Research on the behavior of liquid
fluids atop superhydrophobic gas-bubbled surfaces

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Abstract: Superhydrophobic surfaces play an important role in the development of new product coatings such as cars, but also in mechanical engineering, especially design of turbines and compressors. Thus a vital part of the design of these surfaces is the computational simulation of such with a special interest on variation of shape and size of minor pits grooved into plane surfaces. In the present work, the dependence of the contact angle on the fluid-wall dispersive energy is determined by molecular simulation and static as well as dynamic properties of unpolar fluids in contact with extremely rough surfaces are obtained.

Fluid flow over extremely rough surfaces is governed by non-trivial boundary conditions which can be related to the contact angle as discussed by Voronov et al. (2008). Boundary slip is most relevant for microscopic and nanoscopic flow, while the influence of surface roughness on the contact angle becomes extreme in case of superhydrophobic surfaces. For nanoscopic channel dimensions as well as roughness on the molecular length scale, the accuracy of simulation results can be optimized by applying molecular dynamics (MD), since this approach reflects the actual structure of the material more directly than higher-level methods that rely on aggregated models and properties.

As long as no hydrogen bonds are formed between the wall and the fluid, the interfacial properties mainly depend on the fluid-wall dispersive interaction, even for hydrogen bonding fluids. The truncated and shifted Lennard-Jones (LJTS) potential with a cutoff radius of $r_\mathrm{c} = 2.5\,\sigma$ accurately reproduces the dispersive interaction if adequate values for the size and energy parameters σ and ϵ are specified, cf. Vrabec et al. (2006).

Fluid-wall interactions can be represented by Lennard-Jones-12-6 effective potentials, acting between fluid particles and the atoms of the solid, cf. Battezzati et al. (1975). Following this approach, the LJTS potential with the size and energy parameters $\sigma_\mathrm{fw} = \sigma$ as well as $\epsilon_\mathrm{fw} = W\epsilon$ was applied for the unlike interaction using the same cutoff radius as for the fluid. The wall was modeled as a system of coupled harmonic oscillators with different spring constants for transverse
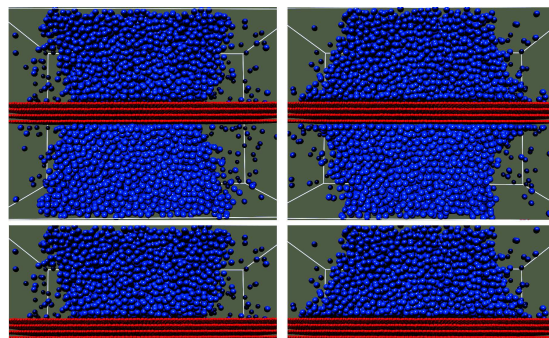

Figure 1: Simulation snaphots for a smooth surface with a reduced fluid-wall dispersive energy W of 0.09 (left) and 0.16 (right) at a temperature of $0.73\,\epsilon/k$. The upper half is reproduced in the bottom to illustrate the effect of the periodic boundary condition.

and longitudinal motion, adjusted to simulation results for graphite with a rescaled variant of the Tersoff (1988) potential. Massively parallel MD simulations were conducted with the program *ls1 mardyn*, cf. Bernreuther et al. (2009). A periodic boundary condition was applied to the system, leaving a channel with a diameter of $27\,\sigma$ between the wall and its periodic image, cf. Fig. 1.

The contact angle was determined from the density profiles by averaging over at least 800 ps after equilibration. A circle was adjusted to the positions of the interface in the bins corresponding to distances between 3 and $11\,\sigma$ from the wall, and the tangent to this circle at a distance of $1\,\sigma$ from the wall was consistently used to determine the contact angle.

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A contact angle – as opposed to total dewetting or wetting – appears only for a relatively narrow range of W values. As the temperature increases and the vapor-liquid surface tension decreases, the contact angle reaches more extreme values, leading to the well-known phenomenon characterized by Cahn (1977) as crtical point wetting, cf. Fig. 2. This plot agrees qualitatively with the results of Giovambattista et al. (2007) regarding the influence of the polarity of hydroxylated silica surfaces on the contact angle formed with water.
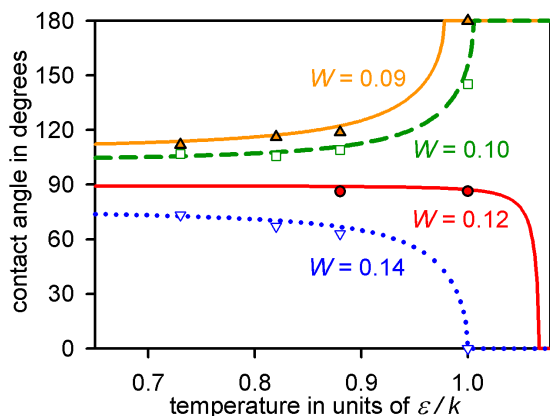

Figure 2: MD simulation results and correlation for the contact angle of the LJTS fluid on a smooth surface in dependence of the temperature with reduced fluid-wall dispersive energy W values of 0.09 (Δ / —), 0.10 ($\Box$ / − −), 0.12 ($\bullet$ / —) as well as 0.14 (∇ / $\cdots$). The entire range between triple point and critical temperature is shown.

For a constant value $W = 0.09$ of the reduced fluid-wall energy, corresponding to a contact angle of about $110°$ for moderate as well as low temperatures, the surface shape and roughness was varied in further simulations, cf. Fig. 3. The stability of the Cassie state as well as the influence of the surface shape on dynamic properties such as the boundary slip length and slip velocity in nanoscopic Poiseuille flow were studied by MD simulation.

The simulation results regard the length scale between 1 and 100 nm and can be reliably extrapolated to the characteristic system dimensions corresponding to typical superhydrophobic surfaces, e.g. about one micron in case of the material manufactured by Steinberger et al. (2008). Thereby, the experimental point of view can be complemented by a theoretical treatment, applying the variant of computational fluid dynamics that is best suited for the investigation of nanopatterned surfaces: MD simulation.

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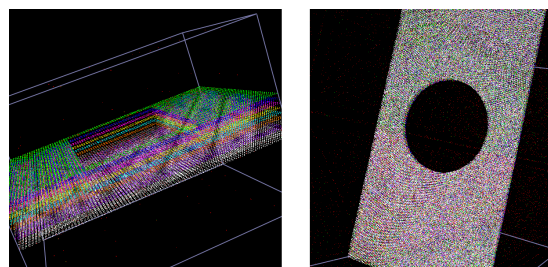
Figure 3: Left: Rectangular elementary cell of a pit grid with rectangular pit for simulation with gaseous and liquid fluids. Right: Rectangular elementary cell (prototype version) with cylindrical bore for simulation of streaming fluids.