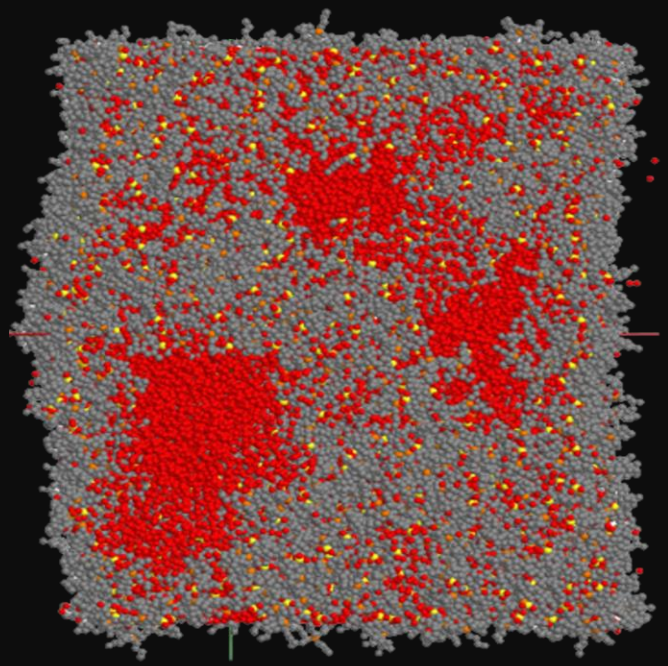
Water Harvesting with Thermoresponsive Ionic Liquids



A Molecular Dynamics Simulation Analysis

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Introduction

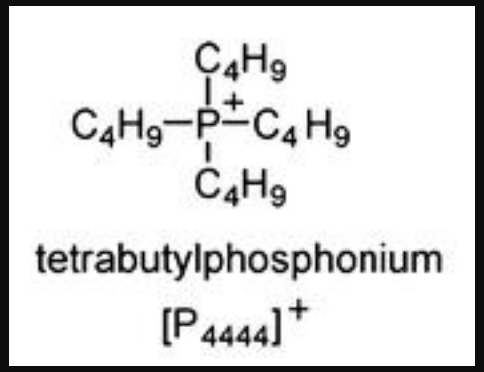
Evaluate:

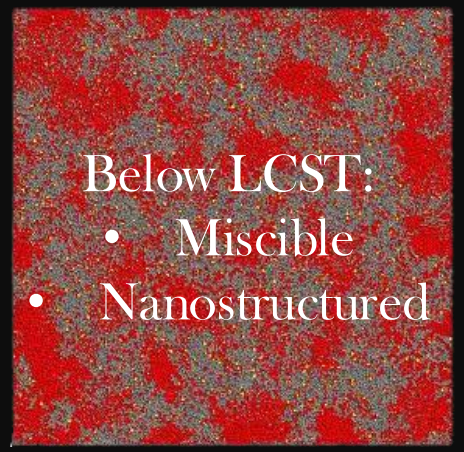
1. ILs as a potential water harvesting method.
2. The ability of brute force simulation to characterise ILs.

My role:

- 12-month European project.
- Analyse data output from the simulated systems.

