Molecular dynamics simulation study of a polymer droplet motion over an array of spherical nanoparticles

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A. Thomas and N. V. Priezjev, Molecular dynamics simulation study of a polymer droplet transport over an array of spherical nanoparticles, *Computational Materials Science* **184**, 109872 (2020).

- In the last couple of decades, there has been a remarkable progress in the field of <u>Nanofluidics</u>.

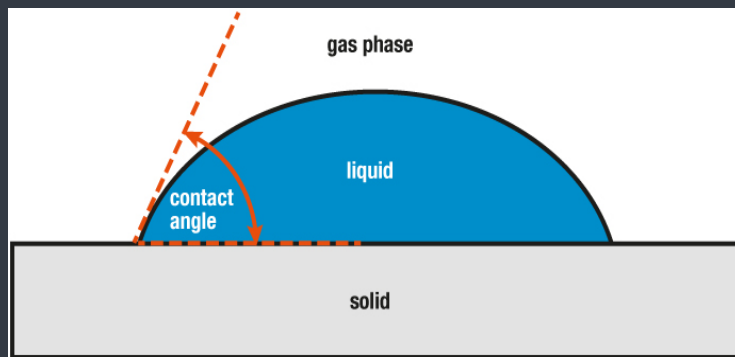**Superhydrophobic Surfaces:**

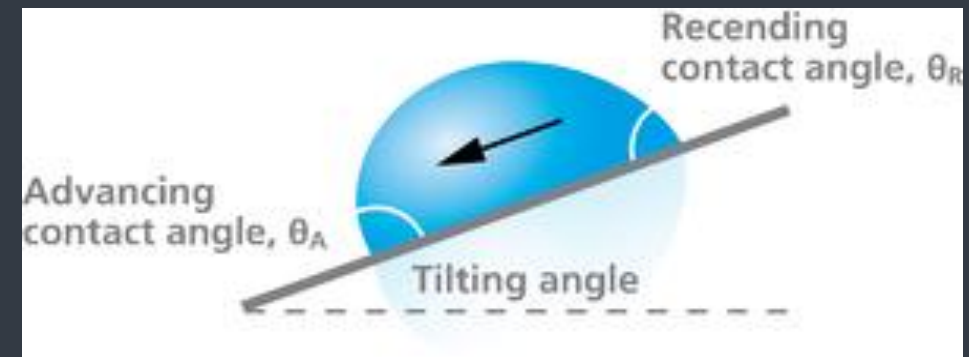➢ What is a superhydrophobic surface?

Contact angle > 150° and contact angle hysteresis < 5°.

(i) Contact angle: The angle at a line where a liquid – vapor interface is in contact with a solid surface.

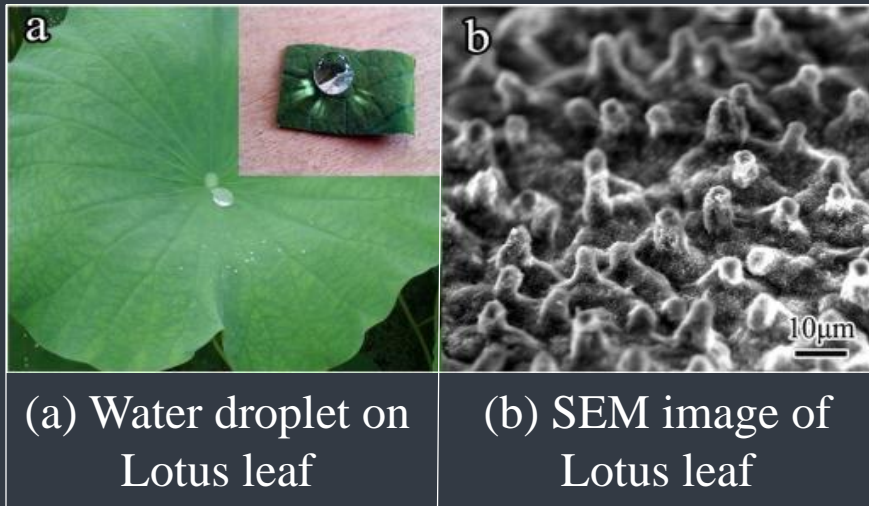(ii) Contact angle hysteresis = θ_A - θ_R
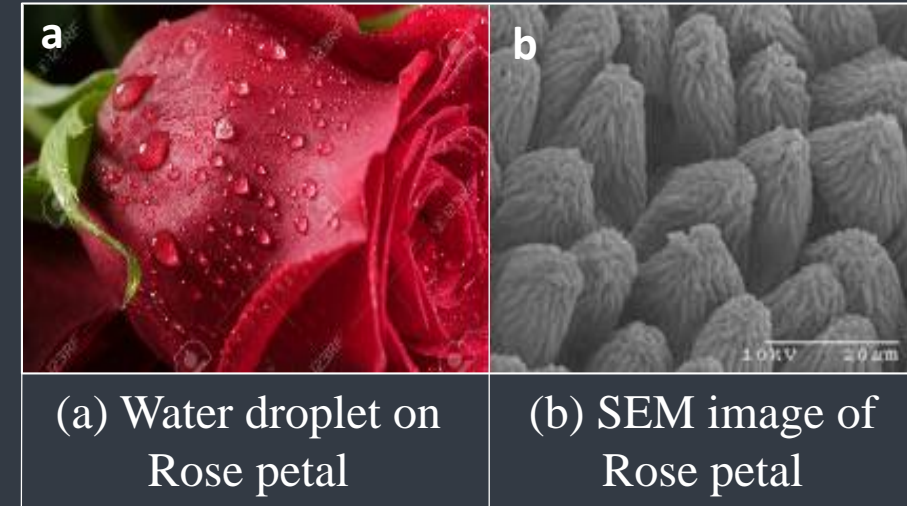

