WRIGHT STATE UNIVERSITY

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WETTING PROPERTIES OF STRUCTURED INTERFACES COMPOSED OF SURFACE-ATTACHED SPHERICAL NANOPARTICLES

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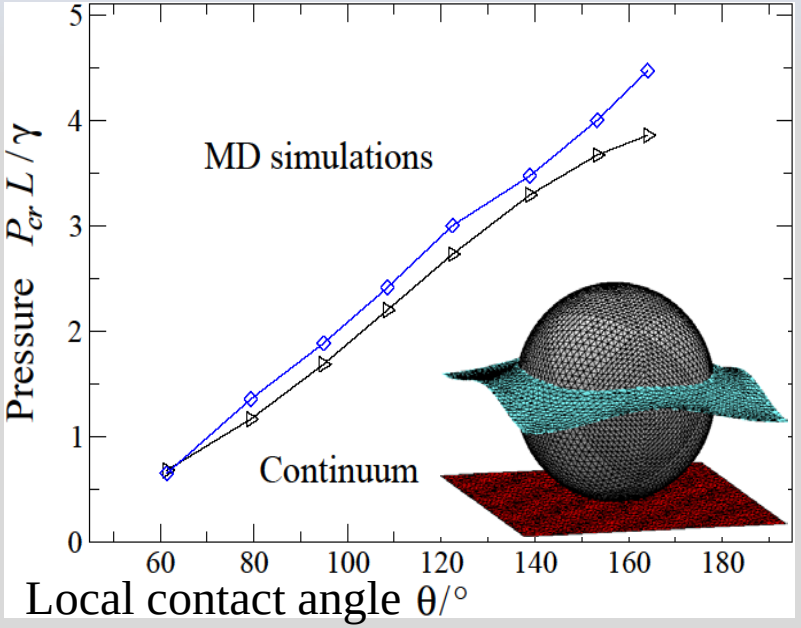


B. Bhattarai and N. V. Priezjev, Wetting properties of structured interfaces composed of surface-attached spherical nanoparticles, *Computational Materials Science* **143**, 497 (2018).

Outline

- Introduction
- Simulation details
  - Molecular dynamics (MD) simulations

    MD Results
  - Surface Evolver simulation

    Continuum results
- Conclusions

Introduction

- In the last few decades, there has been a remarkable progress the field of ‘nanotechnology’.
  - Designing and fabricating Superhydrophobic Surfaces

Lotus leaf, 10μm

- Superhydrophobic Surface: large contact angle > 150° and low contact angle hysteresis (about 5°) .
  - Applications: self-cleaning surfaces, non-fouling surfaces, drag reduction, stain-free clothing, etc.
  - Example: oil on Teflon (Hydrophobic surface)
    water on lotus leaf (Superhydrophobic surface)

Condensation heat transfer

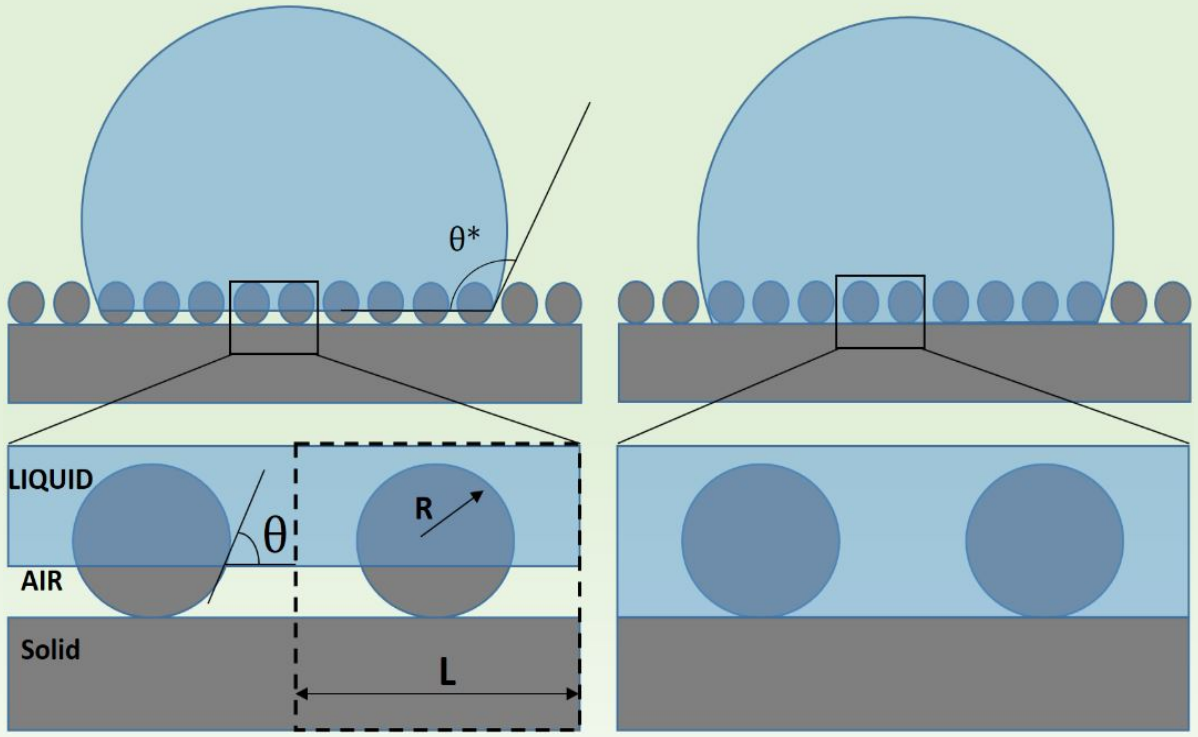
- We study wetting properties of Nano-Structured Surfaces (array of spherical particles)

Cassie-Baxter and Wenzel States

In this case, spherical nano-structured superhydrophobic surface keeps the liquid interface suspended on the asperities (spherical protrusion), reducing the liquid-solid contact area.

Small pockets of air get trapped between the surface and the liquid.

We study the influence of the external pressure and surface energy on wetting transition.



(Cassie-Baxter state) (Wenzel state)

B. Bhattarai and N. V. Priezjev, Wetting properties of structured interfaces composed of surface-attached spherical nanoparticles, *Computational Materials Science* **143**, 497 (2018).

Cassie-Baxter and Wenzel States

Liquid droplet on a textured surface:

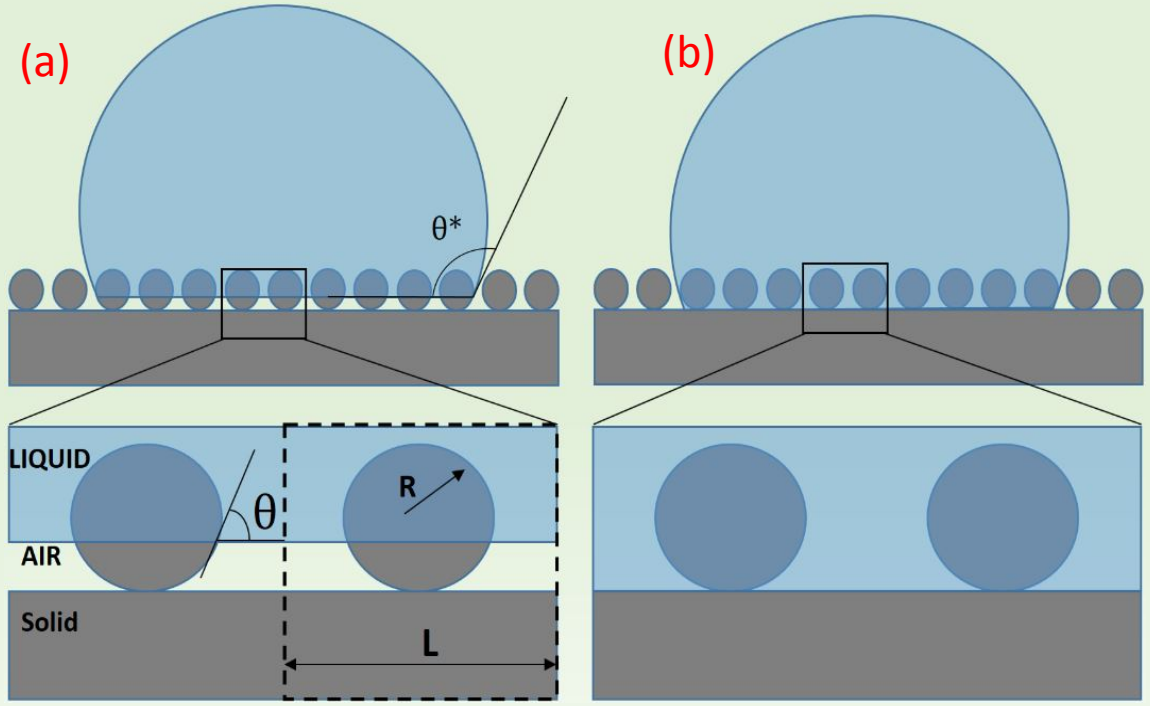
- Cassie-Baxter state (the liquid is supported at composite interface) figure (a)
- Wenzel state (fully wetted)- figure (b)

The local contact angle θ: angle measured between interior of liquid and a solid sphere.