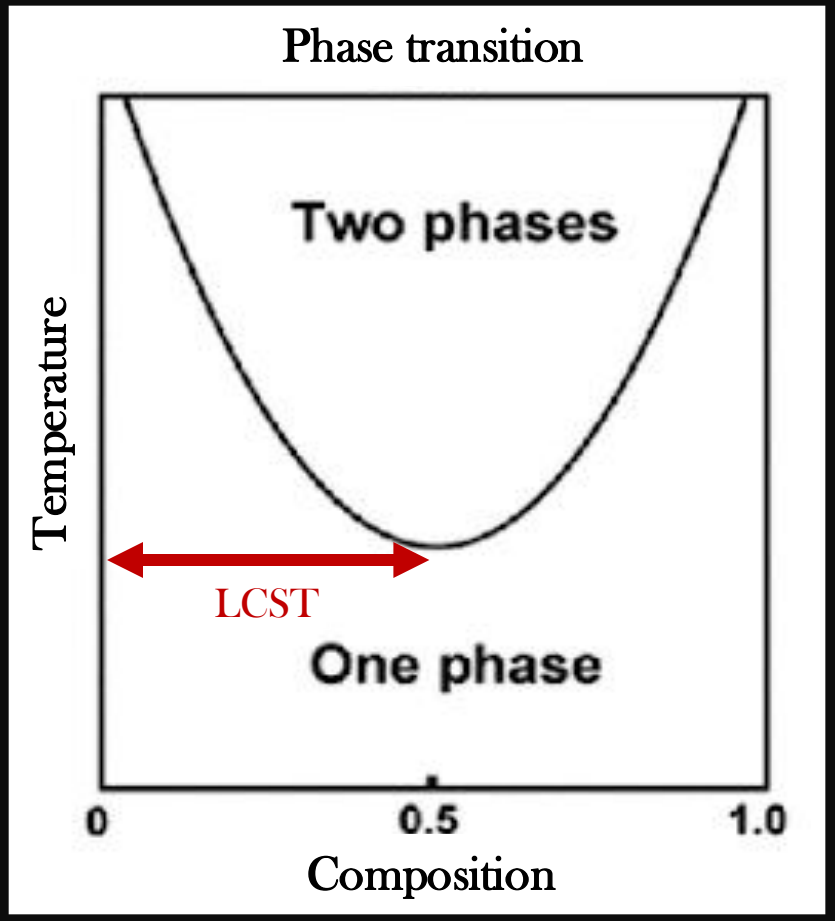
Thermoresponsive Ionic Liquids



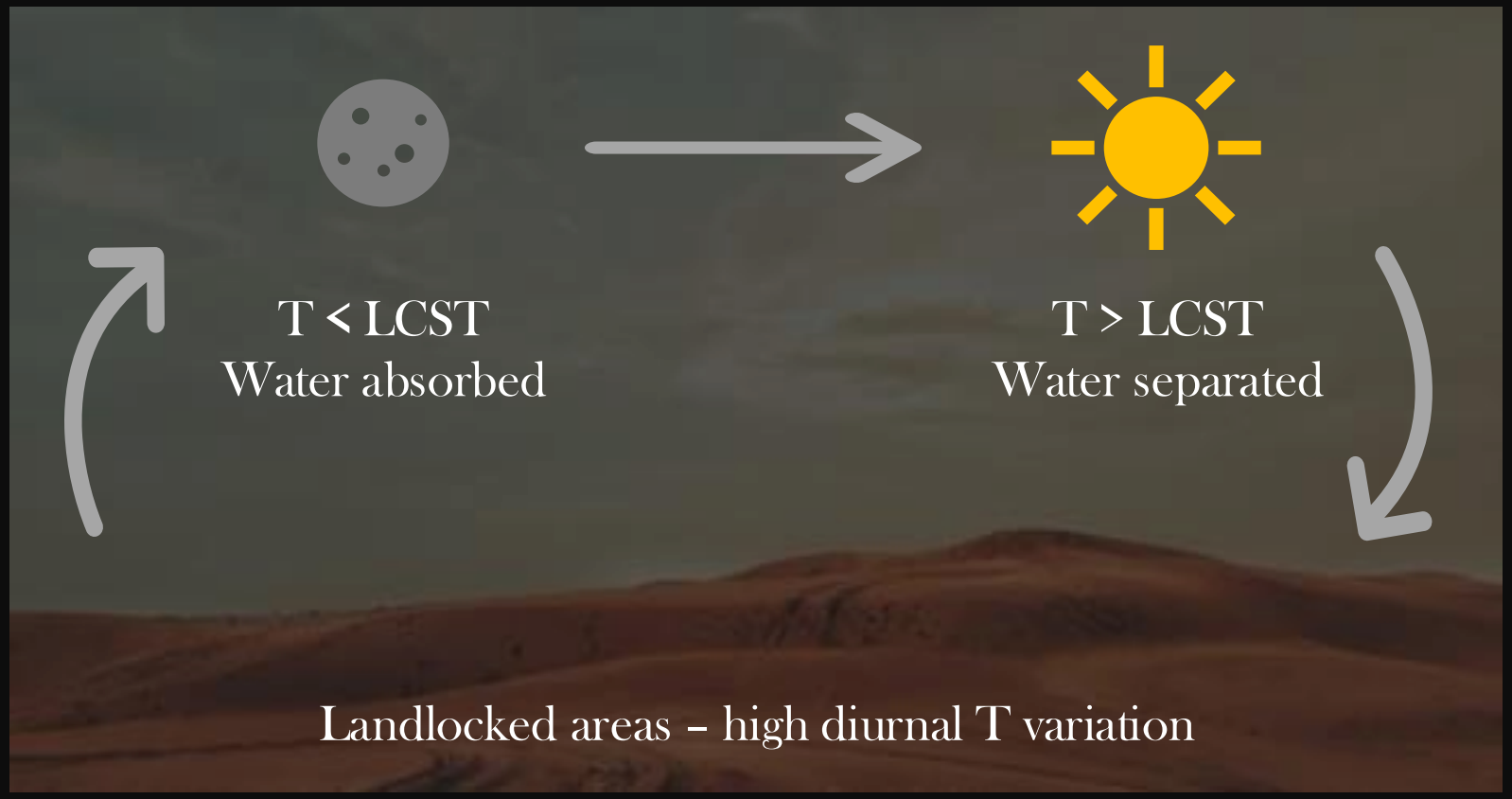


$[P_{4444}][DMBS]$:

- LCST = Lower Critical Solution T
- LCST ~ 40°C / 313 K
- Glass transition < 0°C / 273 K



Motivation of Simulation



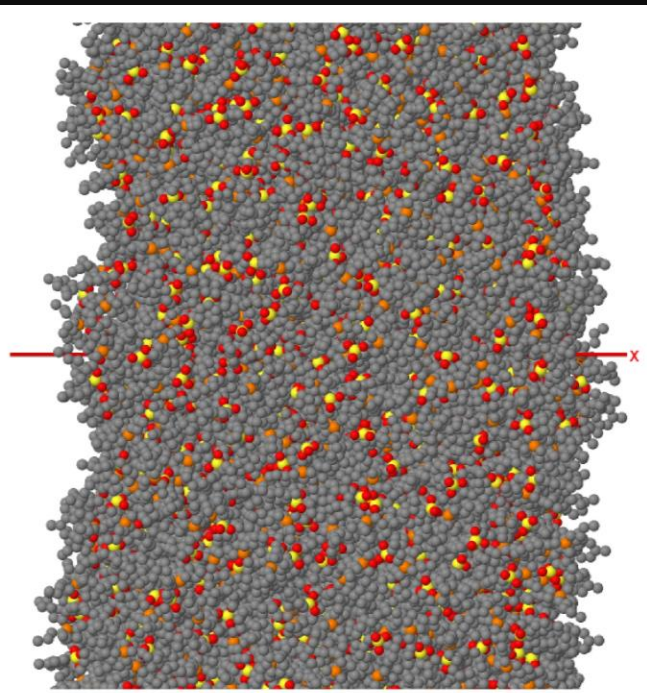
Simulation Stages:

