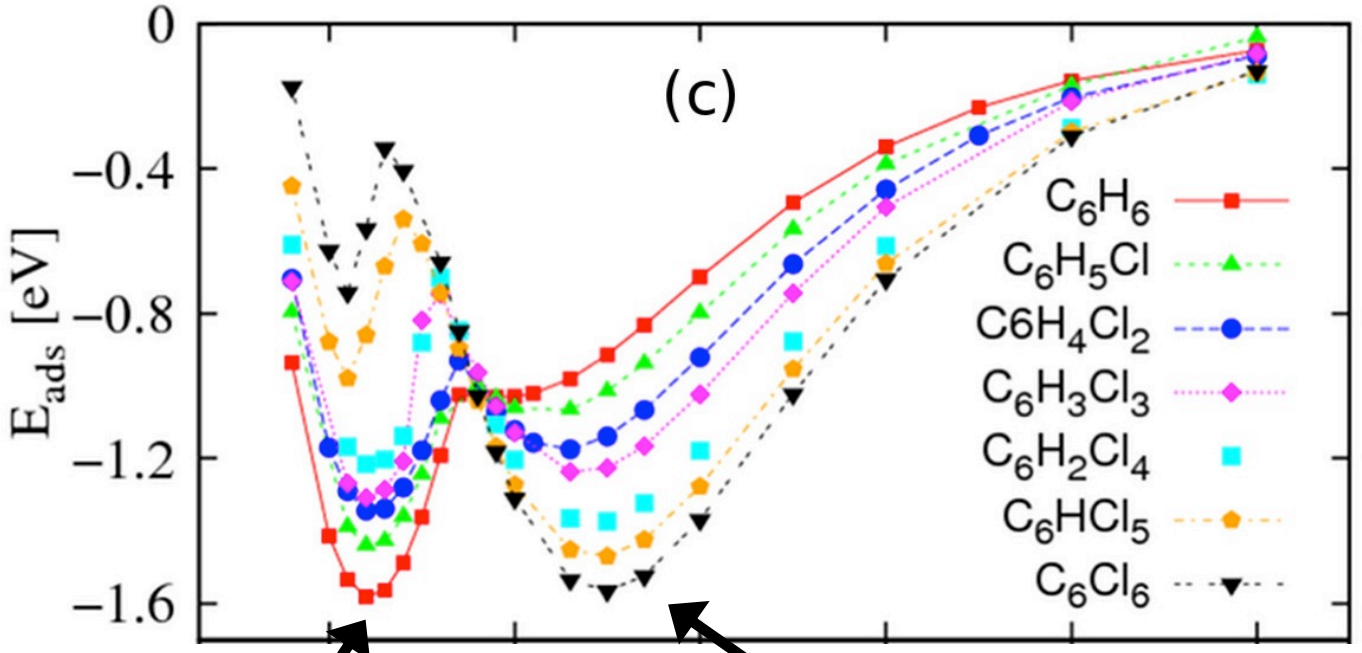


Physisorbed



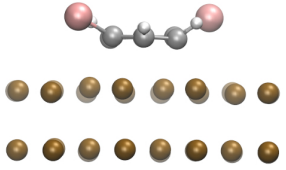
Chemisorbed

DFT results of how chlorination affects adsorption on Pt(111)

