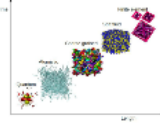
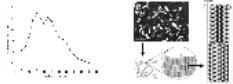


Transferable coarse-grained force field for modeling of crystallization in alkanes

Valentina Drastava

Why CG?



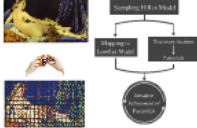
Theory of CG

Top Down

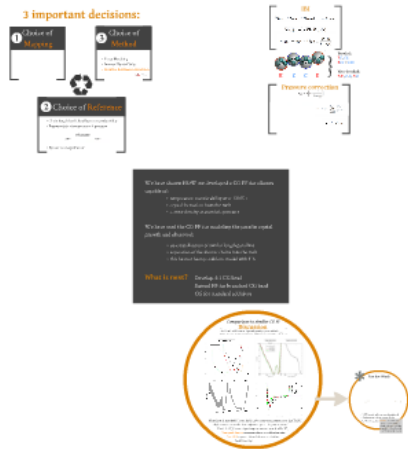


SAFT DPD ...

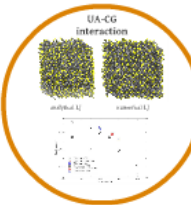
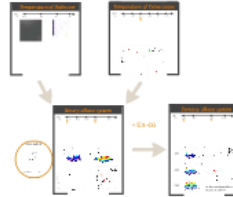
Bottom Up



Thanks to
The Math Works in the course
for their constructive
feedback



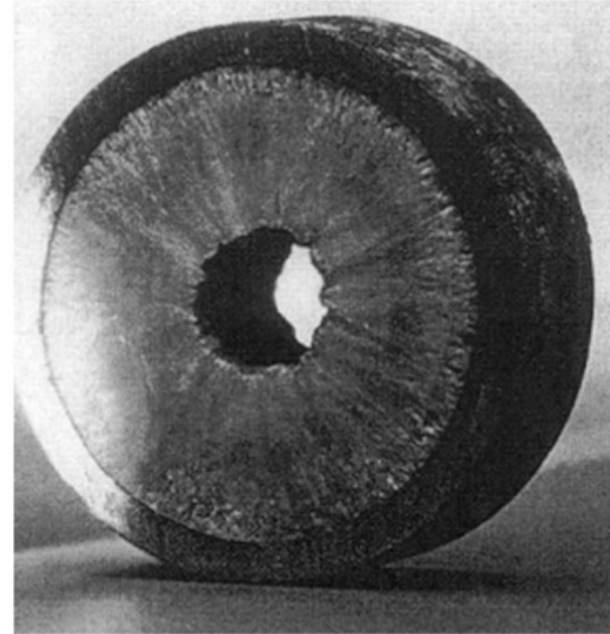
Validation of the CG force field:

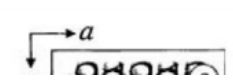
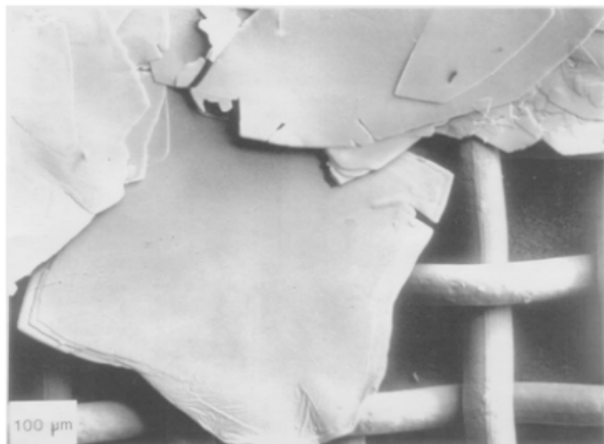


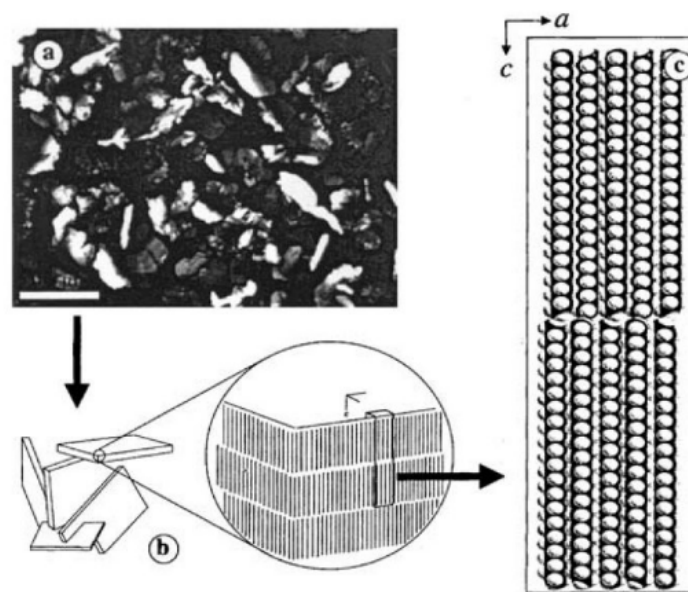
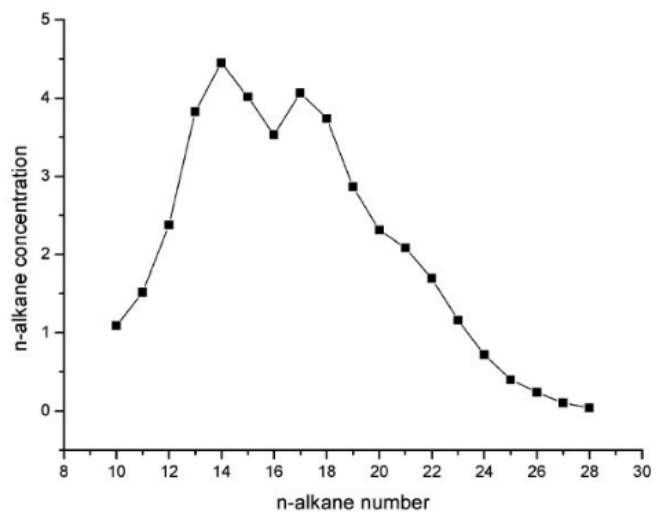
**Transferable coarse-grained
force field for
modeling of
crystallization in alkanes**

Valentina Erastova

Why CG?







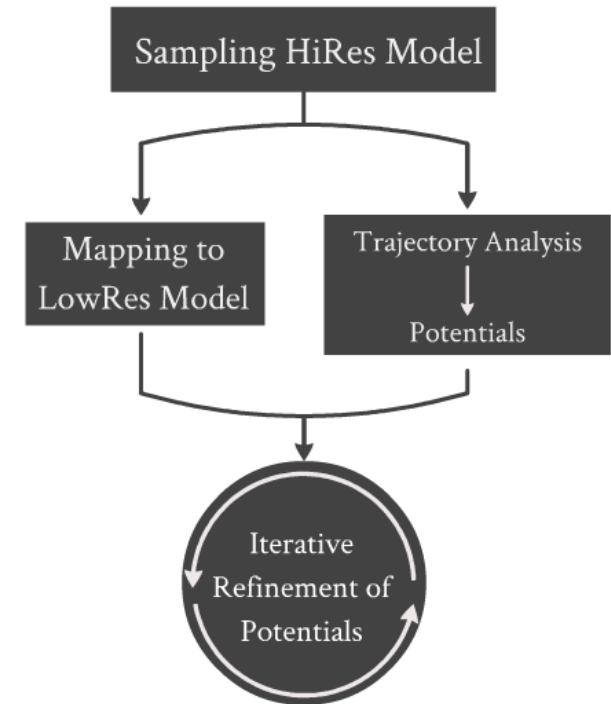
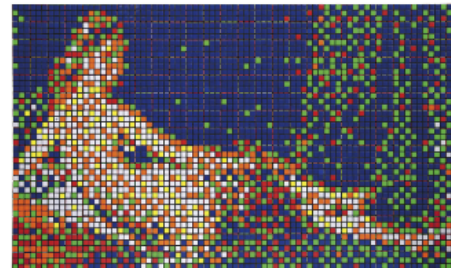
Theory of CG

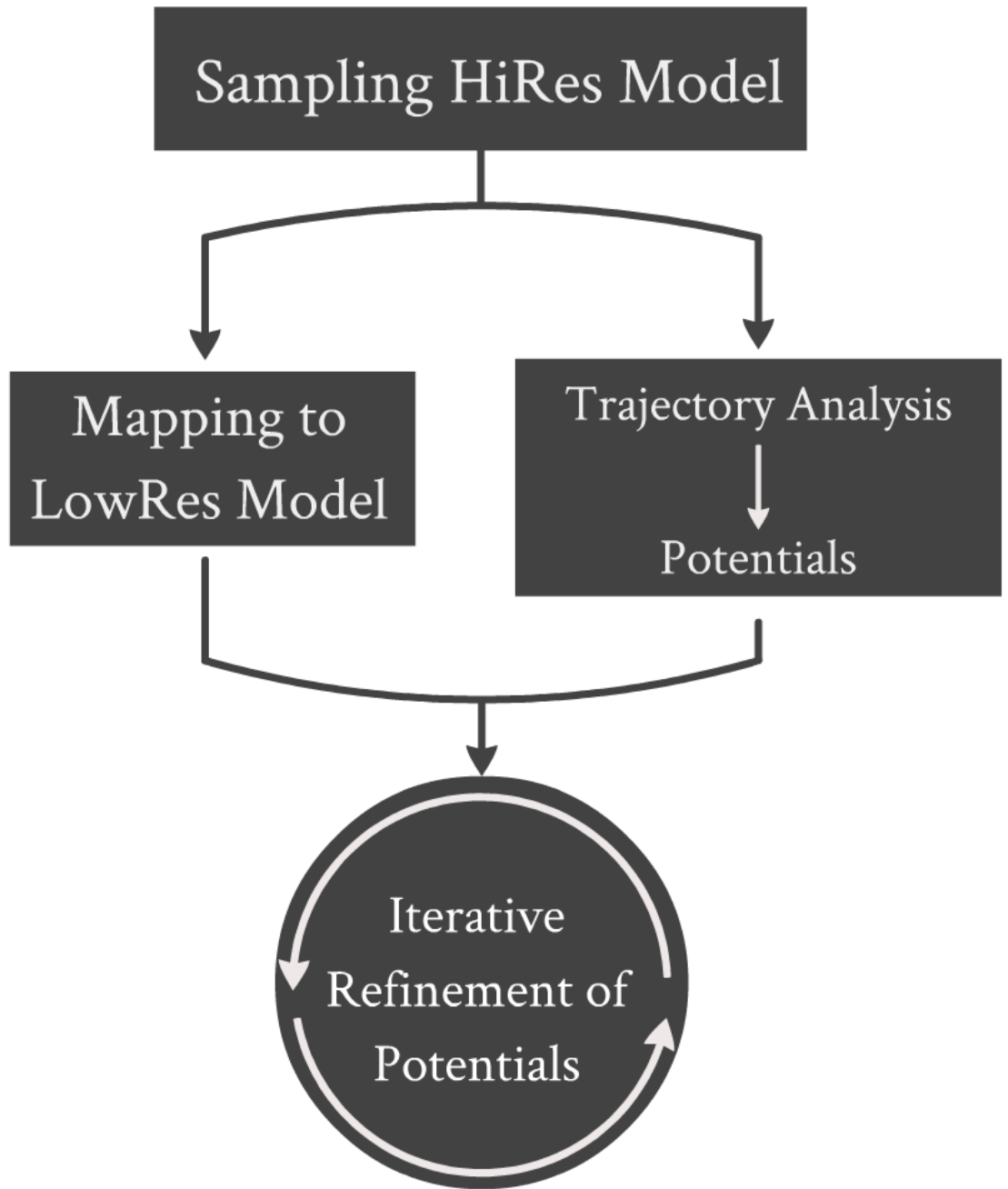
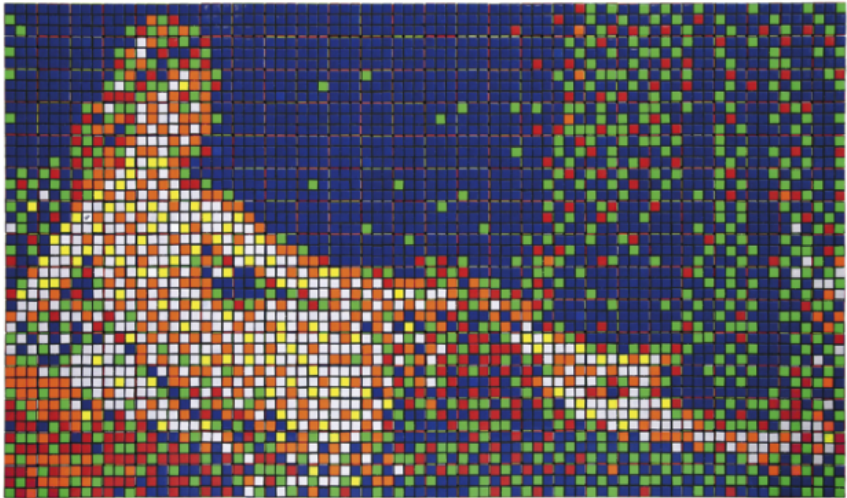
Top Down



SAFT DPD ...

