Multiscale modeling approach towards understanding coronene self-assembly

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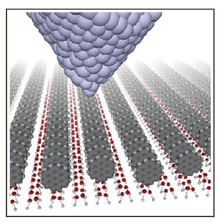
Motivation

Task

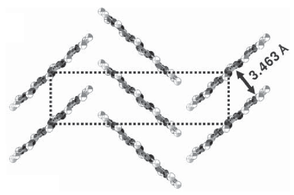
creation of an effective pair interaction potential of coronene molecules

Long term goals

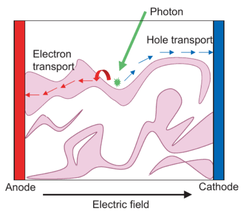
- simulating larger time scales ($10\,ns$) and length scales ($100\,nm$)
- understanding the growth of coronene layers



Coronene-layer arrangement is shown on Ge (001) [3].



The herringbone structure is characteristic for crystalline coronene [1].

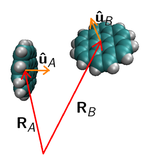


Understanding the self-assembly of organic molecules can tune the hole transport in organic solar cells [2].

Effective pair potential $\mathbf{U_{eff}}$

Coarse-grained coordinates

- $R := |\mathbf{R}|; \mathbf{R} = \mathbf{R}_B - \mathbf{R}_A$
- $a := |\hat{\mathbf{u}}_A \cdot \mathbf{R}|$
- $b := |\hat{\mathbf{u}}_B \cdot \mathbf{R}|$
- $c := |\hat{\mathbf{u}}_A \cdot \hat{\mathbf{u}}_B| \cdot$ $\cdot sgn(\hat{\mathbf{u}}_B \cdot \mathbf{R})\, sgn(\hat{\mathbf{u}}_A \cdot \mathbf{R})$



Mapping functions

- calculate the respective coarse-grained coordinate out of atomistic coordinates
- e.g. $\tilde{R} : \{\mathbf{r}\} \mapsto$ center of mass distance

Configuration integral

$$Z = \int_{\mathbb{R}^3} d\mathbf{r}_1 \ldots \int_{\mathbb{R}^3} d\mathbf{r}_N \, e^{-\beta\, U(\{\mathbf{r}\})} \tag{1}$$

$$= \int_{\mathbb{R}_+} dR \ldots \int_{\mathbb{R}} dc \underbrace{\int_{\mathbb{R}^3} d\mathbf{r}_1 \ldots \int_{\mathbb{R}^3} d\mathbf{r}_N \, \delta(R - \tilde{R}(\{\mathbf{r}\})) \ldots \delta\,(c - \tilde{c}(\{\mathbf{r}\}))\; e^{-\beta\, U(\{\mathbf{r}\})}}_{Z(R,a,b,c) = e^{-\beta\, A(R,a,b,c)}}$$

Free energy function $A(R,a,b,c)$ / histogram function $P(R,a,b,c)$

$$A(R,a,b,c) = -\frac{1}{\beta}\, ln\,(Z(R,a,b,c)) = -\frac{1}{\beta}\, ln(\underbrace{\frac{Z(R,a,b,c)}{Z}}_{P(R,a,b,c)} \cdot Z) \tag{2}$$

Configurational entropy [4]

$$S_{conf}(R,a,b,c) = k\, ln\left(\int_{\mathbb{R}^3} d\mathbf{r}_1 \ldots \int_{\mathbb{R}^3} d\mathbf{r}_N \, \delta(R - \tilde{R}(\{\mathbf{r}\})) \ldots \delta\,(c - \tilde{c}(\{\mathbf{r}\}))\right) \tag{3}$$

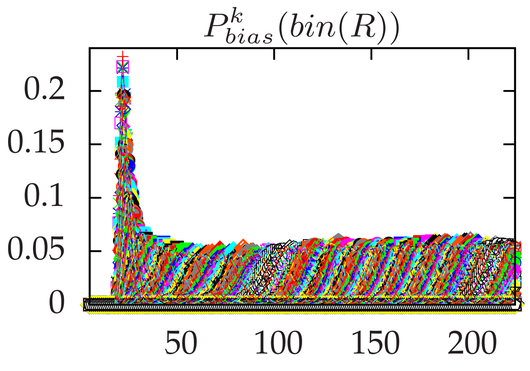
$$\mathbf{U_{eff}}(\mathbf{R},\mathbf{a},\mathbf{b},\mathbf{c}) = \mathbf{A}(\mathbf{R},\mathbf{a},\mathbf{b},\mathbf{c}) + \mathbf{T}\,\mathbf{S_{conf}}(\mathbf{R},\mathbf{a},\mathbf{b},\mathbf{c}) + \mathbf{const} \tag{4}$$

Determine U_{eff} by using $U_{eff}(R,a,b,c) = 0$ for $R \to \infty$.