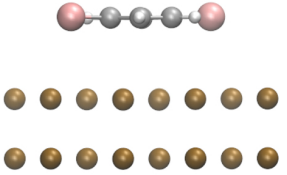


R. Peköz, et al
J. Phys. Chem. C
118 6235 (2014)

Chemisorbed



Physisorbed

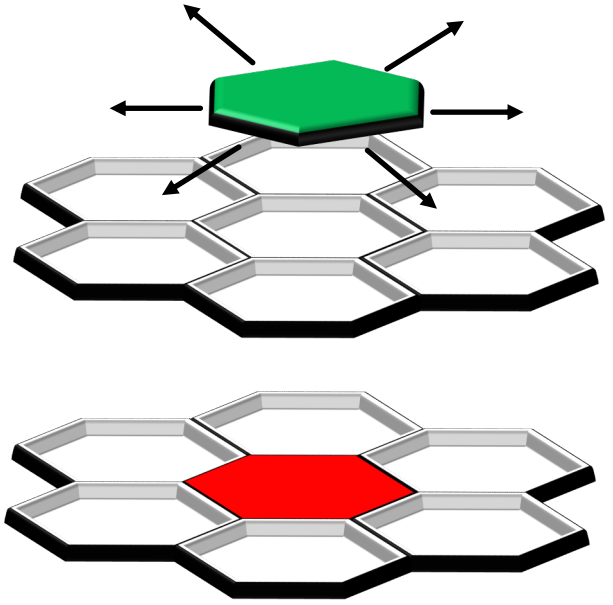


Functionalisation can **tune** the relative depth of the minima.
Can we use this to control self-assembly behaviour?
Develop lattice Monte Carlo (MD) to account for adsorption state.
Use DFT results to parameterise the Lattice MC model.

Hexagonal Lattice Model

Molecule—surface interactions

- Physisorbed or chemisorbed state

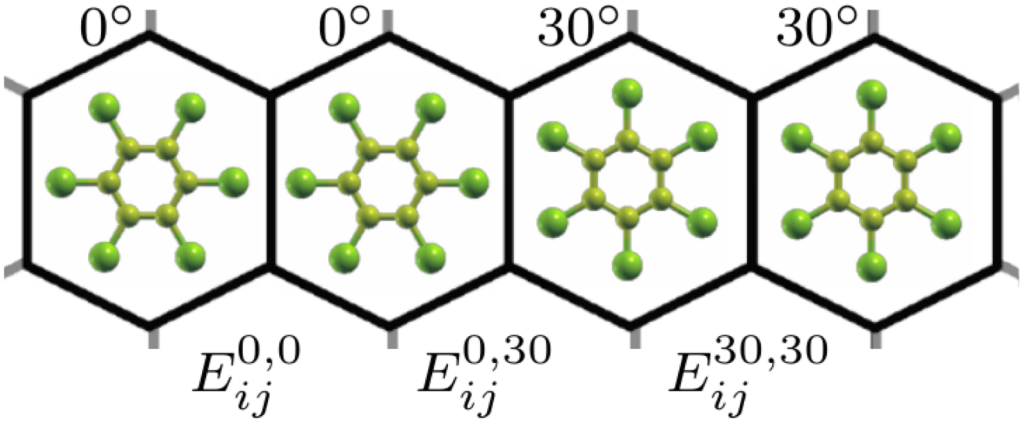


Molecule—molecule interactions

- Relative orientation of molecules

$$H = \sum_{<i>} E_{ads}^{s_i} + \frac{1}{2} \sum_{<ij>} k_{s_i, s_j} E_{ij}^{l_i, l_j}$$

Mol-surf Mol-mol

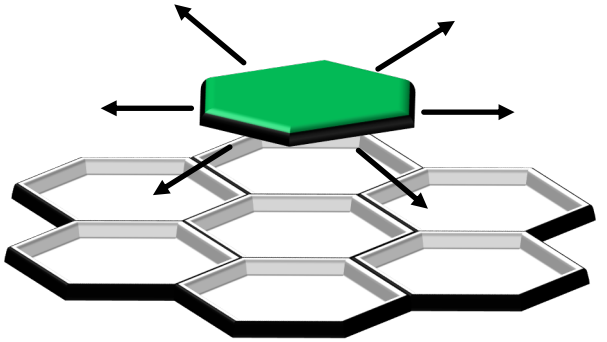


Sara Fortuna, et al., JCP **144**, 134707 (2016)