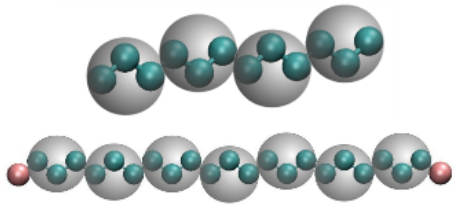
Bottom Up





3 important decisions:


1 Choice of Mapping



The image shows two ball-and-stick molecular models. The top model shows a chain of atoms with a specific mapping of atoms between two different conformations. The bottom model shows the same chain of atoms with a different mapping of atoms between two different conformations.

3 Choice of Method

- Force Matching
- Inverse Monte Carlo
- Iterative Boltzmann Inversion




The VOTKA logo is located at the bottom right of the slide, featuring the word "VOTKA" in a stylized font with a red and white checkered pattern.



2 Choice of Reference

- Chain length has little effect on transferability
- Representative temperature & pressure



The image shows two chemical structures of tricosane. The left structure is labeled "500 K" and shows a highly branched, irregular chain. The right structure is labeled "260 K" and shows a straight, zigzag chain. The word "tricosane" is written between the two structures.

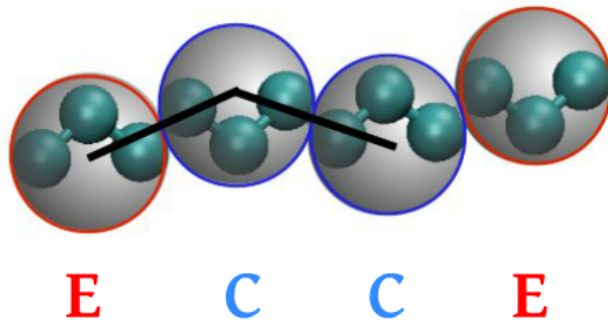
- System is at equilibrium

IBI

$$P_{bond} \rightarrow P_{angle} \rightarrow P_{dihedral} \rightarrow P_{nonbonded}$$

$$V_0(x) = -k_B T \ln P_{ref}(x)$$

$$V_{i+1}(x) = V_i(x) - \lambda k_B T \ln \frac{P_i(x)}{P_{ref}(x)}$$



Bonded:

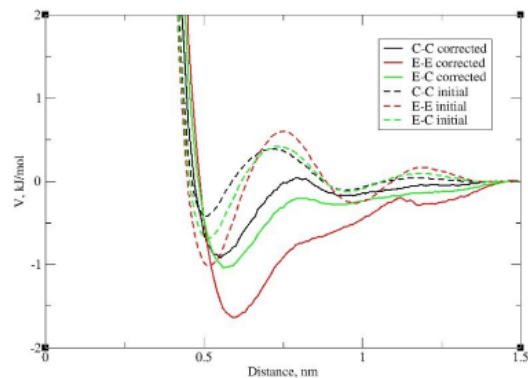
EC, CC
ECC = CCC

Non-bonded:

E-E, C-C, E-C

Pressure correction

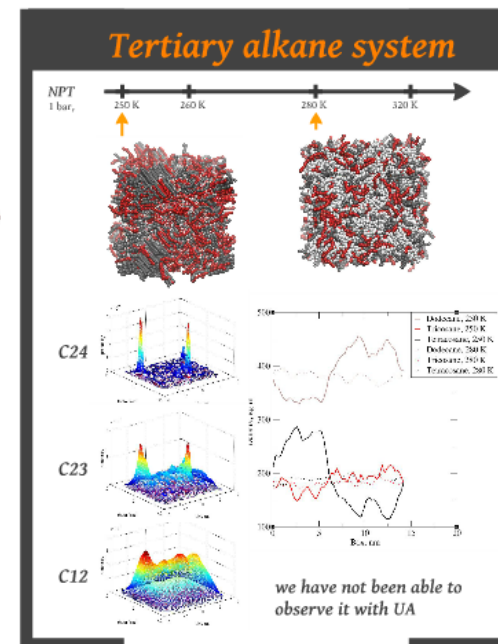
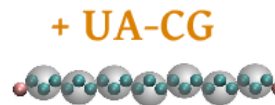
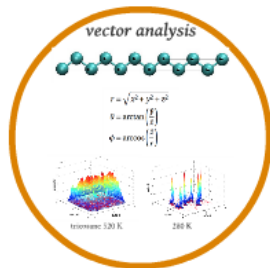
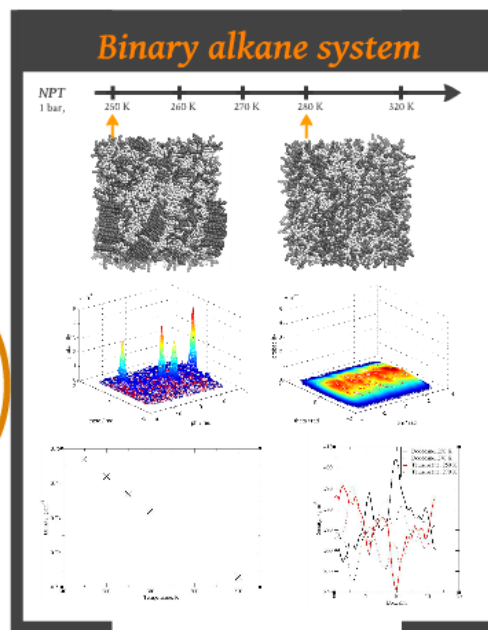
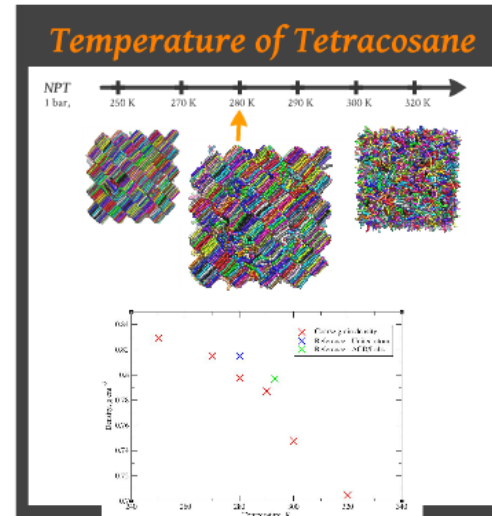
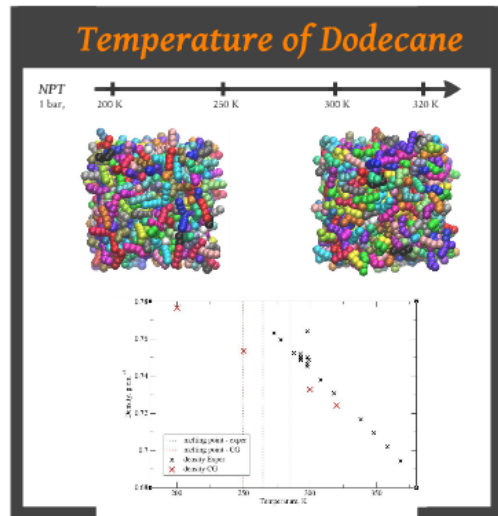
$$V_{att} = A \left(1 - \frac{r}{r_{cutoff}} \right)$$



$$A = -0.1 k_B T \begin{cases} f \Delta P & |f \Delta P| < 1 \\ \frac{f \Delta P}{|f \Delta P|} & |f \Delta P| \geq 1 \end{cases}$$

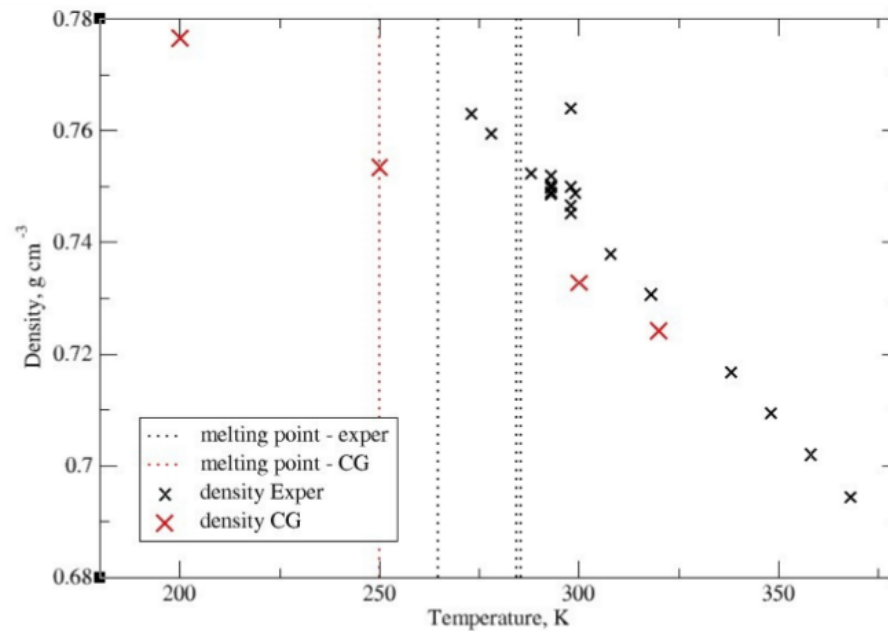
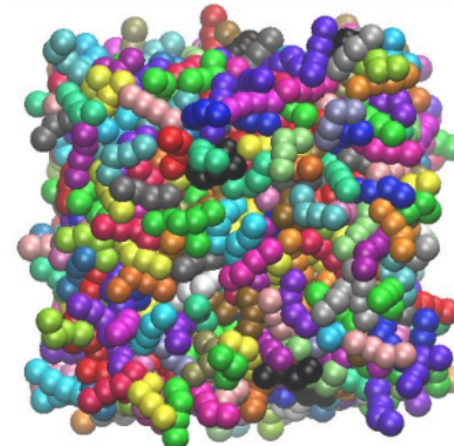
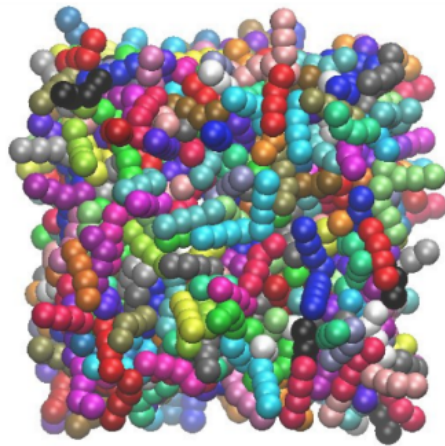
$$\Delta P = P_i - P_{target}$$

Validation of the CG force field:



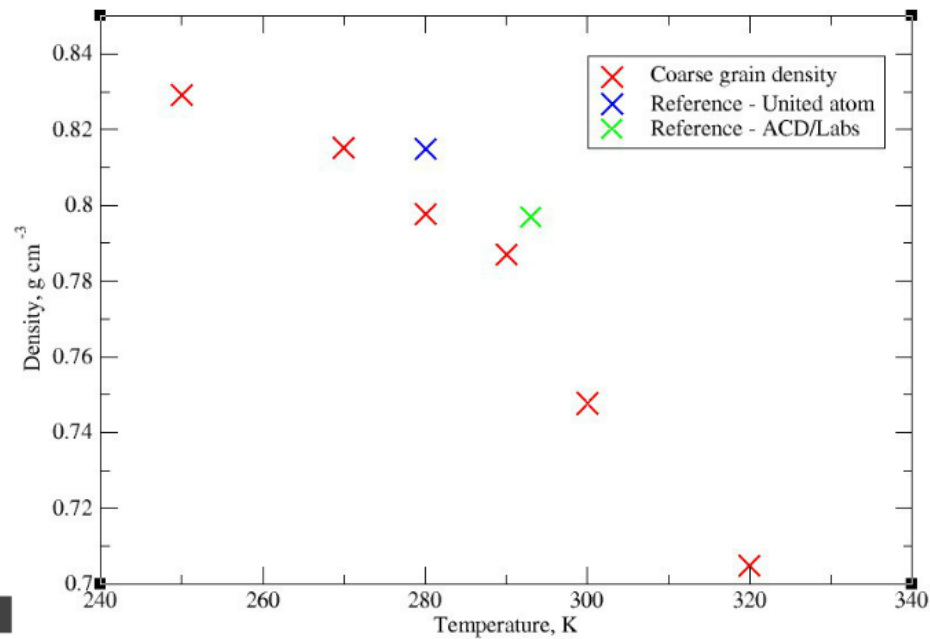
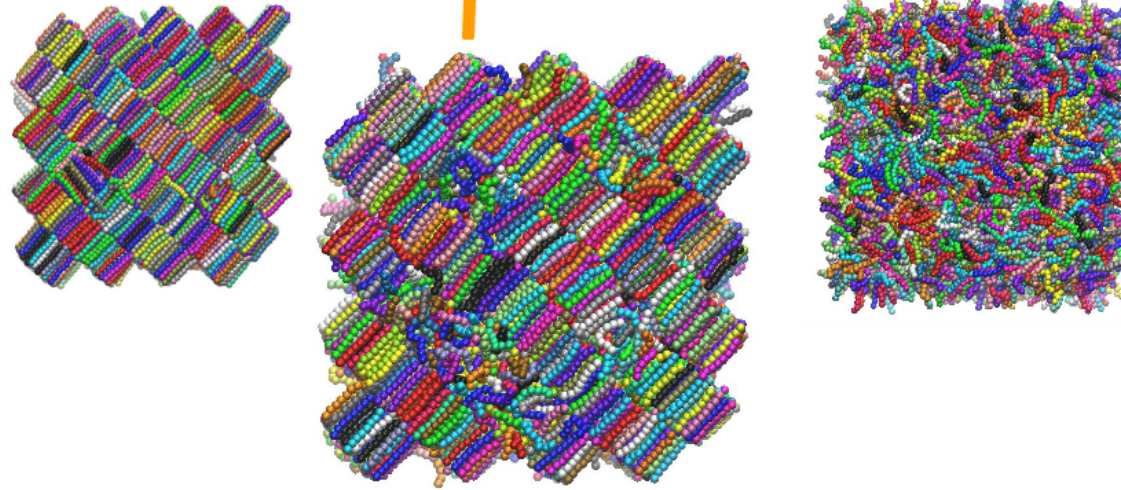
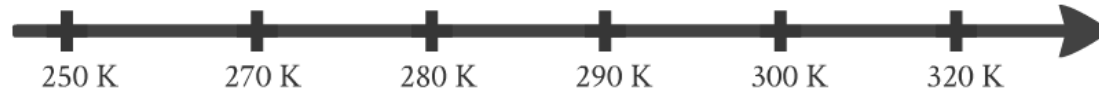
Temperature of Dodecane

