SURFACE FREE ENERGY IN MOLECULAR DYNAMICS AND CLEAVING FOR MOLECULAR CRYSTALS

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Abstract

A study of the properties of interface in Molecular Dynamics (MD) is reported

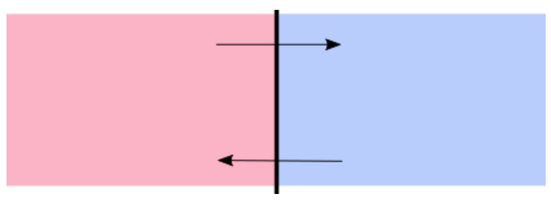
In particular:

- Proof of the relationship between Surface Free Energy (SFE), γ, and Surface Stress (SS), f, (Shuttleworth Equation) with MD
- Derivation of SFE for organic crystals: application to Mannitol
- Different force-fields and structure are tested and compared

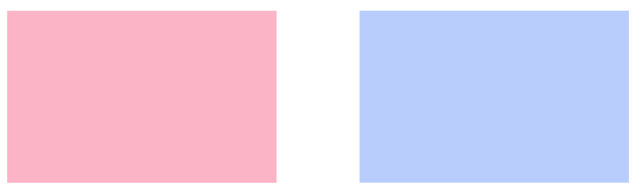
Cleaving Method

Thermodynamic Integration calculates the SFE by integrating over a thermodynamic path parametrised by the parameter λ
In particular:

- λ=1 represents the whole crystal with periodic boundary condition in all the three directions



- λ=0 represents the crystal cut in half where two surfaces are created



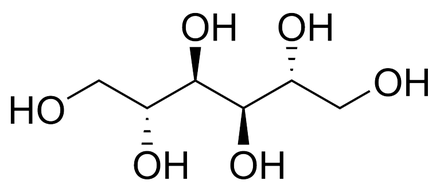
- The interactions between the two sides of the crystal are gradually switched off by changing λ from 1 to zero

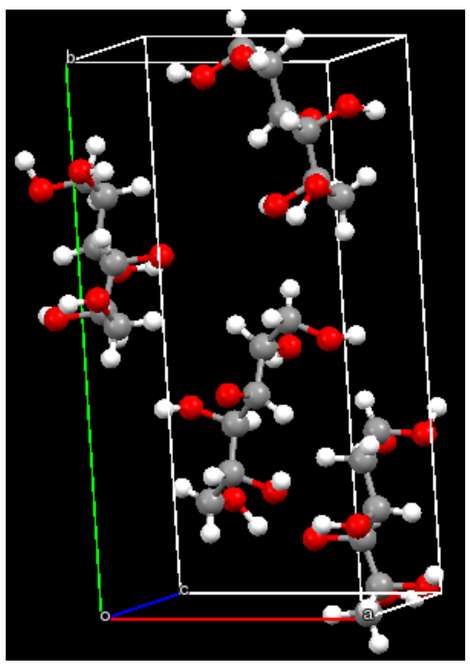
The work per unit area, A, is obtained by calculating the following integral:

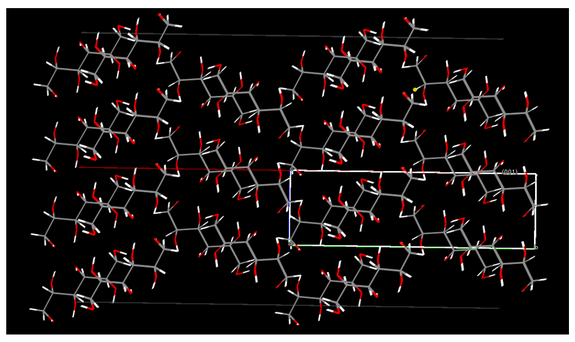
$$\gamma = A^{-1}\int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle d\lambda$$

Mannitol

The test system consists of a mannitol crystal at room temperature and pressure. We apply the cleaving method to the crystal sample by cutting it in half and calculating the reversible work to create the surface. This work per unit area of the surface determines the SFE.







Crystal structure of the mannitol and unit cell with three orthogonal axes highlighted: a (red), b (green), c (blue)

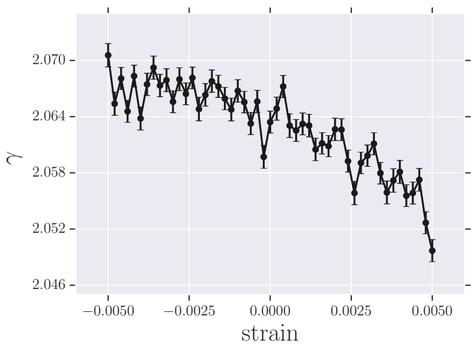
- Crystal structure considered: (001), (010), (100), (011), (120)
- Structure DMANTL, DMANTL 09
- Force-field for MD simulations: GROMOS all-atom, GROMOS united-atom

Free Surface Energy VS Surface Tensor

We verified the Shuttleworth Equation (SE) at finite temperature:

$$f_{ij}^{SE} \equiv \delta_{ij}\gamma + \frac{\partial \gamma}{\partial u_{ij}} = f_{ij}^{SS}, \qquad i,j = x,y$$