Stage 1: Water absorption at low T

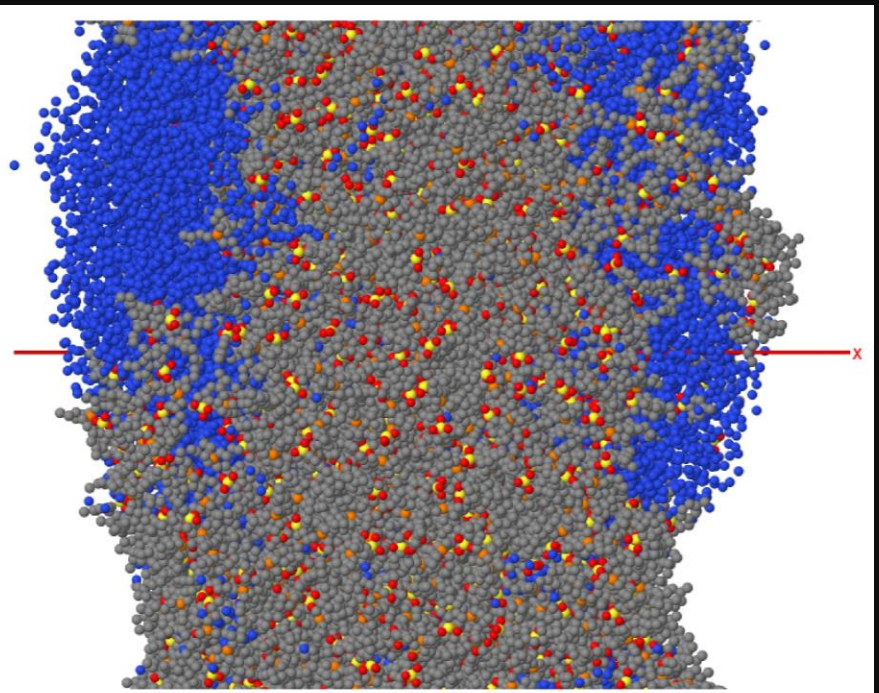
Stage 2: Water separation at high T

Stage 1: Model & Methods

$N_w = 0$



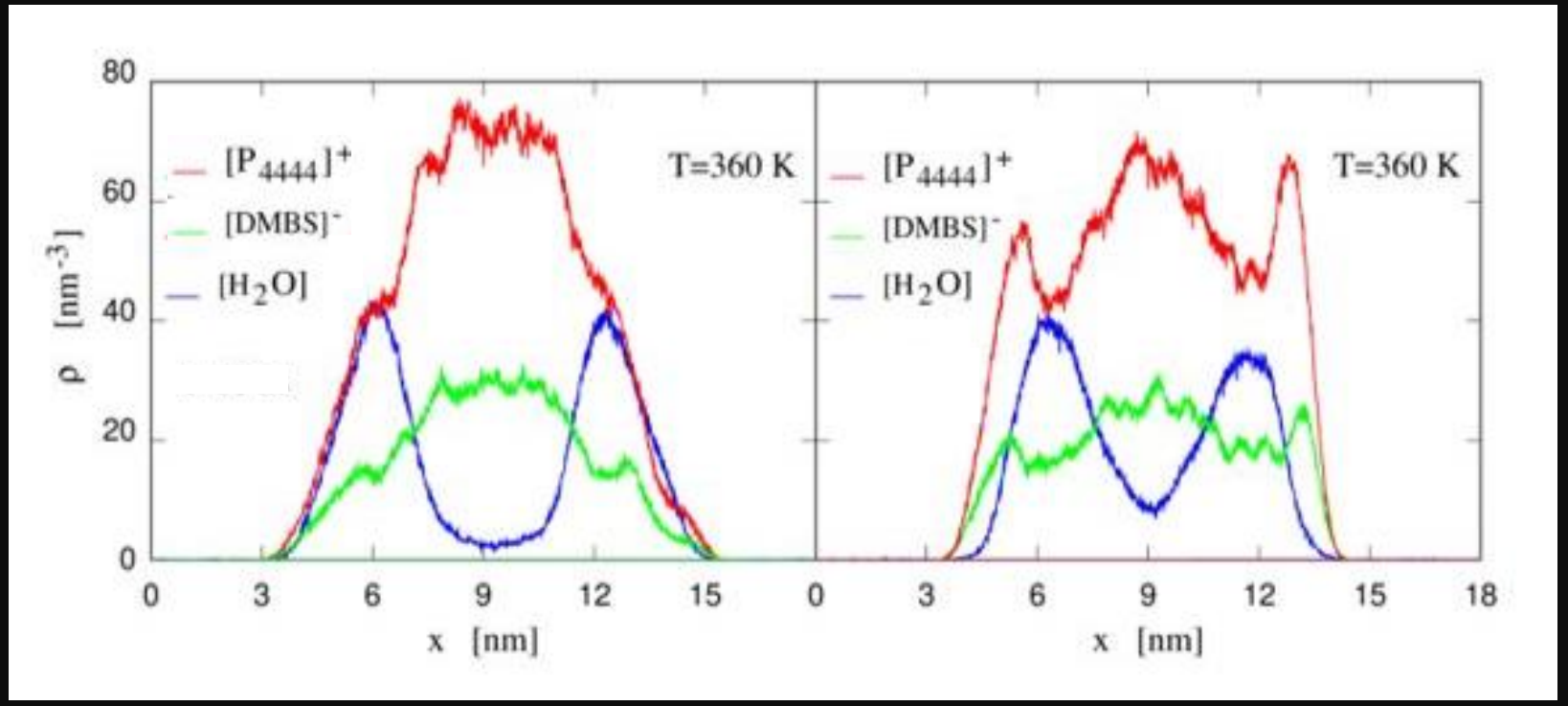
$N_w = 12000$

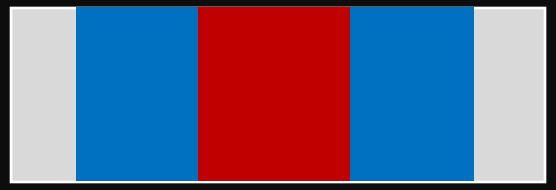


- NVT ensemble & $P = 0$
- X is orthogonal to free surface
- 11 temperatures between 260 **K** and 360 **K**
- 1728 ions & 12000 water molecules