NPT
1 bar,



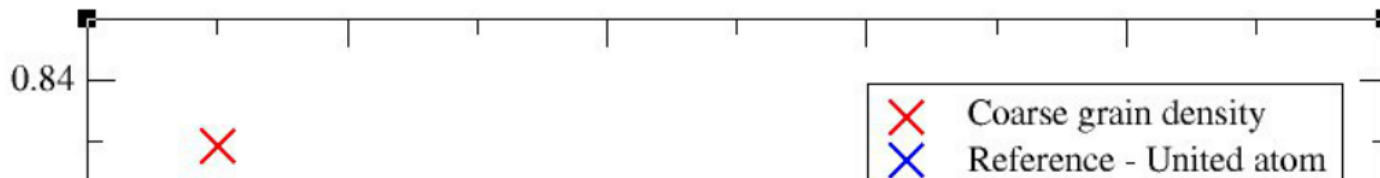
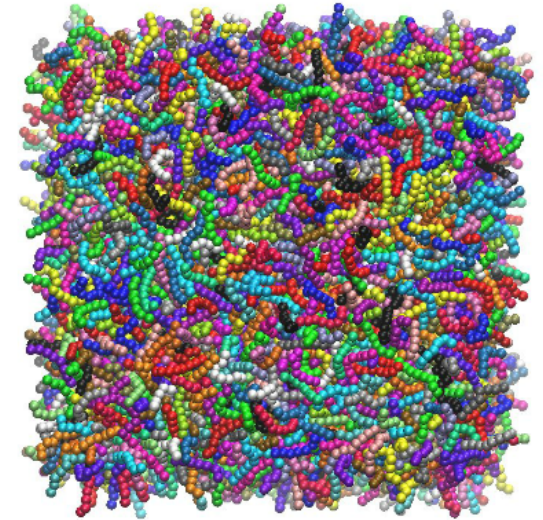
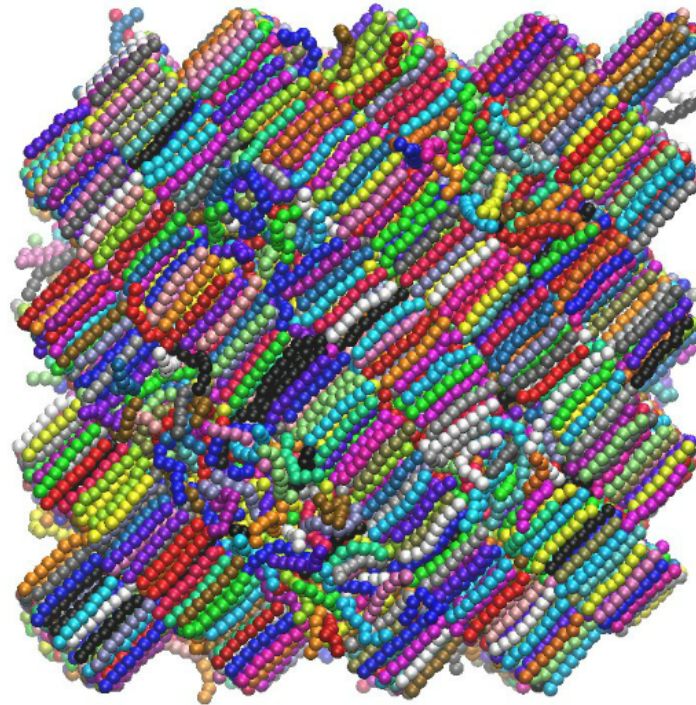
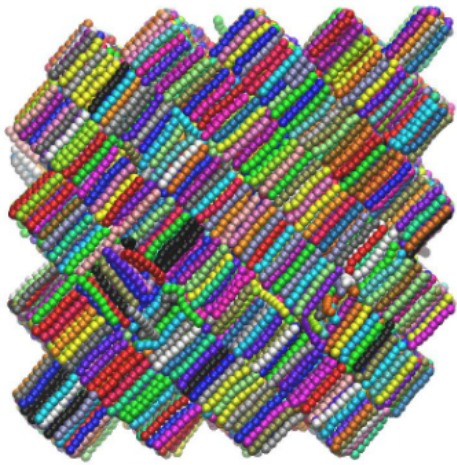
Temperature of Tetracosane

NPT
1 bar,



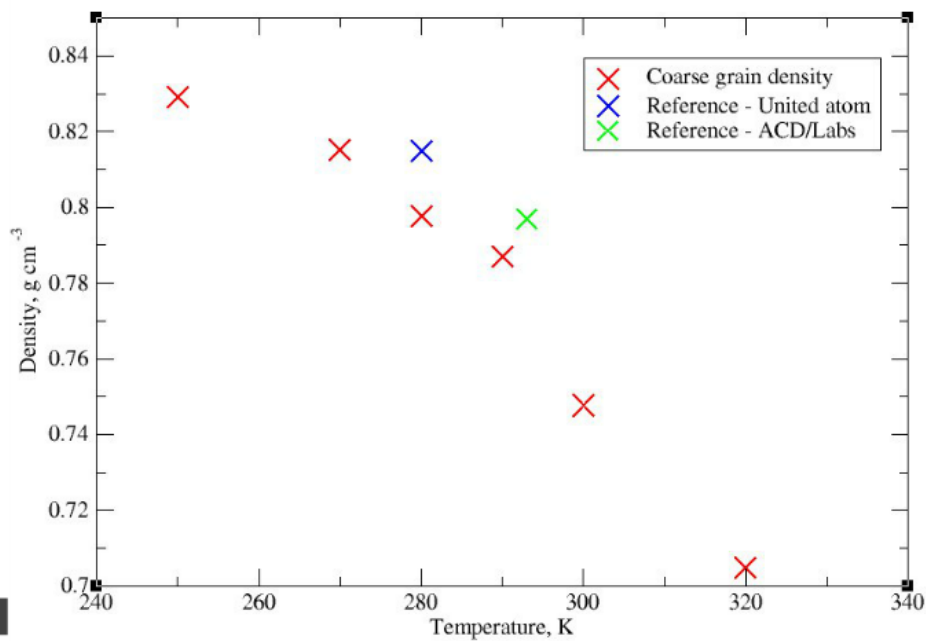
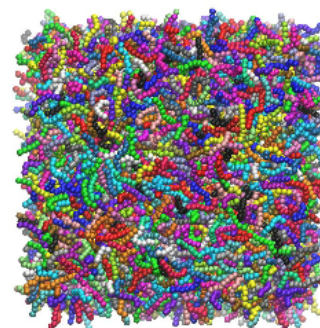
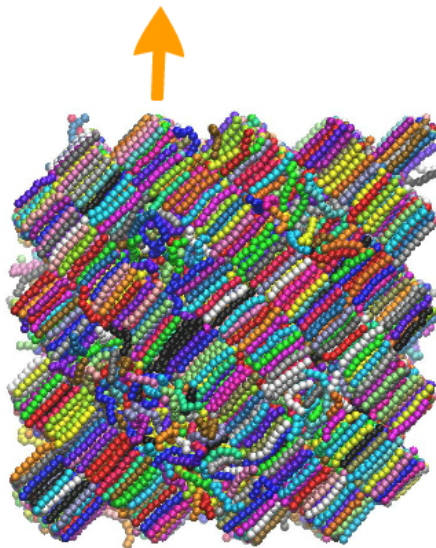
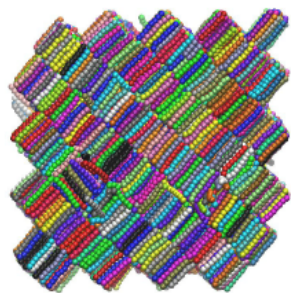
Temperature of Tetracosane

NPT
1 bar,



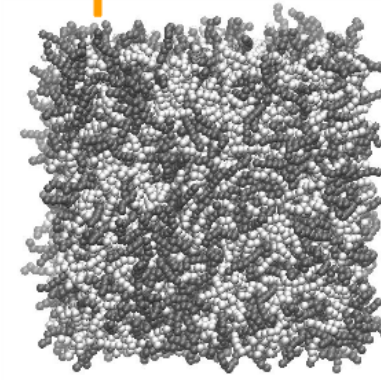
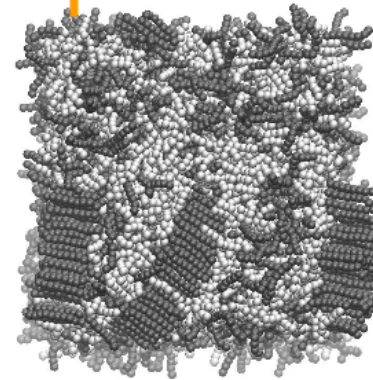
Temperature of Tetracosane

NPT
1 bar,

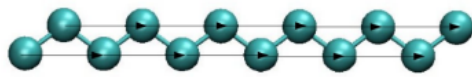


Binary alkane system

NPT
1 bar,



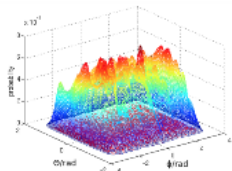
vector analysis



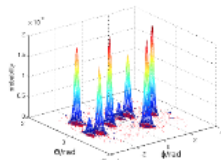
$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \arctan\left(\frac{\hat{y}}{\hat{x}}\right)$$

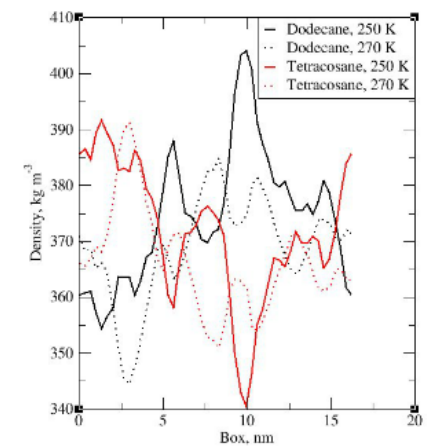
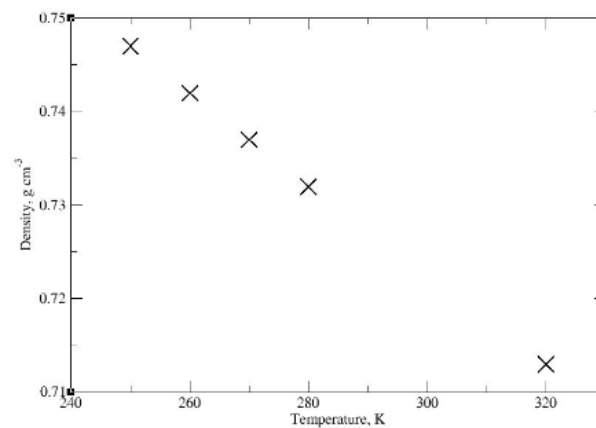
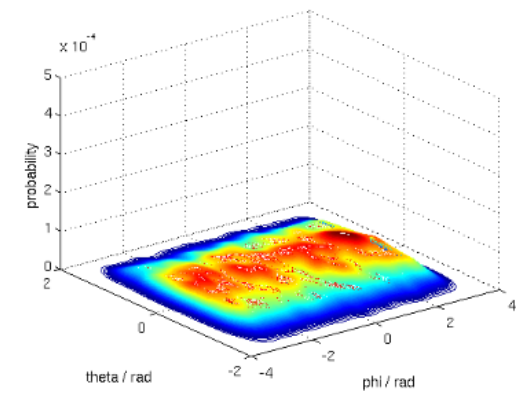
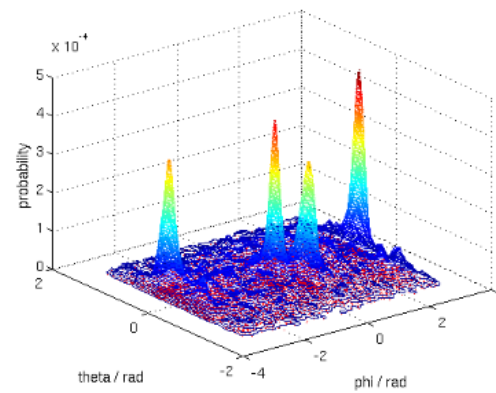
$$\phi = \arccos\left(\frac{\hat{z}}{r}\right)$$