Apparent contact angle, θ^* :

Wenzel relation, $\cos\theta^* = r\cos\theta$

Cassie-Baxter relation, $\cos\theta^* = f_{SL}\cos\theta - f_{LV}$



(Cassie-Baxter State) (Wenzel state)

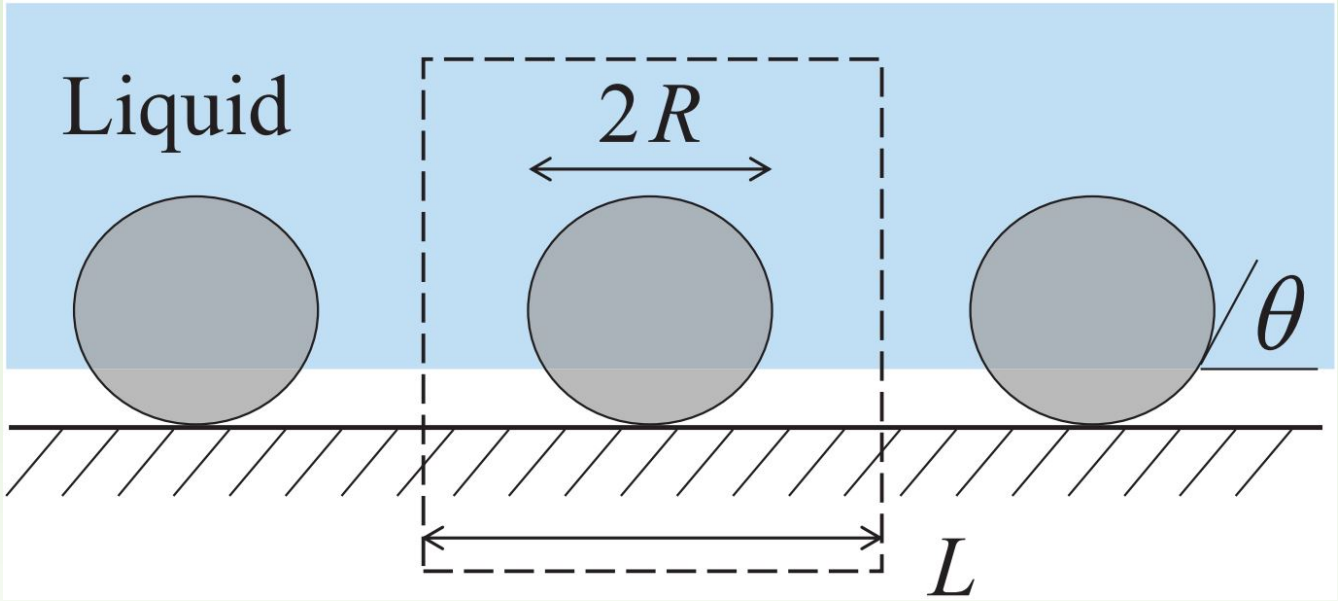
Here, r is the surface roughness, defined as the ratio of the actual surface area to the projected surface area.

Here, f_{SL} is the area fraction of the solid-liquid interface and f_{LV} is the area fraction of the liquid-air interface.

Simulation Details

Wetting properties are studied: structured interface with an array of spherical particles on a solid substrate and a suspended liquid film. The computational domain is indicated by the dashed box in the figure.

Key parameters: external pressure, surface tension, liquid-solid contact angle, R/L ratio



Critical pressure: Maximum pressure at which the liquid-air interface remain suspended above the solid substrate.

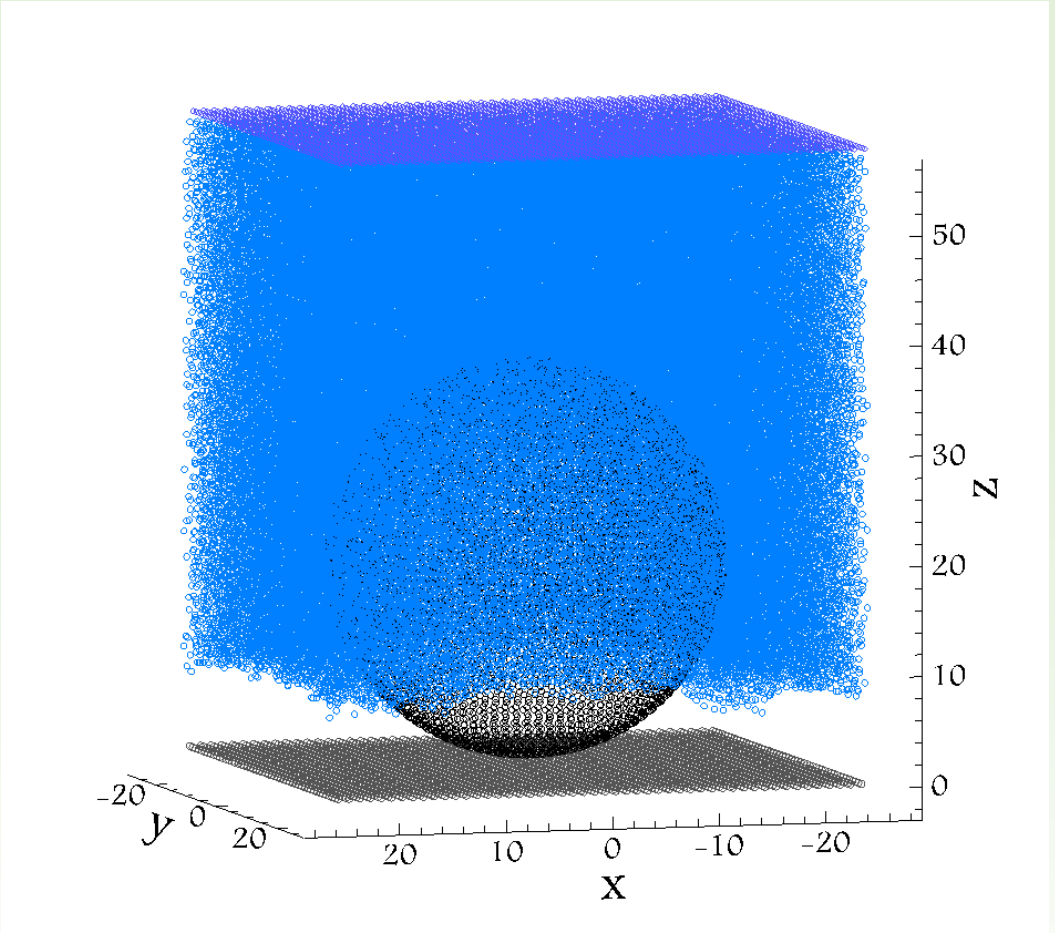
Molecular Dynamics (MD) simulation

Calculation – forces and accelerations for all atoms.

Positions of all atoms are iteratively updated based on velocities and accelerations.

Time-dependent simulations

For our model, MD simulations were carried out using LAMMPS developed at Sandia National Laboratories.



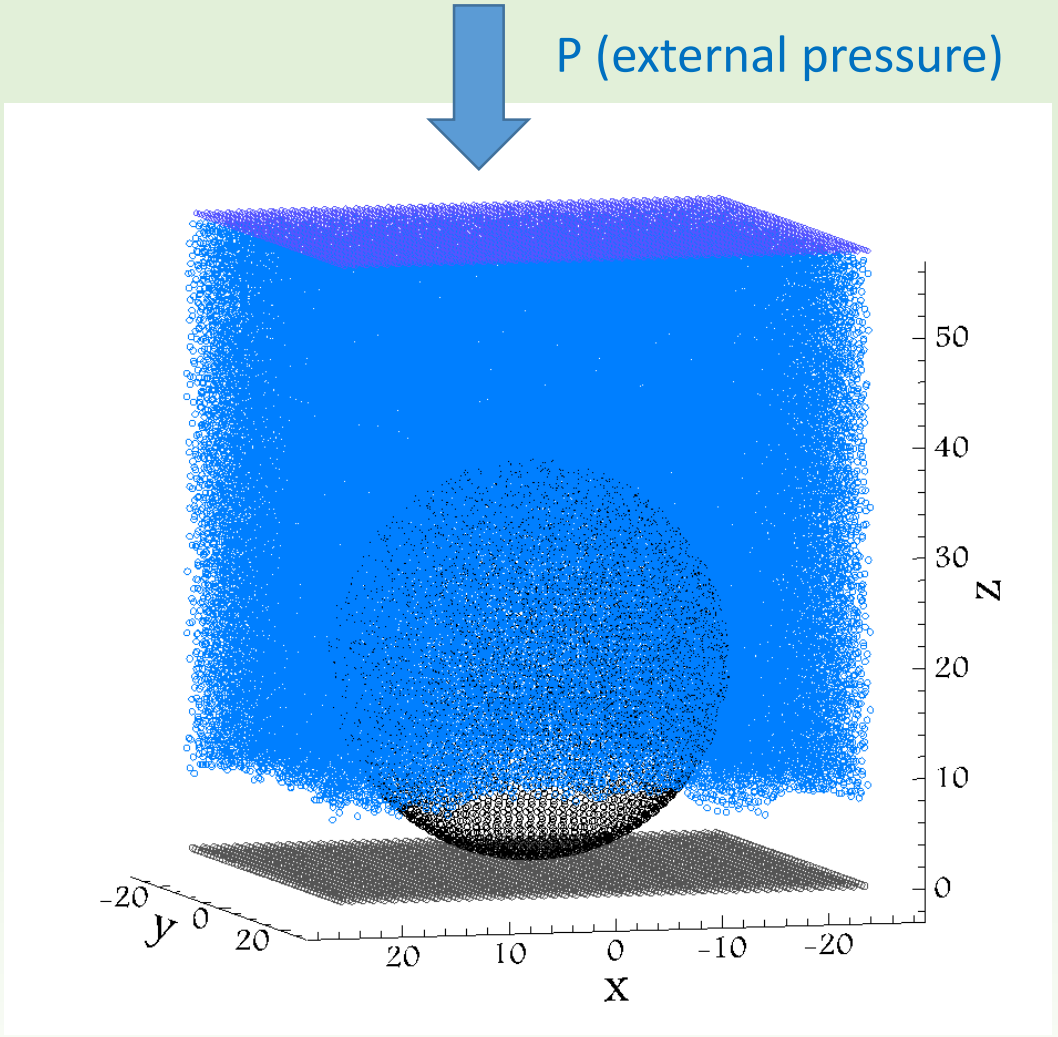
Molecular Dynamics (MD) Simulation

Solid Sphere: 4000 atoms uniformly distributed on a surface with the radius = 17.8σ

Periodic boundary conditions are applied in the x and y directions parallel to the stationary lower substrate. (to mimic a periodic array of spheres and continuous liquid film)

Shape of the liquid-air interfaces are determined by two parameters, i.e., ε_{wf} and P (external pressure).

