# How to Prevent Rebound of a Droplet on a Solid Surface with a Small Amount of Polymer Additives

TECHNISCHE UNIVERSITÄT DARMSTADT


**Eunsang Lee**[1], **Hari K. Chilukoti**[2], **Dejian Qiu**[1], **and Florian Müller-Plathe**[1]

[1]Eduard-Zintl Institute of Inorganic and Physical Chemistry, Technical University of Darmstadt, Alarich-Weiss-Street 8, 64287 Darmstadt, Germany

[2]Department of Mechanical Engineering, National Institute of Technology Warangal, Warangal, Telangana 506004, India


## Motivation and Objectives

- Importance of understanding molecular processes in droplet wetting of a solid surface
- Increasing interest to realistic problems including effects of complex fluids and heterogeneous rough surfaces
- Development and application of non-equilibrium molecular simulation methods for droplets under extreme conditions
- Measurement of appropriate quantitative indicators from simulations and comparison with experiments
- Finding molecular origins of wetting and dewetting phenomena
- Controlling a droplet rebound with a small amount of polymer additives

## Computational Methods

- Non-equilibrium Multi-body dissipative particle dynamics (MDPD) simulations
- Attractive force depending on the local particle density
- $F_{ij}^{C} = B_{ij} w^{B}(r_{ij}) \cdot \boldsymbol{e}_{ij} + A_{ij}(\bar{\rho}_i + \bar{\rho}_j) w^{A}(r_{ij}) \cdot \boldsymbol{e}_{ij}$, where $\bar{\rho}_i = \frac{15}{2\pi r_B^3} \sum_{j \neq i} w^{B}(r_{ij})$
- $w(r)$: Cut-off functions of repulsive and attractive forces with the cut-off distances, 0.75 and 1.0
- Modified velocity-Verlet algorithm for position-velocity integrations

## Results and Discussion

### Rebound Suppression by Elastic Pulling of Adsorbed Polymer

- Investigation of polymer effect on a rebound suppression by using non-equilibrium MDPD simulations
- Small amount of polymer not changing Weber and Reynolds numbers
- Explaining experimental observations of of consistent spreading behavior (spreading diameter) for different polymer contents
- Main difference observed in the hopping stage
- Slow hopping mechanism: polymers adsorbed on a surface acting as a spring during hopping (prevailing in smaller droplets)

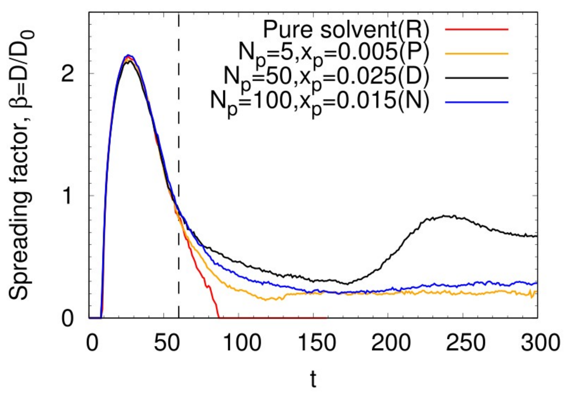


Fig. 1 Spreading factors as a function of time for different polymer contents in a droplets

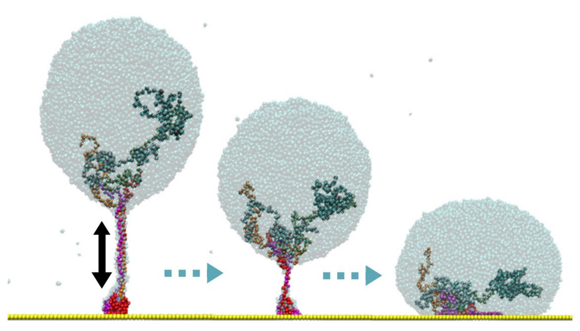

Fig. 2 Simulation snapshot of hopping mechanism

### Rebound Suppression by Large Contact Line Friction during Retraction

- Slow retraction mechanism: polymers retarding a retraction by increasing friction at three phase contact lines (in larger droplets)
- Adsorbed amount of polymer (altered by polymer-surface attraction strength, impact velocity) affecting both mechanisms