(i) Contact angle

(ii) Contact angle hysteresis

Examples of superhydrophobic surfaces

i) Lotus Leaf

| (a) Water droplet on Lotus leaf | (b) SEM image of Lotus leaf |

ii) Rose petal

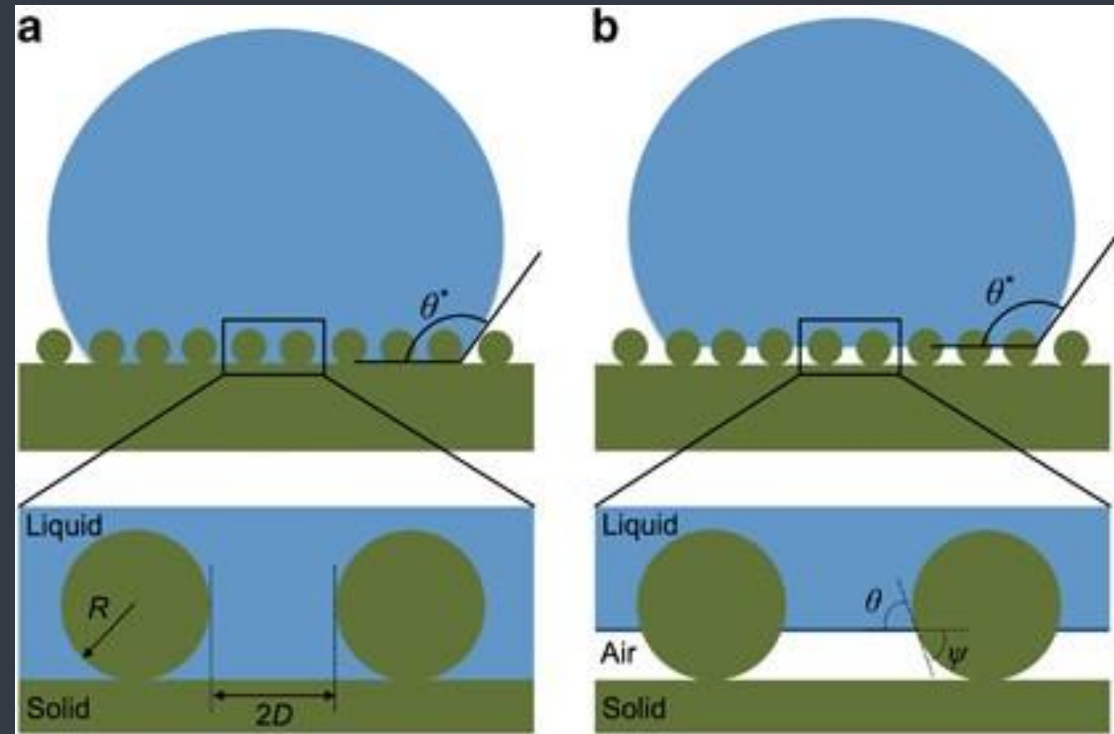| (a) Water droplet on Rose petal | (b) SEM image of Rose petal |

Applications of superhydrophobic surfaces: Non-fouling surfaces, self-cleaning properties, anti-icing properties, drag reduction, stain-free clothing, oil-water separation, etc.

We study the dynamic behavior of a partially wetting polymer droplet over a nanostructured interface.

[1]T. Wang, L. Chang, B. Hatton, J. Kong, G. Chen, Y. Jia, D. Xiong, C. Wong, Preparation and hydrophobicity of biomorphic ZnO/carbon based on a lotus-leaf template, *Materials Science and Engineering* **43,** 310-316 (2014).

- The primary principle behind the *superhydrophobic surface* is to introduce small-scale surface roughness.

- In our case, the surface roughness is introduced via an array of spherical nanoparticles.

- This array of particles allows the formation of air gaps, that keep the liquid suspended above the substrate. This is called as *Cassie – Baxter* state.

- When the liquid droplet completely penetrates into the substrate, this is referred to as *Wenzel* state.

(a) Wenzel state[2]   (b) Cassie – Baxter state[2]

$$\left[\theta^* = \text{Apparent contact angle} \right]$$

[2] Kota, A., Kwon, G. & Tuteja, A. The design and applications of superomniphobic surfaces. *NPG Asia Mater* **6,** 109 (2014).

Details of molecular dynamics simulations and parameter values

MD Simulations were carried out using LAMMPS code developed at Sandia National Laboratories.

- **Liquid droplet consists of 880,000 atoms.**

- The interaction between any two atoms is

  described using Leonard- Jones (LJ) potential.

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

where r = distance between two interacting particles.

   ε = LJ energy scale.

 σ = LJ molecular scale length.

- Liquid monomers are connected to form short polymer (10-mer)

  chains via FENE (finitely extensible nonlinear elastic) potential.

  $$V_{FENE}(r) = -\frac{k}{2} r_o{}^2 ln\left[1 - {r^2}/{r_o{}^2}\right]$$

- Each sphere consists of 4000 atoms.

- Radius of each Sphere = 17.8 σ.

- The solid wall consists of 22,000 atoms.

