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Adaptive Wetting: Surface ordering-induced wetting transition and vapor-controlled drop transport on thermos-responsive oleophilic polymer brushes

Oleophilic polymer brushes serve as liquid-infused slippery surfaces that facilitate e.g. the motion of water drops. Similarly, they can act as flexible surface-grafted transport layers for oil in advanced lubrication techniques. In this lecture, I discuss the wetting properties of poly n-alkyl methacrylate bottle brushes with variable length of the n-alkyl side chains. Brushes with short lauryl side chains (P12MA) are liquid-like at room temperature, swell easily and display near-complete wetting for pure alkanes with contact angles well below 5° [1]. In contrast, brushes with longer octadecyl side chains (P18MA) are solid at room temperature and remain collapsed upon exposure to alkanes with contact angles of approximately 30°.
I will first describe a mechanism of drop mobilization for volatile alkanes enabled by controlling the local vapor concentration above the drop on P12MA. For these samples, the contact angle decreases from 2° to 1° between low and saturated vapor concentration, which induces drop motion. High resolution interferometric measurements of local swelling profiles and contact angles reveal a peculiar non-monotonic distribution along the contact line of the moving drops, which results from a local balance of viscous dissipation and imbalanced Young forces.
Alkane drops on the longer chain P12MA brushes display a two-stage melting and wetting transition upon increasing the temperature: first the bulk of the brush layer melts, while a thin CH3-terminated surface layer remains solid, as evidenced by non-linear optical sum frequency generation (SFG). This first transition leads to partial swelling of the brush layer while the contact angle hardly changes. A few ℃ higher, the surface layer melts and the contact angle drops to near-zero values, as evidenced by the loss of order in the SFG signal concomitant with a strong increase in AFM adhesion.

Our experiments suggest a use of brush layers as a versatile platform for controlled drop motion as well as local entrapment and release of femtoliters of fluids.

[1] Ö. Kap, S. Hartmann, H. Hoek, S. de Beer, I. Siretanu, U. Thiele, F. Mugele, 'Nonequilibrium configurations of swelling polymer brush layers induced by spreading drops of weakly volatile oil', J. Chem. Phys. 158, 174903 (2023).

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