Hexagonal Lattice Model

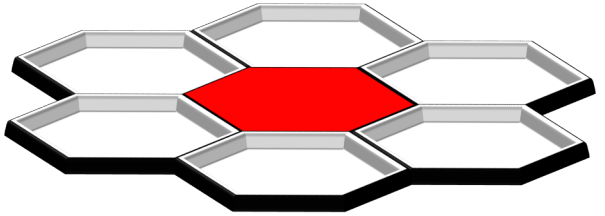
Possible moves:

- **Physisorbed** to/from **chemisorbed** state
- **Translation** only when physisorbed
- **Rotation** by 30˚ only when physisorbed



At every simulation step, a move is attempted and accepted/rejected following the Metropolis acceptance probability:

$$P_{old \to new} = \min\left[1, \exp\left(\frac{E_{old} - E_{new}}{k_B T}\right)\right]$$



Sara Fortuna, et al., JCP **144**, 134707 (2016)

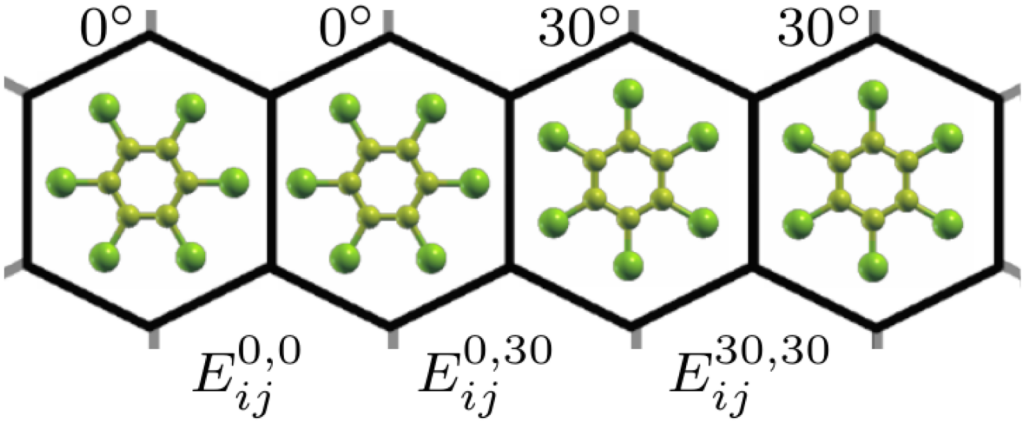
Hexahalogenated molecules on platinum

Consider first:

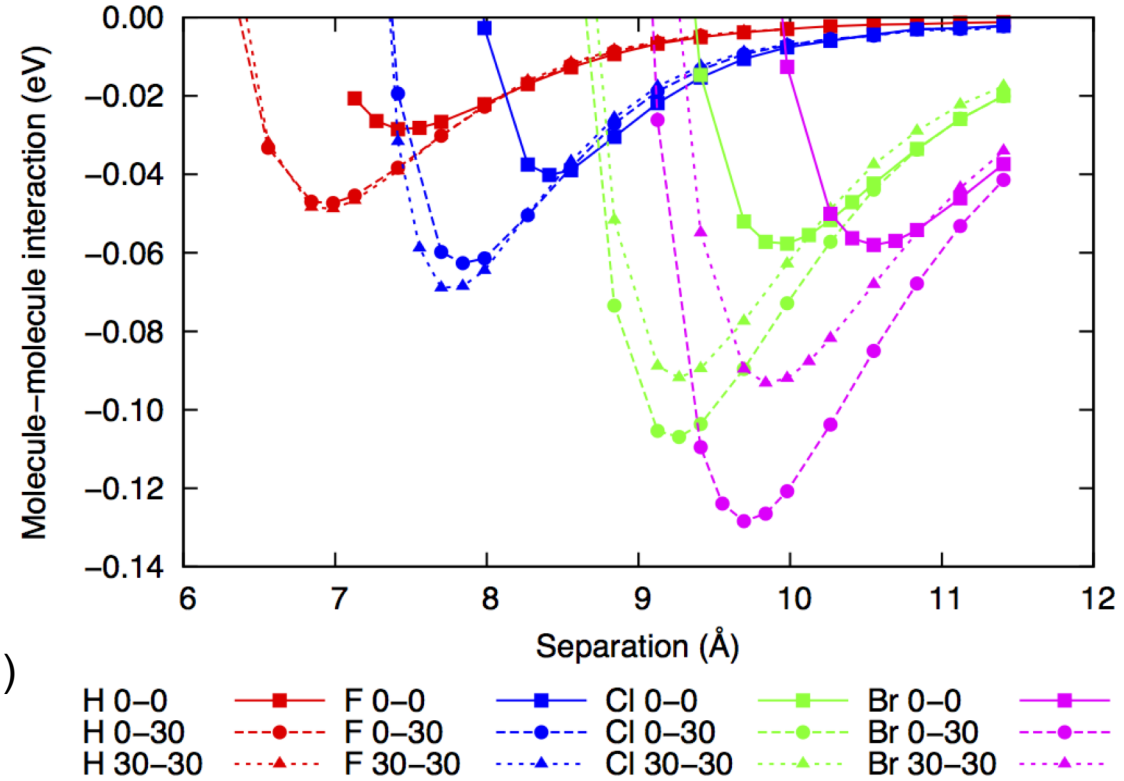
C_6H_6, C_6F_6, C_6Cl_6, C_6Br_6

Mol-mol orientations:

0-0, 0-30, 30-30



- **All**: 0-0 least favorable
- **Br, Cl**: 0-30 most attractive
- **F:** 30-30 slightly more attractive than 0-30
- **H**: 0-30 equal to 30-30



Sara Fortuna, et al., JCP **144**, 134707 (2016)

Hexahalogenated molecules on platinum

Consider first:

C_6H_6, C_6F_6, C_6Cl_6, C_6Br_6

Mol-surf orientations:

Phys vs chem

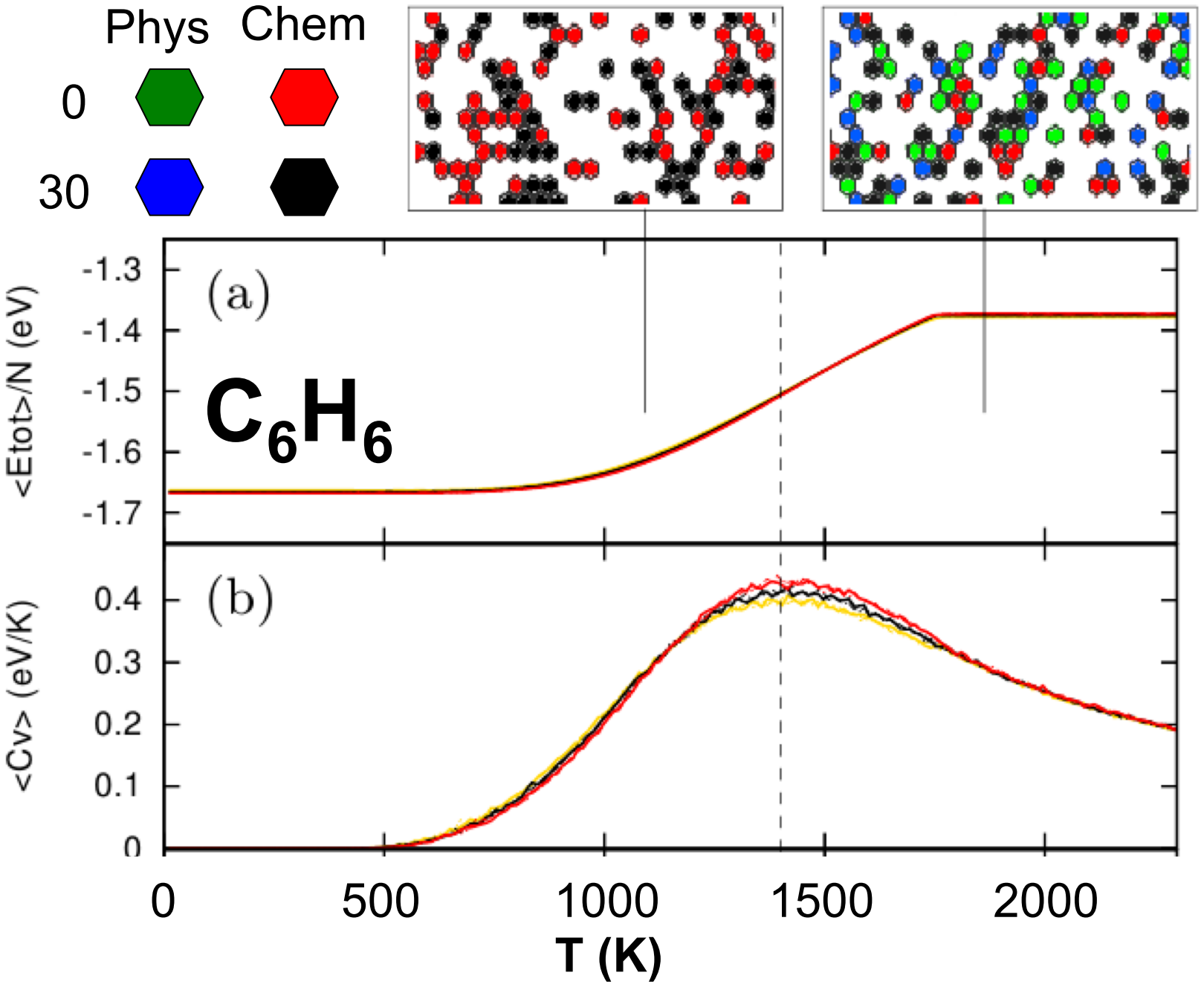
	Echem (eV)	Ephys (eV)
C_6H_6	-1.61	-1.03
C_6F_6	-1.37	-1.02
C_6Cl_6	-0.85	-1.56
C_6Br_6	-1.67	-1.89