Effects of gravity and entrapped gas are not considered.



MD Results

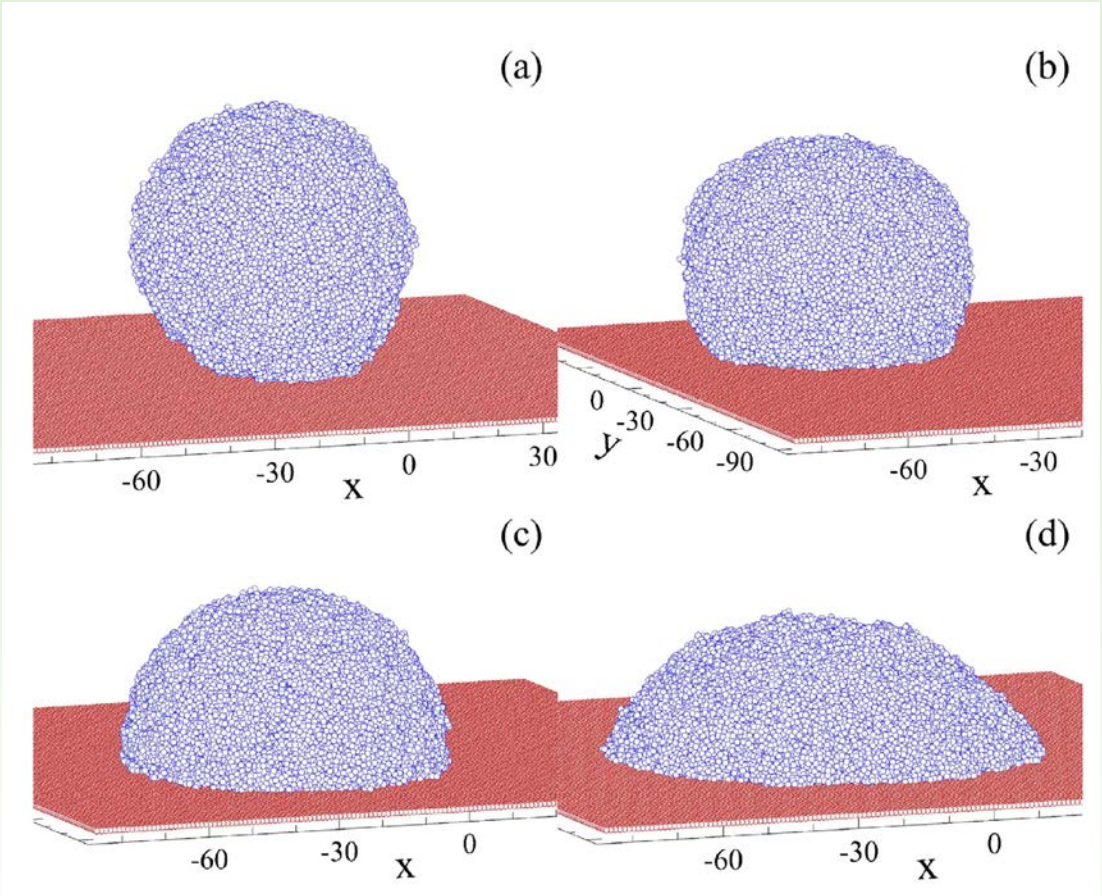
Snapshots of the (polymeric chains N_p=10 units) liquid droplet at the solid substrate obtained in **MD simulations**: wall-fluid interaction energy ε_{wf} is the input parameter.

(a) ε_{wf} = 0.2 ε

25,600 solid atoms on a square lattice 160σ x 160σ

(c) ε_{wf} = 0.6 ε

Contact angle is obtained by fitting the spherical cap



Snapshot of the liquid droplet partially wetting the solid substrate

(b) ε_{wf} = 0.4 ε

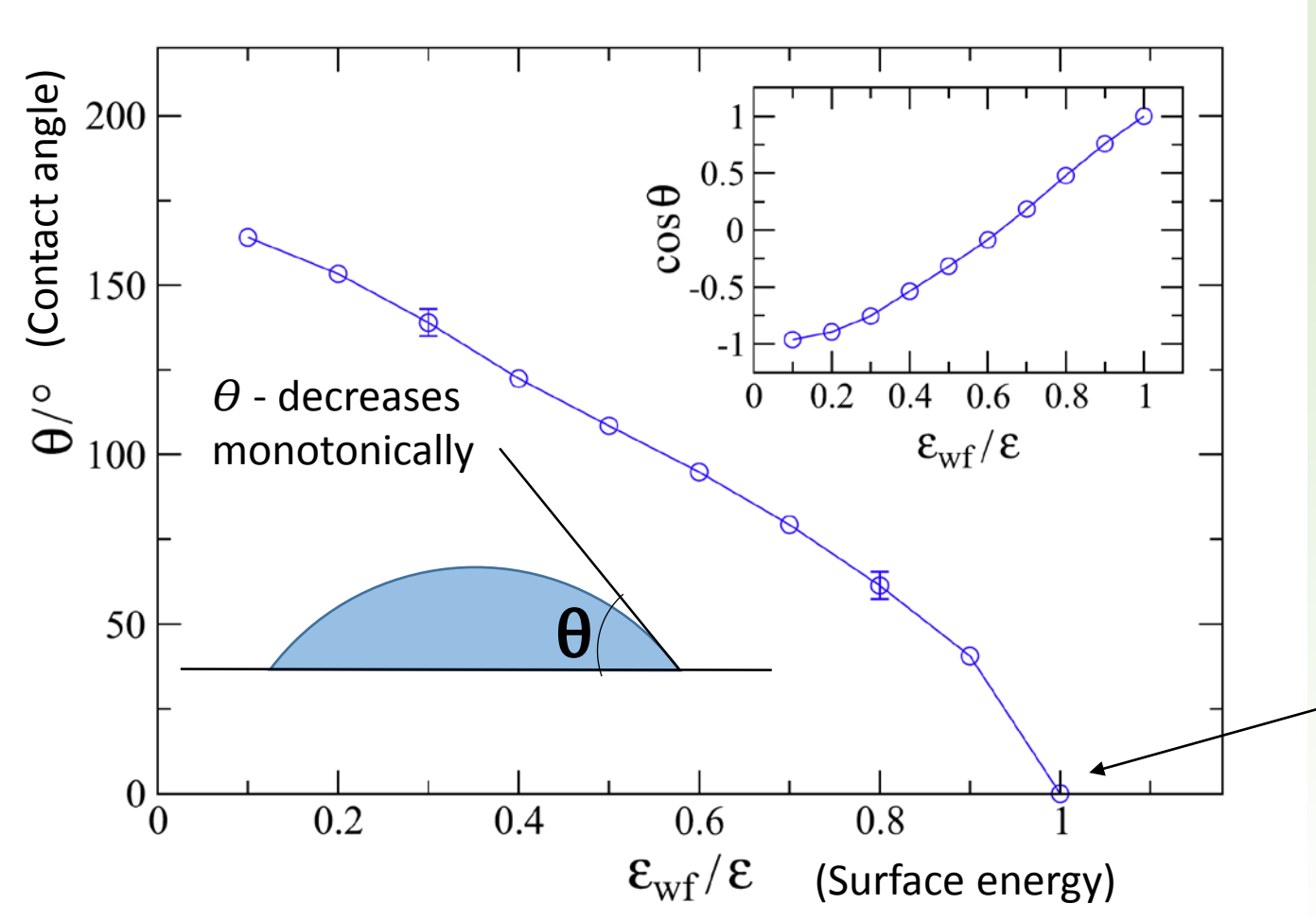
85,000 monomers
8,500 polymer chains of length N_p=10 units

(d) ε_{wf} = 0.8 ε

For higher surface energy,
L-V interface - less curved
L-S contact area - increases

Dependence of the contact angle on surface energy

The dependence of the contact angle as a function of the surface energy for liquid droplets residing on a crystalline substrate. These values of contact angle from MD simulations are used as input parameters for continuum simulations.