tricosane 520 K

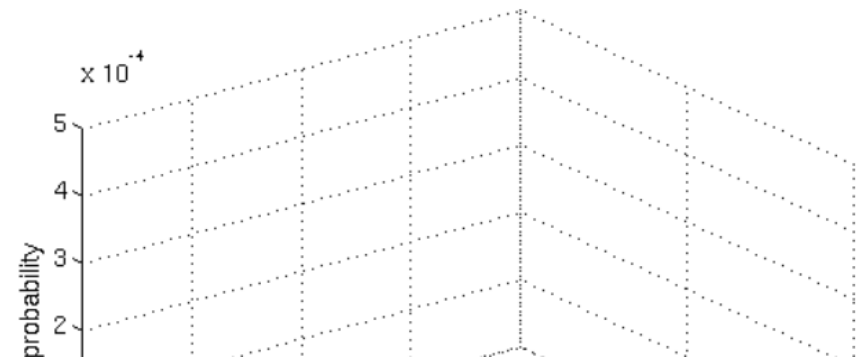
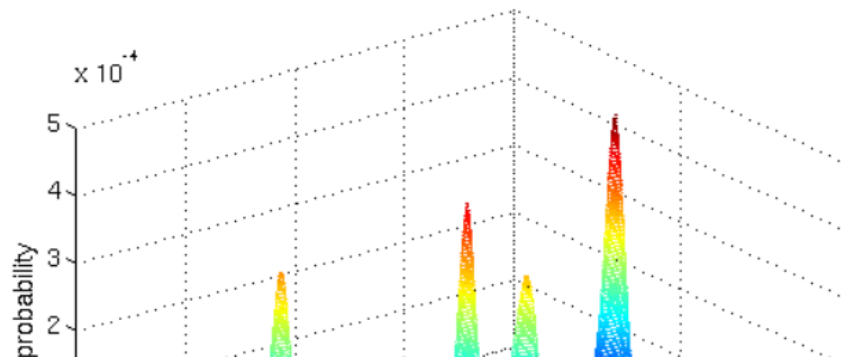
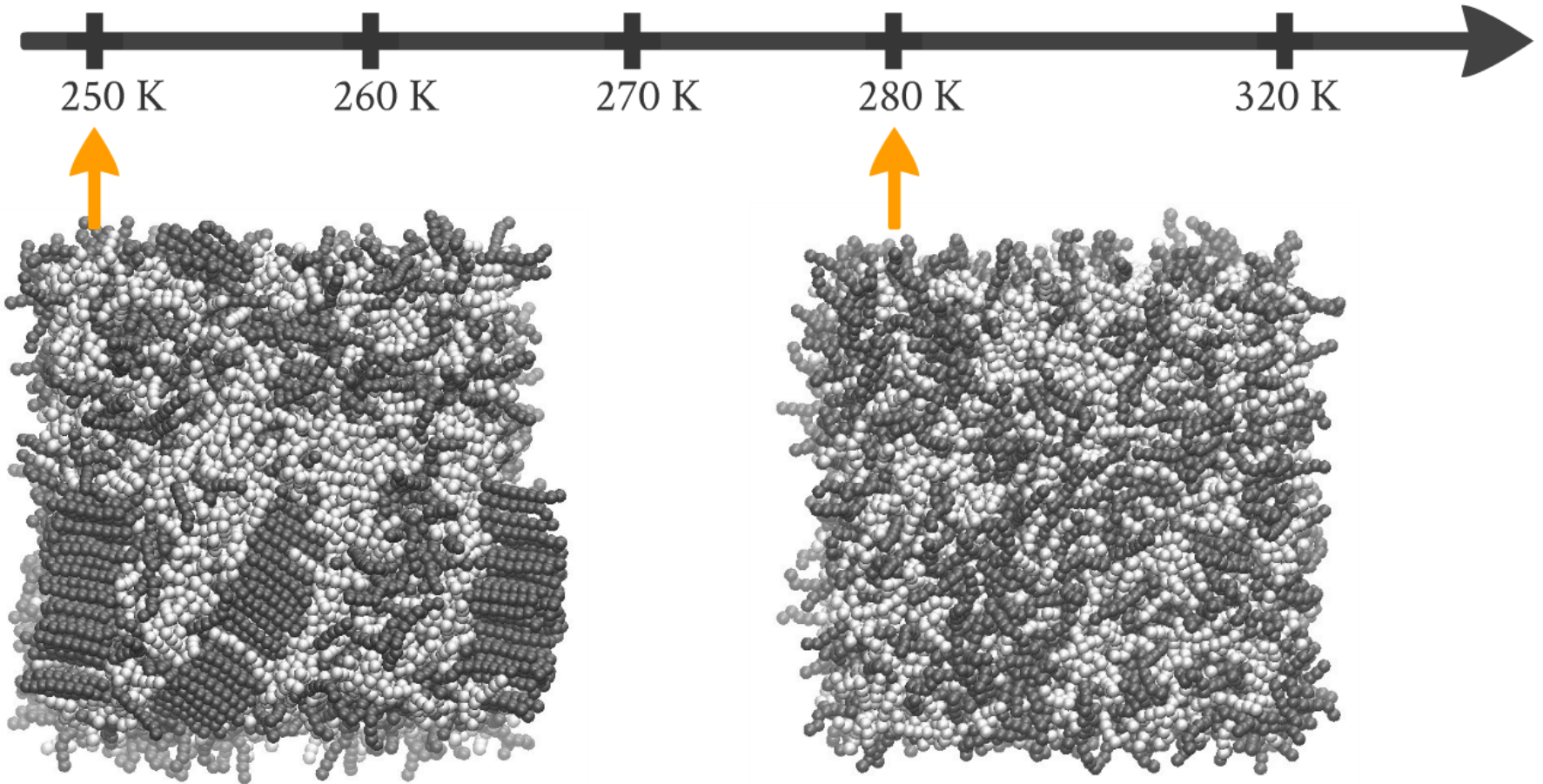


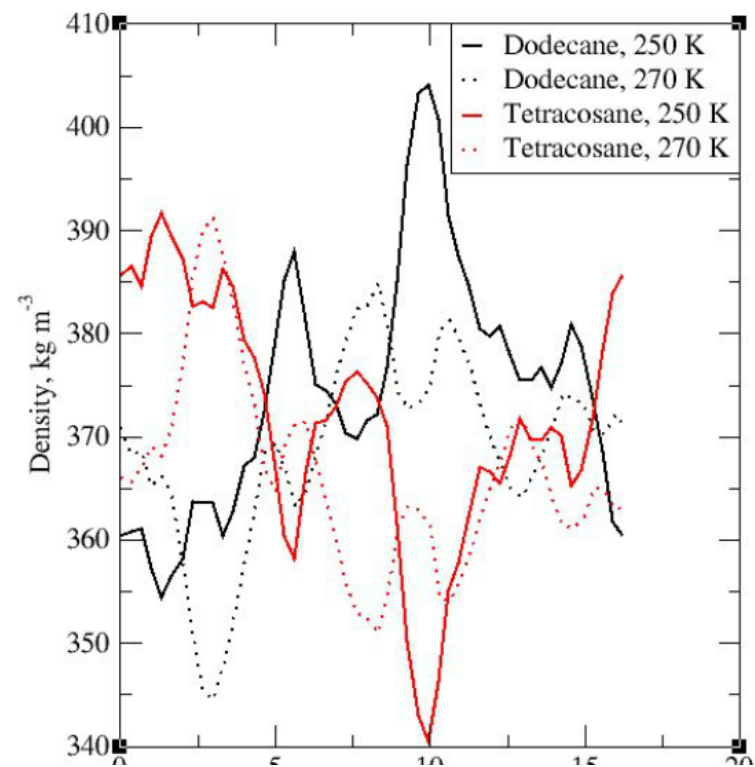
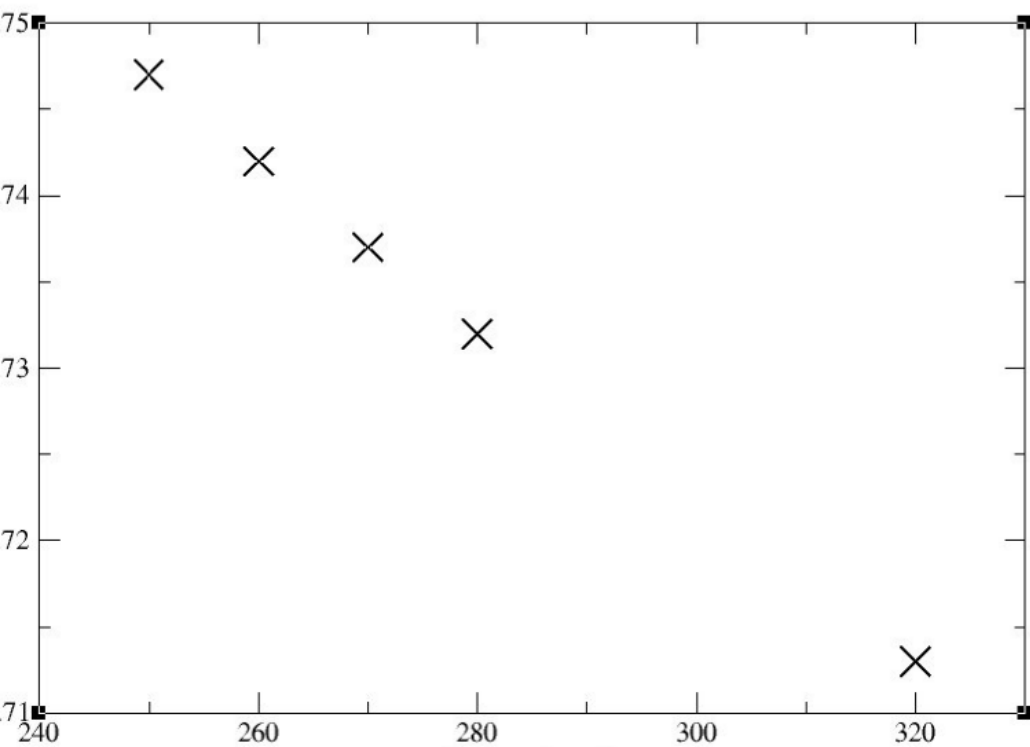
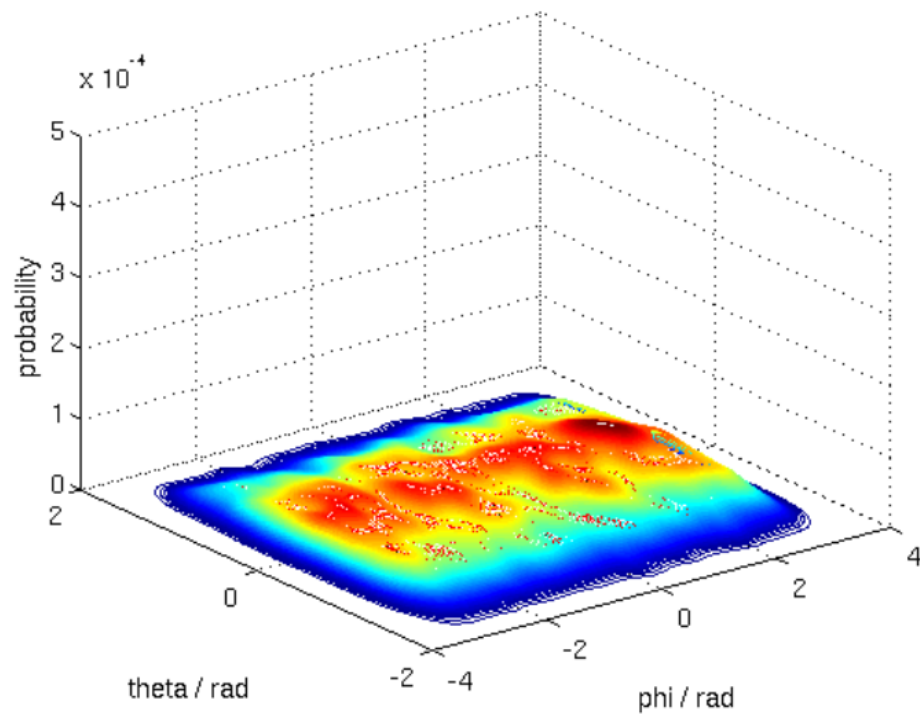
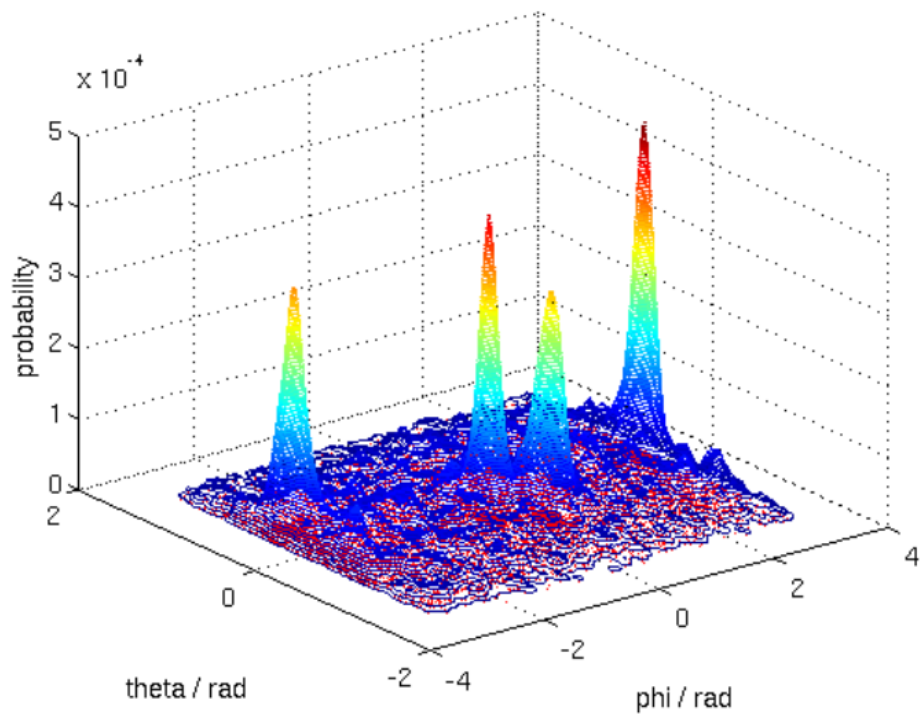
280 K