Methods

$\mathbf{U_{eff}}$ from stochastic simulations with umbrella sampling simulations

1. A tracking of biased histograms $P^k_{bias}(R,a,b,c)$ for each simulation (450 simulations - each uses a different spring connecting the molecules) is performed.



The bin probability functions for the first 200 bins are shown for 300K.

2. Weighted Histogram Analysis Method [5]

$$P(R) = \sum_{k=1}^{N_w} \gamma_k(R)\, P^k_{\text{bias}}(R)$$

$$\text{weights: } \gamma_k(R) = \frac{n_k}{\sum_{i=1}^{N_w} n_i\, e^{-\beta W^i(R)} \left(\frac{Z^i_{bias}}{Z}\right)^{-1}}$$

$$\frac{Z^k_{bias}}{Z} = \int_{\mathbb{R}_+} dR\, e^{-\beta W^k(R)}\, P(R)$$

$$\Rightarrow P(R,a,b,c) = \sum_{k=1}^{N_w} \gamma_k(R)\, P^k_{\text{bias}}(R,a,b,c)$$

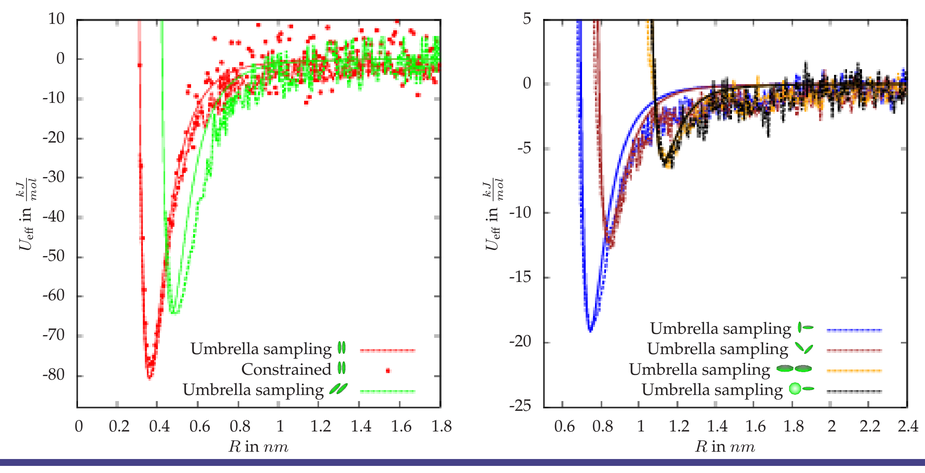
$$\Rightarrow U_{eff}(R,a,b,c) \text{ with (2), (3) and (4)}$$

$\mathbf{U_{eff}}$ from steered stochastic simulations (with constrained pulling)

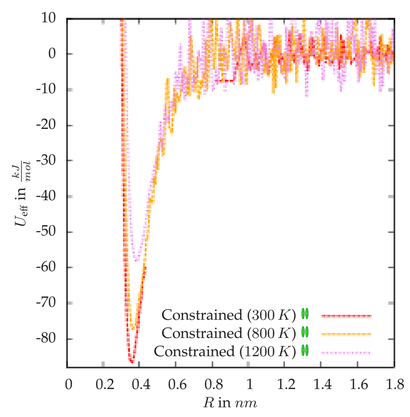
thermodynamic integration $\overset{[6]}{\Rightarrow} A(R) + const = \int_{R_0}^{R} dR' \, \langle F_C(R') \rangle$
with F_C-constraint force => $const \cdot P(R)$ determined
=> $P(R,a,b,c) = P_{Pull}(R,a,b,c) \cdot P(R)$=> $U_{eff}(R,a,b,c)$