Liquid film suspended on a solid sphere

Snapshots of the liquid film suspended on a solid sphere obtained in **MD simulation**:

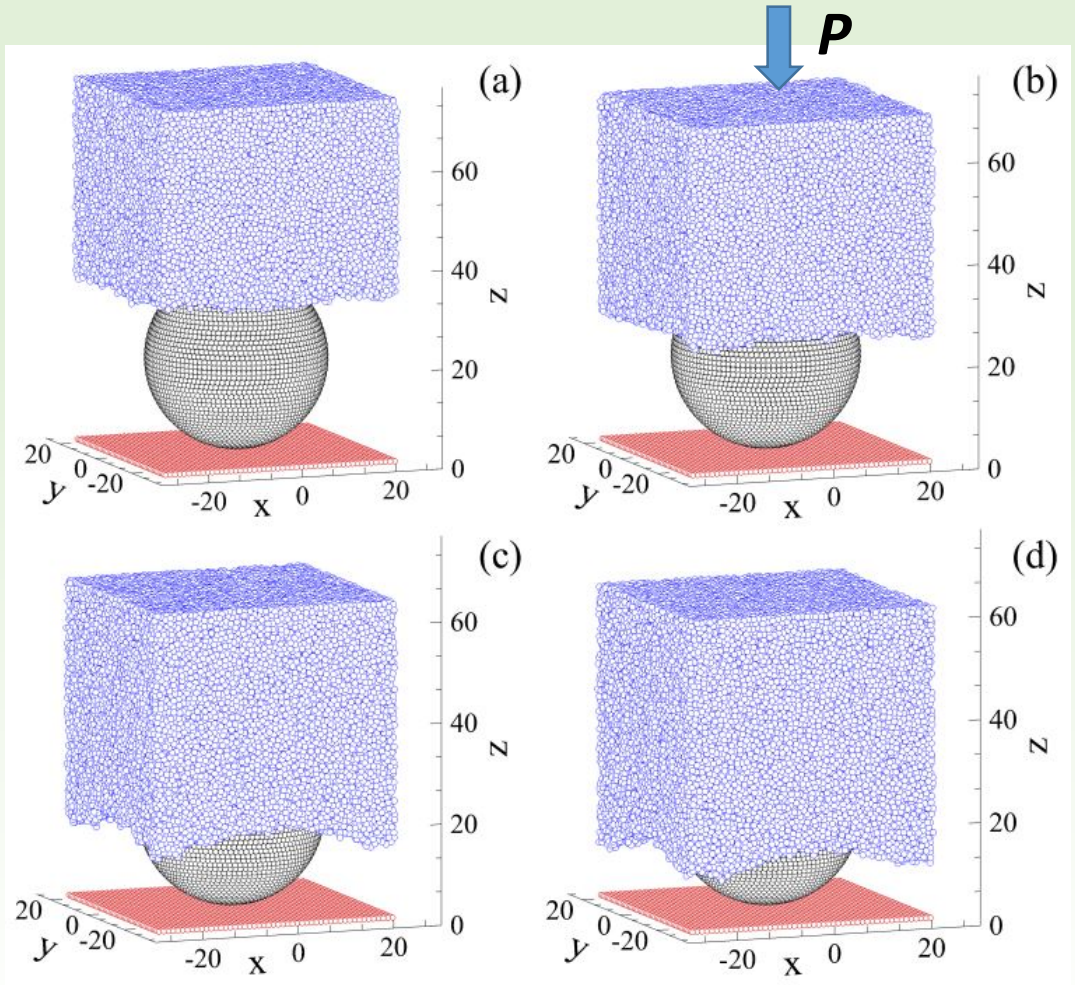
Local contact angle θ: 138.94° and the wall-fluid interaction energy $\varepsilon_{wf} = 0.3\ \varepsilon$

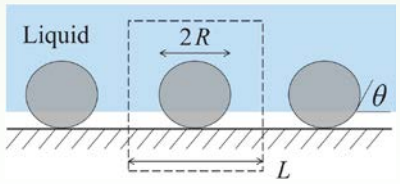
(a) $P = 0$

(b) $P = 0.02\ \varepsilon\ \sigma^{-3}$

(c) $P = 0.05\ \varepsilon\ \sigma^{-3}$

(d) $P = 0.055\ \varepsilon\ \sigma^{-3}$





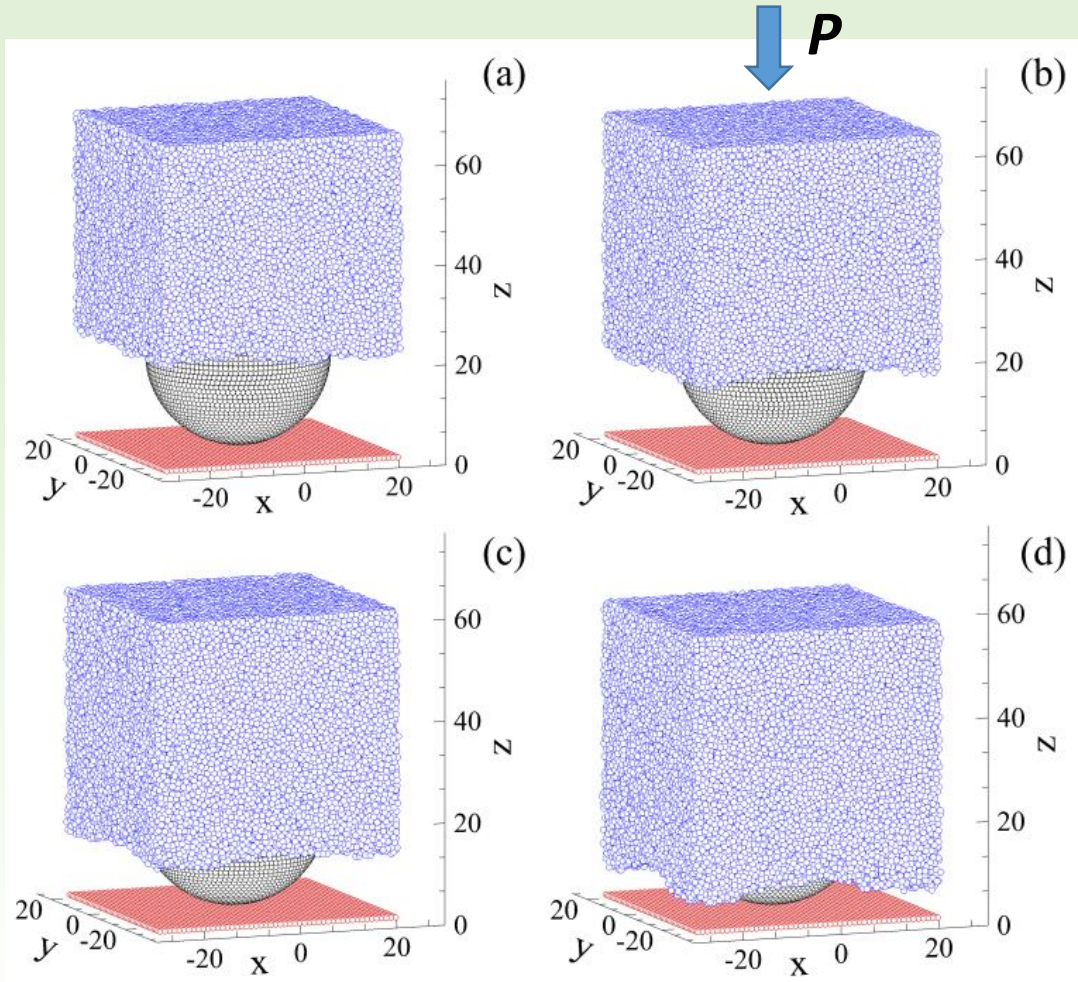
Liquid film suspended on a solid sphere

Snapshots of the liquid film suspended on a solid sphere obtained in **MD Simulation**:

Local contact angle θ: 94.86° and the wall-fluid interaction energy $\varepsilon_{wf} = 0.6\,\varepsilon$