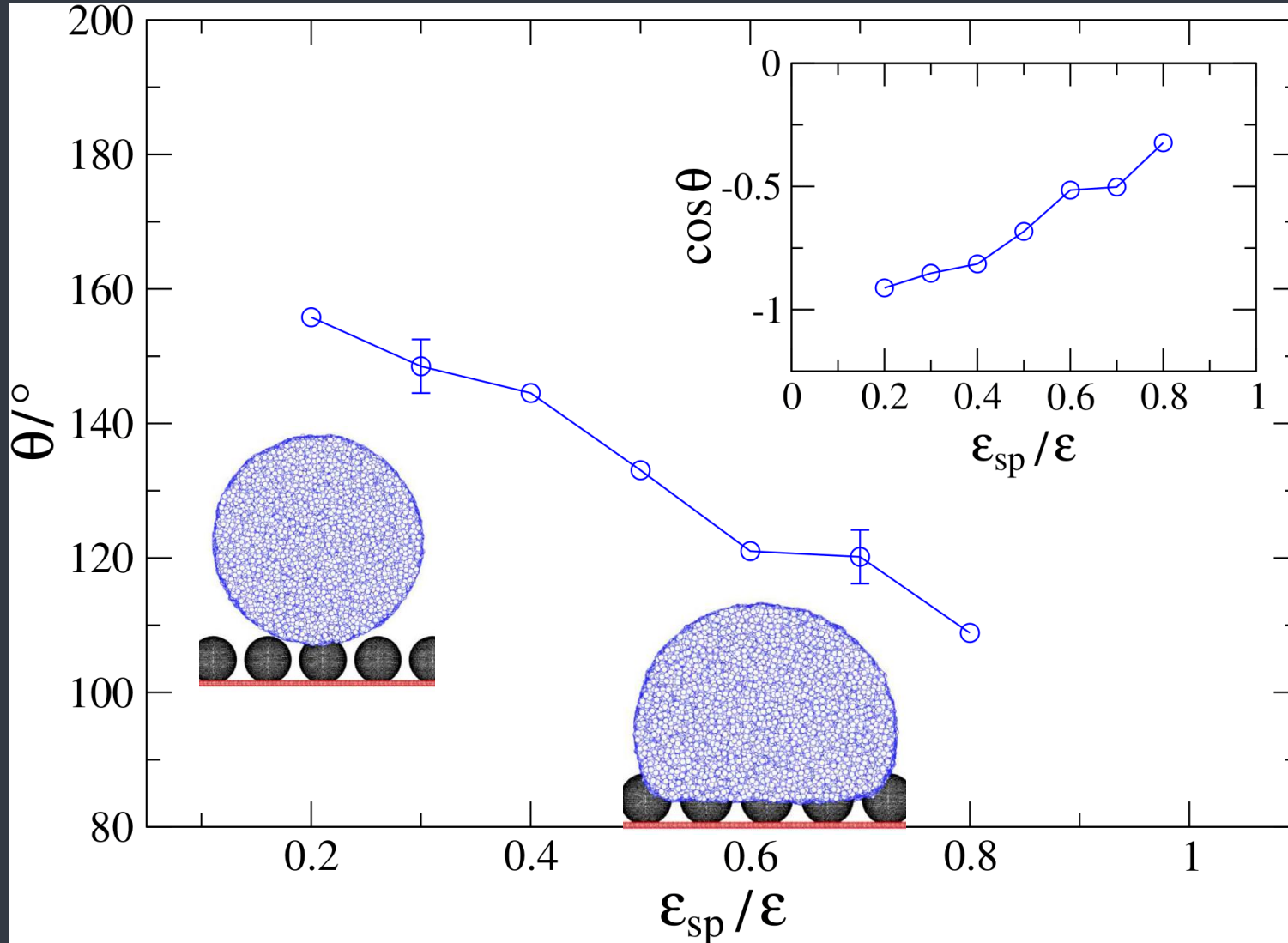- Substrate dimensions : 440 σ * 50 σ
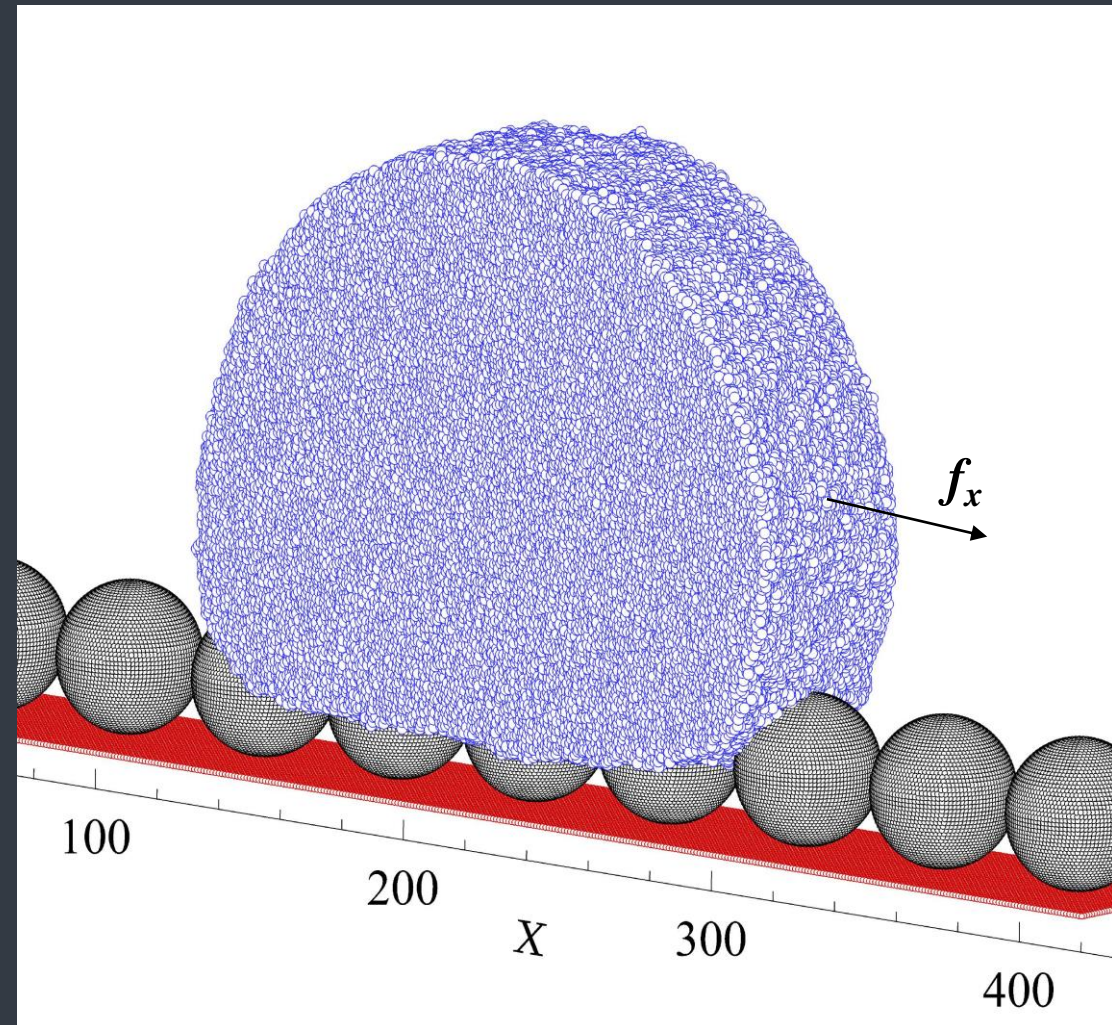
Droplet shapes for various surface energies (no external force)