Binary alkane system

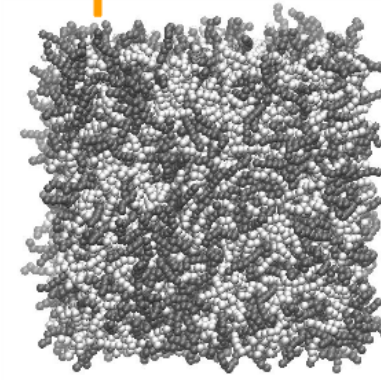
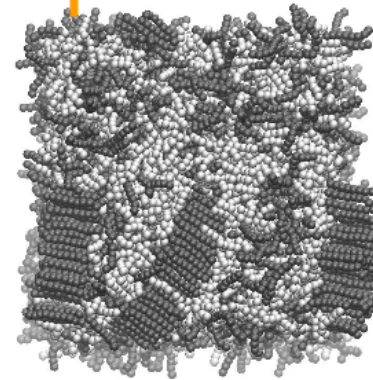
NPT
1 bar,



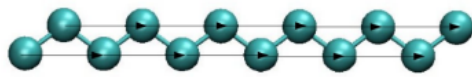


Binary alkane system

NPT
1 bar,



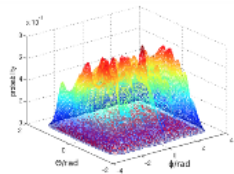
vector analysis



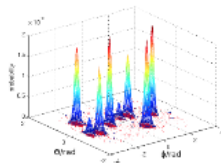
$$r = \sqrt{x^2 + y^2 + z^2}$$

$$\theta = \arctan\left(\frac{\hat{y}}{\hat{x}}\right)$$

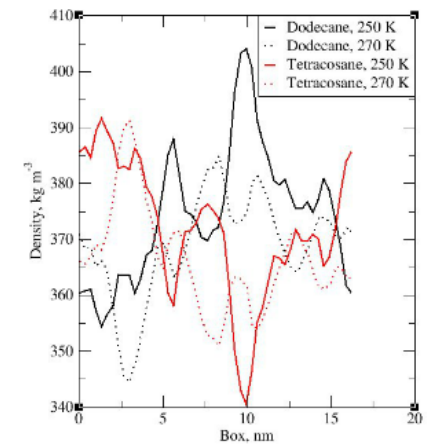
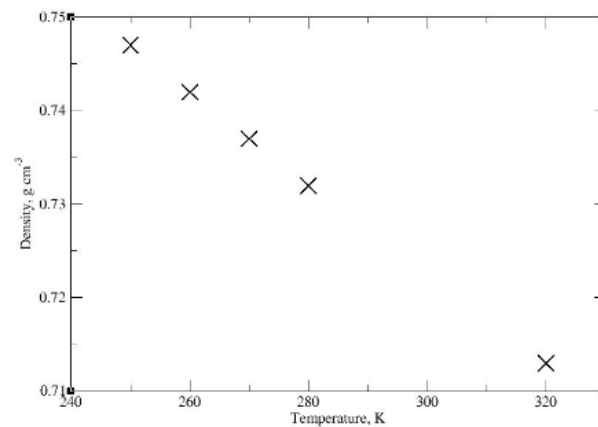
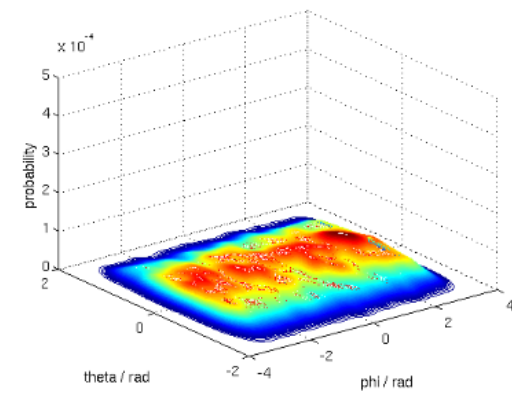
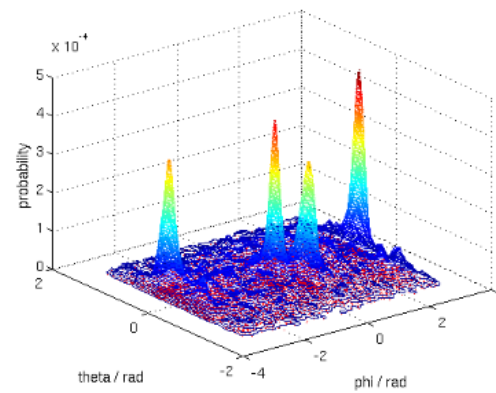
$$\phi = \arccos\left(\frac{\hat{z}}{r}\right)$$



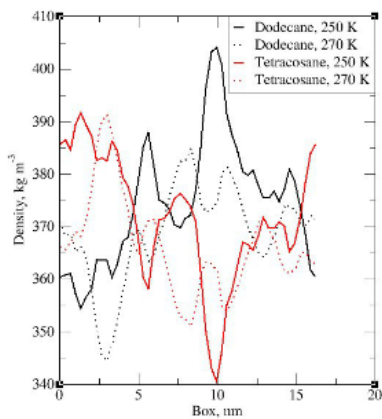
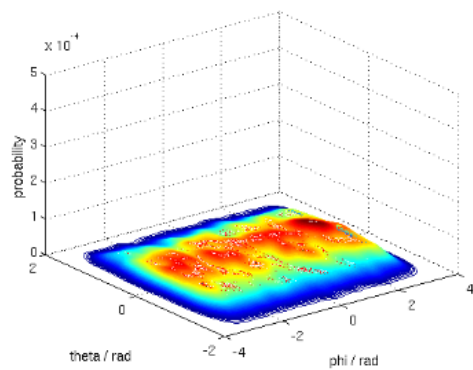
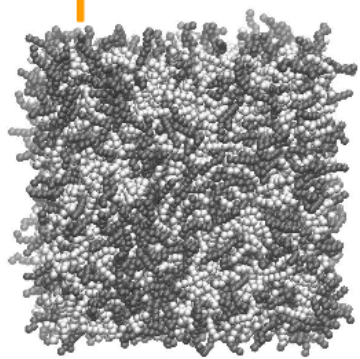
tricosane 520 K



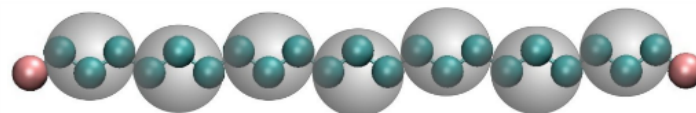
280 K



alkane system

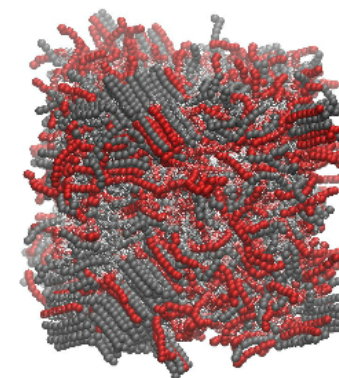


+ UA-CG

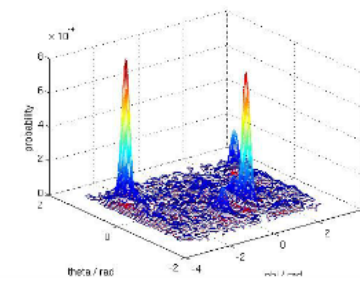


Tertiary alk

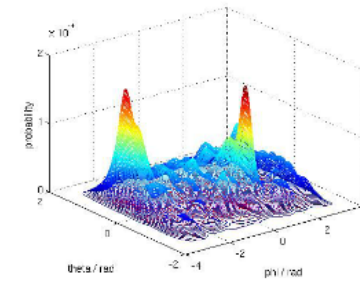
NPT
1 bar,



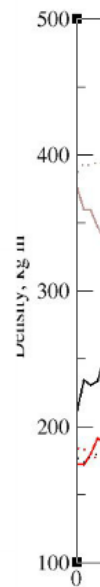
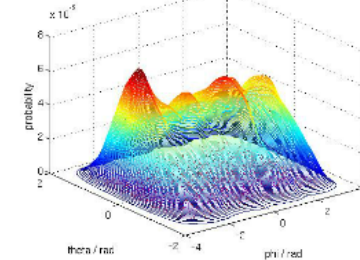
C24



C23

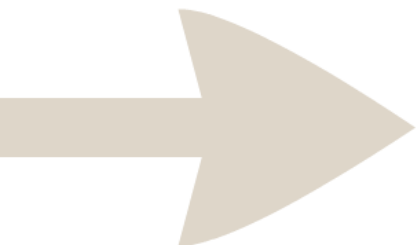
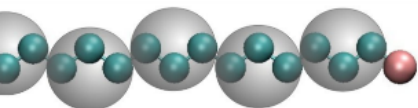


C12

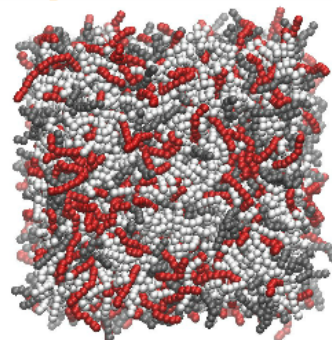
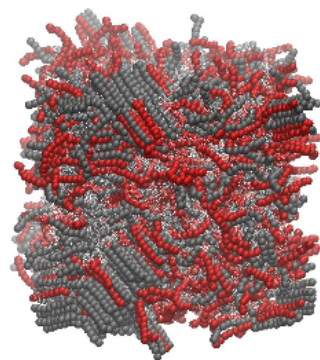


Tertiary alkane system

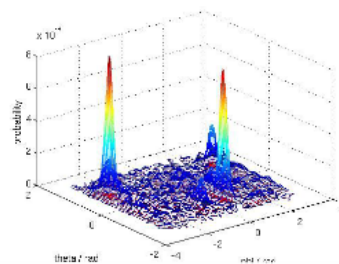
A-CG



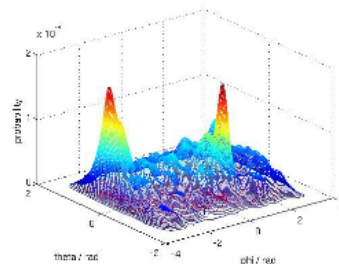
NPT
1 bar,



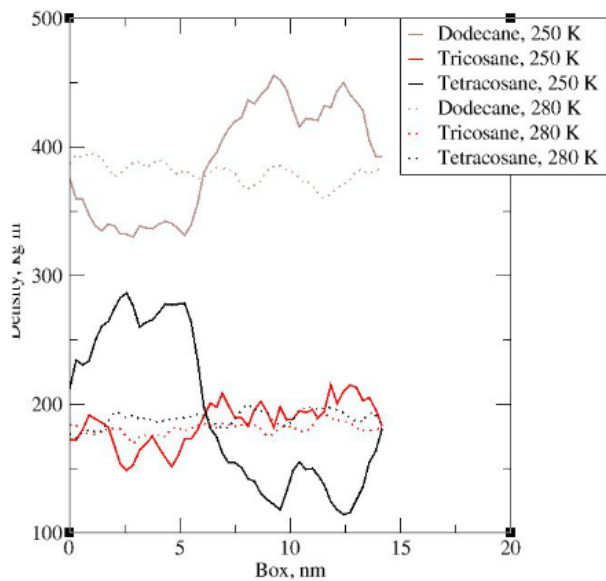
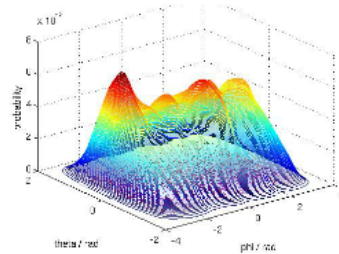
C24



C23



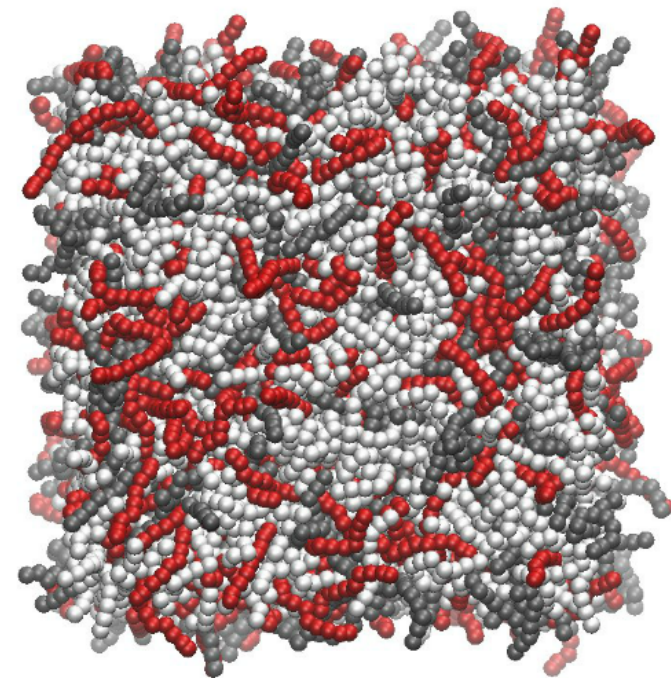
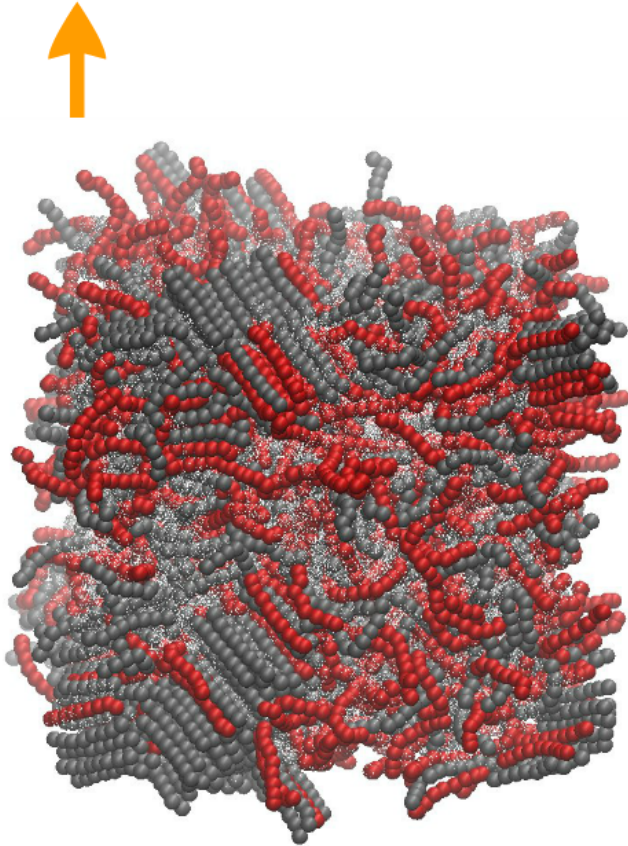
C12