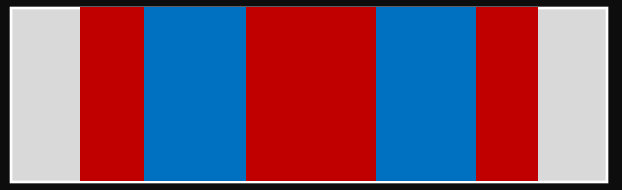
Stage 1: Time-Dependent Profiles

$t = 10\ ns$ $t = 135\ ns$





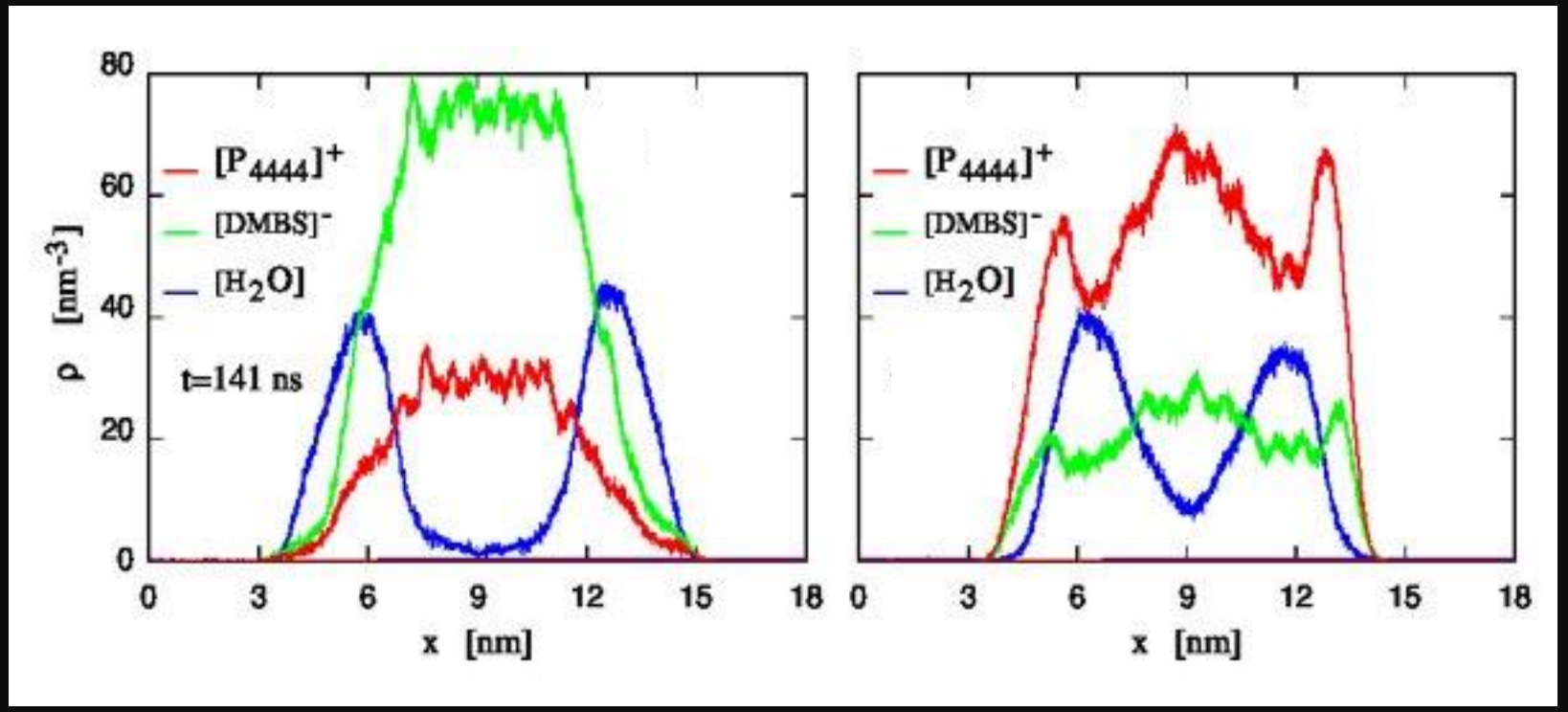
V-W W-IL

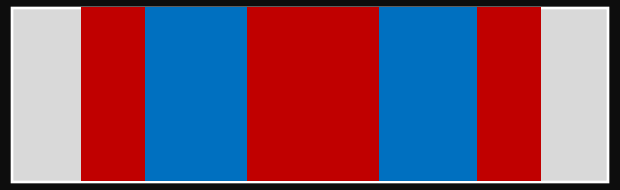


V-IL 2(W-IL)

Stage 1: Temperature-Dependent Profiles

$T = 320\ K$ $T = 360\ K$





V-IL 2(W-IL)

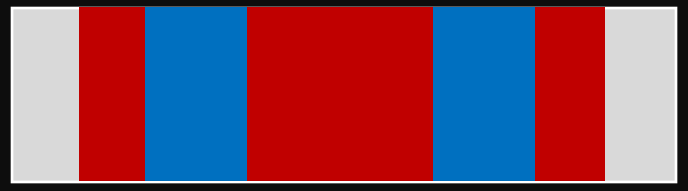
Stage 1: Surface Energies

Why does the system restructure?

W-V W-IL

2 interface pairs:

$\gamma_{tot} = 2(\gamma_{w-v} + \gamma_{w-IL})$



IL-V 2(IL-W)

3 interface pairs:

$\gamma_{tot} = 2(\gamma_{IL-v} + 2\gamma_{IL-w})$

Surface energy decreases after restructuring if:

$\gamma_{IL-W} < \gamma_W + \gamma_{IL}$

Must calculate all 3 γs

Stage 1: Surface Energies

$$\gamma_{IL-W} < \gamma_W + \gamma_{IL}$$

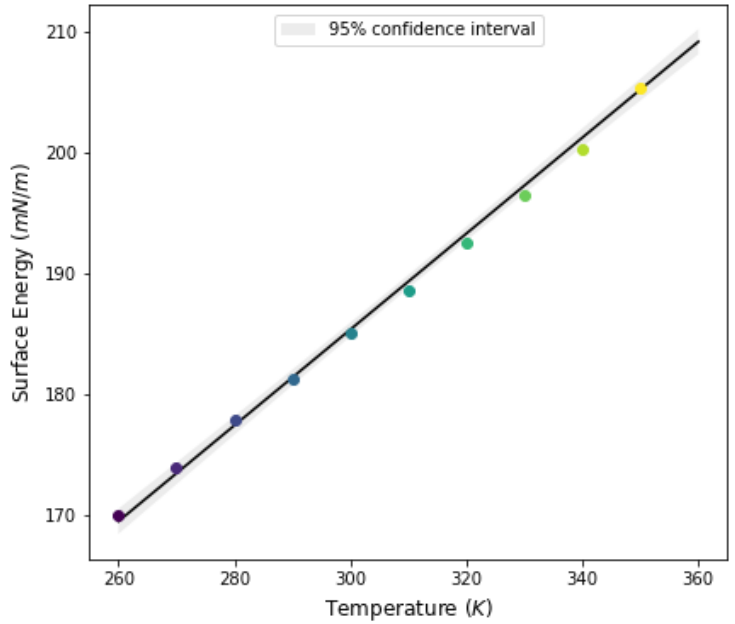
Surface Energy:

$$\gamma = \frac{U_{bulk} - U_{slab}}{2A_s\, N_A}$$

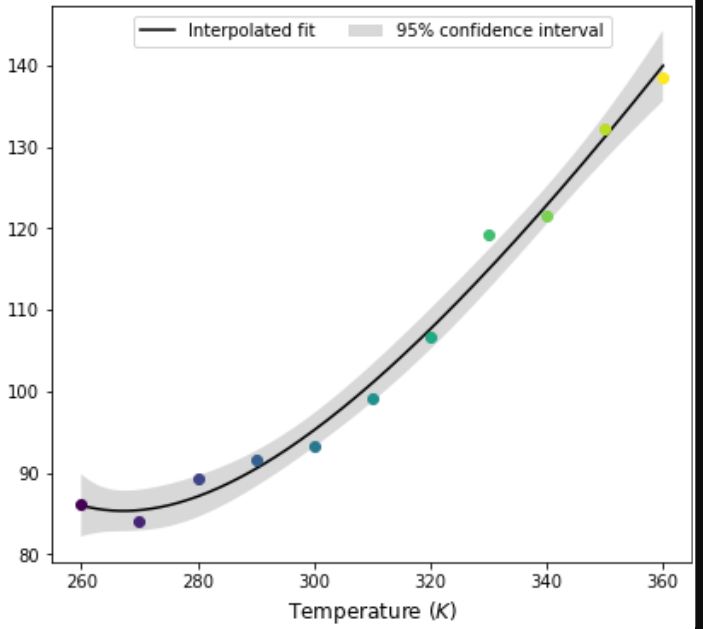
Young equation:

$$\gamma_{IL-w} = \gamma_{IL} - \gamma_w \cos(\theta_C)$$

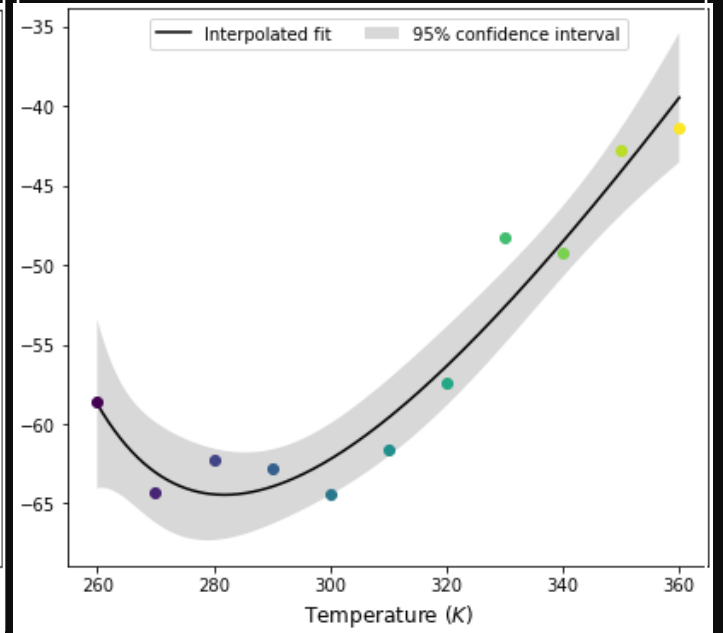
Water (γ_W)



Salt (γ_{IL})

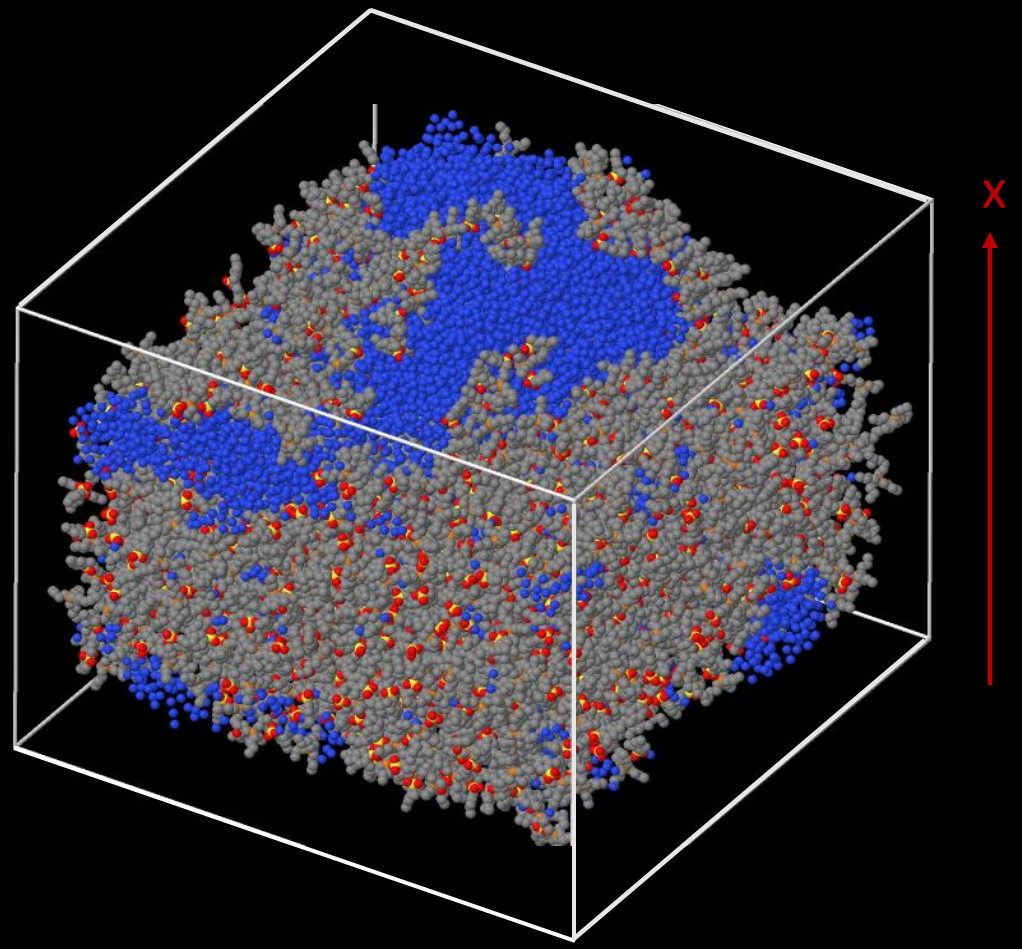


Salt-Water (γ_{IL-W})