(a) 0.2

(b) 0.3

(c) 0.4

(d) 0.6
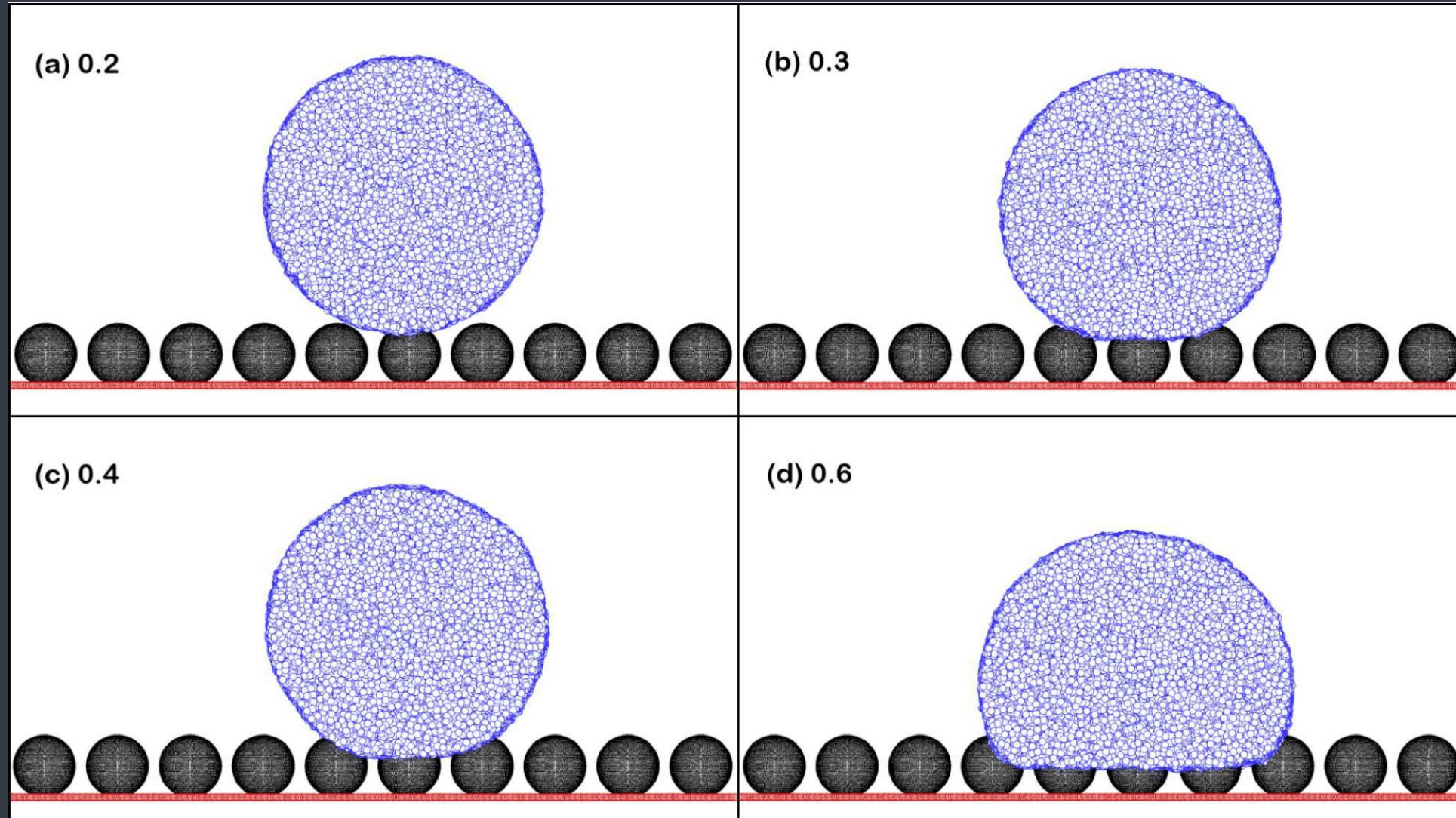
Droplet shape varies from nearly circular, i.e., $\varepsilon_{sp} = 0.2\ \varepsilon$ [fig a] to semicircular for $\varepsilon_{sp} = 0.6\ \varepsilon$ [fig d]

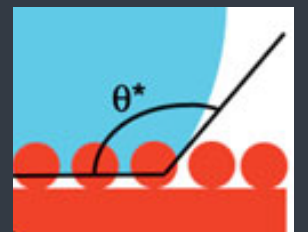# The apparent contact angle as a function of surface energy

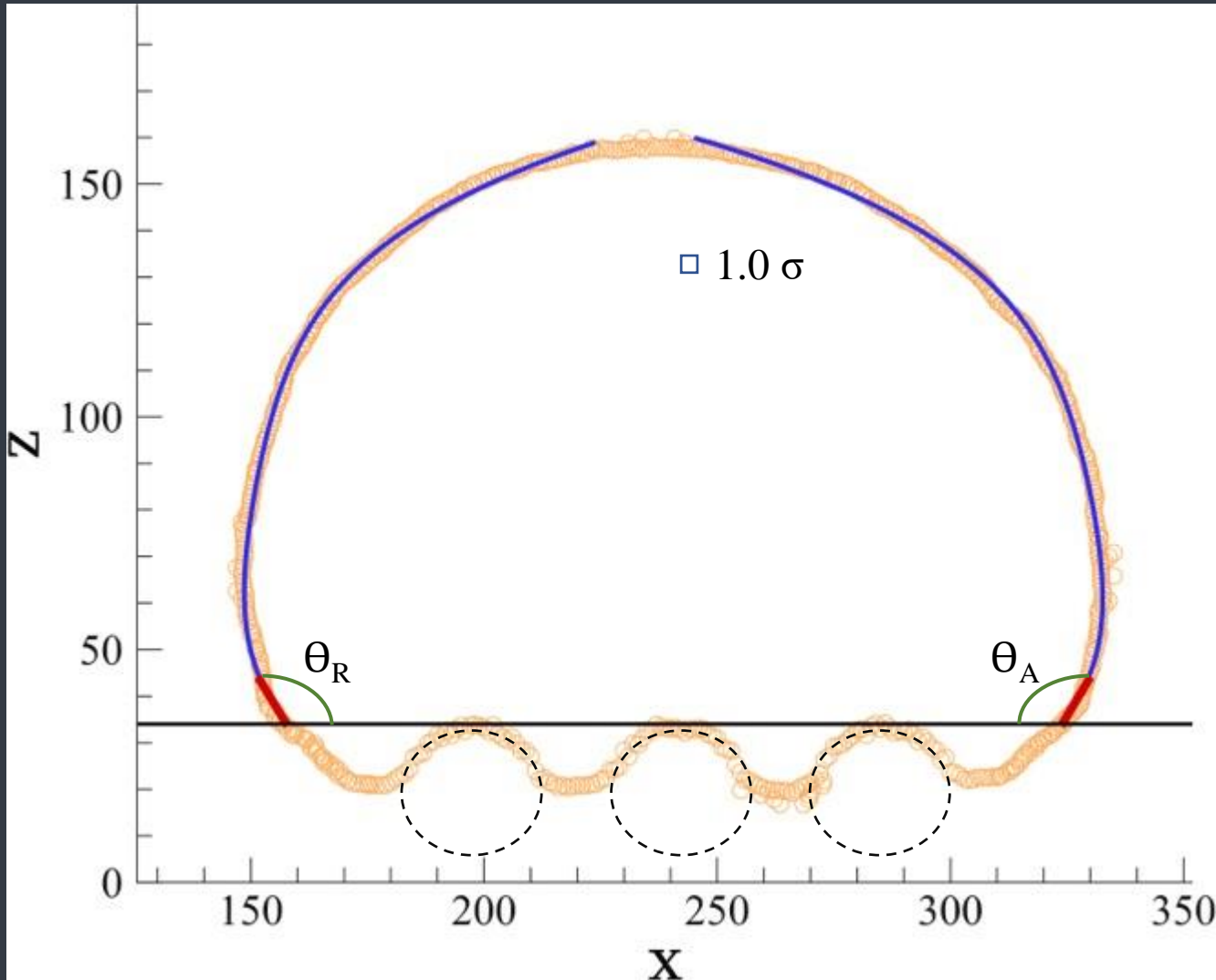The contact angle decreases monotonically as the surface energy increases.

The polymer droplet is in partially wetting state for $\varepsilon_{sp} \leq 0.8\ \varepsilon$

Apparent contact angle:

- The computational domain was divided into thin narrow slices of thickness 1.0 σ, parallel and perpendicular to the solid wall. The local density of each slice was computed and the droplet profile was obtained [orange circles].