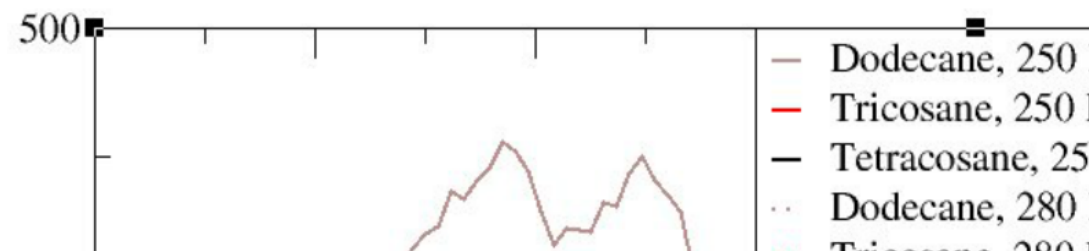
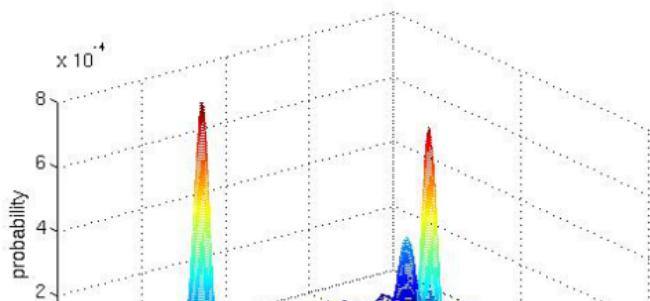
we have not been able to observe it with UA

Tertiary alkane system

NPT
1 bar,

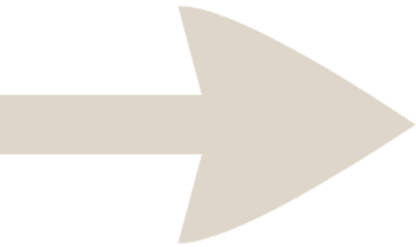
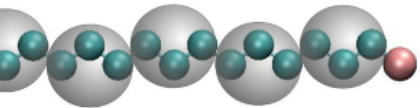


C24

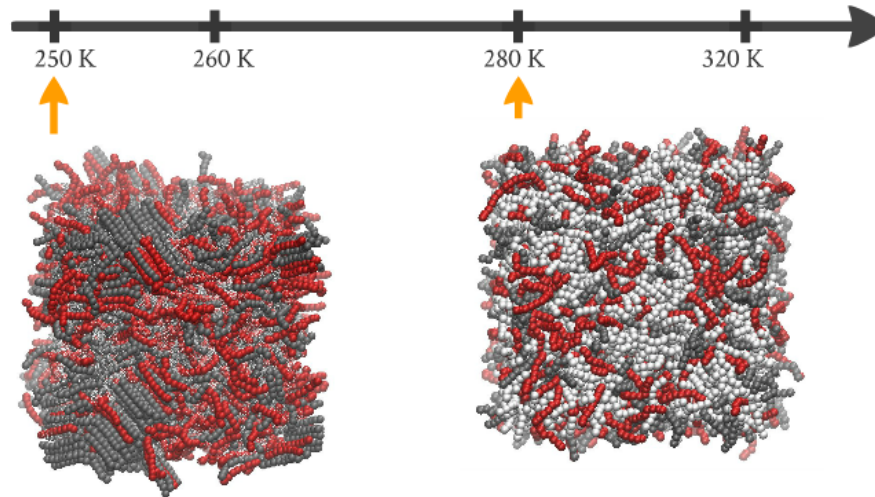


Tertiary alkane system

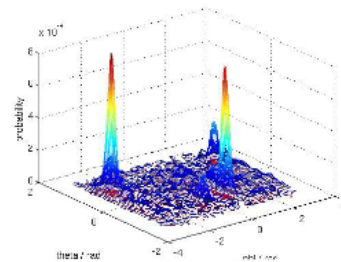
A-CG



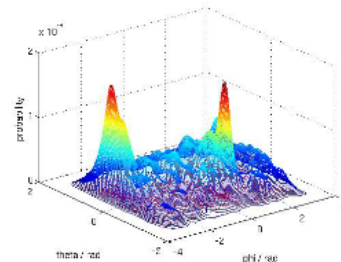
NPT
1 bar,



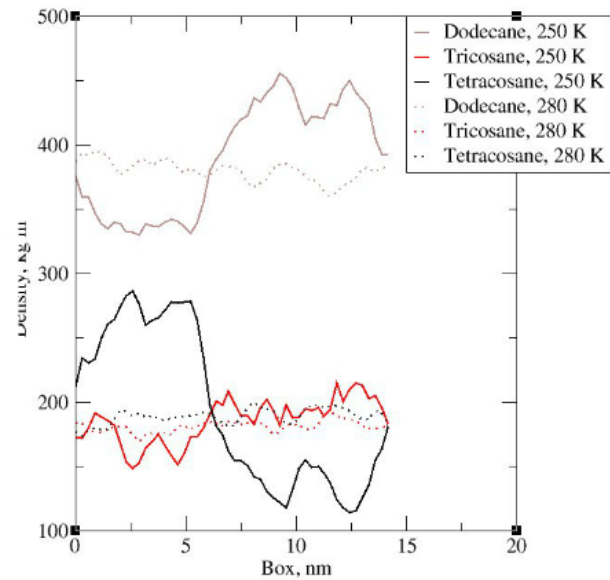
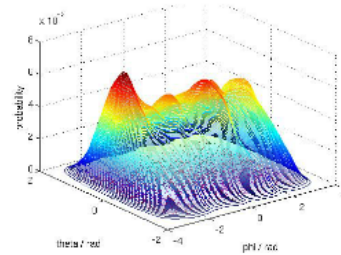
C24



C23



C12

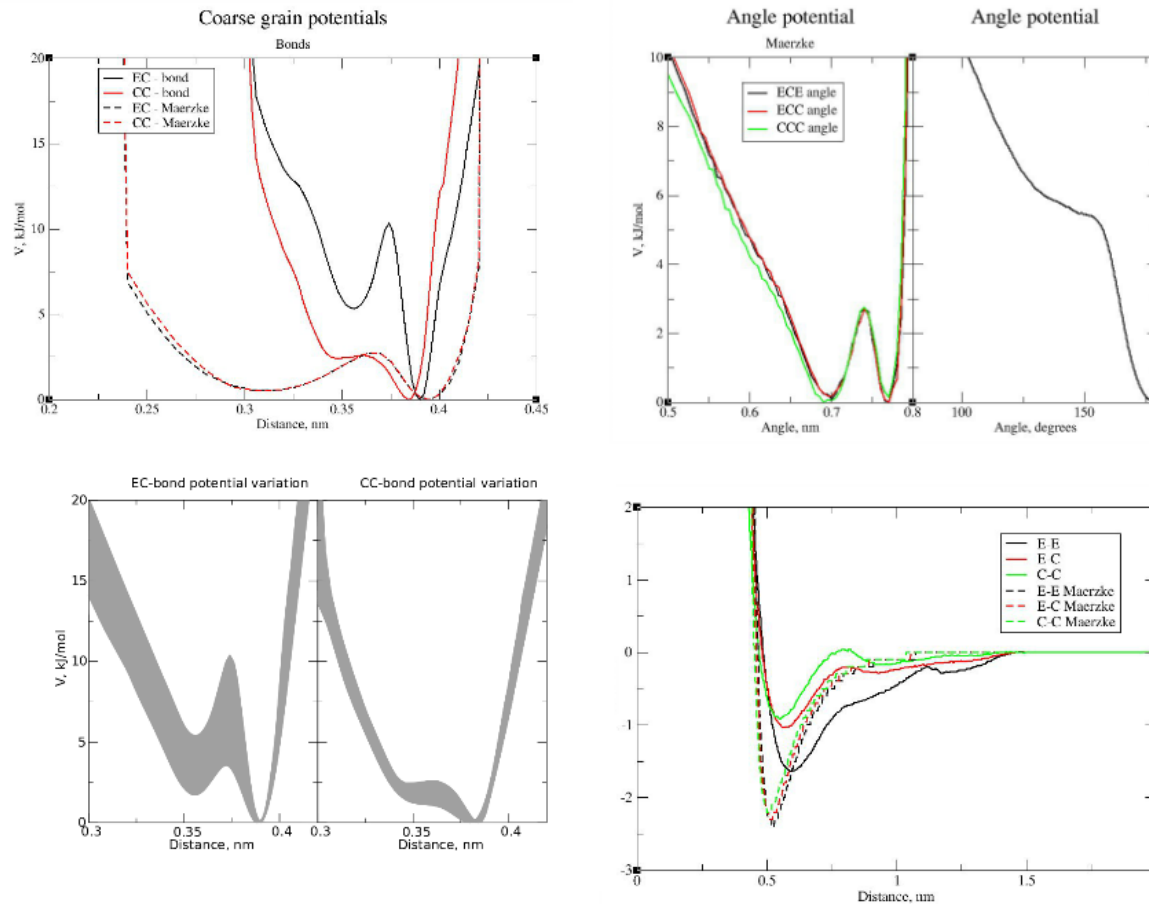


we have not been able to observe it with UA

Comparison to similar CG FF

Discussion

[K.A. Maerzke and J.I. Siepmann. Transferable potentials for phase equilibria: coarse-grain description for linear alkanes. The Journal of Physical Chemistry B, 2011.]



Maerzke et al. matched FF over the liquid-vapour co-existence curve, like TraPPE

Higher emphasis on the thermodynamic properties, not structural

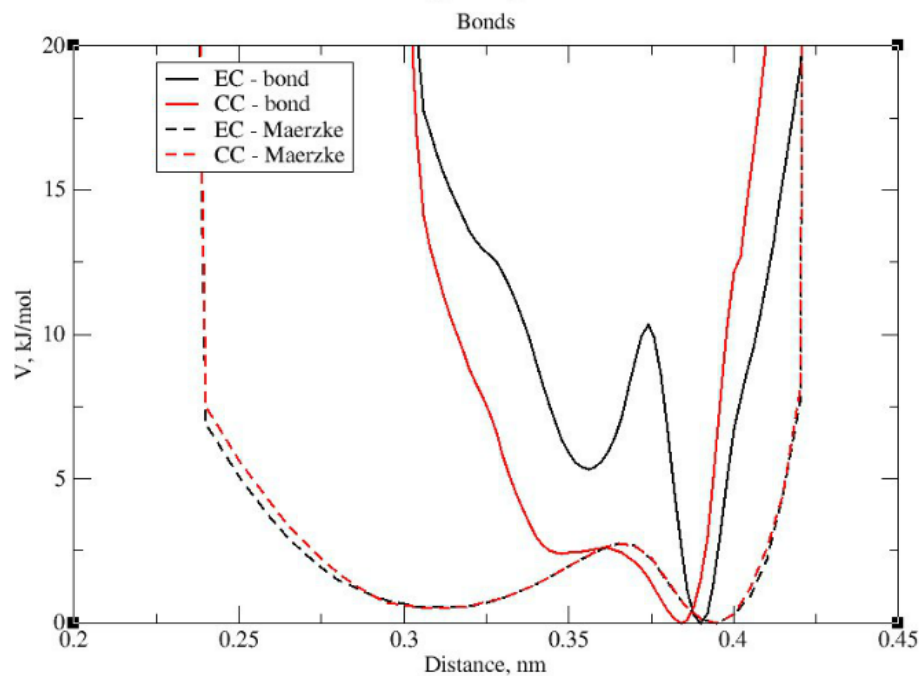
Used 12-6 LJ [best for liquid-vapour transition within UA FF]