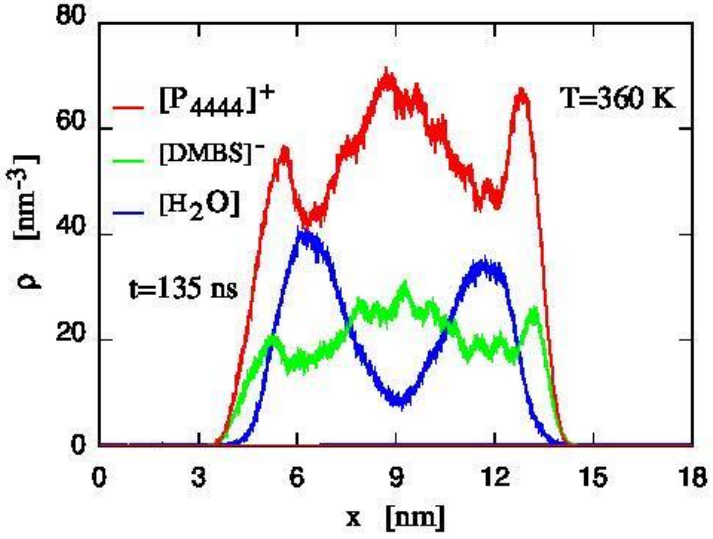
Stage 1: Surface Energies

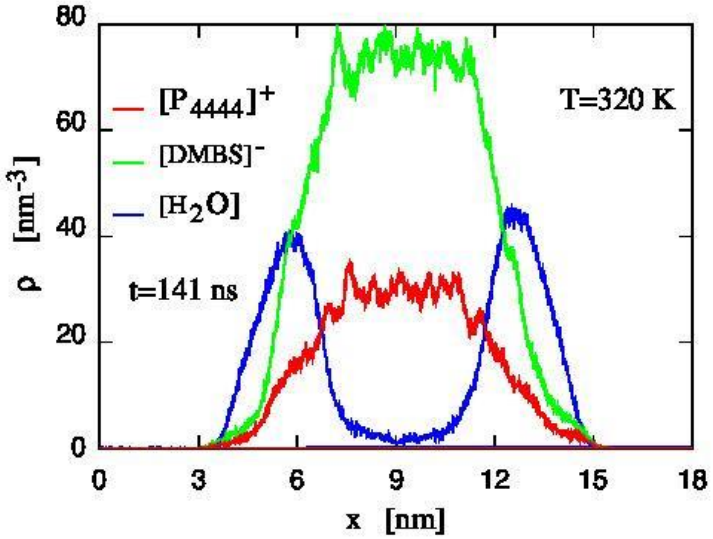
The system decreases its surface energy (γ_{IL-v}) by orientating the hydrocarbon tails outwards from the water slab.



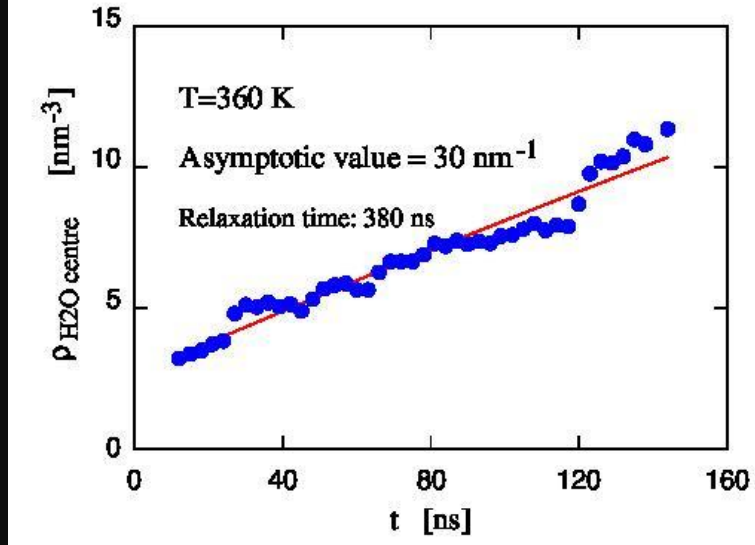
320 K

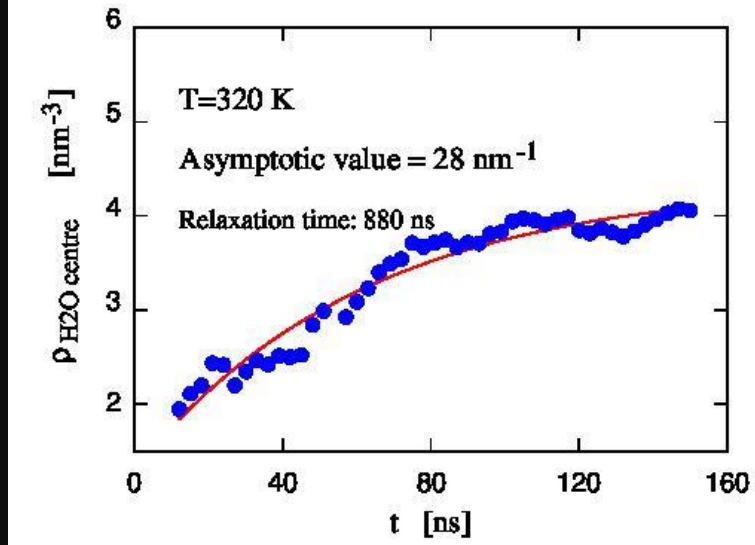
Stage 1: Relaxation Times





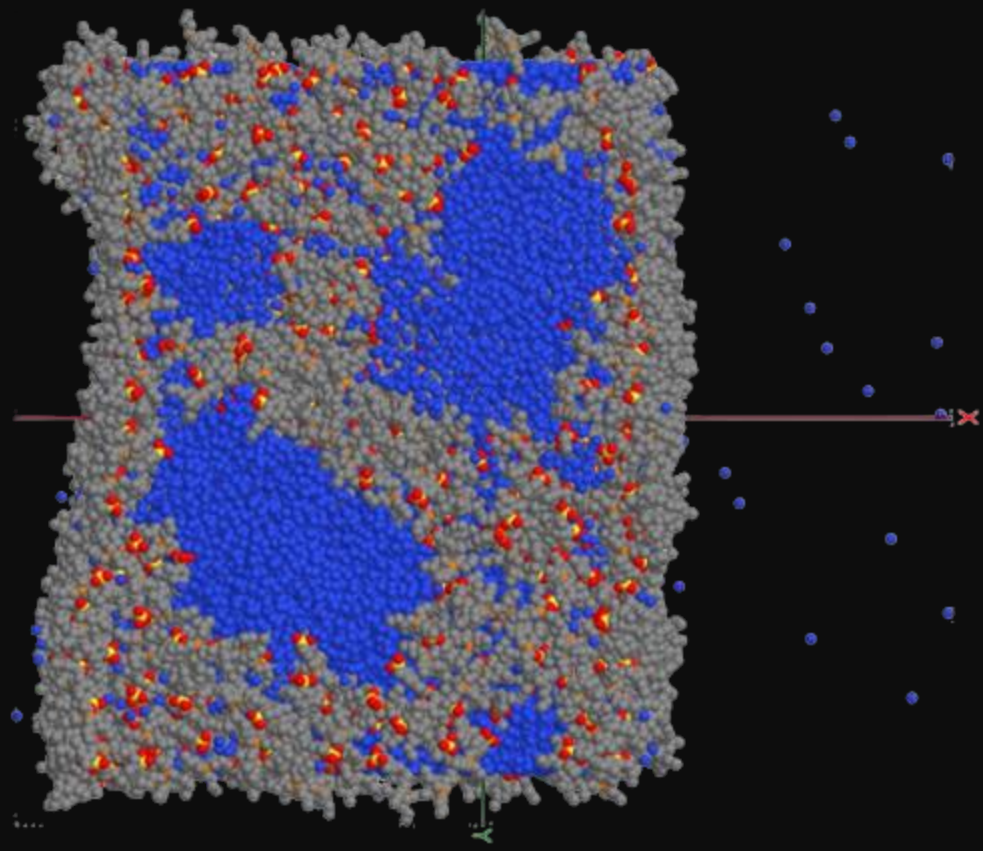
- <ρ>: Average water density in the center of the slab
- Extrapolate <ρ> to long times.
- Validity to be tested.