- 4th order polynomial curve was fit over the droplet profile [blue curve].

- Tangent at intersection with reference plane [black line] was obtained using first 10 data points [red line].
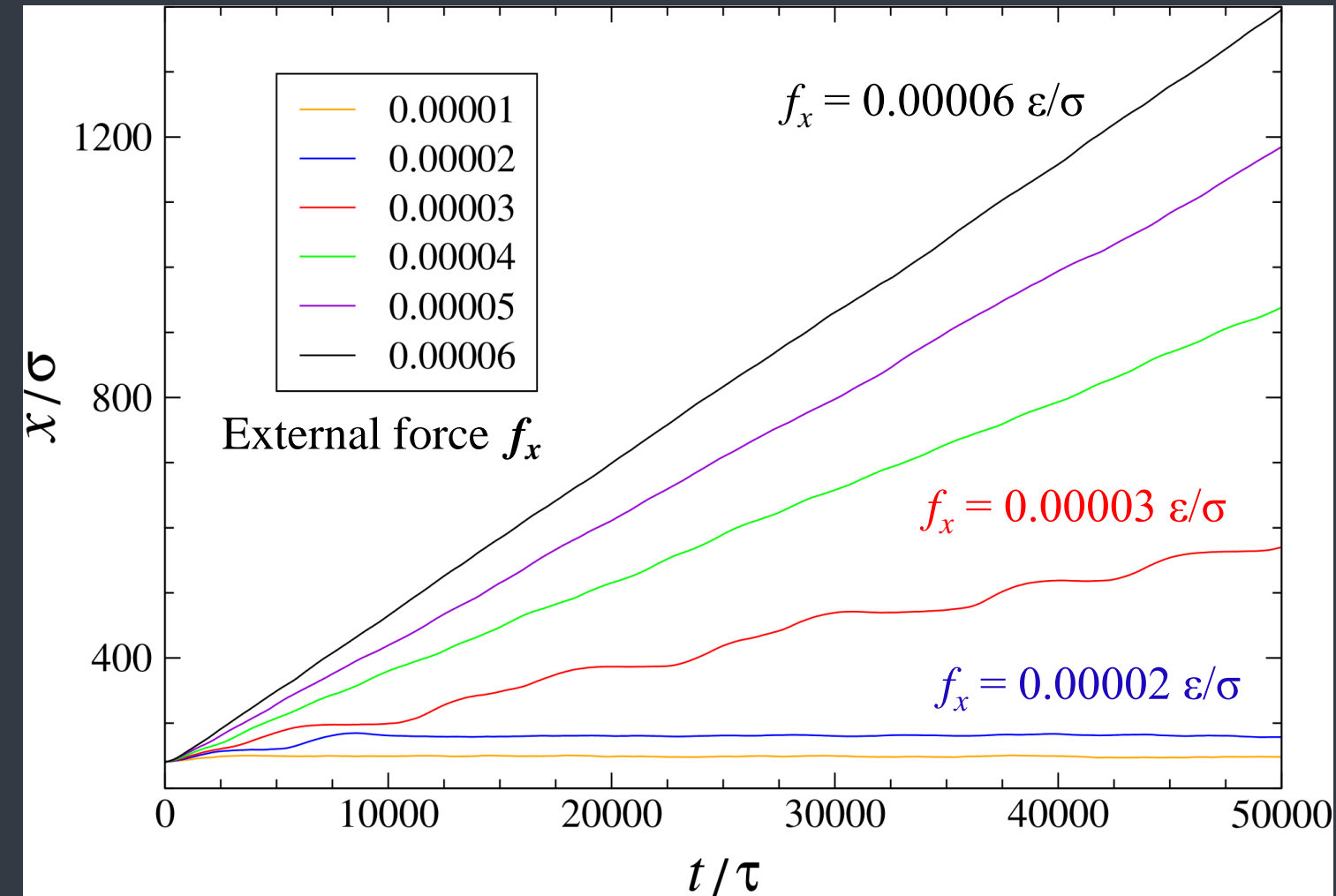
- The droplet is initially at equilibrium at time t = 0.

- At small values of forces [$f_x \leq 0.00002 \ \varepsilon/\sigma$] the droplet is initially displaced between the neighboring sphere, but remains pinned during the time interval 50,000 τ.

- At the larger value of the force, $f_x = 0.00003\varepsilon/\sigma$, the droplet becomes temporarily pinned at the particle surface and then there is rapid motion between spheres.

- As the force is increased [$f_x \geq 0.00004 \ \varepsilon/\sigma$], the droplet is displaced linearly during the time interval 50,000 τ.