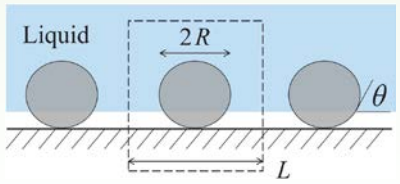
(a) $P = 0$

(b) $P = 0.01\,\varepsilon\,\sigma^{-3}$



(c) $P = 0.02\,\varepsilon\,\sigma^{-3}$

(d) $P = 0.03\,\varepsilon\,\sigma^{-3}$

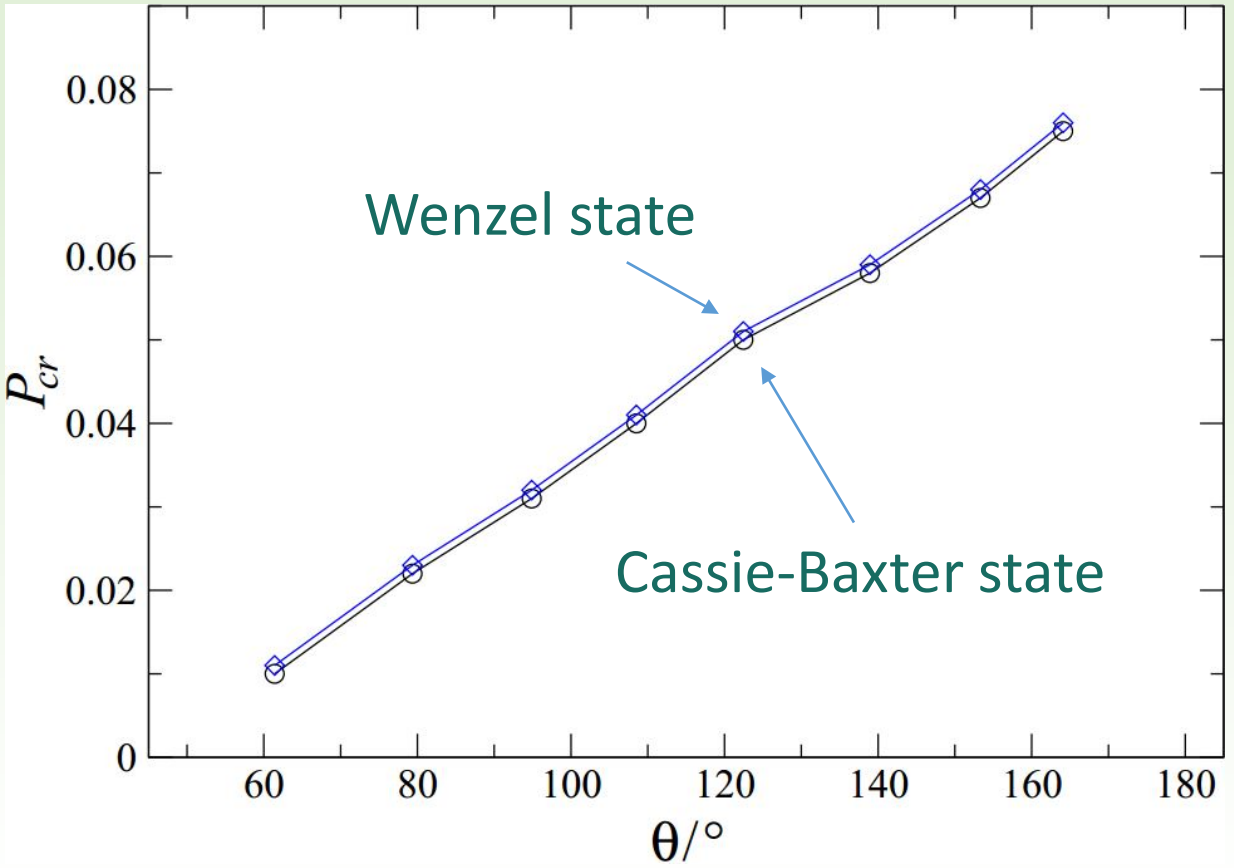


Wetting Transition

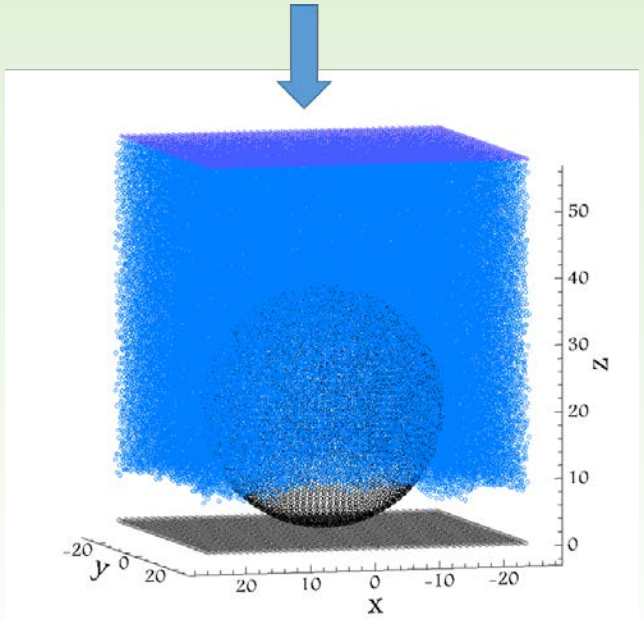
The plot shows the critical pressure as a function of the local contact angle obtained from **MD Simulations**.

- Black line is the critical pressure (the liquid interface is still suspended).
- Blue line is the threshold pressure associated with a wetting transition to the Wenzel state.

Pressure is measured in LJ units $\varepsilon\ \sigma^{-3}$



Pressure



Continuum Simulations (Surface Evolver)

To compare the results of MD simulations, the continuum analysis of liquid film trapped by the spherical surface protrusion was performed using the Surface Evolver.

Surface Evolver is a freely available software (designed by Dr. Kenneth A. Brakke) and it is written in C programming language.

It uses gradient descent method to evolve the surface towards minimum energy, subject to constraints.

A surface is a union of triangles.

Continuum Simulation Details

Continuum simulation (Surface Evolver):

What is a surface in surface evolver? - vertices, edges, facets, and bodies

Geometry:

The initial surface is created in a text file in any standard text editor.

- Vertices are defined
- Edges: defined by the line segments joining those vertices.
- Faces: defined by the loop of edges with proper orientation.
- Bodies: defined by it's oriented faces.

Continuum Simulation Details

Geometry:

(A simple example of a 3D – cube)

When we run this data file command in Surface Evolver, we get a cube as shown in the image

Untitled - Notepad

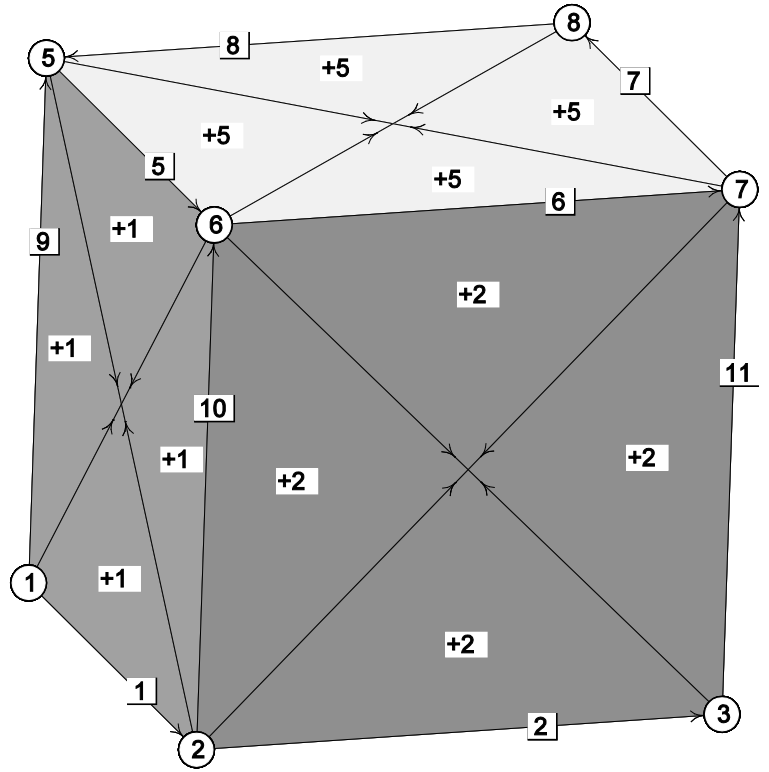
File Edit Format View Help

```
vertices
1   0.0 0.0 0.0
2   1.0 0.0 0.0
3   1.0 1.0 0.0
4   0.0 1.0 0.0
5   0.0 0.0 1.0
6   1.0 0.0 1.0
7   1.0 1.0 1.0
8   0.0 1.0 1.0

edges
1    1 2
2    2 3
3    3 4
4    4 1
5    5 6
6    6 7
7    7 8
8    8 5
9    1 5
10   2 6
11   3 7
12   4 8

faces
1    1 10 -5  -9
2    2 11 -6 -10
3    3 12 -7 -11
4    4  9 -8 -12
5    5  6  7   8
6   -4 -3 -2  -1

bodies
1    1 2 3 4 5 6  volume 1
```

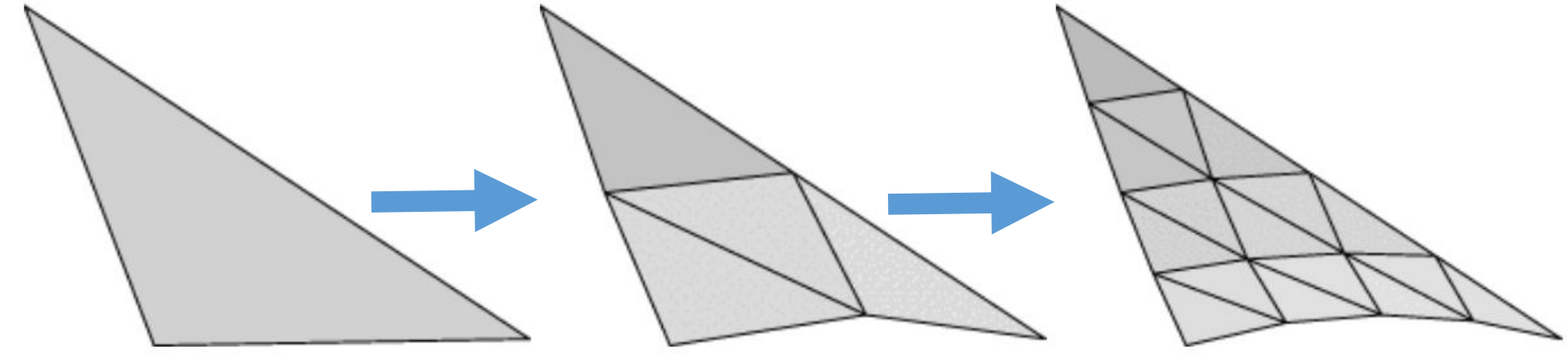


Continuum Simulation Details

Meshing in Surface Evolver:

In Surface Evolver, the grids are triangular in shape. With one ‘r’ command, one step refinement is performed. (Refines all faces).