Stage 2: Results

- Homogeneous, nanostructured, bulk sample.
- Phase separates and a film forms.
-
- Gravity/mechanical method for collection.
- Limited simulations yet promising results.



50 ns at 360 K

Summary

- MD simulations reveals a complex interplay of surface effects, mixing/de-mixing, and nanostructuring.

- Slow kinetics at all T; Brute simulation is not sufficient; requires extrapolation of results.

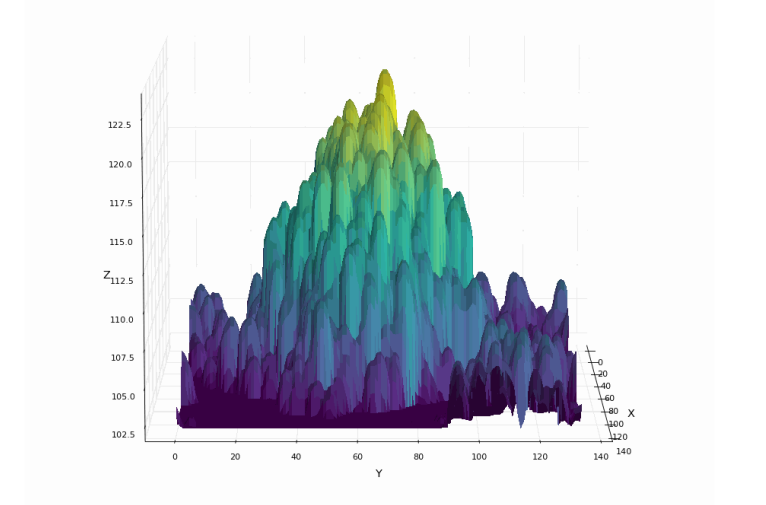
- Gained insight into various system properties:
  - Temporal and thermal evolution
  - Surface energies
  - Contact angle

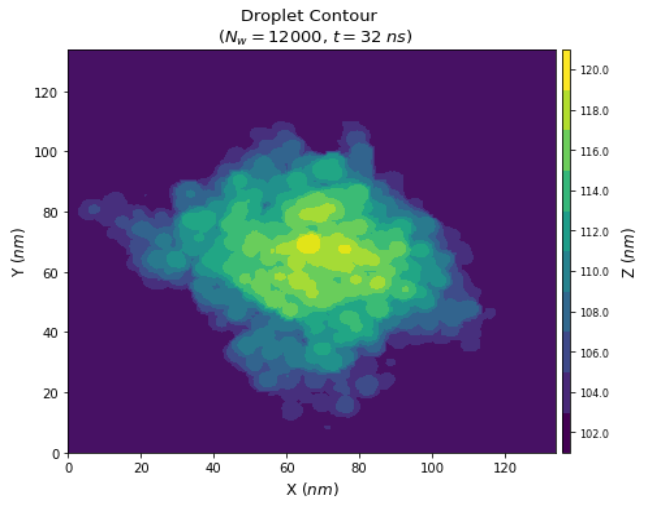
- These insights are potentially useful for developing water harvesting technologies.

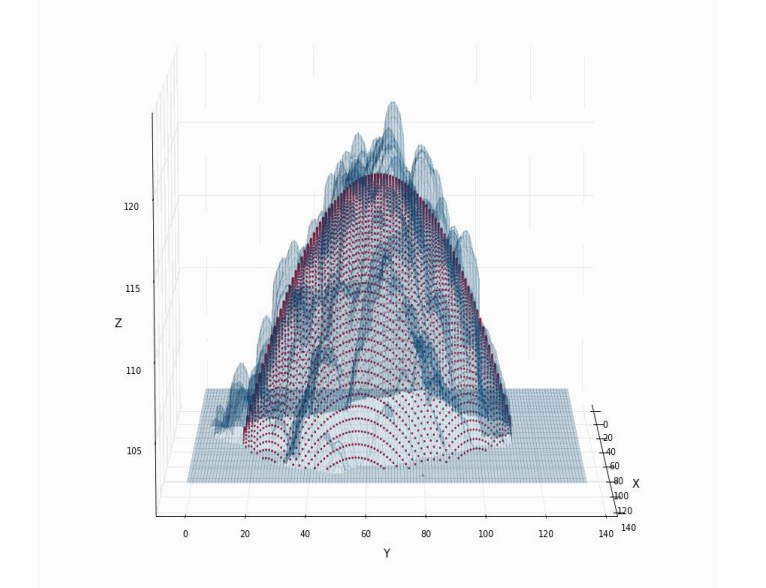
Thank you for listening.

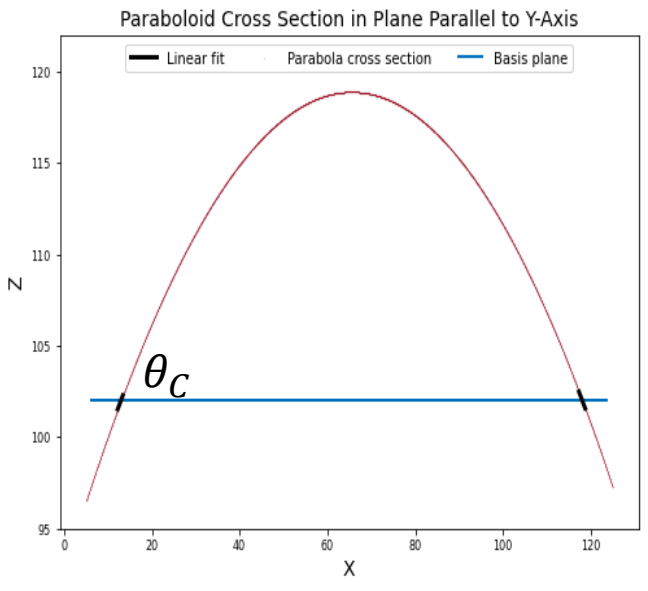
Questions?