Results for uncharged coronene

Potential energy curves for 800 K and its Gay-Berne-like potential fits

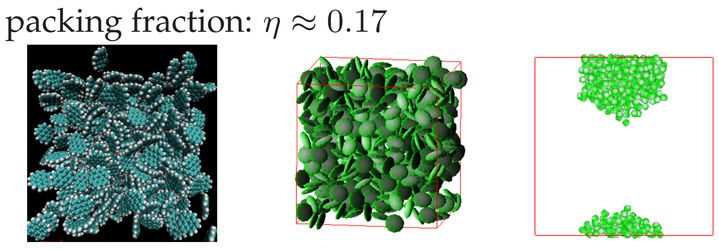


Face-face configuration for different temperatures



High temperature regime - 1500 K

packing fraction: $\eta \approx 0.17$



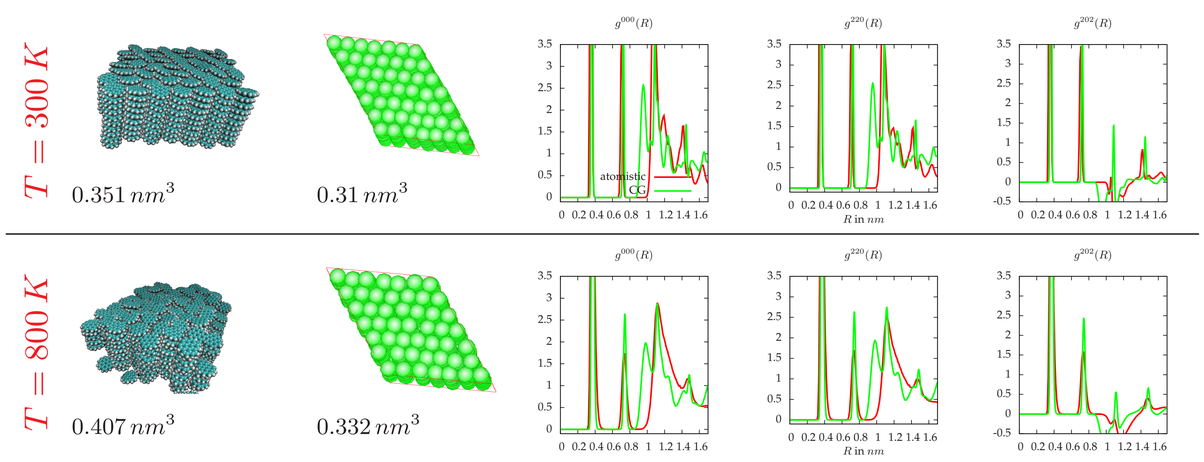
atomistic $U_{eff}(R,a,b,c)$ $U_{eff}(R)$

no isotropic phase for $U_{eff}(R)$
$\Longrightarrow$ Angle dependency is important!

Hexagonal nematic phase (atomistic vs. coarse-grained)

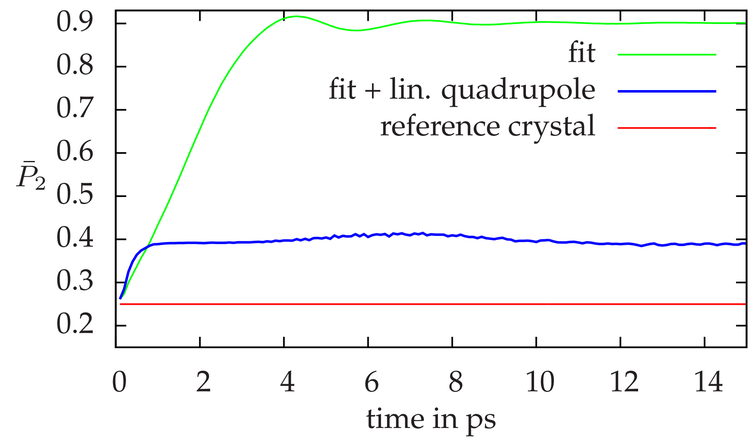
unit cell volume

rotational invariant coefficients of the pair distribution function



Crystal stability (300K) => linear quadrupole improves the leak of electrostatics

nematic order parameter: $\bar{P}_2 = < \frac{1}{N} \sum_i P_2(\hat{\mathbf{u}}_i^T \hat{\mathbf{n}}) >$



Conclusions

- coarse-graining methods are applicable to coronene
- U_{eff} can be fitted with a modified Gay-Berne potential (corrections for: a) well width [7], b) contact distance for [8], c) [9])
- coronene crystal can be stabilized using an additional quadrupole moment

References

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