Very good density agreement above crystallisation point

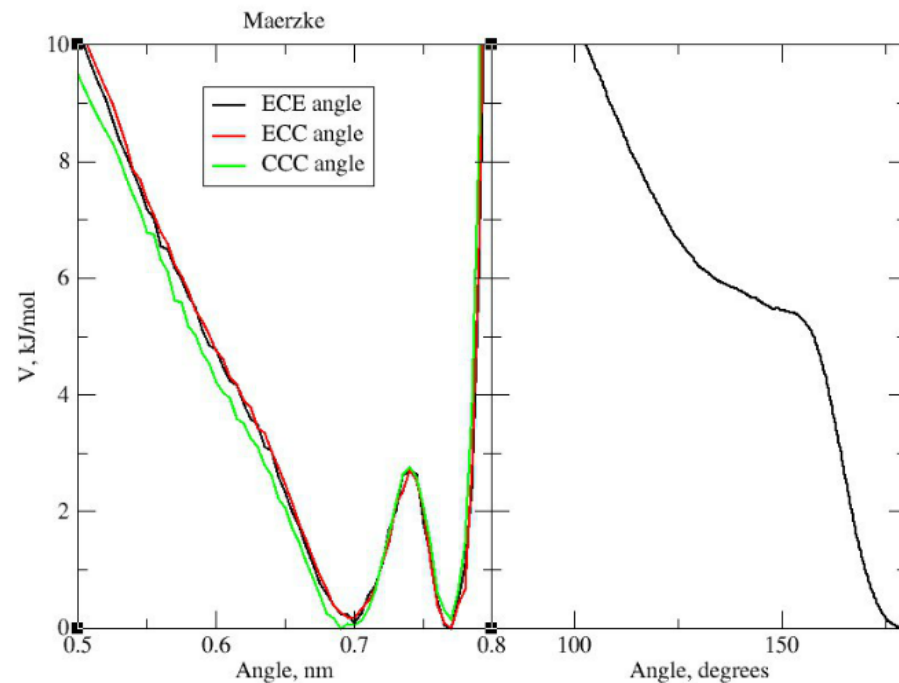
Poor RDF representation below crystallisation