Each refinement reduces the error in the area by a factor of 4, at the expense of a 4-fold increase in the number of vertices.



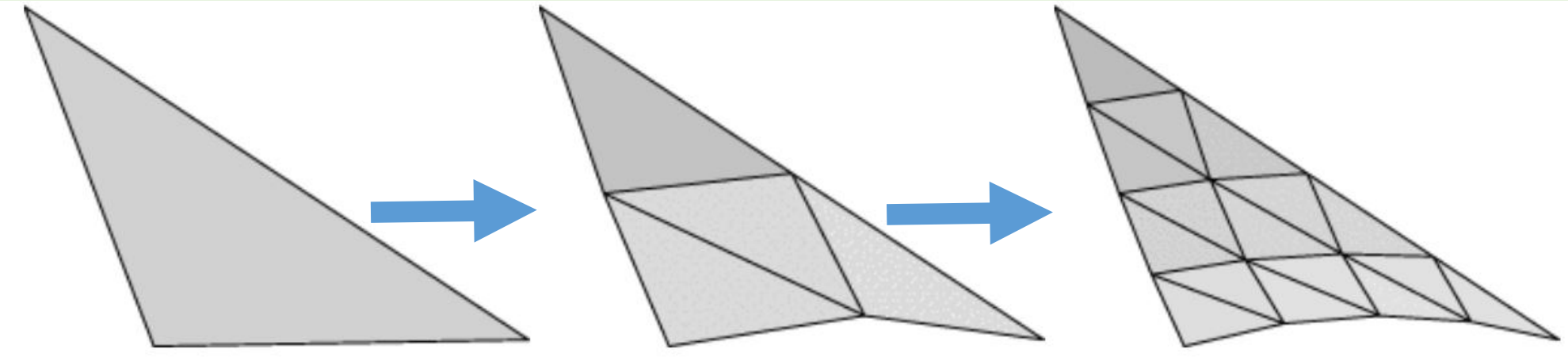
Geometry refinement

Continuum Simulation Details

Meshing in Surface Evolver:

We performed the grid size independency check for our model.

To obtain the stable results, we performed all the calculations with sufficiently refined grid sizes. Calculations were performed with 11760 facets (triangles).



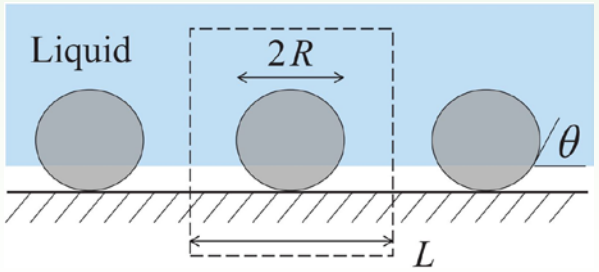
Continuum Simulation Details

Continuum simulation (Surface Evolver):

An iteration is one evolution step (energy minimization by gradient descent).

- the force on each vertex is calculated from the gradient of the total energy of the surface as a function of the position of that vertex. The force gives the direction of motion.
- the force is made to conform to the constraints that are applied.
- the actual motion is found by multiplying the force by a global scale factor.

We take the same ratio, 'R/L = 0.366', in both MD simulation and in Surface Evolver for comparison.

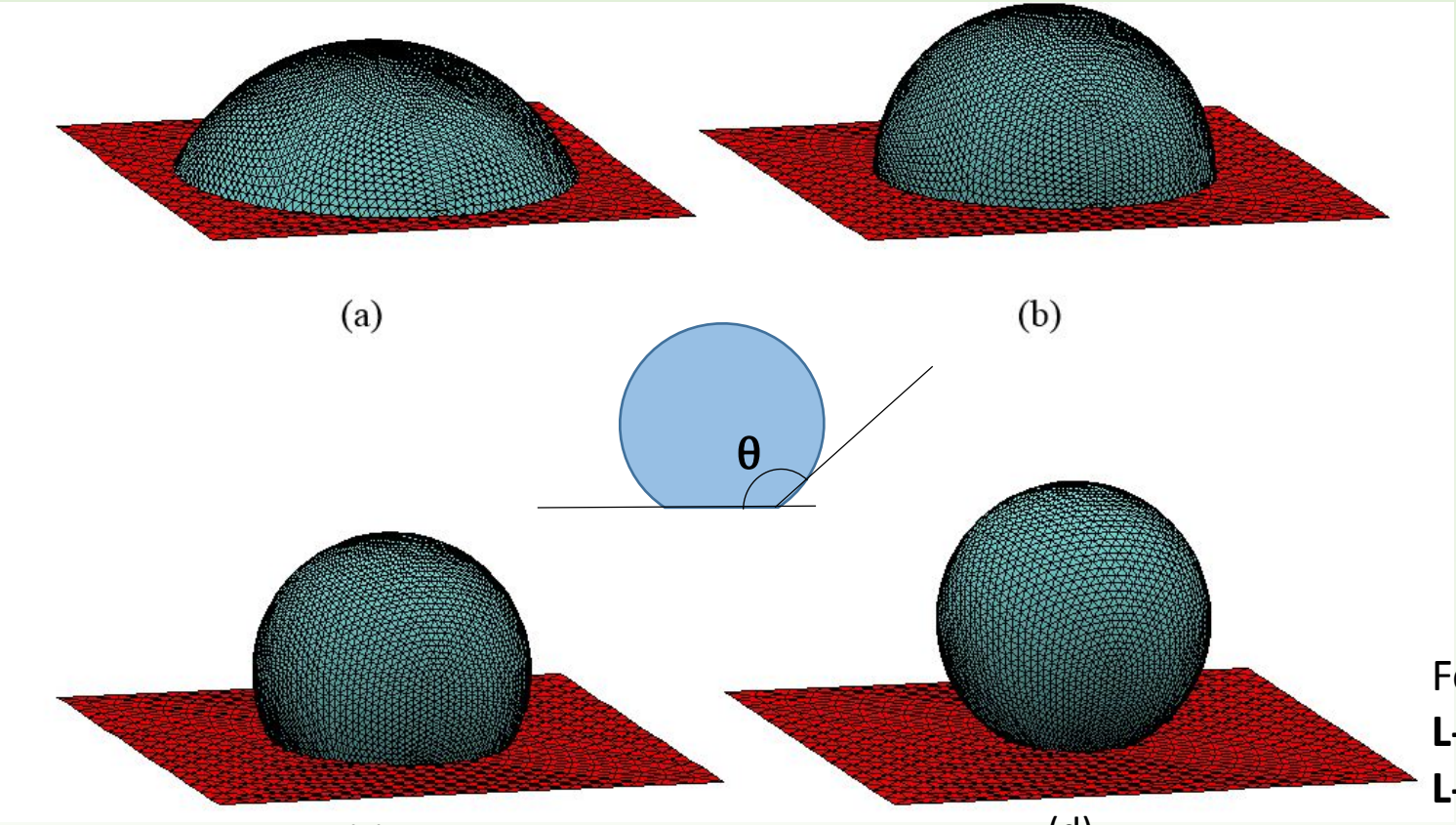


Liquid droplet on a solid surface

Snapshots of the liquid droplet on a solid substrate for different contact angles obtained from **Surface Evolver**. Liquid-Vapor surface tension: 1N/m

(a) $\theta = 60°$

(b) $\theta = 90°$



(c) $\theta = 120°$

(d) $\theta = 150°$

For higher contact angle,
L-V interface - more curved
L-S contact area - decreases

Surface Tension

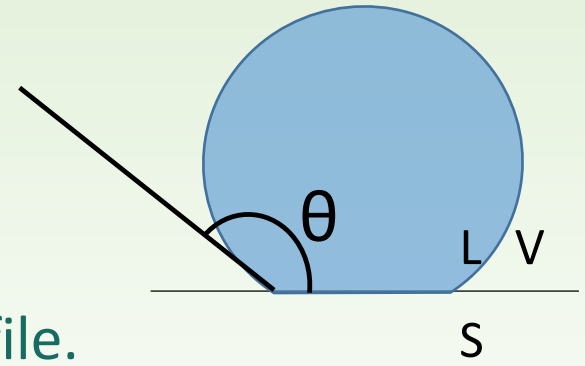
Continuum simulation (Surface Evolver):

Surface Tension:

The surface tension energy is always included in the total energy by default.
The surface tension of the facet; the default is 1. However, the user can define the value.

We specify the Liquid-vapor tension in the following equation:

(liquid-solid tension) = (Liquid-vapor tension)*cos(angle)



which is included in the energy integrand of the Surface Evolver datafile.

For our calculation, we used Liquid-vapor surface tension = 1 (N/m)

The local contact angle

Continuum simulation (Surface Evolver):
Our Model:

Contact angle:

- Angle is measured interior to the liquid.
- Angle < 90 degrees
- Angle > 90 degrees

Positions of the interface is determined by the local contact angle.