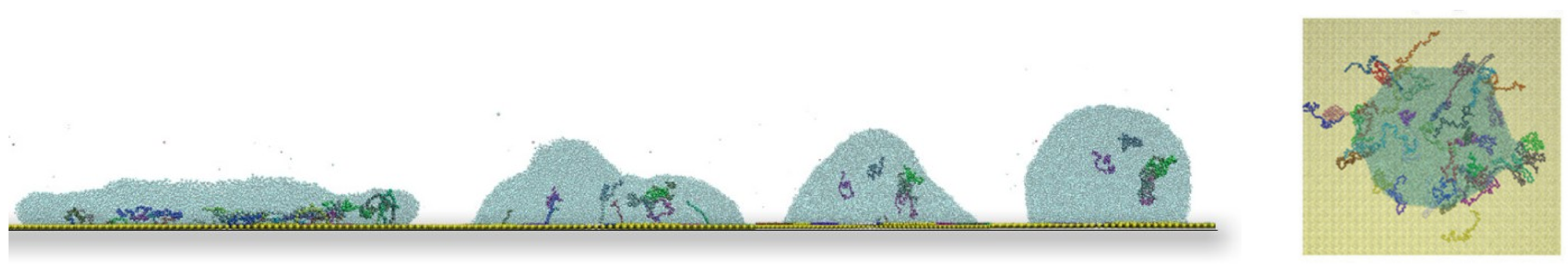

Fig. 3 (left) Simulation snapshots of slow retraction mechanism. Small contact angle by a strong friction manifests during the retraction. (right) Top view simulation snapshot during the retraction.

- Molecular kinetic theory (MKT) of wetting for contact line friction

$$v_{CL} = 2\kappa_0 \lambda \sinh\left(\frac{\gamma(\cos\theta_0 - \cos\theta)}{2nk_B T}\right) \approx \gamma(\cos\theta_0 - \cos\theta)/\zeta_{CL}, \quad \text{where} \quad \zeta_{CL} = nk_B T/\kappa_0 \lambda$$

- Relation between contact angle-contact line velocity
- Slow retraction mechanism: Large contact line friction retarding retraction and resulting in droplet deposition
- Coexisting both mechanisms

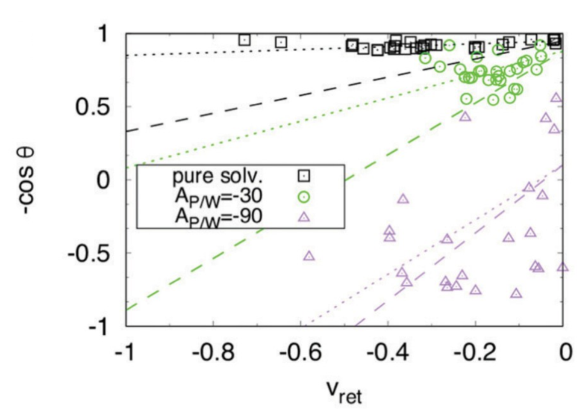


Fig. 4 Contact angle as a function of contact line velocity during retraction for different polymer-wall attraction strengths. Dotted lines represent the fitted function of each data, and the dashed lines indicate the friction coefficient calculated from MKT.

## Contact Line Friction and Dynamic Contact Angle by Polymer Adsorption

- Investigation of a contact line friction of a capillary bridge under steady shear using non-equilibrium MDPD
- Derivation of an equation of molecular kinetic theory of wetting modified by local polymer concentration adsorbed on a contact line region
  $\gamma_{lv}(\cos\theta_e - \cos\theta_d(v_{cl})) = \gamma_{lv}(\cos\theta_e^{(s)} - \cos\theta_e^{(p)})(\tilde{x}_p(v_{cl}) - \tilde{x}_{p,e}) + v_{cl}\zeta_{cl}(v_{cl})$
  where $\zeta_{cl}(v_{cl}) \equiv \tilde{x}_s(v_{cl})\zeta_{cl}^{(s)} + \tilde{x}_p(v_{cl})\zeta_{cl}^{(p)}$
- Only a receding contact line affected by polymer
- Explaining a slow retraction mechanism of the rebound suppression by polymer without altering spreading dynamics

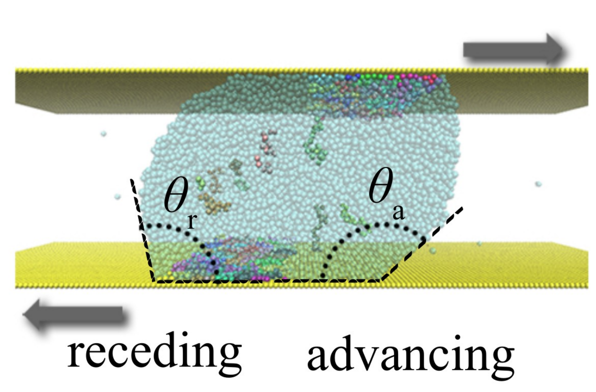


Fig. 5 Simulation snapshot of a capillary bridge under steady shear. Polymer molecules are adsorbed on receding contact lines.

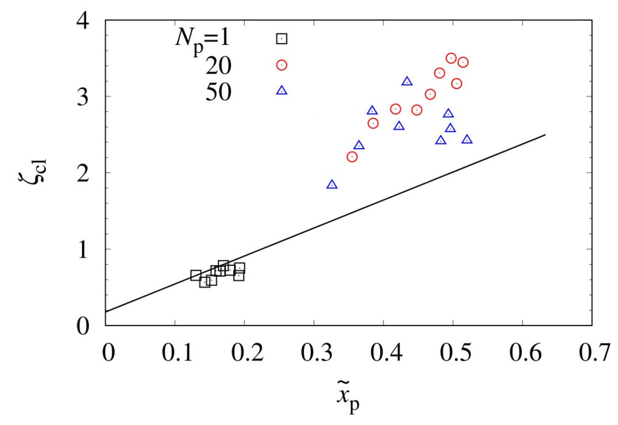


Fig. 6 Friction coefficients calculated from the local polymer concentration and dynamic contact angle. Solid line indicates the analytical prediction of the contact line friction coefficient above.