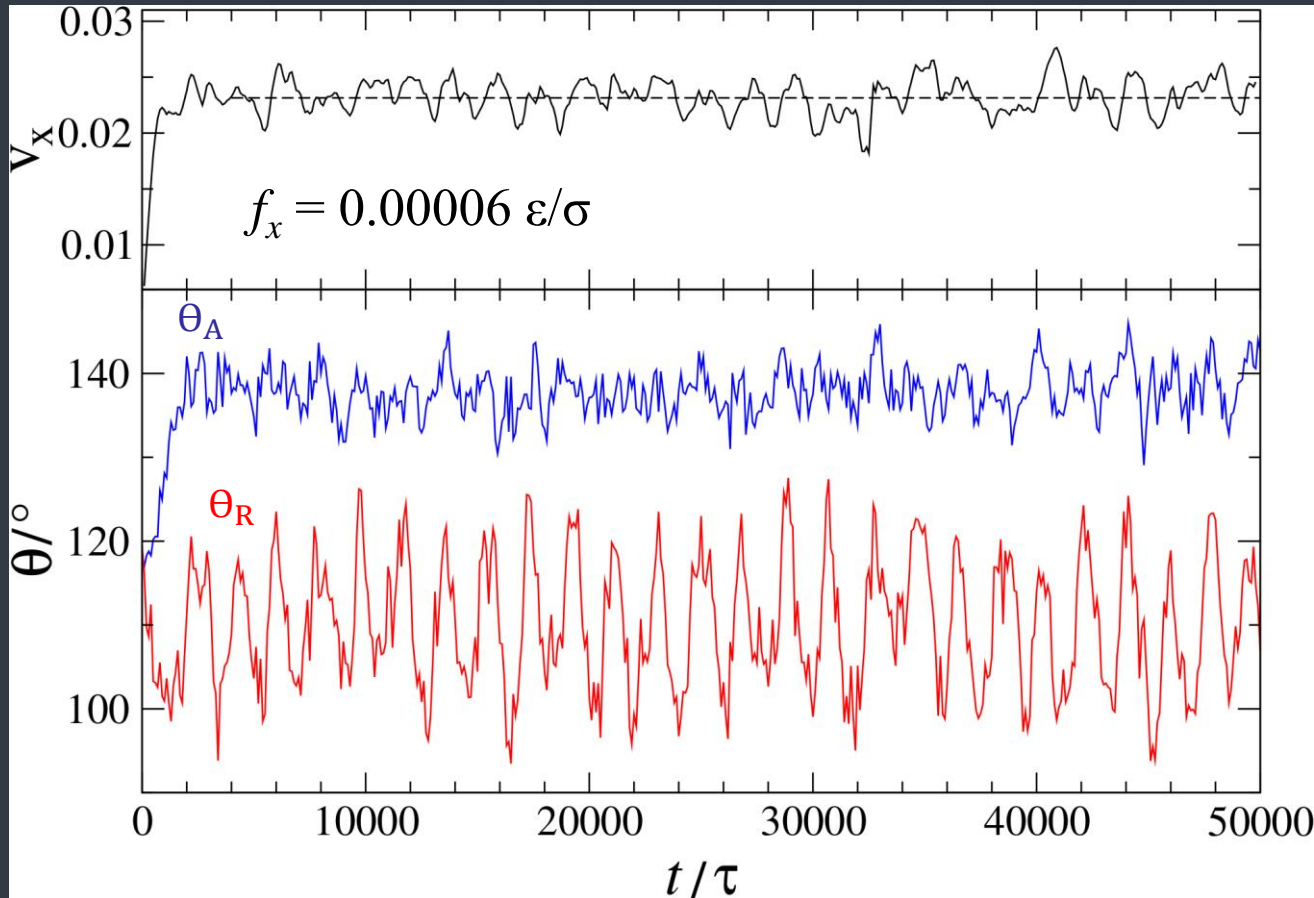# Advancing and receding contact angles and the velocity of COM
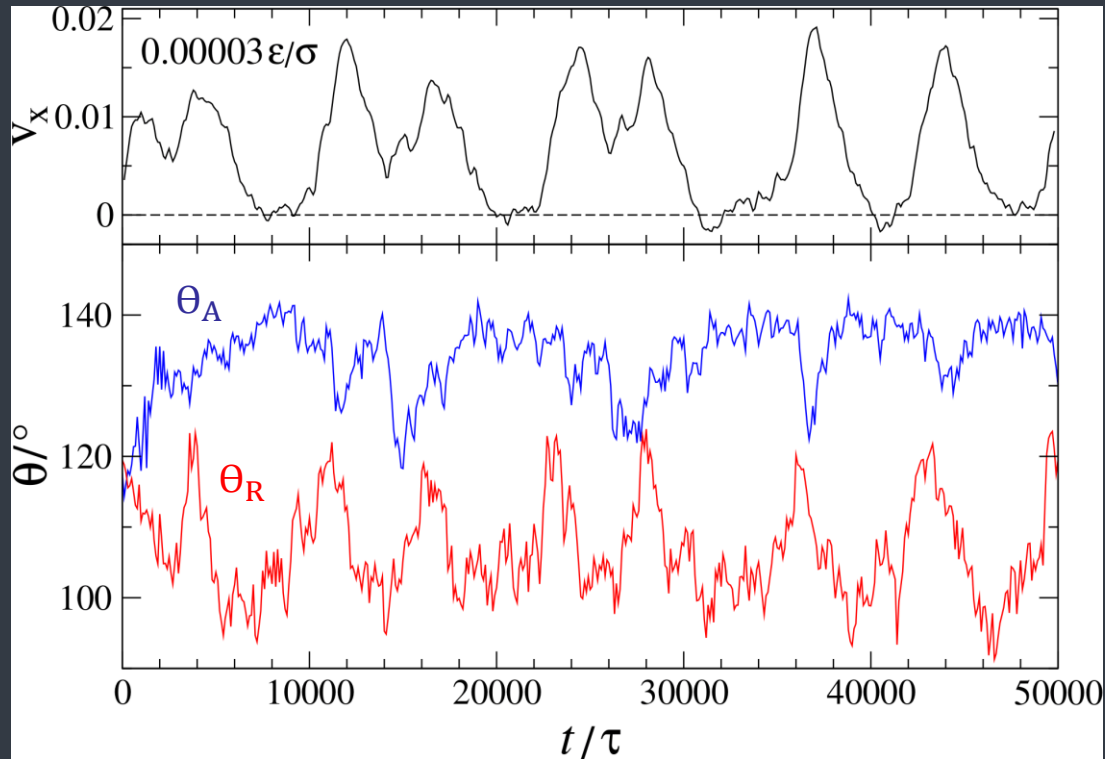
(i) $f_x = 0.00003\ \varepsilon/\sigma$
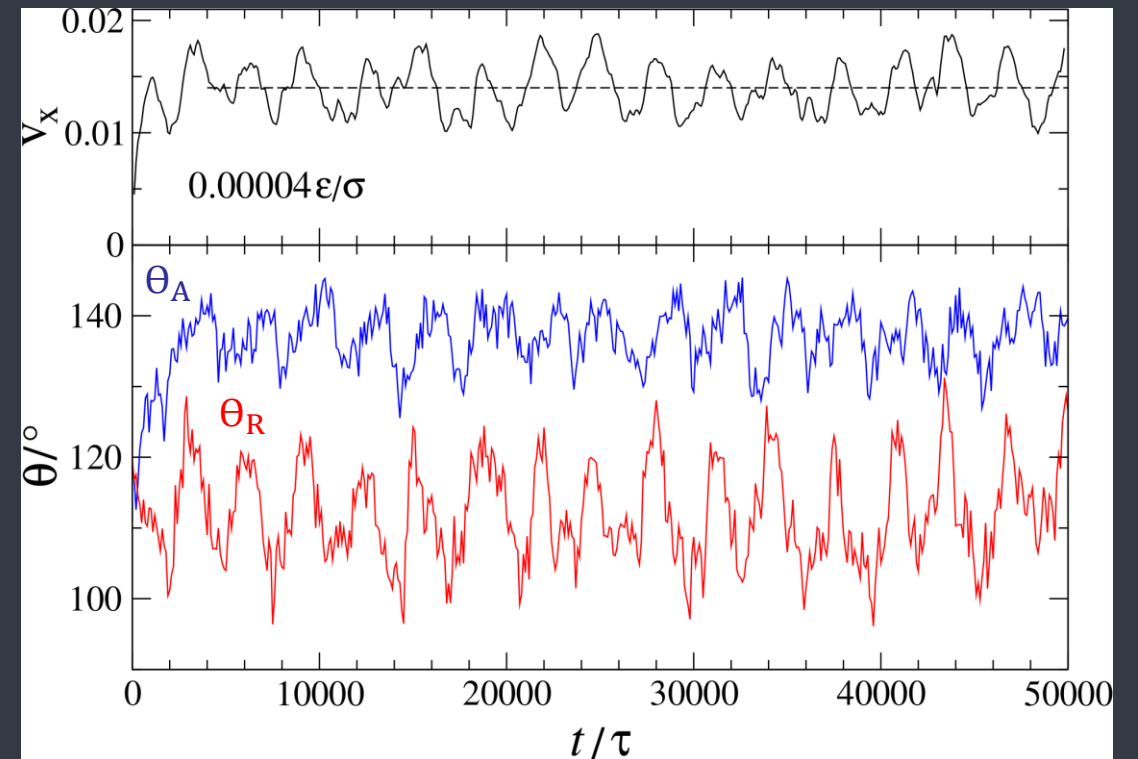
(ii) $f_x = 0.00004\ \varepsilon/\sigma$