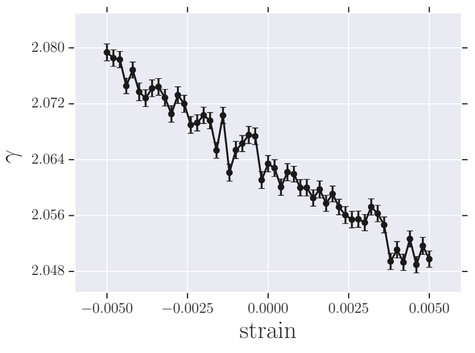
We tested the different possible routes on a simple system:
Lennard-Jones crystal fcc (110), T=0.3 (LJ units)

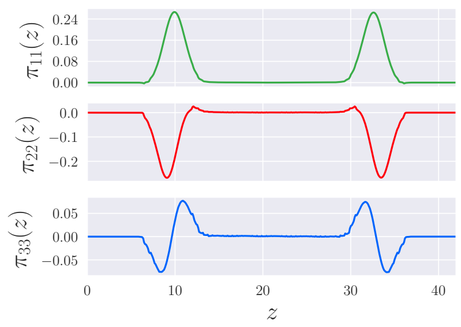


Surface Free Energy, γ, for different strains of the crystal

x direction

y direction





Pressure profile in the three directions from which f_{SS} is obtained

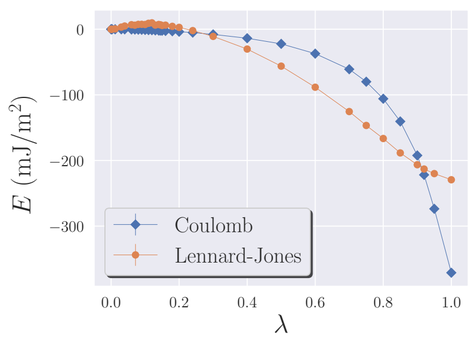
Different components of the Shuttleworth equation and comparison with the calculated surface stress

γ	$\frac{\partial \gamma}{\partial u_{ii}}$	f_{ii}^{SS}	f_{ii}^{SE}
2.063±2	-2.87 ± 6	-0.783±2	-0.81±6
2.063±2	-1.38 ± 1	0.69±2	0.68±6

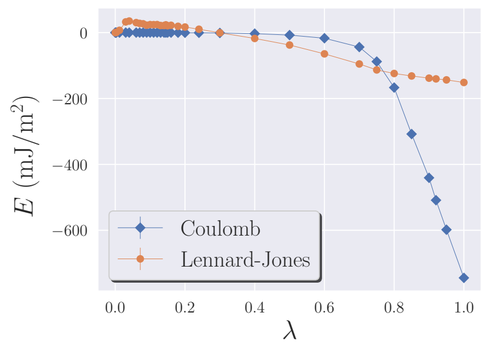
Results in $(\boldsymbol{\varepsilon\sigma^{-2}})$. First row: $i = x$, second row : $i = y$

SFE for Mannitol with Cleaving

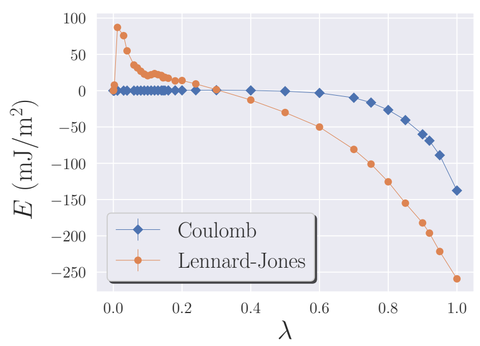
Thermodynamic path for the creation of an interface perpendicular to b direction



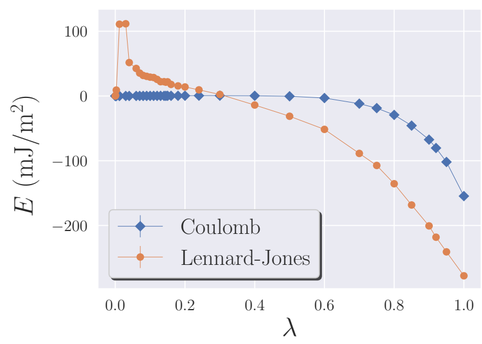
DLMANT GROMOS All-Atoms



DMANTL09 GROMOS All-Atoms



DLMANT GROMOS United-Atoms



DMANTL09 GROMOS United-Atoms

SFE [mJ/m²]	All-Atoms	United-Atoms
DMANTL	141 ± 1	70 ± 1
DMANTL09	155 ± 1	75 ± 1

For Mannitol we can use cleaving to calculate γ, the pressure tensor to calculate f, and the difference in energy between bulk and slab to estimate the Surface Free Energy

For Cleaving we can split the interaction into two components: Coulomb interactions and Lennard-Jones interactions

Conclusions

- Calculations for orientations (010) and (011) shows a behaviour consistent with experiment
- The difference with experiments may be due to the particular force-field employed, further analysis with different force-fields is needed
- We can now assign to each model its exact physical meaning in terms of Surface Free Energy or Surface Stress

Acknowledgements
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