Small time step

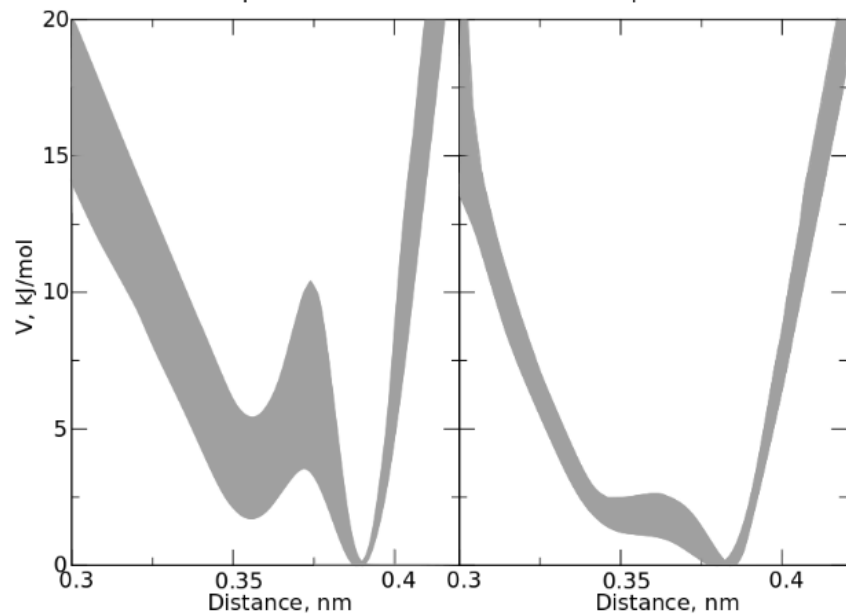
Coarse grain potentials



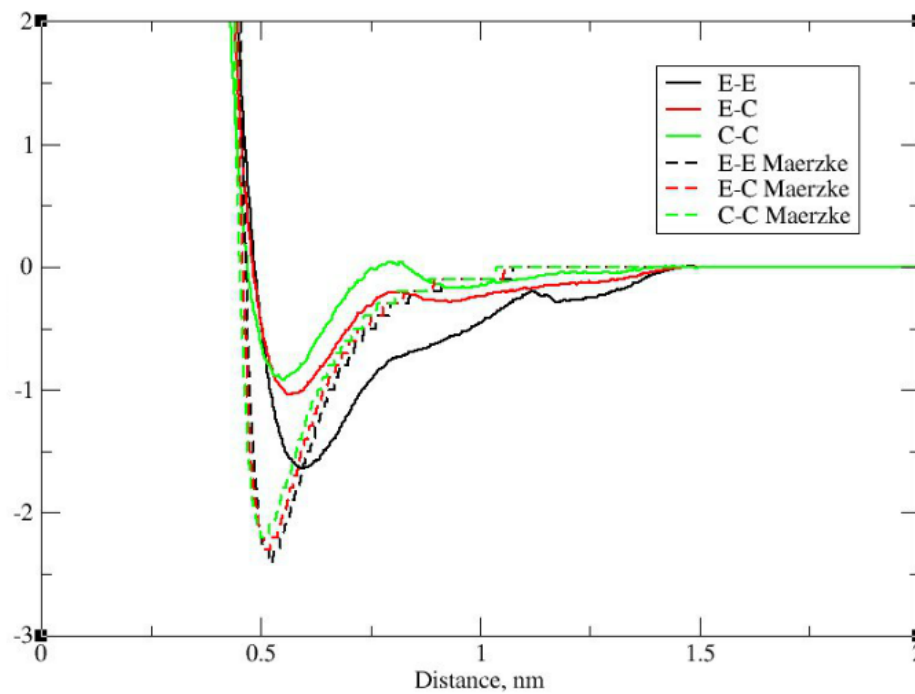
Angle potential



EC-bond potential variation

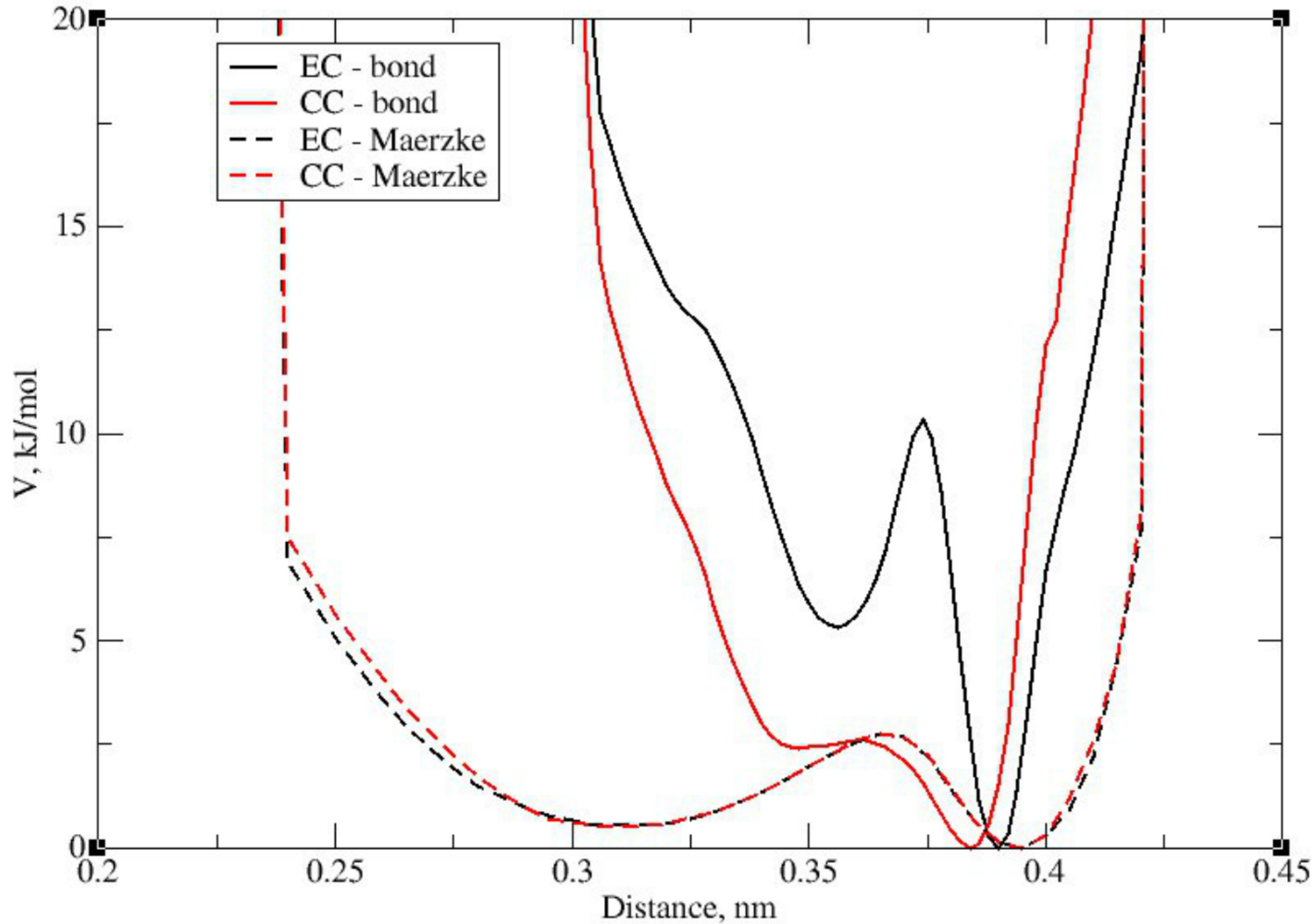


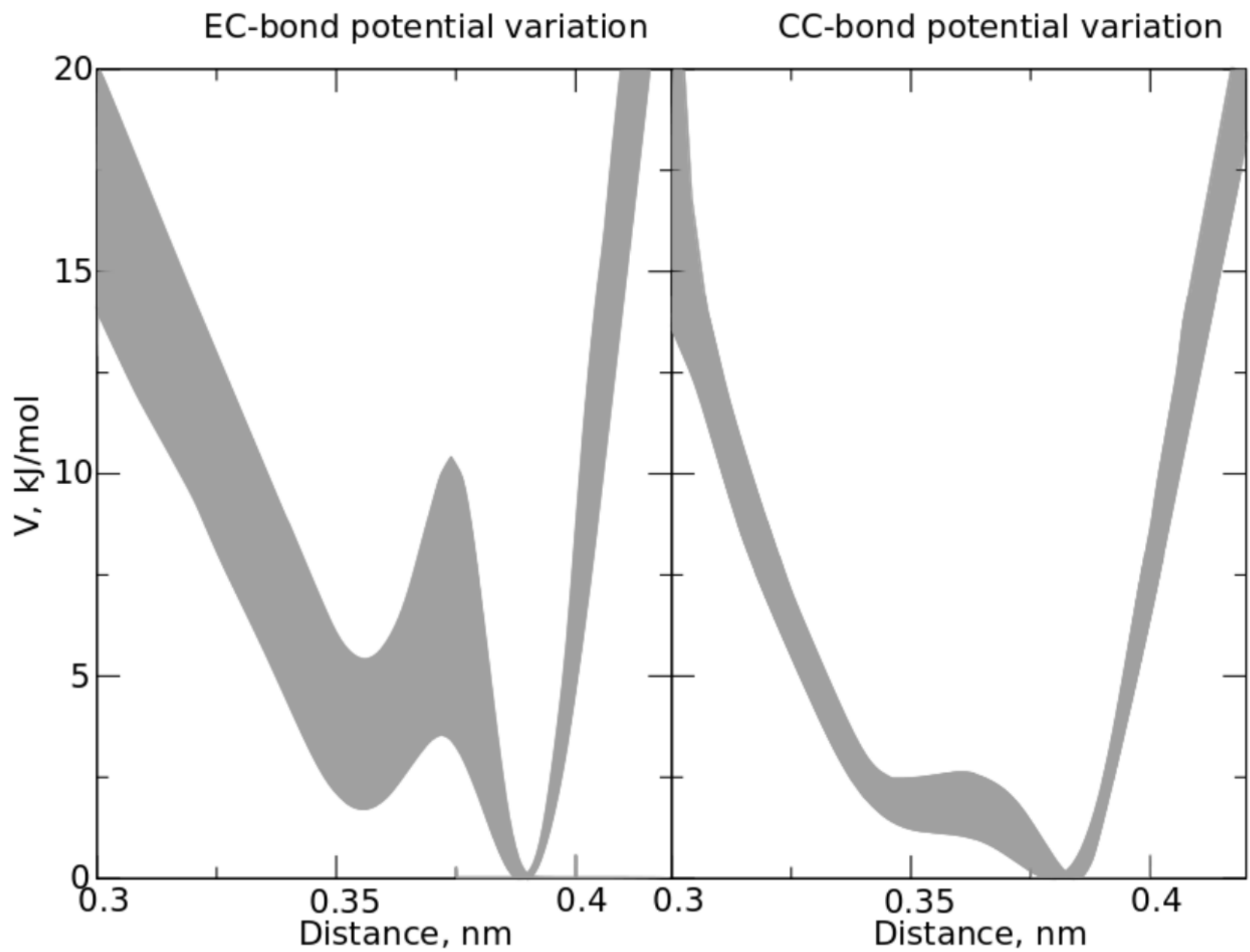
CC-bond potential variation



Coarse grain potentials

Bonds

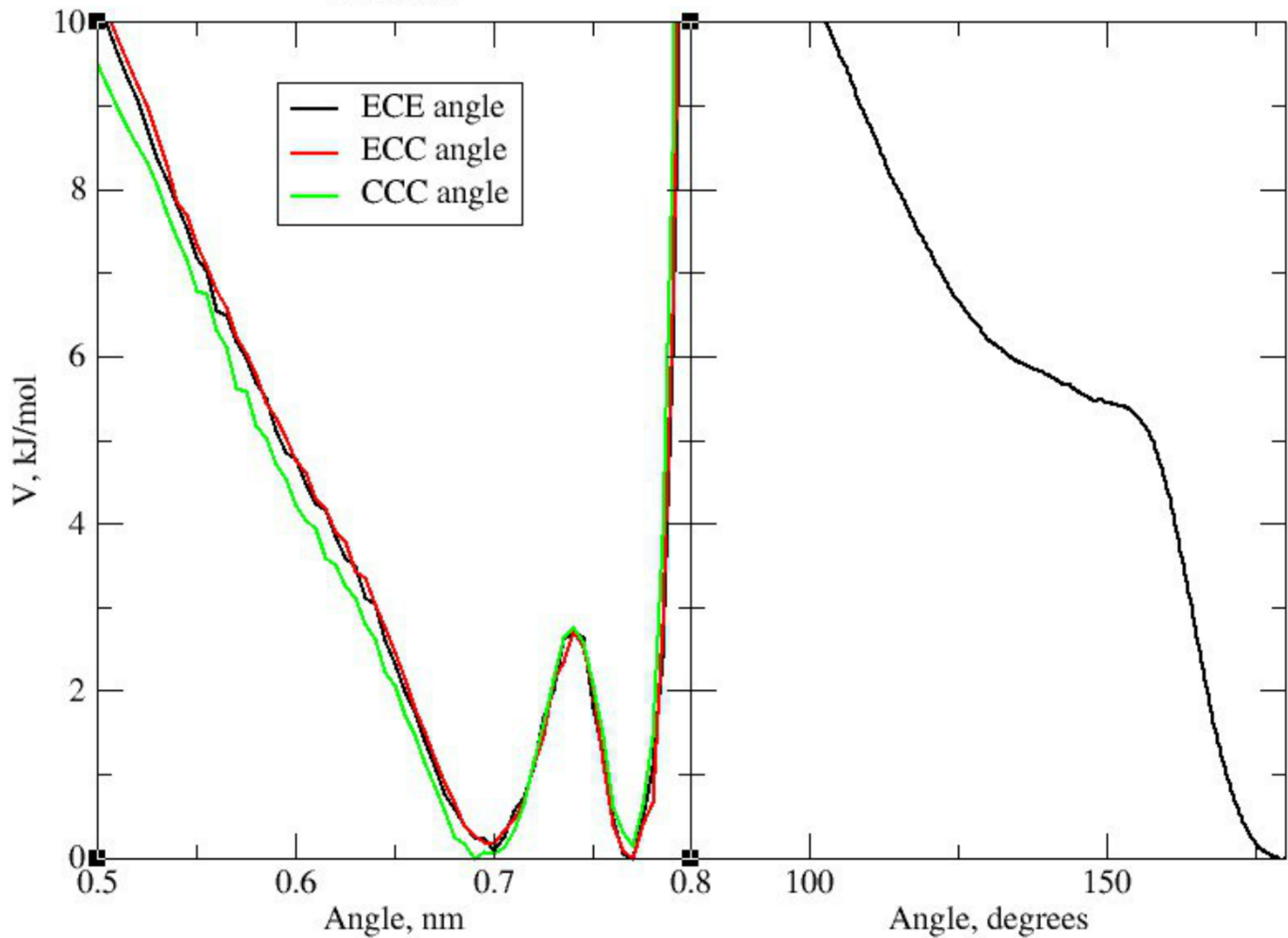


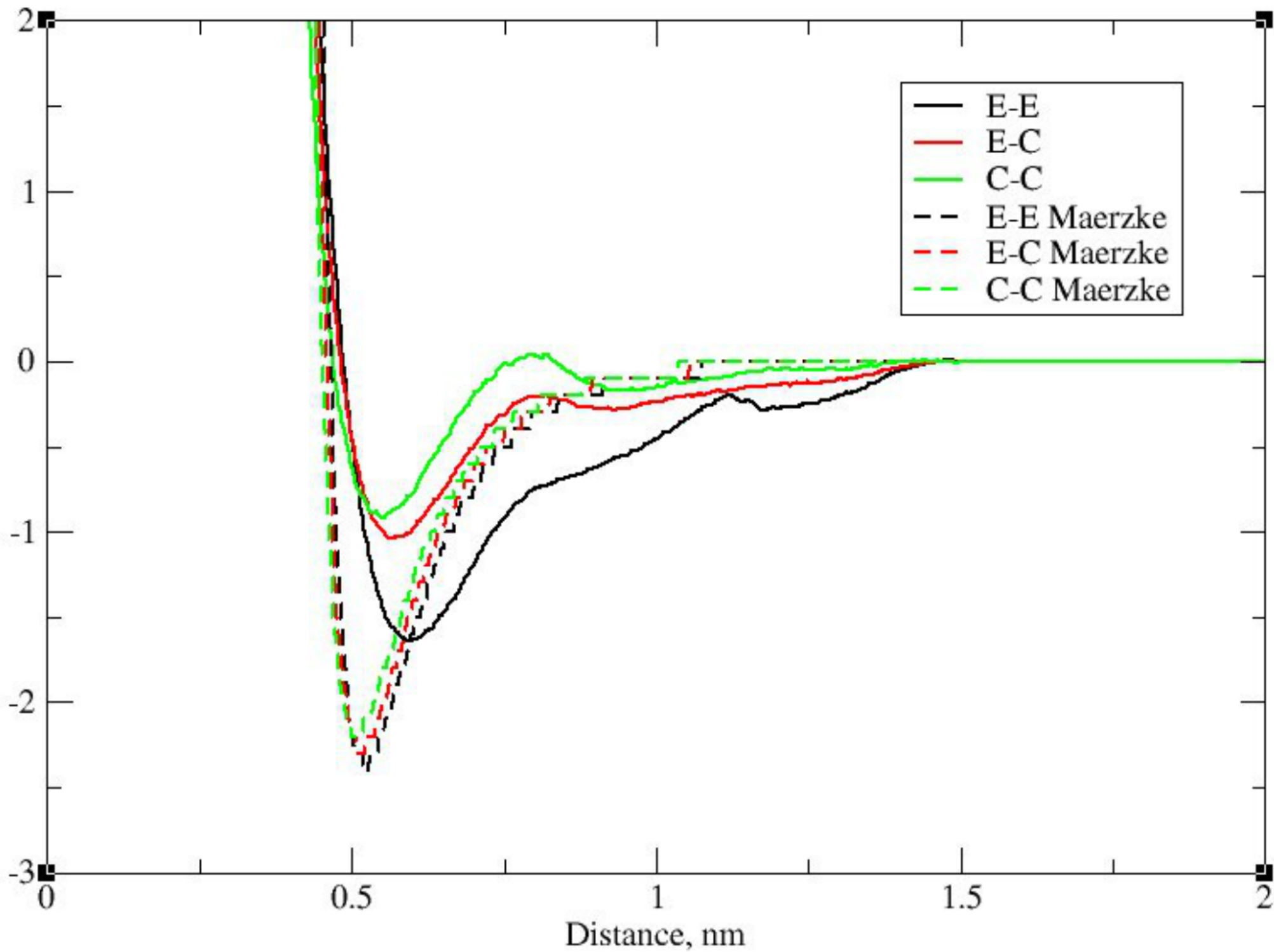


Angle potential

Maerzke

Angle potential







Van der Waals

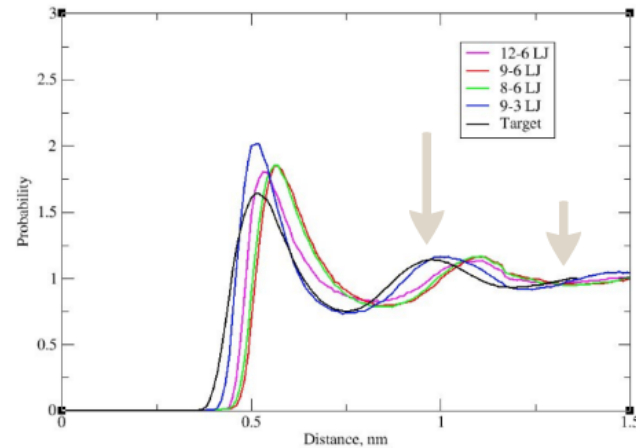
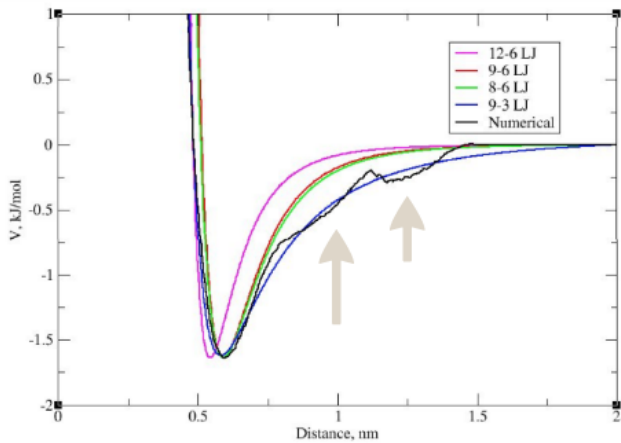
$$E_{pair}(r) = \left(\frac{n}{n-m}\right) \left(\frac{n}{m}\right)^{m/(n-m)} \epsilon \left[\left(\frac{\sigma}{r}\right)^n - \left(\frac{\sigma}{r}\right)^m \right]$$

$$E^{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

$$E^{LJ} = \epsilon \left[2\left(\frac{r_m}{r}\right)^9 - 3\left(\frac{r_m}{r}\right)^6 \right]$$

$$E^{LJ} = \epsilon \left[3\left(\frac{r_m}{r}\right)^8 - 4\left(\frac{r_m}{r}\right)^6 \right]$$

$$E^{LJ} = \frac{3\sqrt{3}}{2} \epsilon \left[\left(\frac{\sigma}{r}\right)^9 - \left(\frac{\sigma}{r}\right)^3 \right]$$



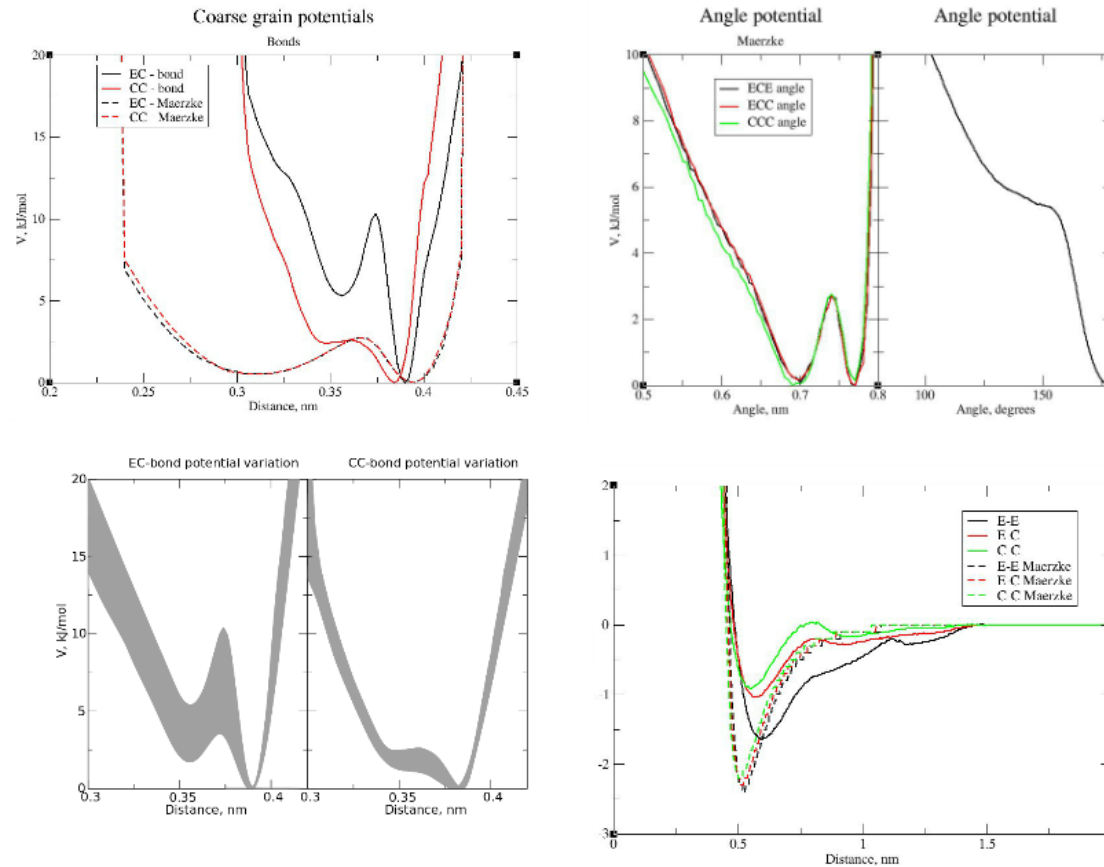
- VdW are not well represented analytically
- Combination rules are unsuitable for lamellar structures

Timestep is defined by the STEEPNESS of the potentials
 Maerzke et al. use 12-6 LJ, that steepness is ~ to bond potential

Comparison to similar CG FF

Discussion

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We have shown HOW we developed a CG FF for alkanes capable of:

- temperature transferability over 120 K +
- crystal formation from the melt
- correct density at atomistic pressure

We have used the CG FF for modeling the paraffin crystal growth and observed:

- co-crystallisation of similar length paraffins
- separation of the shorter chains into the melt
- this has not been possible to model with UA

What is next?

Develop 4:1 CG bead

Extend FF for branched CG bead

CG for standard additives

Thanks to:

Prof Mark Wilson & the group

Durham University

Infineum