- For $f_x = 0.00003\ \varepsilon/\sigma$, (a) the advancing contact angle reduces as the receding contact angle increases during transient motion along spheres.
  (b) The COM velocity becomes negative during successive displacements indicating slight oscillatory movement due to surface tension force.
  (c) The contact angle hysteresis varies from $\theta_A - \theta_R \approx 45°$ during periods of pinning to nearly zero during rapid displacements.

- For $f_x = 0.00004\ \varepsilon/\sigma$, (a) after the initial jump, the droplet is steadily propelled with an average velocity of $v_x = 0.014\ \sigma/\tau$.
  (b) The maximum value of contact angle hysteresis is nearly the same as $f_x = 0.00003\ \varepsilon/\sigma$, i.e., $\theta_A - \theta_R \approx 45°$.
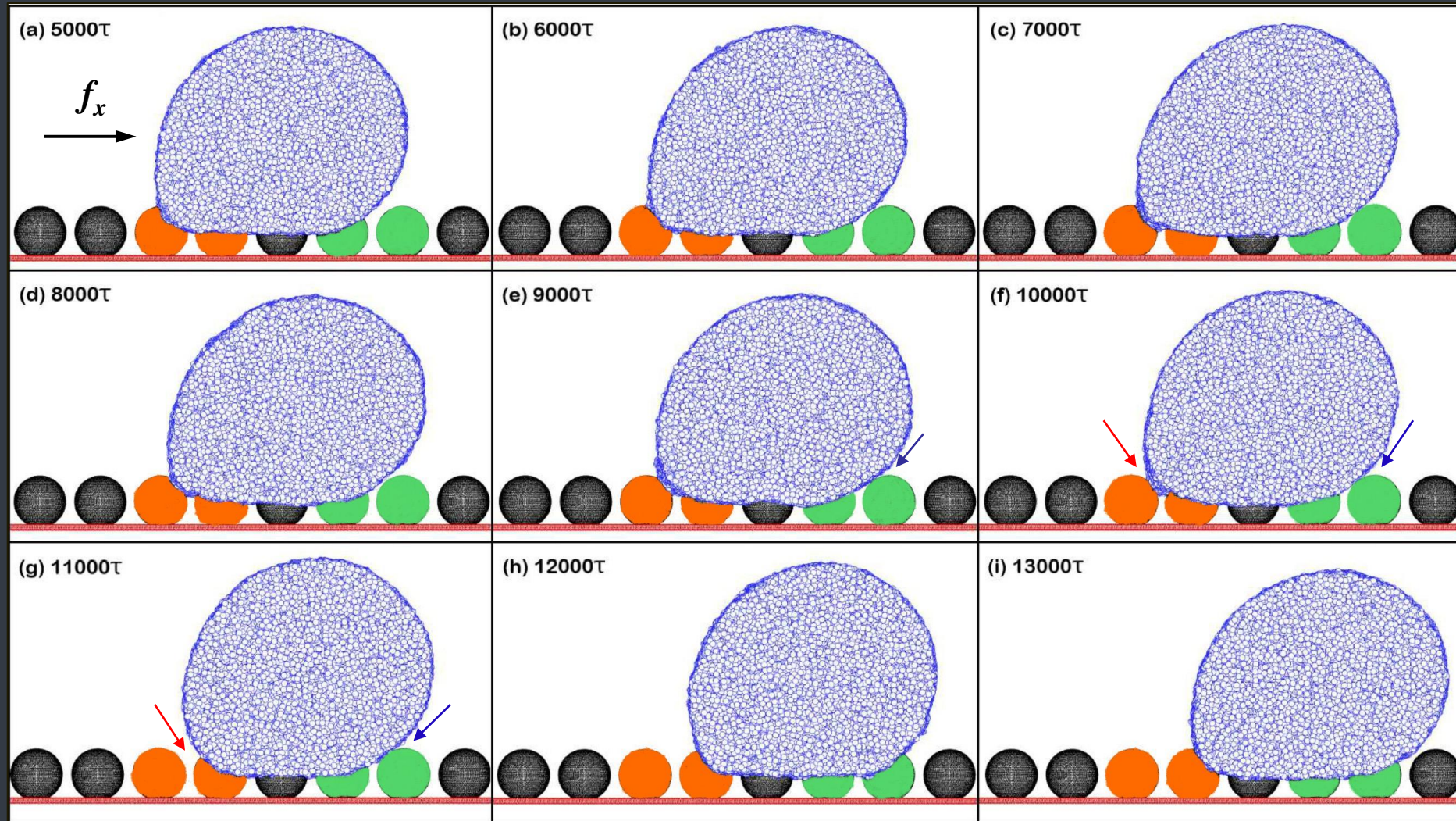
(iii) $f_x = 0.00006\ \varepsilon/\sigma$

For large value of the force, $f_x = 0.00006\ \varepsilon/\sigma$, (a) the average velocity of the droplet increases to $v_x = 0.023\ \sigma/\tau$.