## Contact Line Dynamics of a Capillary Bridge on a Rough Superhydrophobic Surface

- Investigation of the effect of surface roughness on the contact line dynamics of a capillary bridge in the Cassie-Baxter superhydrophobic state using non-equilibrium MDPD
- Contact angle hysteresis originating from pinning force as well as shear force from the whole liquid-solid interface
- Strong liquid/solid interface friction caused by liquid particles slightly penetrating into the grooves which act like solid particles

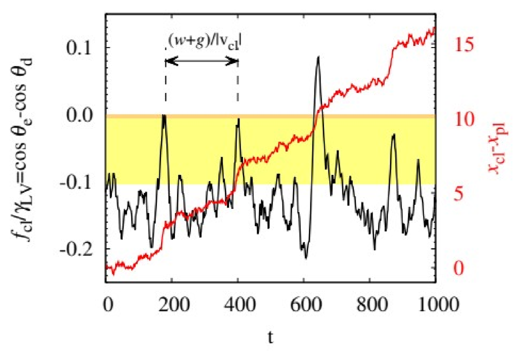

Fig. 7 (Black) Instant contact line friction force and (red) the distance traveled by contact line from the position of the reference solid particle as a function of time

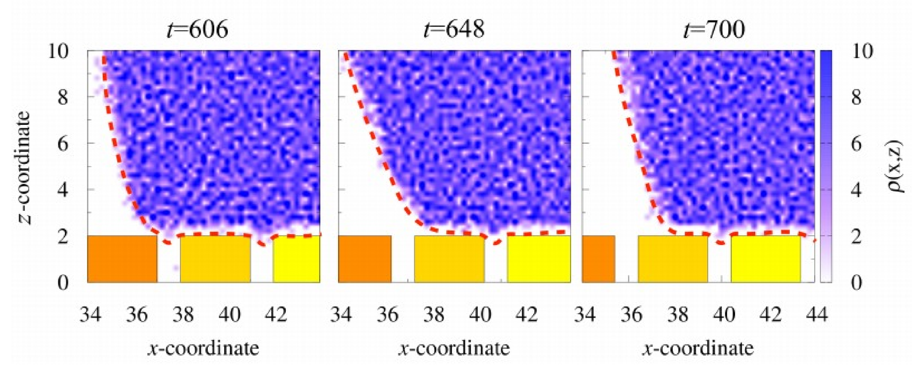


Fig. 8 Particle density map at three different stage of dynamic wetting, (left) pinning, (center) depinning, and (right) sliding. Red dashed lines indicate an liquid-vapor interface and colored squares show pillars moving toward left.

## Conclusions

- Droplet rebound can be suppressed by a small amount of polymer additives through slow hopping and slow retraction mechanisms.
- The amount of polymer adsorption is a key to determine the rebound suppression.
- The friction of the retracting contact line increases due to the adsorbed polymer.
- The contact line friction can be formulated as a function of local polymer concentration at the contact line.
- The intermediate state between Wenzel and Cassie-Boxter states has to be considered to understand the contact line friction on a rough surface.

## Acknoledgement


- GCS Collaborative Research Centre Transregio 75, Droplet Dynamics in Extreme environments of the Deutsche Forchungsgemeinschaft
- GCS Supercomputer JUWELS at Jülich Supercomputing Centre (JCS)


## Project Publications


[1] Lee, E., Chilukoti, H. K., Müller-Plathe, F., "Rebound suppression of a droplet impactig on a supersolvophobic surface by a small amount of polymer additives" *ACS Macro Letters* 10, 192-196, 2021

[2] Lee, E., Chilukoti, H. K., Müller-Plathe, F., "Suppressing the rebound of impacting droplets from solvophobic surfaces by polymer additives: polymer adsorption and molecular mechanisms" *Soft Matter* 17, 6952-6963, 2021

[3] Lee, E., Müller-Plathe, F., "Effect of polymer on the contact line friction of a capillary bridge" *Macromolecules* 55, 2649-2658, 2022

[4] Lee, E., Müller-Plathe, F., "Contact line friction and dynamic contact angles of capillary bridge between superhydrophbic nanostructured surfaces" *J. Chem. Phys.* 157, 024701, 2022

[5] Lee, E., Chilukoti, H. K., Müller-Plathe, F., "Stopping droplet with polymer addtives: A molecular viewpoint" in *Droplet Dynamics under extreme ambient conditions*, Springer, Cham. 87-106, 2022