Sharp Transition between Coalescence and Noncoalescence of Sessile Drops

Supplemental Material

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Substrate Cleaning

As substrates served single-sided polished silica wafers with a natural oxide layer (Si(100), p, 30 Ωcm, SILCHEM, Freiberg, Germany) that were cut into pieces of approximately 2 cm × 2 cm. The substrates were cleaned in a piranha solution (hydrogen peroxide 30 % with sulfuric acid, volume fractions 1 : 3, respectively) for approximately 30 min. After flushing with copious amounts of water, the samples were sonicated in a low power supersonic bath for about 10 min to remove traces of the acid and dust. Finally the samples were stored under fresh water for at most four hours before usage. Immediately before the experiments, they were dry blown with clean nitrogen (purity 5.0). The surface roughness was about 0.3 nm as determined by non-contact atomic force microscopy and x-ray reflectivity.

Measurement of dynamic contact angles

Dynamic contact angles during drop spreading were determined very accurately ($\approx \pm 0.1^\circ$) by combining top- and side-views: The evolution of the drop height was measured from the side aspect, the footprint diameter from the top aspect. This information defines the (mostly) circular contour of the spreading drop[1]. Thus its volume respective dynamic contact angle can be determined. The biggest remaining uncertainty is the vertical offset of the (substrate-) baseline, which can be eliminated by considering the drop volume as approximately constant. Typical corrections to the measured drop heights are 10...30 µm, resulting in fluctuations of the measured volume smaller than ±1 %.

[1]The contour is not perfectly circular since capillarity and viscous dissipation interact. However, this effect is relevant only close to the contact line ($\propto h^{-3}$), and the relevant part of the contour remains circular. Strictly speaking, a dynamic contact angle is not well defined if one approaches microscopic scales [1, 2]; the commonly used definition of an "apparent dynamic contact angle" is provided by fitting such a circle.

Measurement of profile evolution

The drops are images from the side with a telecentric lens (0.5x magnification) and telecentric background illumination. The pixel size of the CMOS camera is $\approx 5\,\mu m$, which translates into a spatial resolution of $\approx 10\,\mu m/px$. The profile is extracted from the data via a threshold value. The threshold was chosen in the middle between the average bright- and the average dark values of the image. Due to the high contrast from the telecentric imaging, the gray scale values of the pixels just above and below the threshold can be used to achieve sub-pixel resolution in the extracted height information. The resolution of relative height changes is basically limited only by the contrast between the average bright and dark values (≈ 200 of 256 possible intensity values) compared to the noise in the image (≈ 5 intensity values for the imaging rate of $\approx 60\,fps$). Thus we expect the resolution for relative height changes to be in the (sub-)micron range (compare the height fluctuations in Fig. 3 of the manuscript). The absolute height information is slightly less precise and depends on the measurement of an offset value. The latter is obtained from the profile of a substrate without drops.

Liquid Combinations from Fig. 4 of the manuscript

Liquids	$\overline{\gamma}$	$\Delta\gamma$	$\Delta\gamma/\overline{\gamma}$
Pentadecane - Hexadecane	27.32	0.44	0.016
Tetradecane - Pentadecane	26.83	0.53	0.020
Tetradecane - Hexadecane	27.12	0.87	0.032
Pristane - Hexadecane	27.11	1.25	0.046
Tridecane - Hexadecane	26.77	1.56	0.058
Squalane - Squalene	29.83	3.35	0.11
Pristane - Squalene	28.87	5.20	0.18

Videos

The supplement contains four videos, showing immediate coalescence and noncoalescence for two different liquid combinations:

`c14+c15_immediate.avi`	tetradecane (left) vs. pentadecane (right),	$\overline{\Theta}_a \approx 7.6°$
`c14+c15_noncoalescence.avi`	tetradecane (left) vs. pentadecane (right),	$\overline{\Theta}_a \approx 5.8°$
`c14+c16_immediate.avi`	tetradecane (left) vs. hexadecane (right),	$\overline{\Theta}_a \approx 10.0°$
`c14+c16_noncoalescence.avi`	tetradecane (left) vs. hexadecane (right),	$\overline{\Theta}_a \approx 7.9°$

The movies of tetra- vs. hexadecane correspond to the images shown in figure 2 of the manuscript. The contrast in these movies is larger as compared to those of tetra- vs. pentadecane: the perimeters of the drops appear dark. This comes from the larger contact angles and the aperture angle of the illumination setup.

Simulations

Equations (4) and (8) of the main manuscript were integrated numerically within the framework of the software packet "Mathematica".

The highly nonlinear character of the equations however necessitates several manual adaptations of the basic routines from the software. The simulation grid was nonuniform and adaptive. Every time unit t_0 (or after a maximum of 500 iterations), the grid was redefined after the following scheme. The magnitudes of the relevant derivatives of h and c were used to determine the desired local grid spacing. For h, third and fourth spatial derivatives enter the evolution equations; for c, first and second derivatives are relevant. The actual spacing was selected as the minimum grid spacing from the four criteria, surrounded by a region of at least $12l_0$ with no larger spacing. This ascertains that the profile can evolve for at least one time unit without loss of precision. The maximum grid spacing is set to $6l_0$. Larger values cause numerical instabilities in regions with a flat precursor film. The minimum grid spacing is limited to $0.125l_0$, which was sufficient for the studied topography. To obtain suitable precision for the finite difference approximations of the derivatives (especially on the regions with larger grid spacings), centered finite difference formulas of order 8 were used.

The simulations were initiated with profiles that originated from simulations with a disjoining pressure $\Pi = \frac{1}{3}\left(\xi^{-6} - \xi^{-3}\right)$ and apex heights $\xi_{\text{Apex}} = 501$. The equilibrium for this disjoining pressure is a drop of contact angle 1 and footprint length of $\chi_{\text{Footprint}} \approx 2000$ on a precursor film of $\xi_{\text{Precursor}} = 1$. The coalescence simulations were initiated with two such drops. They were placed at an initial apex-apex distance of 2200, yielding an initial distance between the contact lines of 200. The initial concentration gradient is localized between the two drops by assuming $c(\chi) = (\tanh(0.1\chi) + 1)/2$. M_0 was iterated from 0 to 3 in steps of 0.25 at some distance to $\widetilde{M}_t$, and with steps down to 0.0625 close to the threshold. Simulations were performed for $\widetilde{D} \in \{6.25 \cdot 10^{-2}, 1.25 \cdot 10^{-1}, 2.5 \cdot 10^{-1}, 5 \cdot 10^{-1}, 1\}$. The effect of different values for v_c and Θ_0 can be obtained from the performed simulations by rescaling time, space, and aspect ratio appropriately and selecting the corresponding M and $\widetilde{D}$ from the performed simulations.

Without the disjoining pressure, the drops spread freely and eventually come into (macroscopic) contact. Because the drops spread until they come into contact, $\overline{\Theta}_a$ is smaller than Θ_0. Accordingly $\widetilde{M}$, the Marangoni number in the moment of contact, is larger than M_0 ($\widetilde{M} = M_0/\overline{\Theta}_a^2$, Eq. (5) from the manuscript).

The simulations were advanced with a stiffness-switching method. The time step was selected automatically from the local error estimate of the temporal derivative (see [3] and links to the respective subtopics).

References

[1] J. Eggers. Hydrodynamic theory of forced dewetting. *Phys. Rev. Lett.*, 93:094502, 2004.

[2] J. Eggers. Toward a description of contact line motion at higher capillary numbers. *Phys. Fluids*, 16: 3491–3494, 2004.

[3] `http://reference.wolfram.com/mathematica/tutorial/ndsolveoverview.html`.