These contact angles shown in the figure are generated with ZERO external pressure

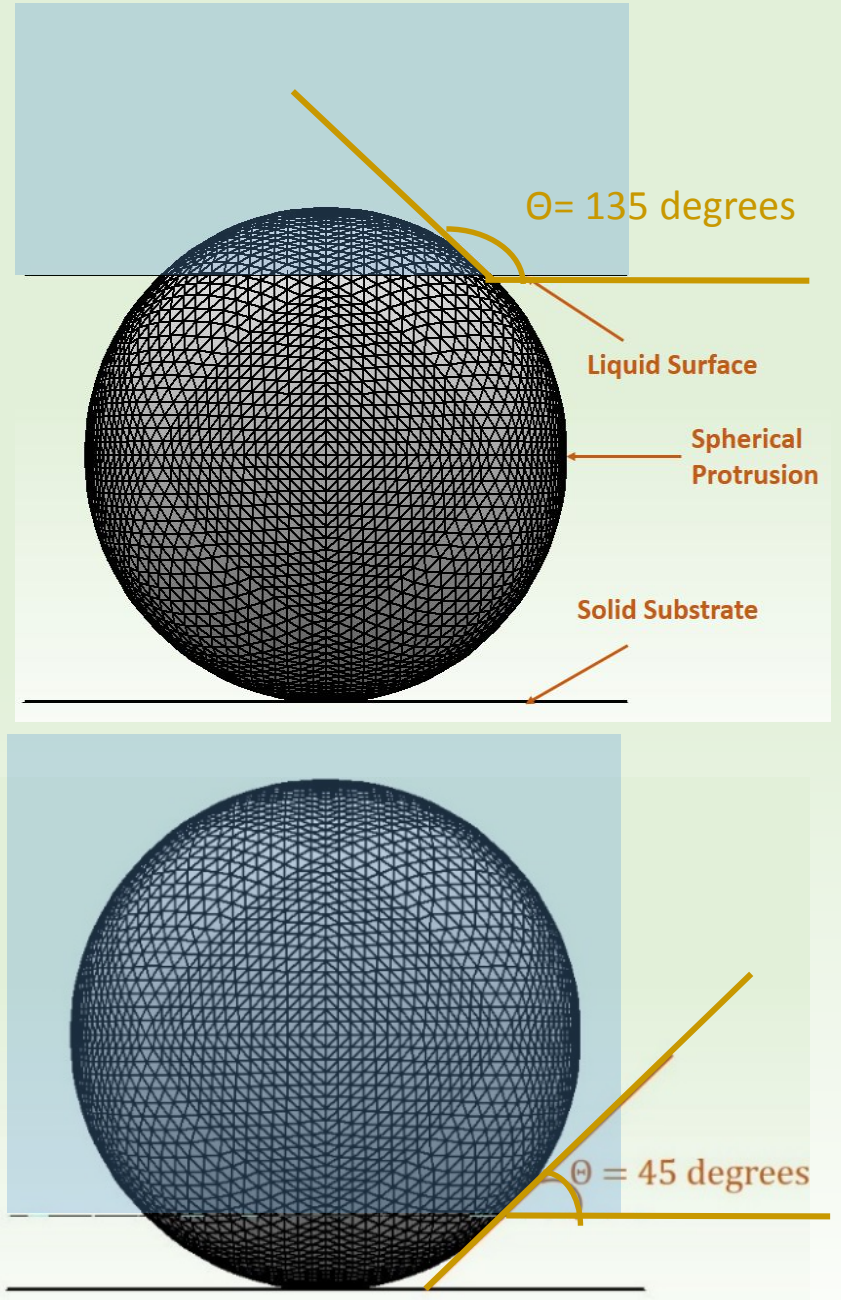


Fig. Snapshots of L-V interface on solid sphere

Periodic Boundary Conditions

Continuum simulation (Surface Evolver):

To specify Periodic boundary condition to a model in Surface Evolver the keyword TORUS_PERIODS is used in the datafile.

Periodic boundary conditions are applied in the lateral x and y directions. (Simulate liquid film on an array of spherical particles)

We define the computational domain of length (L) = 2.7322 x R (where R is the radius of the spherical protrusion)

Thus, the ratio, R/L = 0.366

Continuum Simulations Results

We obtain the steady state (time independent) shape of the liquid interface.

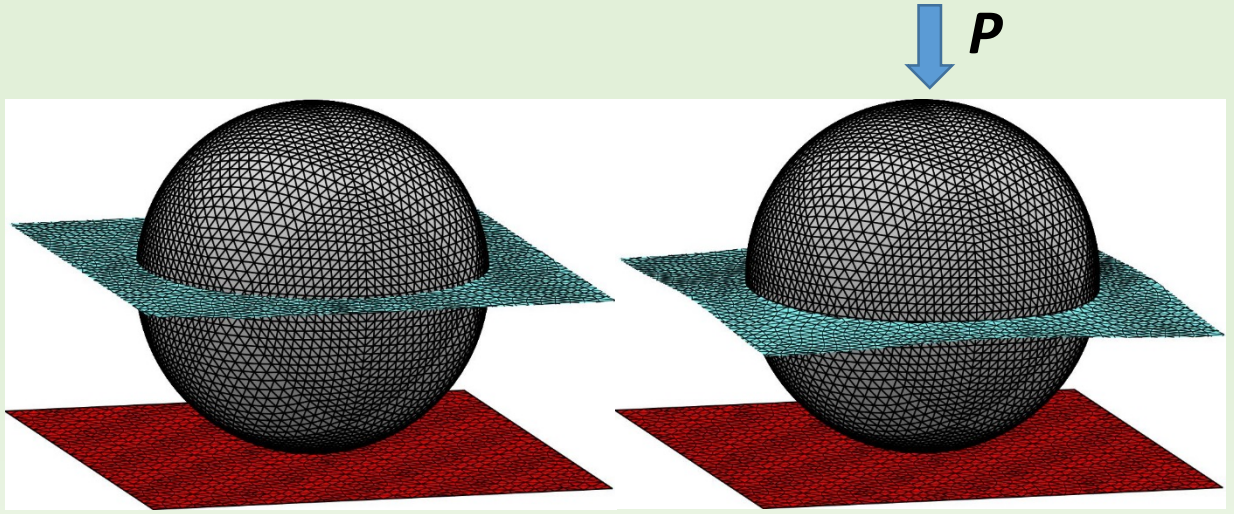
Next, we find the Critical Pressure (Cassie-Baxter to Wenzel) using Surface Evolver.

Our results are illustrated in the following figures.

Shape of liquid-vapor interface under applied pressure

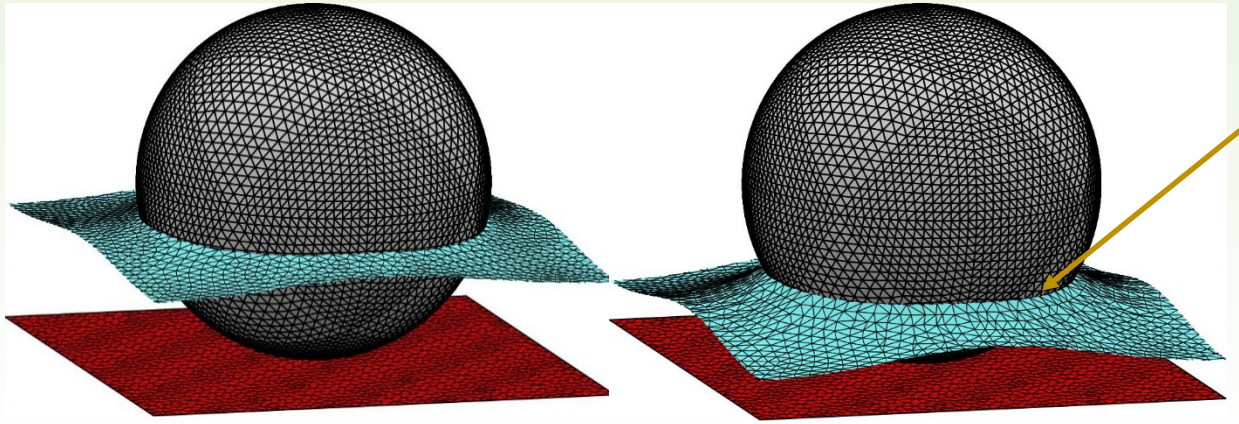
Snapshots of the liquid-vapor interface obtained in **Surface Evolver.**