Stage 1: Contact Angle









Young equation:

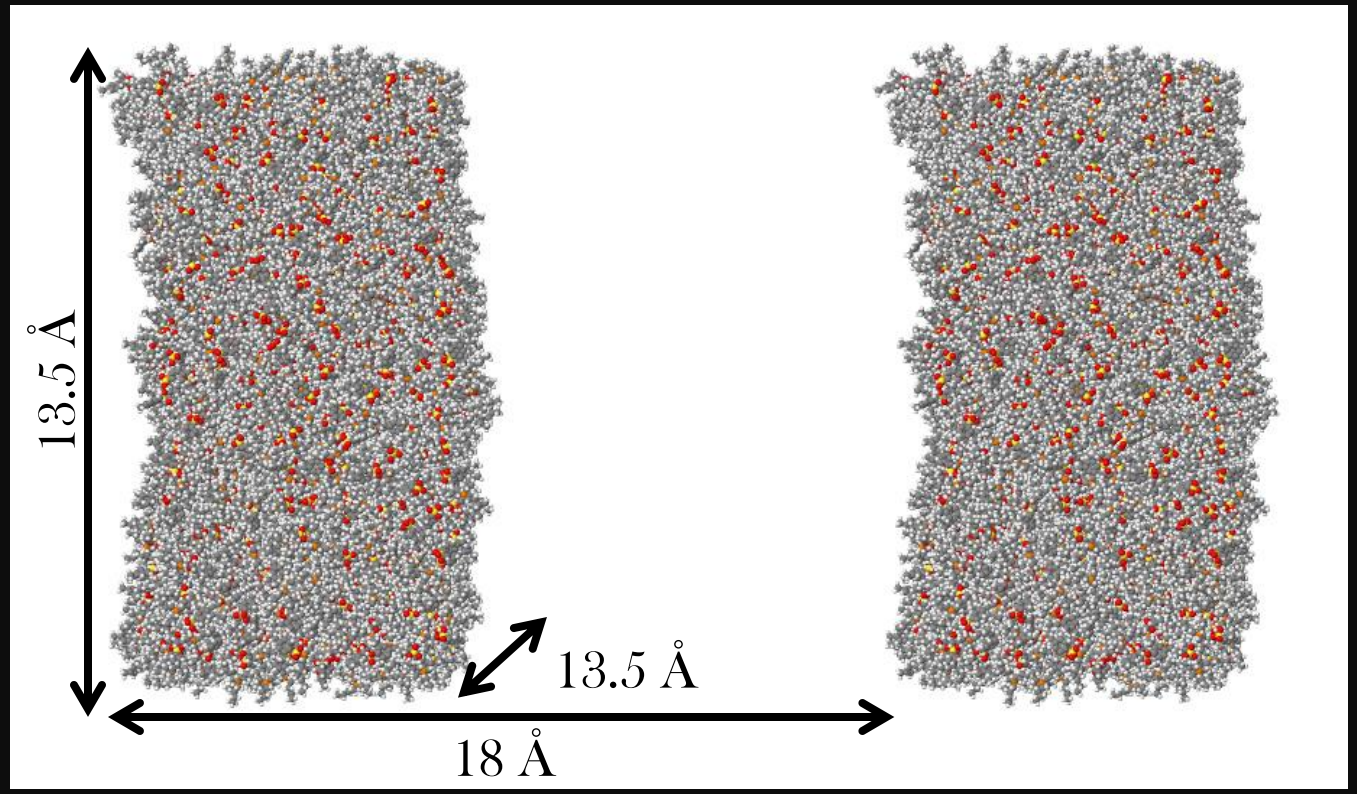
$$\gamma_{IL-w} = \gamma_{IL-v} - \gamma_{w-v}\cos(\theta_C)$$

Paraboloid:

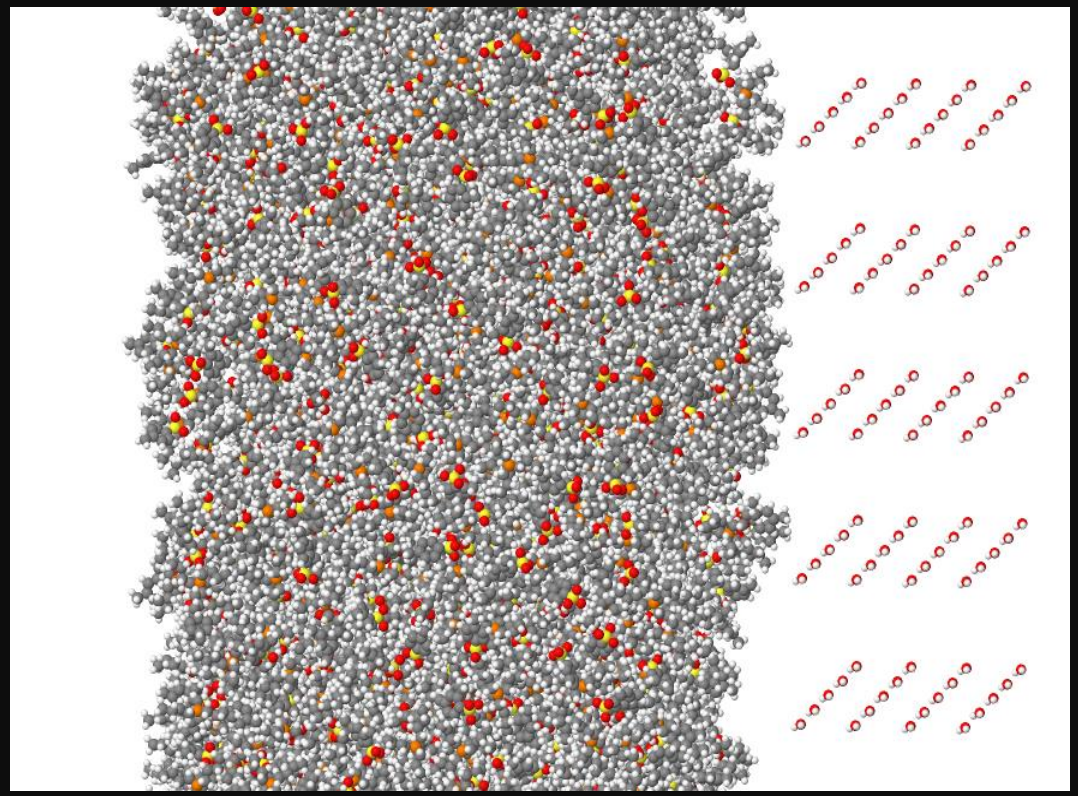
$$z = Ax^2 + By^2 + Cxy + Dx + Ey + F$$

$$\theta_C = 34° \pm 5°$$

Model & Methods: Stage 1



Set-Up



Slab Hydration