(b) The fluctuations in COM velocity and the advancing contact angle are reduced. However, the oscillation amplitude of the receding contact angle remains relatively large and is comparable to the cases $f_x = 0.00003\ \varepsilon/\sigma$ and $f_x = 0.00004\ \varepsilon/\sigma$.
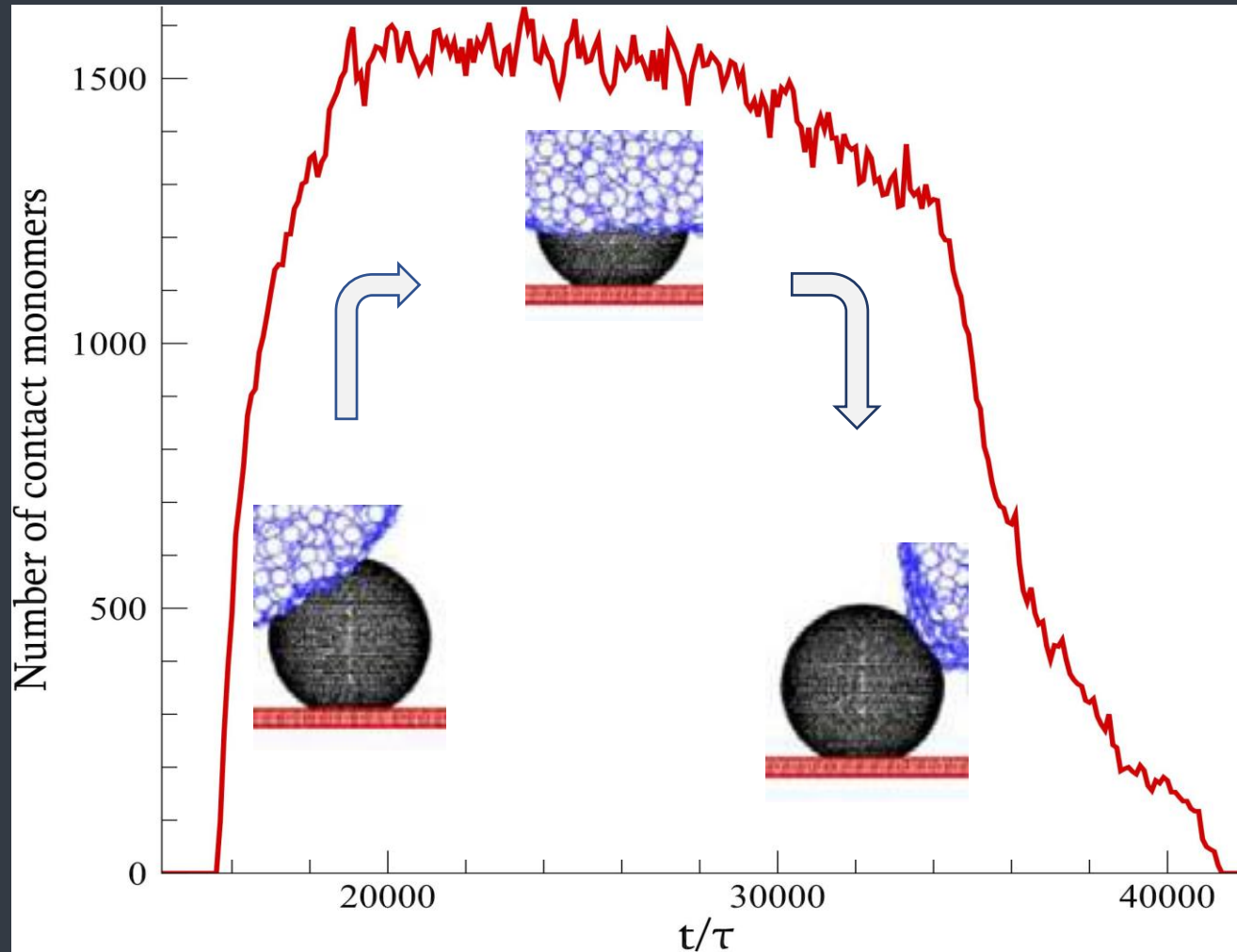
- The green spheres show the attachment process of the droplet interface from one sphere to the next one.
- The orange sphere shows the detachment process of the droplet interface from the surface of the sphere.

Fluid monomers in contact with surface atoms of a spherical particle

$\varepsilon_{sp} = 0.6$ and $f_x = 0.00003 \ \varepsilon/\sigma$
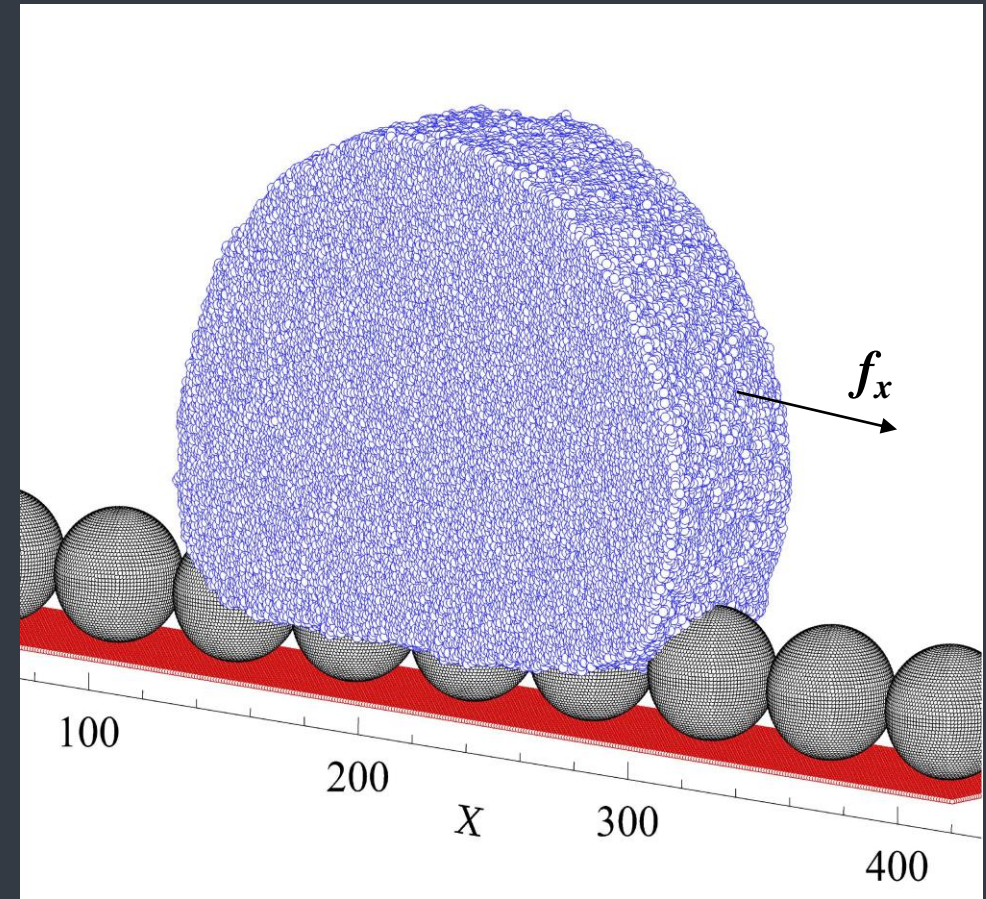
- The number of monomers in contact with the sphere, first increases rapidly and then saturates to a quasi – plateau, followed by a slow decay.

- The plateau level represents about half of the surface area in contact with the liquid droplet.

- The slow decrease in number of contact monomers describes the detachment of progressively narrowing neck that temporarily pins the whole droplet.

CONCLUSIONS

- From our simulations, the polymer droplet remains pinned at the surface of nanoparticles at sufficiently small values of external force.

Above the threshold force, the droplet moves intermittently along the interface via successive rapid displacements and periods of pinning.

- With increasing external force, the variation of advancing contact angle is reduced, whereas the oscillation amplitude of the maximum contact angle hysteresis remains nearly unchanged.

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