The local contact angle θ: 94.86° and the surface tension coefficient γ: 1.0 N/m



(a) $P = 0$

(b) P = 205 Pa



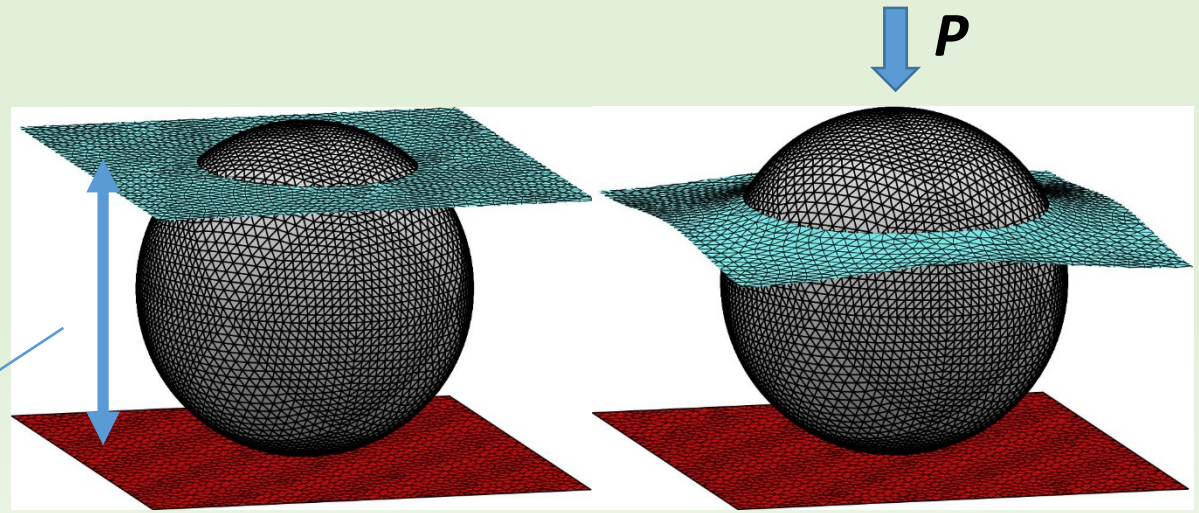
(c) P = 410 Pa

(d) P = 610 Pa

Shape of liquid-vapor interface under applied pressure

Snapshots of the liquid-vapor interface obtained in **Surface Evolver.**

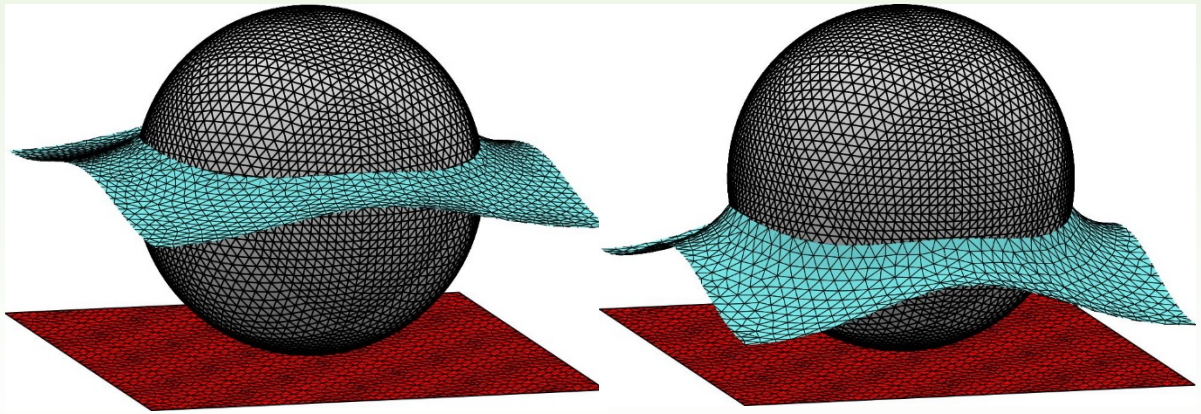
The local contact angle θ: 138.94° and the surface tension coefficient γ: 1.0 N/m



(a) ***P*** **= 0**

(b) ***P*** **= 400 Pa**

Distance b/w interface and solid substrate



(c) ***P*** **= 800Pa**

(d) ***P*** **= 1200 Pa**

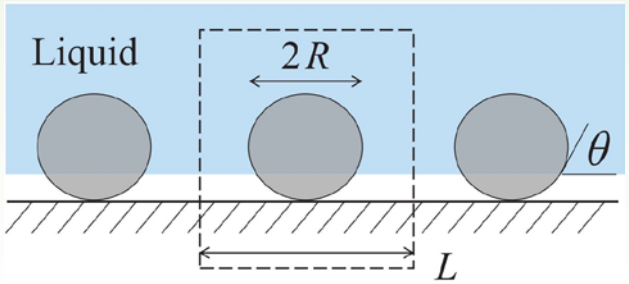
Results

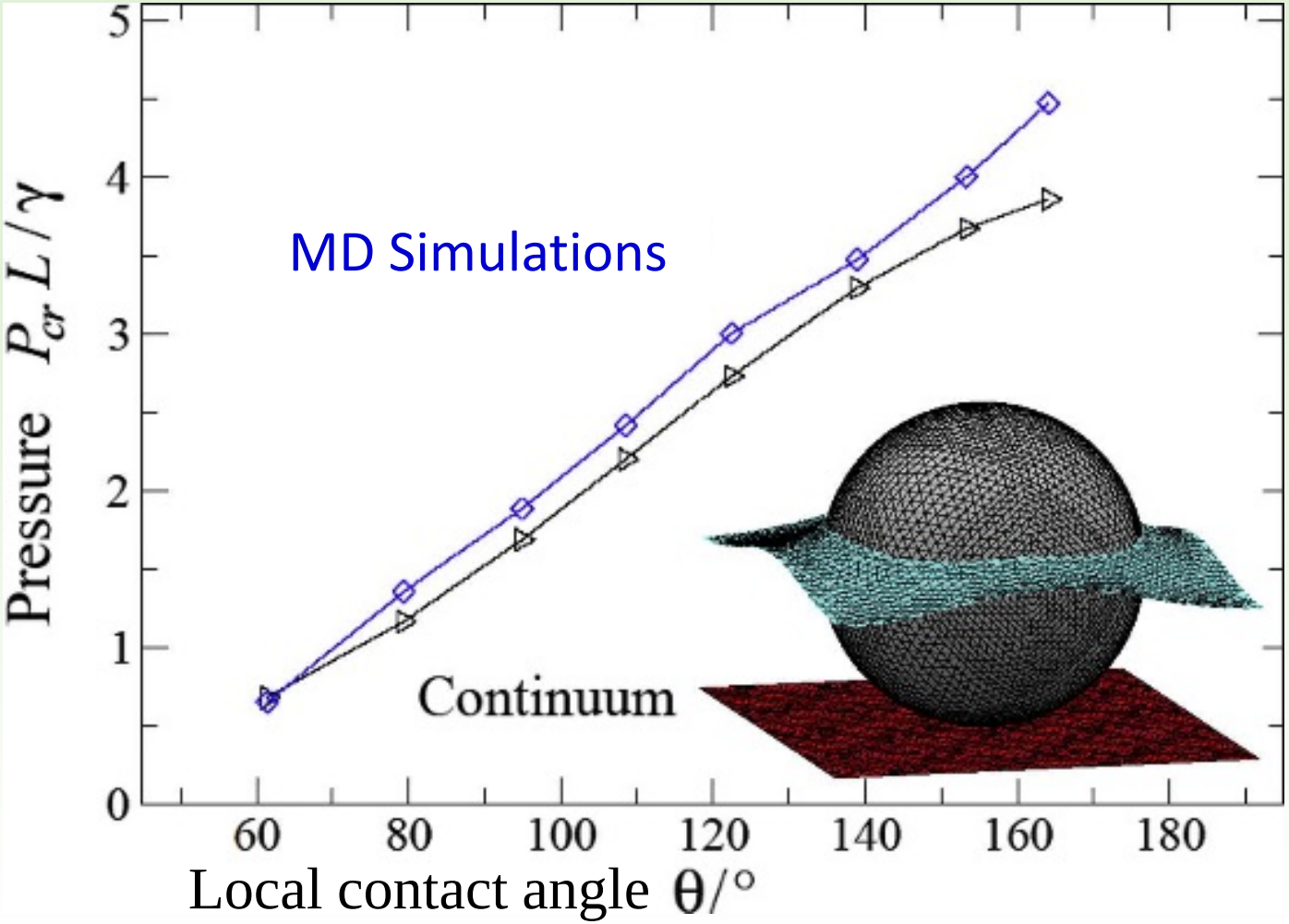
We use dimensionless variable $P_{cr}L/\gamma$ as a function of the local contact angle θ.
Good agreement between MD results (blue line) and continuum results (black line).
Continuum stability analysis of partially wetting states hold at length scales of about 20 nm.

L is the linear size of the solid substrate (simulation cell)

L = 2.73 mm and γ = 1 N/m

$L = 50\,\sigma$ and $\gamma = 0.85\,\varepsilon/\sigma^2$





Conclusions

In our project, based on MD simulations and continuum simulations, we find that the liquid-vapor interface is flat in the absence of external pressure.

The position of the interface is then determined by the local contact angle, i.e., the local angle between the liquid interface and the solid sphere.

When external pressure is applied, the liquid-vapor interface becomes curved. Higher the pressure, more curved the liquid-vapor interface.

The three phase contact line on the sphere shifts downwards until the external pressure reaches the critical pressure.

Conclusions

The shape of liquid interfaces and the critical pressure of permeation to the solid substrate obtained from MD simulations agree well with the results of the numerical minimization of the interfacial energy using Surface Evolver.

Obtained results can be useful for modeling partially wetting states on hierarchically textured surfaces.

Further research can be done on the micro- or nanostructured surfaces (with different shapes and parameters of surface texture) that helps to trap a thin air layer and reduce the interaction between the solid surface and liquid film.

B. Bhattarai and N. V. Priezjev, Wetting properties of structured interfaces composed of surface-attached spherical nanoparticles, *Computational Materials Science* **143**, 497 (2018).