R. Peköz, et al J. Phys. Chem. C **118** 6235 (2014)

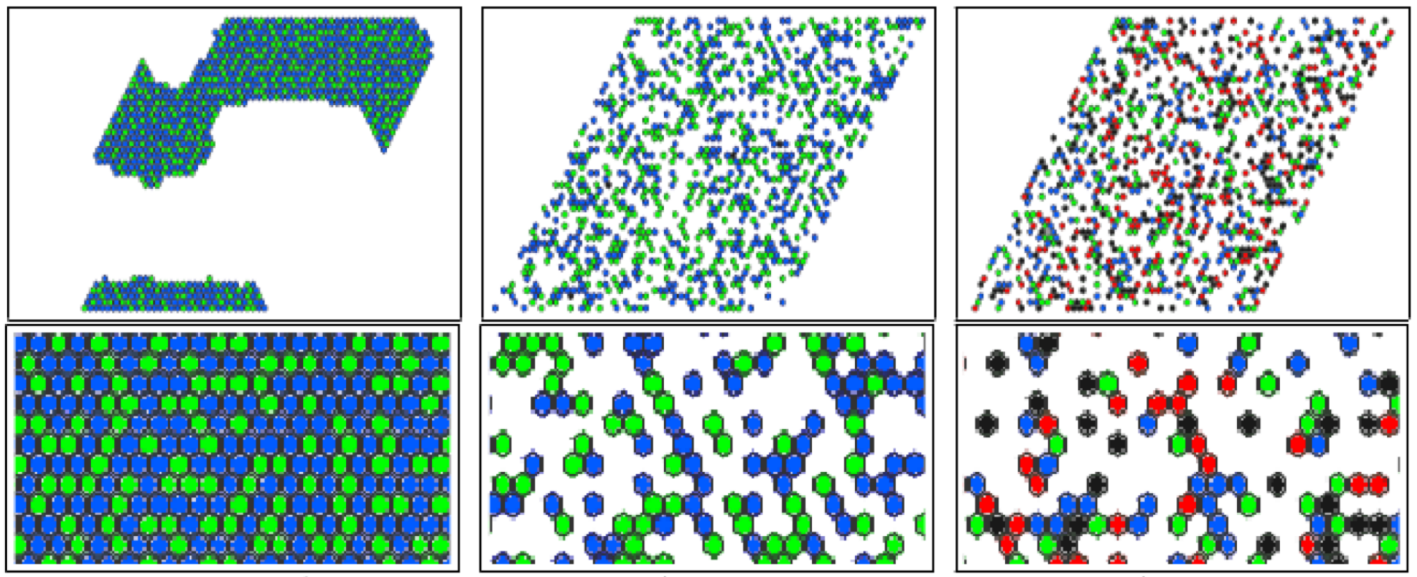
- **Br, Cl**: Physisorption stable
- **F, H:** Chemisorption stable

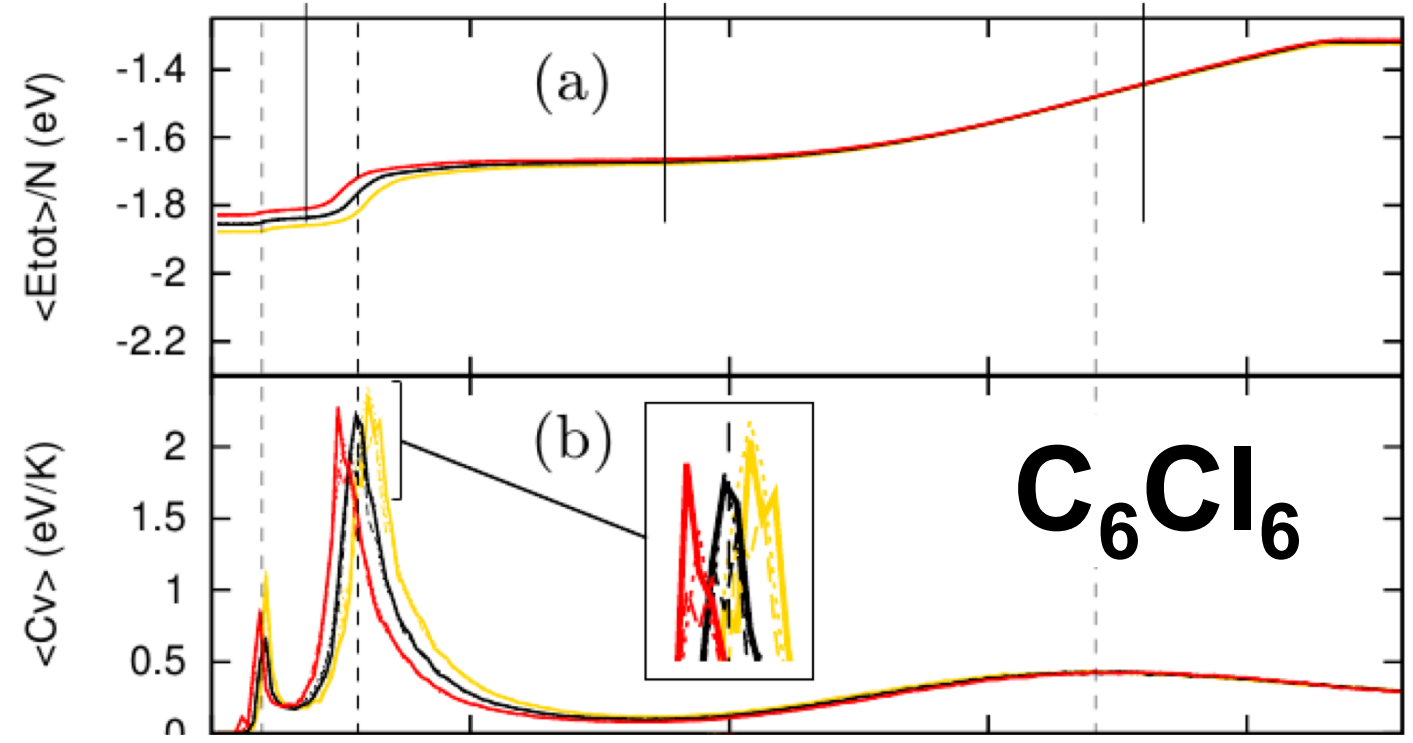
Lattice MC simulations:

- 50x50 lattice with N=1025 molecules
- Initial random state, position and orientation
- Begin simulation at high T, run 5000N steps, reduce T



- Single phase transition
- Arrested disordered chemisorbed monolayer

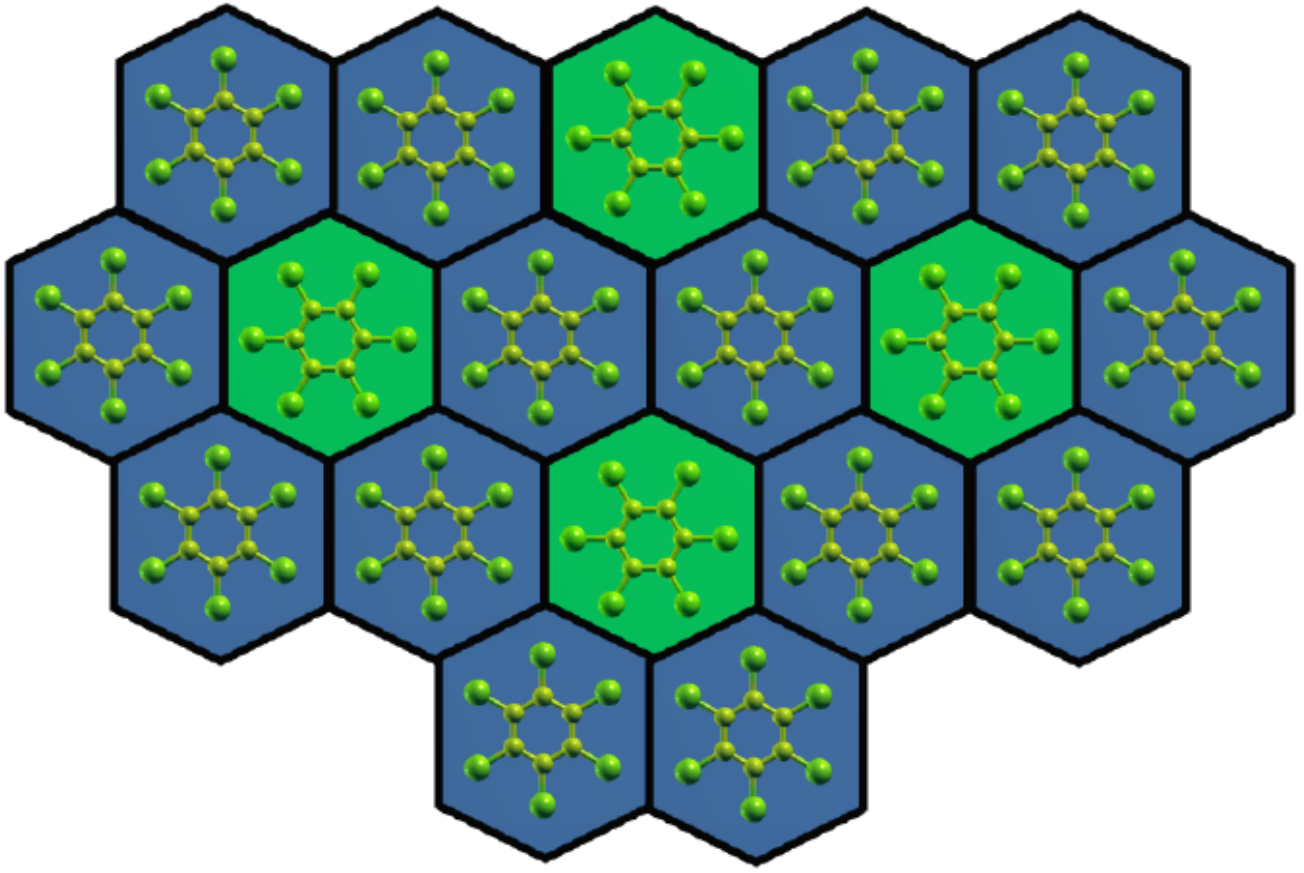




C_6Cl_6

- Three phase transitions
- Low temperature ordered physisorbed monolayer

Low temperature state for C_6Cl_6 and C_6Br_6



- C_6H_6 and C_6F_6 arrested disordered chemisorbed states
- C_6Cl_6 and C_6Br_6 ordered, packed physisorbed states

Limitations and validation

Model does not account for desorption or dissociation
Model should be extended to lower symmetry molecules
Extend lattice to account for multiple adsorption sites

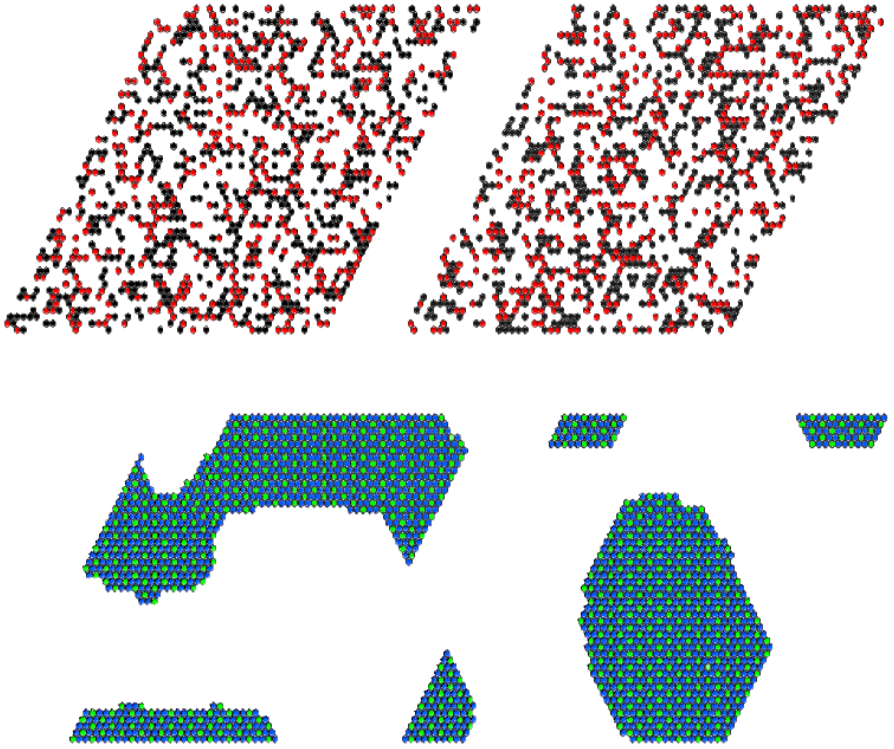
Experimental comparisons:

a) Benzene forms disordered structures on Pt(111) [1,2]
b) Fluorination results in more ordered monolayers for pentacene on Cu(100) and for copper phthalocyanine on Cu(100), Au(100) and Au(111) [3,4,5]

[1] Wander et al. Surf. Sci. **249**, 21 (1991)
[2] Yau et al. J. Am. Chem. Soc. **118**, 7795 (1996)
[3] de Oteyza et al. Chem. Phys. Lett. **490**, 54 (2010)
[4] de Oteyza et al. J. Chem. Phys. **133**, 214703 (2010)
[5] Krauss et al. ChemPhysChem **10**, 2445 (2009).

Self-assembled monolayers summary

- Halogenated aromatic molecules show bistability on Pt(111)
- Developed a lattice model to investigate phase behaviour
- C_6H_6 and C_6F_6 get stuck in disordered chemisorbed states
- C_6Cl_6 and C_6Br_6 form ordered packed physisorbed states



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